Research article

# Role of dry watercourses of an arid watershed in carbon and nitrogen processing along an agricultural impact gradient

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ABSTRACT

In the Mediterranean arid region such as Southeast (SE) Spain, a considerable part of the fluvial network runs permanently dry. Here, many dry watercourses are embedded in catchments where agriculture has brought changes in carbon (C) and nitrogen (N) availability due to native riparian vegetation removal and the establishment of intensive agriculture. Despite their increasing scientific recognition and vulnerability, our knowledge about dry riverbeds biogeochemistry and environmental drivers is still limited, moreover for developing proper management plans at the whole catchment scale. We examined $CO_2$ and $N_2O$ emissions in five riverbeds in SE Spain of variable agricultural impact under dry and simulated rewetted conditions. Sediment denitrifying capacity upon rewetting was also assessed. We found that, regardless of agricultural impact, all riverbeds can emit $CO_2$ under dry and wet conditions. Emissions of $N_2O$ were only observed in our study when a long-term rewetting driving saturated sediments was conducted. Besides, most biogeochemical capabilities were enhanced in summer, reflecting the sensitiveness of microbial activity to temperature. Biogeochemical processing variation across rivers appeared to be more controlled by availability of sediment organic C, rather than by agriculturally derived nitrate. We found that the studied dry riverbeds, agriculturally affected or not, may be active sources of $CO_2$ and contribute to transitory $N_2O$ emissions during rewetting phenomena, potentially through denitrification. We propose that management plans aiming to support ecosystem biogeochemistry through organic C from native vegetation rather than agricultural exudates would help to reduce anthropogenic greenhouse gases emissions and excess of nutrients in the watershed and to control the nitrate inputs to coastal ecosystems.

## 1. Introduction

In water stressed landscapes a vast extension of the fluvial network runs dry most part of the time. The most extreme hydrological-type of non-perennial watercourses, also known as dry rivers, are characterized by the prevalence of dry conditions (i.e. absence of surface water) lacking of aquatic features and only transport water after floods events (Vidal-Abarca et al., 2020). Despite commonly found in arid regions, rivers and streams experiencing natural drought are worldwide distributed (Messager et al., 2021). Approximately of 18% of global surface area is covered by drying inland waters (Pekel et al., 2016); a fraction subjected to grow in response to the exacerbated use of water by human purposes and global warming. Due to the limited information

about their ecological and functional values, dry riverbeds are still poorly considered by society and watershed managers. Consequently, they are merely seen as irrelevant ecosystems within the landscapes vulnerable to be anthropogenically impacted (Cottet et al., 2023; Vidal-Abarca et al., 2020). Advancing in their study is a paramount aspect in the research agenda of fluvial ecosystems in the future scenario of water scarcity (Zimmer et al., 2022). Our knowledge about the role of dry riverbeds at global scale has emerged in the last decade, specially for carbon (C) gaseous emissions (Keller et al., 2020; Paranaíba et al., 2022), but rates and environmental drivers of processing of both C and nitrogen (N) in arid riverbeds are not well understood yet. Besides, most of information in arid regions derives from desert and arid soils and, despite soils and dry sediment being comparable habitats (Arce et al.,

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2019), lack of empirical information in arid rivers prevents a complete picture about the role of drying rivers in biogeochemical cycling.

Exposed sediments may represent a substantial source of greenhouse gases to the atmosphere, especially for C dioxide ($CO_2$) (Keller et al., 2020; Marcé et al., 2019). At local and regional scale, gaseous fluxes are spatially and temporally driven by geochemical factors often related by landuse (and delivery organic matter and nutrients), temperature or water content (Ni et al., 2020). Indeed high release of $CO_2$ to atmosphere in dry riverbeds has been attributed to an active microbial respiration of organic matter in dry sediments together with an increased gas diffusion due to air exposition (Arce et al., 2021; Gómez-Gener et al., 2015, 2016; Keller et al., 2020; Koschorreck et al., 2022). Biotic controls may therefore also exert a fundamental role in gaseous emissions rates (Marcé et al., 2019), especially in arid regions where low availability of organic matter and water often limit microbial abundance and activity (Schimel, 2018).

In terms of N cycling, the release of nitrous oxide ($N_2O$) to atmosphere can occur simultaneously as a function of aeration and C and N availabilities (Congreves et al., 2019; Liang et al., 2015). Recent research demonstrates that $N_2O$ emissions is prone to decrease in drying rivers (Tonina et al., 2021). Yet, during the temporal transition of wet to dry, $N_2O$ emissions from sediments can happen when humidity is not limiting microbial activity and both oxic and anoxic microsites co-occur (Pinto et al., 2021). While anaerobic pathways, such as denitrification (the $NO_3^-$ reduction to $N_2$), is often neglected in drying sediments (Arce et al., 2018; Gómez et al., 2012). Aerobic ammonia oxidation and production of nitrate ($NO_3^-$) can be also favored in exposed sediments (Gómez et al., 2012; Merbt et al., 2016). Nonetheless, the processing rate of this pathway has been seen to decrease in riverbed sediments under very low humidity as desiccation increases (Arce et al., 2018).

As in desert or arid soils, much of biogeochemical processing in dry riverbeds is concentrated in brief periods of high activity following wetting events (Collins et al., 2008; Zaady, 2005). Similar to *"Birch effect"* described in soils (Birch, 1958; Kim et al., 2012), rapid fluxes of $CO_2$ due to increased respiration have been described in dry riverbed sediments upon rewetting (Sponseller, 2007; von Schiller et al., 2019), being considered as *"Ecosystem Control Points"* across temporal and spatial scales (*sensu* Bernhardt et al., 2017). The precedent desiccation degree strongly shapes the magnitude of the release on $CO_2$ (Arce et al., 2021) as well as $N_2O$ to atmosphere upon rewetting (Arce et al., 2018; Gallo et al., 2014). Also, the duration of rewetting in dry ecosystems seems to be key to boost $N_2O$ emissions since it controls $O_2$ depletion and anaerobic conditions to support denitrification (Arce et al., 2015; Reverey et al., 2016; Zaady et al., 2013). Denitrification is considered a paramount ecosystem function preventing anthropogenic N pollution; its activation during rewetting is particularly critical to alleviate the excess of N stored in riverbed sediments and its release after floods (Arce et al., 2015). Nonetheless, sediments upon rewetting being potential hot spots for $N_2O$, a potent greenhouse gas, deserve evaluation as a plausible side effect of $NO_3^-$ removal from the ecosystem (Beaulieu et al., 2011). Up-to-date estimates of riverine $N_2O$ emissions highlight an increase due to agricultural N application, yet, they do not consider the dry part of the fluvial network (Yao et al., 2020).

The fluvial network of Campo de Cartagena watershed (Southeast Spain) is mainly configured by dry watercourses, which run through an irrigated agricultural landscape (Álvarez-Rogel et al., 2020). The supply of native organic matter and C in most dry rivers is limited to scarce and scatter terrestrial vegetation sparsely growing within the river channel. Due to changes in geomorphology, the lack of a well-developed riparian zone in the more impacted agricultural sites led to a constrained buffering capacity for any terrestrial pollutants arising from the agricultural activity. Besides, intensive agriculture runoff is rich in inorganic N, especially $NO_3^-$ (Álvarez-Rogel et al., 2020), which ends reaching the riverbeds following precipitations. From here, most of the $NO_3^-$ enters in the Mar Menor, the largest hypersaline coastal lagoon of the Mediterranean basin, which in the last years suffers from a severe eutrophication crisis due to the excess of $NO_3^-$ (Álvarez-Rogel et al., 2020). However, no previous research exists on the potential of riverbed sediments in Campo de Cartagena to denitrify and control elevated levels of $NO_3^-$, which is essential to gain a complete knowledge of the catchment and to design proper management policies in favor of reducing agricultural loads and greenhouse gases emissions.

In this study we examined different C and N processing rates under dry and rewetted conditions in sediments of dry watercourses with variable agricultural pressure of the Campo de Cartagena watershed. We combined a field and laboratory study to assess the $CO_2$ and $N_2O$ gaseous fluxes in response to a short- and long-term rewetting. We expect that dry sediments may emit $CO_2$ but low $N_2O$ due to well aerated conditions. We also expect that while short-term (hours) rewetting will boost $CO_2$ fluxes, a longer-term (days) rewetting will be needed to trigger fluxes of $N_2O$ in dry riverbeds. Finally, we expected that rivers subjected to higher agricultural landuse in the catchment will support larger potential denitrifying activity and $N_2O$ production as a result of a higher $NO_3^-$ content in sediments. As $CO_2$ and $N_2O$ fluxes are temperature and sediment moisture sensitive (Liang et al., 2016), our study covered summer and winter to visualize the potential variation in the magnitude of biogeochemical responses between the most deferring seasons. We provide direct and potential insights on the biogeochemical capabilities of dry riverbeds in arid regions to impact C and N budgets under different moisture scenarios. We hope our results are useful for further research of adaptation and mitigation strategies of agriculturally modified and N-polluted landscapes in arid climates where dry watercourses are often neglected from a functional and management perspective.

## 2. Methods

### 2.1. Study area

We selected five rivers located in Campo de Cartagena (Region of Murcia, southeast Spain) having a variable landuse percentage of irrigated agriculture in their respective sub-watersheds as well as a different degree of anthropogenic disturbances (Fig. 1, Table 1 Supp. Material). Overall, the study sites CA and MU were the sites least affected by agriculture and kept features close to pristine conditions in terms of channel morphology and structure of riparian vegetation (Fig. 1, Table 1 Supp. Material). The rest of the sites, AL, FA and JI, presented an increasing agricultural impact, respectively, yet similar disturbances in relation to the river morphology alterations; that is channelization and removal of native riparian vegetation (Fig. 1, Table 1 Supp. Material). The surface of Campo de Cartagena watershed is 1,316 $Km^2$, and is the drainage watershed to the Mar Menor (135 $Km^2$, mean depth 4 m), the largest hypersaline lagoon in Europe (Fig. 1). The climate is Mediterranean semiarid with average annual rainfall and temperature and evapotranspiration of 300 mm, 18 °C and 1,275 mm, respectively (Jiménez-Martínez et al., 2011). Campo de Cartagena agriculture changed in the earlier 1970s from dry lands to intensive irrigated crops being an important supply point of vegetables to the European market. As a consequence of the use of N-fertilizers, including the addition of manure to soils, drainage surface waters and subsurface waters are polluted by $NO_3^-$ (Álvarez-Rogel et al., 2020). Most of this $NO_3^-$ is also transported by the rivers during rainfalls and when intense, the discharge may reach loads of 1000 kg $NO_3^-$-N d$^{-1}$ (data recorded in January 2017 after intense precipitation) (Álvarez-Rogel et al., 2020). These watercourses run mostly dry and the presence of surface water is subjected to rainfalls yet without generating a surface flow. The absence of a steady surface flow allows terrestrial shrubs from small to high size to grow within the river channel (e.g. *Tamaris* sp., *Nicotiana glauca*, *Carduus* sp.). The intense agricultural activity nearby has profoundly modified the natural riparian zone in many of them and vegetation is almost absent (Table 1 Supp. Material). With some exception, most of the study riverbeds sediments had a sandy texture mixed by small
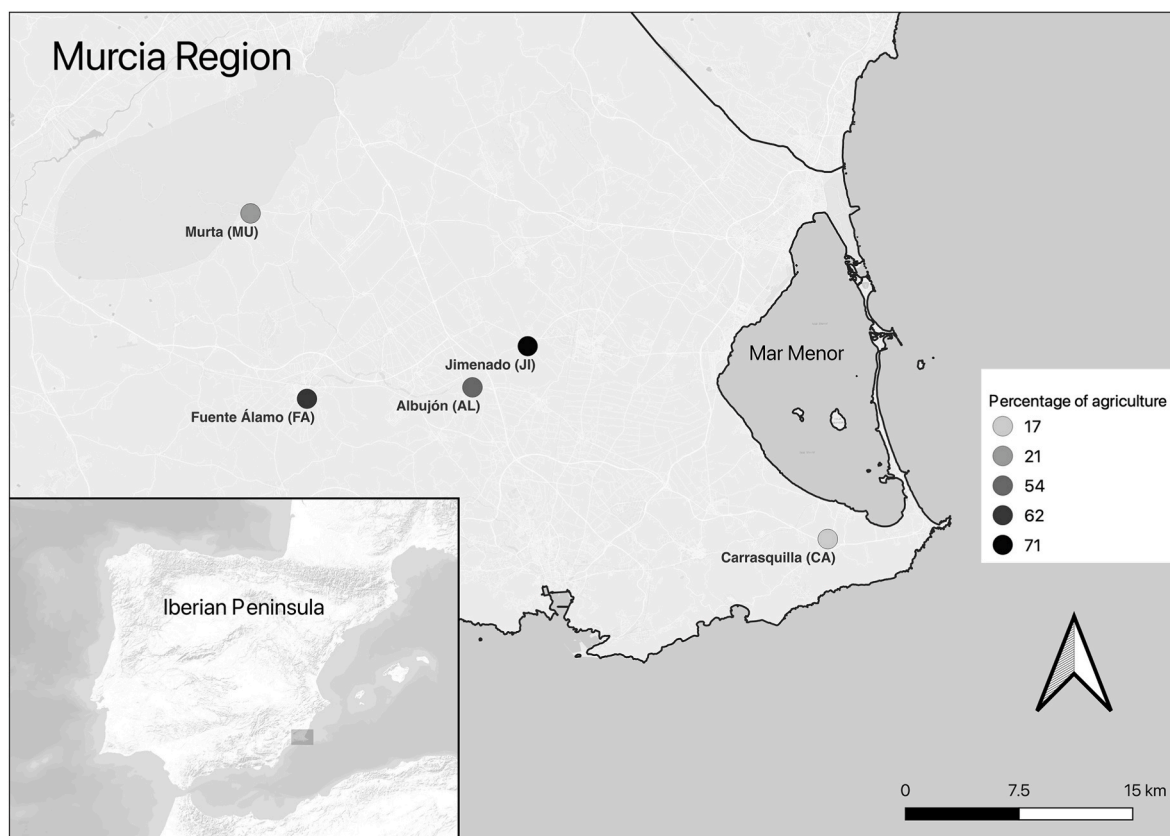
**Fig. 1.** Campo de Cartagena watershed. The location of the selected sampling points in five riverbeds is shown by circles. The extent of agricultural land use (expressed in %) is also indicated and represented by a grayscale in each sampling point. Basemap sources: ESRI Light Gray and ESRI Terrain.

gravels (Table 1 Supp. Material). Sediments are characterized by an organic matter content ranging from 3.3 to 1.1% and by conductivity which varied from 328 to 102 μs/cm. Sediment pH was less variable, ranging from 8.1 to 9.0 (Table 1 Supp. Material).

### 2.2. Watershed delineation and land cover characterization

Specific watershed boundaries for each point were delineated from a 20 m raster digital elevation model (DEM) using the multiple flow direction algorithm implemented in GRASS GIS 7.8 (GRASS Development Team, 2020). Watersheds' area ranged from 920 ha to 41,108 ha. Percentage of irrigated cropland areas in each watershed was calculated using the CORINE land cover map from year 2012 of 100 m resolution (EEA, 2016).

### 2.3. Field survey and sampling collection

Field sampling was performed twice to cover summer (July 2018) and winter (January 2019) processes. In both dates, the five study sites were dry, i.e., with absence of surface water. Three replicate points were established along a 50 m reach in each site to assess the effect of short-term rewetting on gaseous fluxes and to collect sediment samples for the different laboratory analysis.

To allow the short-term rewetting study in the field, 3 PVC-soil gas chambers (height = 11 cm, diameter = 30 cm, volume 7.7 L) were built. One month in advance, a permanent collar of similar dimensions was placed into sediments with help of a shovel to allow sediment structure to be stable before gas sampling. Collars were kept in the study sites over the whole study with the purpose of avoiding the disturbance of in-situ conditions before examining gas fluxes.

Sediments were collected in each study site with a hand shovel nearing to the PVC chambers. Sediments were sieved (2 mm mesh) and stored in plastic bags for their transport to laboratory and analyzed within the next 24–48 h.

### 2.4. Short- and long-term rewetting experiments

$CO_2$ and $N_2O$ fluxes under dry and short-term rewetting conditions were studied in each river and date. The PVC- soil collars (n = 3) previously installed in each sampling site were closed using the PVC chambers provided by a gas tight material around (Parkin and Venterea, 2010). Once chambers were installed, three gas samples were collected during 1.5 h of accumulation for characterizing the rate of $CO_2$ and $N_2O$ fluxes during dry (pre-wetting) conditions. Following that, chambers were removed to allow air circulation over sediments and a short rainfall of 20 mm was applied by watering the sediment chamber area by using pure water. This rainfall amount was selected based on the most frequent precipitation of the study area over a year. Immediately after water addition, chambers were again placed on the collar and four gas samples were collected over 2 h for characterizing $CO_2$ and $N_2O$ fluxes upon wetting. Gas samples were taken by using a 20 mL plastic syringe and stored in 12 mL pre-evacuated gas vials (Exetainer Labco Limited, UK). Gas samples were transported to laboratory and analyzed within the next 24 h using Gas Chromatography (VARIAN CP-4900 Micro-GC, Palo Alto, CA, USA).

$CO_2$ and $N_2O$ fluxes under dry and long-term rewetting conditions over a 16- days -period were also studied in the laboratory. Approximately 100 g of dry sediment (n = 3 replicates in each study site) were placed in incubation polypropylene bottles (250 mL) provided with septa caps to allow head-space gas sampling. Sediments were wetted by using pure water until achieving a saturation of 80% expressed as Water Field Pore Space (WFPS), high enough to maintain sediments wetted over the course of the experiment.

Gaseous fluxes were monitored during dry conditions (t = −0.5

days), immediately after water addition (t = 0 days) and several times during post wetting (t = 0.5, 1, 2, 3, 4, 5, 6, 9, 11, 14 and 16 days) by directly measuring the head-space gas concentrations in the Gas Chromatograph. In each monitoring event, bottles were closed for 30 min to measure the head-space gas concentrations. Between sampling times, bottles were open and aerobically incubated in a climate chamber under dark conditions at 25 °C. Bottles were weighted at each sampling time to monitor changes in %WFPS over time. Unlike the short-term rewetting performed in the field, with this experiment we mimic a rainfall-induced rewetting that drives sediments to long-term saturation, which may help anoxic conditions to temporally develop and trigger a potential $N_2O$ flux derived from denitrification. Sediments were characterized for $NO_3^-$ content (see section below) prior to incubation and after the end of the incubation (t = 16 days) to examine the net variation in the concentrations if compared with dry conditions (t = −0.5 days). Thus, in each site and date a delta value ($\Delta NO_3^-$) was calculated to express the net changes in $NO_3^-$ concentrations as:

$$\Delta NO_3^- = NO_{3\,t-0.5}^- - NO_3^-$$

where positive values indicated a net loss of the nutrient at the end of rewetting.

All measured gas concentrations in both field and lab experiments were converted to mass units through the application of the Ideal Gas Law:

$$n = (P \times V) / (R \times T),$$

where $n$ is the number of moles/volume concentration (e.g. moles $C–CO_2\,L^{-1}$ or $N–N_2O$ enclosure), $P$ is the barometric pressure, $V$ is the vol/vol concentration (trace gas concentration expressed in ppmv or μL $C–CO_2\,L^{-1}$), $R$ is the universal gas constant (0.0820575 L atm $K^{-1}$ $mol^{-1}$), and $T$ is the air temperature expressed in K. By using the molecular weight of the trace gas species (e.g. 12 μg $C–CO_2$ per μmol $CO_2$) the number of moles were converted to concentration values ($C_m$). They were then used to calculate gaseous fluxes via linear regression of headspace gas concentration versus time elapsed since the plug placement and considering field chamber headspace and the sediment area by means of the following equation:

$$f = (\Delta C_m / \Delta t \times V_{hs}) / A,$$

where $f$ is gas flux as mass of C or N as $CO_2$ or $N_2O$, respectively per area and time expressed as mg C $m^{-2}\,h^{-1}$, $\Delta C_m/\Delta t$ is the change in concentration of gas ($C_m$) over the enclosure period time expressed as mg C $m^{-3}$ $h^{-1}$, $V_{hs}$ is internal volume of the headspace expressed as $m^3$ and $A$ is the sediment area expressed as $m^2$.

In the case of laboratory experiment, gas fluxes were calculated as ng C or N $h^{-1}\,g^{-1}$ DM (dry mass) considering the change in concentration of gas ($C_m$) over the enclosure period time expressed as ng C L$^{-1}$ h$^{-1}$, $V_{hs}$ as laboratory chamber headspace expressed as L and mass of dry sediment expressed as g. We also calculated cumulative N and C emissions from each incubation assuming linear changes in fluxes between adjacent monitoring points (Velthof et al., 2003).

### 2.5. Chemical and biogeochemical analyses

In each date, sediment samples (n = 3 replicates) of each study site were characterized by water content (WC), organic matter (OM) percentage, extractable inorganic N ($NO_3^-$ and $NH_4^+$), dissolved organic C (DOC), and for the following biogeochemical processes: denitrifying enzymatic activity (DEA), substrate induced respiration (SIR) and ammonia oxidation. Sediment WC and OM % were calculated, respectively, after drying 10 g of subsample for 24 h at 100 °C and after combustion of dried subsamples for 4 h at 550 °C.

Sediment inorganic N and DOC were extracted in a proportion 1:5 (sediment: liquid). Ammonium ($NH_4^+$) was extracted by using KCl 2 M

while $NO_3^-$ and DOC were extracted by using ultrapure water. Approximately 10 g of sediment was agitated during 2 h in 50 mL Falcon® inert tubes by using a rotary shaker. Afterwards, tubes were centrifuged at 3400 rpm and the supernatant was filtered through pre-combusted Whatman GF/F filter (England, UK). Subsamples for $NH_4^+$ were immediately determined by using the colorimetric method based on Berthelot's reaction (Sommer et al., 1992). Subsamples for $NO_3^-$ and DOC were frozen and further determined by ionic chromatography (HPLC, model 861, Metrohm AG, Herisau, Switzerland) and a TOC-analyzer (Analytik jena multi N/C 3100, Germany), respectively. They were expressed as μg or mg of N or C per g of dry mass (DM). These amounts are considered soluble nutrient and C potentially released from sediments after a rewetting event to water column when flow resumes. SIR was measured by incubating in the dark and in an orbital shaker (100 rpm) 20 g of field-moist sediment subsamples with a 20 mL of C-glucose solution (1.5 mg C $g^{-1}$ DM) in 25 mL flasks provided with septum caps (Fromin et al., 2010). Head-space gas was sampled four times over 6 h of incubation period to determining concentrations of $CO_2$ using a gas chromatograph (VARIAN CP-4900 Micro-GC, Palo Alto, CA, USA). SIR was expressed as mg C–$CO_2$ $h^{-1}$ $g^{-1}$ DM.

DEA was determined according to Čuhel et al. (2010). Briefly, sediment slurries were made by mixing 25-g field-moist soil samples in 120-mL serum bottles with 25 mL of a solution containing 1 mM glucose, 1 mM $KNO_3$ and 1 g $L^{-1}$ chloramphenicol. Bottles were capped with rubber stoppers, evacuated, and flushed four times with 99.99% He. The slurries were then incubated without (DEA-) and, subsequently, with acetylene ($C_2H_2$) (DEA+) to block the conversion of $N_2O$ to $N_2$ (10%, v/v) on an end-to-end shaker at 25 °C. After 30 and 60 min $N_2O$ was quantified using gas chromatography (VARIAN CP-4900 Micro-GC, Palo Alto, CA, USA). Finally, DEA was calculated from the $N_2O$ increase during half an hour incubation (30–60 min) from the $C_2H_2$ treated sediments. The fraction of $N_2O$ converted into $N_2$ fraction was calculated as the difference between $N_2O$ concentration in the slurries incubated with $C_2H_2$ and the same slurries incubated without $C_2H_2$.

Ammonia oxidation was measured following the $C_2H_2$ gas inhibition method at a partial pressure of 100 Pa (Offre et al., 2009). This method allows measurements in sediments under actual humidity, which is not possible when using other methods that involve the addition of the inhibitor in a water solution (Merbt et al., 2016). For each sediment replicate, two flasks (125 mL) fitted with septa caps were incubated with 10 g of sediments for 72 h, with or without $C_2H_2$ (inhibited/control flasks). Every 24 h, all bottles were opened for 30 min to ensure continuous aerobic conditions for ammonia oxidation. Afterwards, $C_2H_2$ was added again to the blocked flasks. At the end of the incubation, sediment $NH_4^+$ concentration was analyzed after conducting a KCl extraction as previously described. The quantity of $NH_4^+$ oxidized was calculated as the difference in extractable $NH_4^+$ between the inhibited and control flasks after incubation. Ammonia oxidation rates were expressed as μg $NH_4$–N $g^{-1}$ DM $h^{-1}$. Negative values involved a net ammonia production during incubation (that is, ammonification).

### 2.6. Data processing

To examine differences on the study variables between rivers in dependence of the date, we used two-way repeated measure analyses of variance (RM-ANOVA) (SPSS software, IL, USA). *Date* (summer and winter) was set as the within-subject factor while *river* was included as between-subject factor. Similarly, differences between dry and short-term rewetting on gaseous fluxes across rivers were accounted by two separated RM-ANOVA in each date. In these analyses, the factor *dry-rewet* (that is gas flux under dry conditions and after water application) was set as within-subject factor and *river* was set as between-subject factor. The change of $CO_2$ and $N_2O$ fluxes rates in response to the long-term rewetting were examined graphically over the monitoring events (t = −0.5, 0, 0.5, 1, 2, 3, 4, 5, 6, 9, 11, 14 and 16 days) (SigmaPlot, Systat Software, CA, USA).

A Principal Component Analyses (PCA) (PRIMER software, England, UK) with the agricultural landuse (AG) % and the chemical and biogeochemical variables was done to explore their relationship and visualize their variation at once across the study rivers and seasons. All variables were standardized to mean 0 and variance 1 before being included in the PCA. The significance of each variable on the axes was determined through Pearson correlations between variables and axes scores. Besides, simple linear regressions were also done to assess the significance of the relationship between variables (SPSS software, IL, USA).

Variables were log(x) transformed when necessary to meet the criteria of normality of the data distribution and of homogeneity of variance analyses. Significant values were considered at P < 0.05 and marginally significant when 0.1 < P < 0.05.

## 3. Results

### 3.1. Short-term rewetting effects on gas fluxes

The water applied to simulate the short-term rewetting in the field led to a variable increase in the sediment WC % among rivers; between 2.5 and 14 times in summer and between 1.4 and 6.5 times in winter (Fig. 2a and b). During the dry conditions and following the short-term rewetting we only detected fluxes for $CO_2$, while $N_2O$ fluxes were no observed for any river during our study. Overall, $CO_2$ fluxes were lower in winter than summer in all rivers both under dry and after water application (Fig. 2c and d). Besides, a significant effect of short-term

rewetting on $CO_2$ fluxes were only found during summer (Fig. 2c), which depended on the study river (RM-ANOVA interaction term *dry-rewet x river*: F = 12.62, P = 0.001). In this season, $CO_2$ fluxes raised after rewetting in some impacted (AL and JI) and non-impacted sites (CA) (Fig. 1), while in the rest of rivers, fluxes decreased after the water pulse, especially in MU (Fig. 2c). In winter, fluxes of $CO_2$ after rewetting were not significantly different if compared with dry conditions in all sites (P > 0.05) (Fig. 2d).

### 3.2. Long-term rewetting effects on gas fluxes

The initial WFPS of 80% hardly decreased after 16 days of incubation reaching final values of average 76% (±0.13, SE) and 77% (±0.16, SE) in summer and winter, respectively (Data not shown). Unlike short-term rewetting, long-term rewetting in laboratory triggered marked changes in the rates of both $CO_2$ and $N_2O$ fluxes in all study rivers. Yet, the behavior of fluxes as rewetting time progressed was not the same for all rivers (Fig. 3a,b,c,d).

Rewetting increased fluxes of $CO_2$ in all sites immediately (t = 0 days) and during post-wetting especially in the summer experiment (Fig. 3a and b). In this season, both the least and most agriculturally-impacted sites (CA and JI, Fig. 1) showed the highest fluxes which peaked with average values of 2,350 and 1,680 ng C $h^{-1}$ $g^{-1}$ DM after 6 and 9 days, respectively (Fig. 3a). In the winter experiment (Fig. 3b), however, rewetting triggered $CO_2$ fluxes with a lower magnitude if compared with summer and in fact, negative fluxes were still observed for some study sites upon rewetting at t = 1 day (Fig. 3b). The
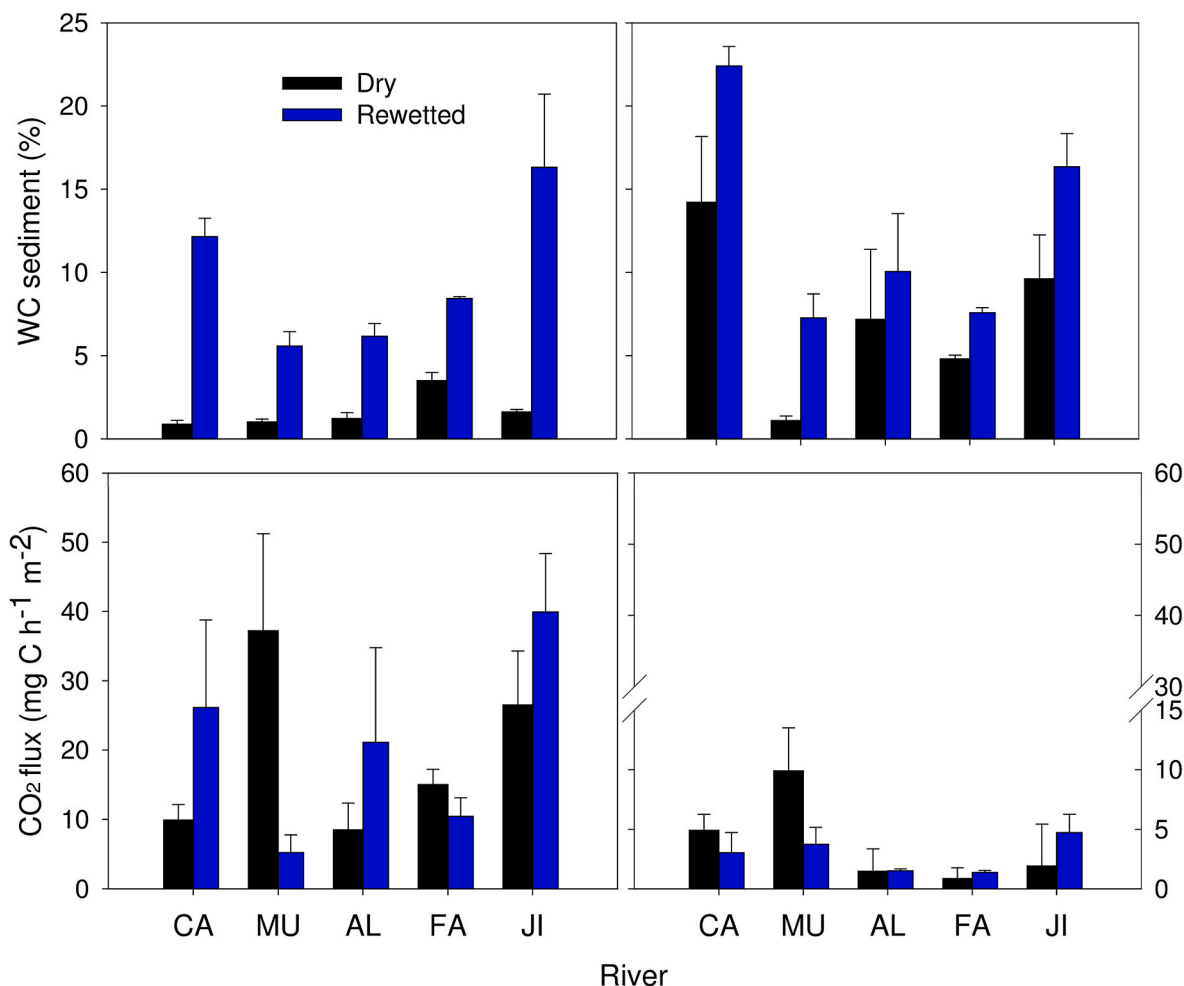
**Fig. 2.** Mean (±SE) sediment water content (WC) % and $CO_2$ fluxes during dry and after the simulated short-term rewetting in field across the study rivers in summer (a,c) and winter (b,d). The study rivers are placed from left to right following the increasing agricultural land use percentage.
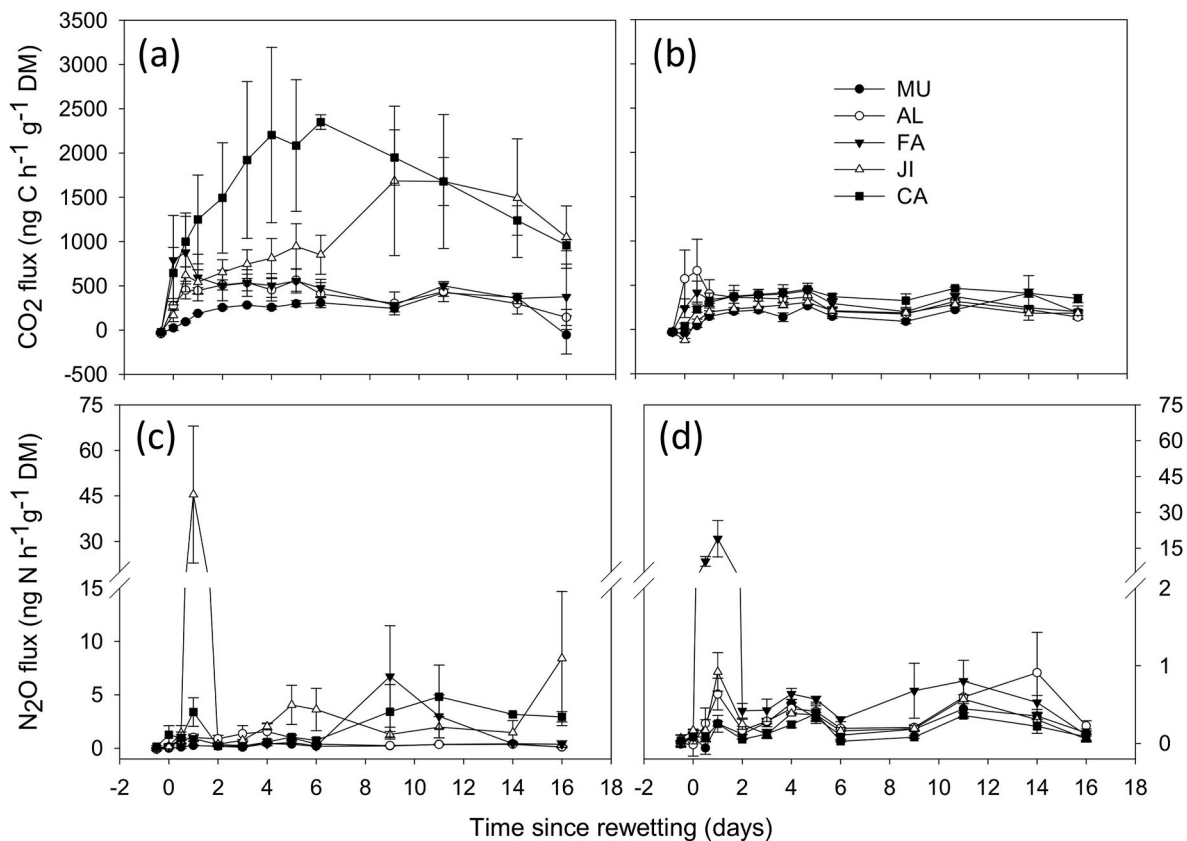
**Fig. 3.** Mean (±SE) $CO_2$ and $N_2O$ fluxes during the simulated long-term rewetting in laboratory in each study river in summer (a,c) and winter (b,d).

cumulative fluxes for $CO_2$ after 16 days rewetting were higher in summer than winter, but they were only significant in the case of the most different study sites CA and JI (Figs. 1 and 4a) (RM-ANOVA interaction term *date x river* F = 6.97, P = 0.006).

In relation to $N_2O$, rewetting also triggered positive fluxes in all study sites with several peak values found over experimental time (Fig. 3c and d). An important peak of 30 ng N $h^{-1}$ $g^{-1}$ DM was observed in the summer experiment after 1 day of rewetting in the most anthropogenically impacted site (JI), followed by the least impacted site (CA) (Fig. 1) which exhibited a $N_2O$ flux of 3.4 ng N $h^{-1}$ $g^{-1}$ DM (Fig. 3c). In winter, the larger fluxes were found in the rivers more impacted, especially in FA with a peak value of 15.4 ng N $h^{-1}$ $g^{-1}$ DM at t = 1 day (Fig. 3d). Following the first day of rewetting, the emissions dropped down to values below 8 and 1 ng $N_2O$–N $h^{-1}$ $g^{-1}$ DM in summer and winter seasons, respectively. (Fig. 3c and d).

Like $CO_2$, cumulated fluxes for $N_2O$ after 16 days of rewetting were also higher in summer than in winter for the least- (CA) and most-impacted site (JI) (Fig. 1), while the rest of rivers showed similar values (RM-ANOVA interaction term *date x river* F = 4.00, P = 0.034) (Fig. 4b).

Also for the least- (CA) and most-impacted site (JI), the positive $\Delta NO_3^-$ values calculated in both seasons between dry conditions (t = −0.5 days) and the last rewetting day (t = 16 days) indicated a net loss of $NO_3^-$ (Fig. 4c). The negative $\Delta NO_3^-$ values observed in the rest of sites indicated net enrichment in sediment $NO_3^-$ at the end of the period (Fig. 4c). Between seasons, two of the most impacted sites (FA and JI, Fig. 1) showed differences in the average $\Delta NO_3^-$, yet, as a result of the high variability of the data, such differences were only marginally significant (RM-ANOVA interaction term *date x river* F = 3.31, P = 0.063).

### 3.3. Biogeochemical features

$N_2O$ emitted when acetylene ($C_2H_2$) was added to the rubber-septa bottles reflects the total denitrifying potential of the studied riverbed sediments (DEA+, Fig. 5a), as $C_2H_2$ blocks the last step of denitrification (from $N_2O$ to $N_2$). Across rivers, both non-impacted and impacted sites (CA and FA, respectively, Fig. 1) had the largest DEA + rates in summer, season when the rivers, in turn exhibited higher rates if compared with winter, with exception of MU (RM-ANOVA interaction *date x river* F = 35, P < 0.001). In fact, no detected DEA+ were found in some rivers during the winter experiment. Compared to DEA+, DEA rates without $C_2H_2$ (DEA-) were very low irrespectively of the study site, and indeed we did not detect derived $N_2O$ emission in winter in most of the rivers (Fig. 5b).

The percentage of $N_2O$ reduced to $N_2$ calculated by the riverbed sediments during the study was generally high, ranging between 80 and 100%, showing the capacity of the sediments to perform the complete denitrification process to $N_2$. Only in summer, the most impacted site (JI, Fig. 1) presented a lower capacity of 50%.

Between seasons, respiration rates (SIR) appeared larger in summer than in winter in the impacted rivers, while in the least disturbed sites (CA and MU, Fig. 1), this process did not appear significantly different (Fig. 6a) (RM-ANOVA interaction term *date x river* F = 7.46, P = 0.005). Across rivers, the highest SIR rates were found in the most contrasted sites, CA and JI in summer (Fig. 6a).

In the case of ammonia oxidation rates (Fig. 6b), RM-ANOVA did not detect differences among seasons and study rivers probably because rates showed a very irregular pattern with most rates close to zero.

In relation to water and nutrient content in sediments, RM-ANOVA detected significant differences across study sites and dates for all variables (interaction term *date x river* P < 0.05, Fig. 7a,b,c,d). WC% in riverbed sediments at the time of sampling was considerably higher in winter than in summer, from 6 to 16 x higher, with the exception of MU and FA where WC% hardly varied (Fig. 7a). Across the rivers (Fig. 1), the most impacted site, JI, showed the largest values in the concentrations of both N species and DOC in summer (Fig. 7b,c,d), while the least
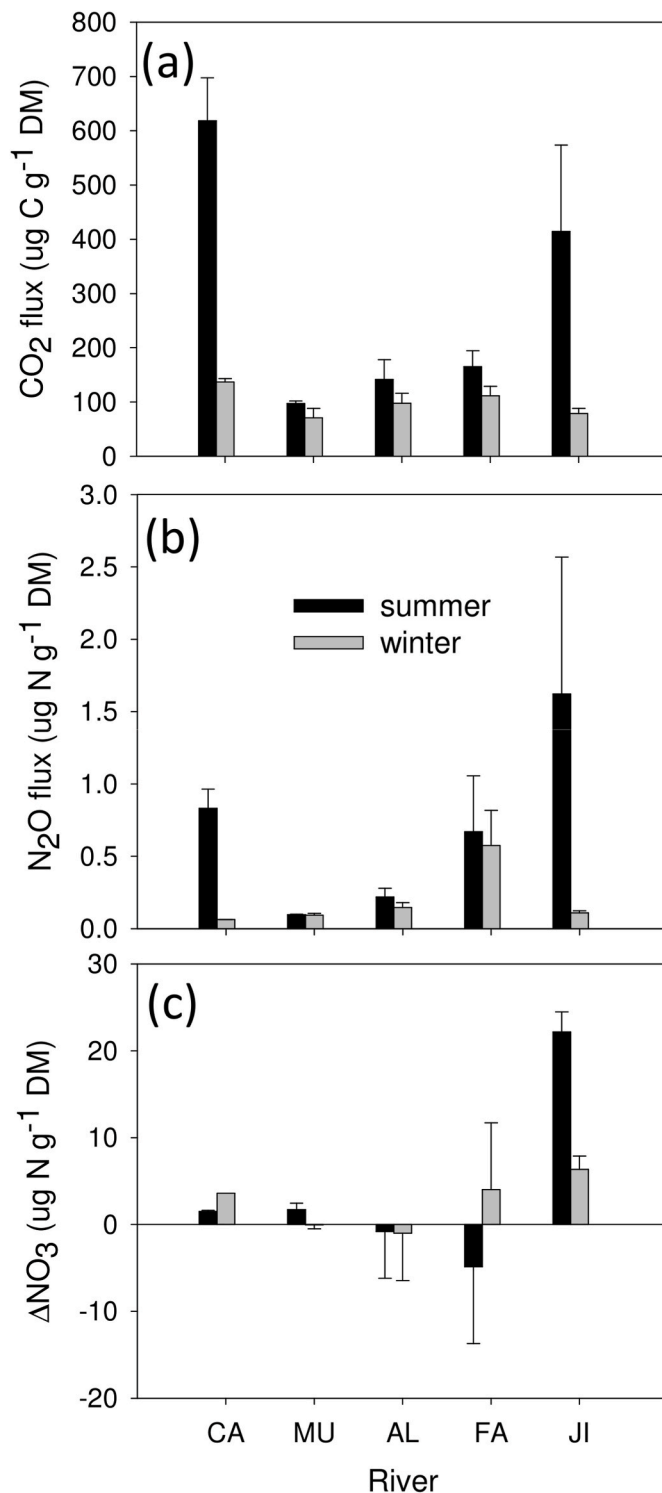
**Fig. 4.** Mean (±SE) cumulative $CO_2$ fluxes (a) $N_2O$ fluxes (b) and net loss of sediment $NO_3^-$ (c) content during the long-term rewetting in each study river and date. The rivers are placed from left to right following an increasing agricultural land use percentage.

impacted site, CA, presented the lowest amount of $NO_3^-$ (Fig. 7b) but moderate levels of $NH_4^+$ and DOC (Fig. 7c and d, respectively). Between seasons, concentrations of $NO_3^-$ and DOC were higher in summer than in winter in all sites (Fig. 7b,d). Concentrations of $NH_4^+$ exhibited the opposite pattern, with exception of the most impacted site JI (Fig. 7c).

### 3.4. Linkages between variables

The PCA explained 66.2% of the variance observed across rivers and seasons (Fig. 8). The axis 1 explained 45.5% of the variance and correlated negatively with DOC, DEA (+), SIR, $CO_2$ fluxes after short-rewetting and cumulative fluxes of CO2 and $N_2O$ after long-term rewetting (Pearson correlations P < 0.05). Through axis 1, PCA well separated streams by dates showing the highest values for most biogeochemical variables in summer than in winter, with exception of MU. The axis 2 condensed 20.8% of the variance and correlated positively with AG%, sediment $NO_3^-$ and $NH_4^+$ and $\Delta NO_3^-$ after long-term rewetting (Pearson correlations P < 0.05). Through axis 2, PCA reflected how the agriculturally impacted rivers (higher AG%); FA and especially JI, tended to have the highest sediment N content and $\Delta NO_3^-$ if compared with the least agriculturally impacted sites (that is, CA and MU) (Fig.1).

## 4. Discussion

### 4.1. Gas fluxes during dry conditions

As expected, rivers in the study region were net emitters of $CO_2$ during dry conditions, especially in summer. These results agree with recent studies that recognize dry inland waters as active sites for $CO_2$ emissions and support the importance of considering these habitats within the global estimations of C emissions (Keller et al., 2020; Marcé et al., 2019; von Schiller et al., 2014).

Our highest $CO_2$ fluxes measured *in situ* in dry riverbed sediments in summer varied from 8.5 to 37 mg C $h^{-1}$ $m^{-2}$, notably lower than fluxes reported in dry sediments of a temperate intermittent stream in Germany (235 mg C $h^{-1}$ $m^{-2}$, Arce et al., 2021) and other dry streambeds of Mediterranean climate in north Spain (390 mg C $h^{-1}$ $m^{-2}$, Gómez-Gener et al., 2016). Moreover, our detected rates are in the lower range reported by Keller et al. (2020) in a recent global survey for other dry inland waters from arid regions (mean ± SD = 118 ± 235 mg C $h^{-1}$ $m^{-2}$ median = 30). Such comparative highlights a lower processing of C in arid climates probably in response of limited availability of water and supply of organic matter (≤3.3% in our study sites). Despite low emissions, our results support the notion that microbial respiration can be maintained at some extent in dry rivers and provide punctually $CO_2$ to atmosphere (Koschorreck et al., 2022). As described in terrestrial soils (Schimel, 2018), extreme water fluctuations in dry riverbeds select taxa capable to live under such conditions (Romaní et al., 2017). Besides, microbes develop strategies to cope with water stress, as for instance thicker cell walls in gram positive bacteria and fungi, and the production of extracellular polymeric substances (Romaní et al., 2017). Other studies have described the existence of extracellular enzyme activity in dry conditions which can exert an important function on the decomposition of organic C and respiration (Pohlon et al., 2018). In winter, despite sediments having more humidity (higher WC%), $CO_2$ emissions decreased, reflecting the sensitiveness of microbial C decomposition to temperature (Keller et al., 2020; Liang et al., 2016). Among all study sites, MU, one of the less impacted rivers (Fig. 1), had the largest $CO_2$ emissions under dry conditions, probably as a result of a high proportion of gravel and sandy in the sediment texture; this being also a considerable factor to support with more or less extent the gas exchange with the atmosphere (Gómez-Gener et al., 2016).

Unlike $CO_2$, we anticipated that desiccated sediments exposed to atmosphere would support low $N_2O$ production based on the notion that denitrifying activity is limited due to lack of anoxic environments, as suggested in other dry riverbeds (Arce et al., 2018; Gallo et al., 2014; Gómez et al., 2012). The undetected $N_2O$ emissions in the study sites during dry conditions confirm this notion. Using $^{15}N$ isotope pairing technique Pinto et al. (2022) found that the process of drying in stream sediments, that is, the transition from wet to dry, may support $N_2O$ production via ammonia oxidation and denitrification. However, the
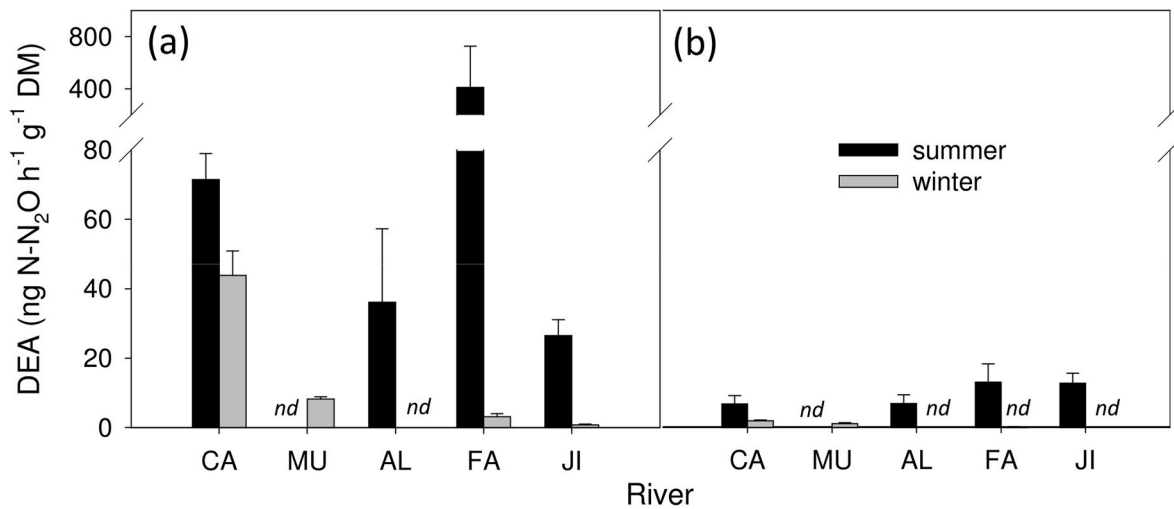
**Fig. 5.** Mean (±SE) denitrifying enzyme activity (DEA) blocked (a) and unblocked (b) with acetylene in each study site and season. The rivers are placed from left to right following an increasing agricultural land use percentage. Nd = non detected values.
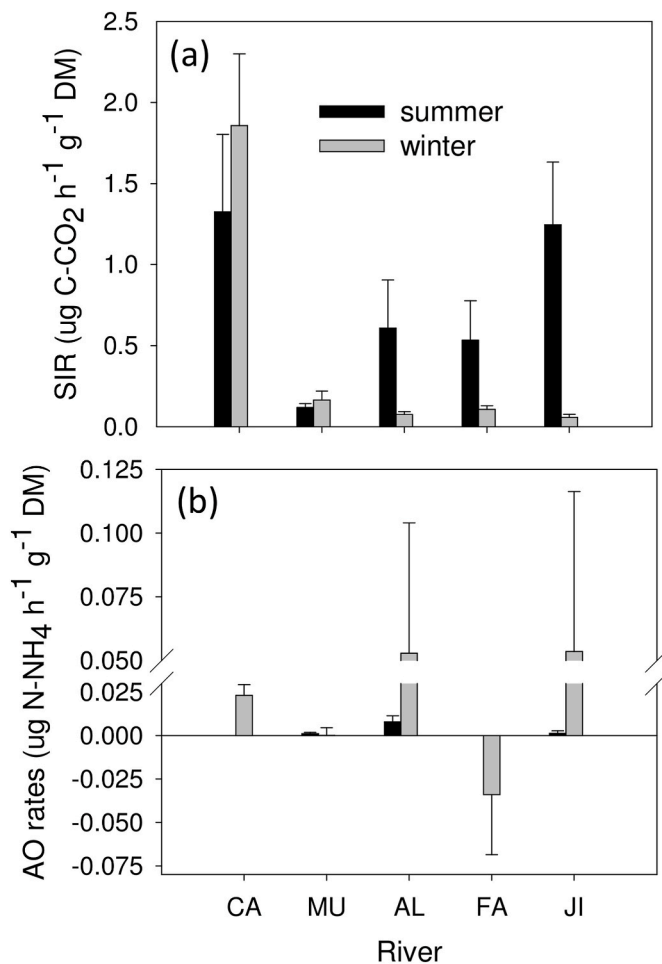


**Fig. 6.** Mean (±SE) substrate induced respiration (SIR) (a) and ammonia oxidation rates (b) in each study stream and date. The rivers are placed from left to right following an increasing agricultural land use percentage.

study locations had sediments extremely dry with a humidity (WC%) ranging from 0.7 to 6% during our study, likely still low to support a substantial microbial processing. In fact, we measured very low ammonia oxidation rates in summer likely due to very low sediment

humidity (low WC%). Ammonia oxidation appeared positively correlated with WC reflecting the importance of humidity for this process as previously reported in other streambed sediments across temporal progression of desiccation (Arce et al., 2018). Thus, given the low ammonia oxidizers activity detected, derived emission of $N_2O$ from this process could be neglected (Liang et al., 2016).

Compared to $CO_2$, we propose that ephemeral watercourses are irrelevant spots of $N_2O$ during extreme desiccation since the potential microbial sources, that is ammonia oxidation and denitrification could be constrained by low water availability and nutrient supply diffusion as it also happens in other water-stressed regions (Manzoni et al., 2012; Sponseller, 2007).

### 4.2. Response of gas fluxes to rewetting

As predicted, short-term rewetting triggered $CO_2$ fluxes in most rivers but no $N_2O$ response was observed. Only when we run the long-term rewetting in the sediments, pulses of $N_2O$ were detected. Our short-term approach developed between 4 and 6 h following a punctuated rewetting of 20 mm which led increases in WC% up to 15% and up to 22% in summer and winter, respectively, was enough to trigger a $CO_2$ flux in the rivers. As initially hypothesized, microbial respiration of C tends to reactivate quickly when water arrives (Placella et al., 2012; von Schiller et al., 2019) in accordance with the "*Birch effect*" described in soils (Birch, 1958); a set of biogeochemical responses that involve the decomposition of labile soil organic matter. Rapid microbial growth and wetting-enhanced substrate availability (Borken and Matzner, 2009) can drive stimulation of C emissions. In fact, variation of DOC and SIR rates, a proxy of microbial C respiration activity in sediments, correlated with $CO_2$ flux upon short-term rewetting across study sites and dates. This finding supports the positive effect of water on microbial metabolism in close association with the availability of organic matter (Sponseller, 2007); this response in turn, favored by warm temperatures of summer, denoting again the sensitiveness of C processing to temperature (Liang et al., 2016). Overall, our results partially agree with previous findings in dry sediments on the effect of short-rainfalls. For instance, in similar studies, large pulses not only of $CO_2$ but also $N_2O$ were detected 2 h after a similar artificial rainfall of 21 mm (Arce et al., 2018, 2021). Yet, these studies were conducted in dry sediments of a temperate -more humid-region than the study watershed, more water stressed and with lower organic matter in the soils which would contribute to explain the contrasted findings.

In semiarid ephemeral watercourses in USA, a climatic region similar to our study area, Gallo et al. (2014) observed maximum pulses of $CO_2$
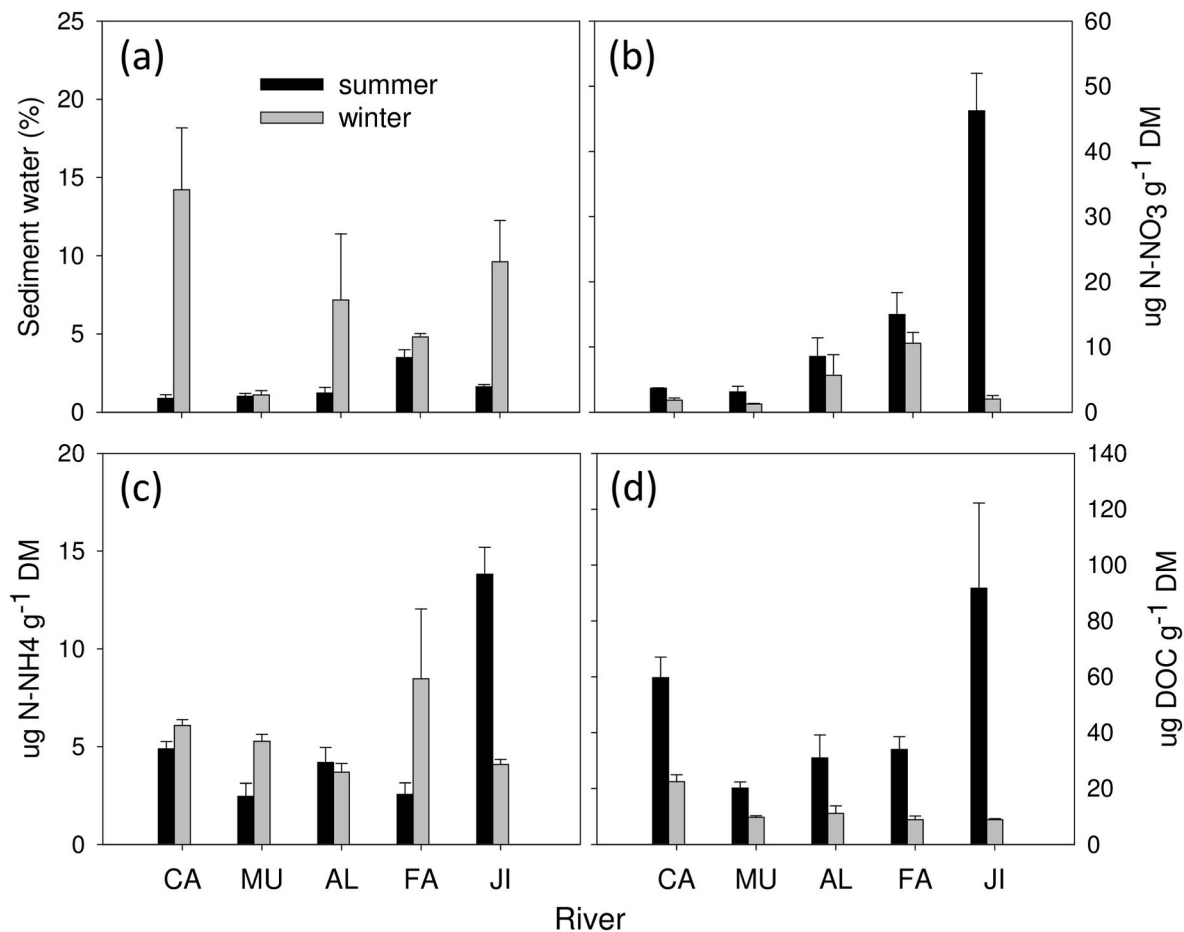
**Fig. 7.** Mean (±SE) sediment water content (%) (a) nitrate (b), ammonium (c) and dissolved organic carbon (DOC) (d) in each study river and season. The rivers are placed from left to right following an increasing agricultural land use percentage.

and $N_2O$ immediately after simulated rainstorm up to 1,588 mg C h$^{-1}$ m$^{-2}$ and 3 µg N h$^{-1}$ m$^{-2}$, respectively. Our maximum fluxes of $CO_2$ upon short-term rewetting were comparatively lower. For instance, the highest increases we found were up to 26 and 40 mg C h$^{-1}$ m$^{-2}$ in the two most different rivers (CA and JI, respectively, Fig. 1) more similar to the mean flux 6 h post-wetting reported also by Gallo et al. (2014) for sandy sediments of dry watercourses (45 mg C h$^{-1}$ m$^{-2}$). Despite being also a semiarid region, the lower amount of water applied in our study could also explain the low flux we measured after short-term rewetting for $CO_2$ and the null flux detected for $N_2O$. We did not simulate a rainstorm, instead we selected 20 mm of precipitation based on the annual mean precipitation of the study area. Despite small and scattered, these precipitation events in the Mediterranean year-round are likely enough to boost high microbial respiration and resultant emissions of $CO_2$ from dry watercourses as observed in other arid regions (Sponseller, 2007).

The response of gas emissions to rewetting is controlled by both biotic and physical factors (Arce et al., 2021). Besides microbial respiration, physical displacement of gases accumulated in sediments during the precedent dry phase can take place after water addition (Kim et al., 2012). We do not discard this physical effect to explain the rapid flux of C we observed in the study rivers. Indeed, the extraordinary large fluxes reported by Gallo et al. (2014) just after water addition in the extremely dry streambed sediments were attributed to a physical evasion.

Surprisingly, despite being strongly water limited systems, $CO_2$ fluxes prior to short-term rainfall in some sites were considerable higher than fluxes measured after water arrival, as found in one of the less impacted site, MU (Fig. 1). In agreement with previous observations (Arce et al., 2021; Looman et al., 2017), the sediment interstitial water

can act as a dilution media for the gas and ultimately buffers the transitory $CO_2$ exchange with atmosphere. The drop in the $CO_2$ observed in MU after rewetting could be attributed to this "dilution" effect favored by the gravels present in the sediments that allow rapid water infiltration.

The long-term rewetting experiment achieving a WFPS of 80% increased the WC% in the sediments in a range between 16 and 30%, relatively similar to the WC% reached in the field experiment. Yet, the laboratory approach allowed us to detect $N_2O$ emission as well as to assess the temporal dynamic and cumulative emissions of both C and N. Not surprisingly, $CO_2$ fluxes also increased in response to laboratory rewetting in most rivers, supporting the activation of microbial metabolisms upon re-hidratation. Besides, like the short-term rewetting, the response of $CO_2$ to long-term rewetting was also temperature sensitive (Liang et al., 2016) since all rivers exhibited low fluxes in winter. In our experiment, we observed a rapid increase in $CO_2$ fluxes after either the first or the second day of rewetting followed of a plateau state of no longer rise. This behavior agrees with the response of soils to rewetting when there is no extra source of substrate once those nutrients available during rewetting favoring respiration are consumed (Congreves et al., 2019; Fierer and Schimel, 2002). Importantly, we found increasing fluxes up to late rewetting in some instances. In our study, microbial activity (approached by SIR) and cumulative fluxes of $CO_2$ upon long-term rewetting appeared correlated in association with DOC availability. Thus, the increasing pattern observed the first days of rewetting in the summer experiment in the most differing sites within the study gradient; CAand JI (Fig. 1), suggested a strong support of respiration due to larger DOC availability until a threshold moment, when rates started to drop, consistent with the consumption of the
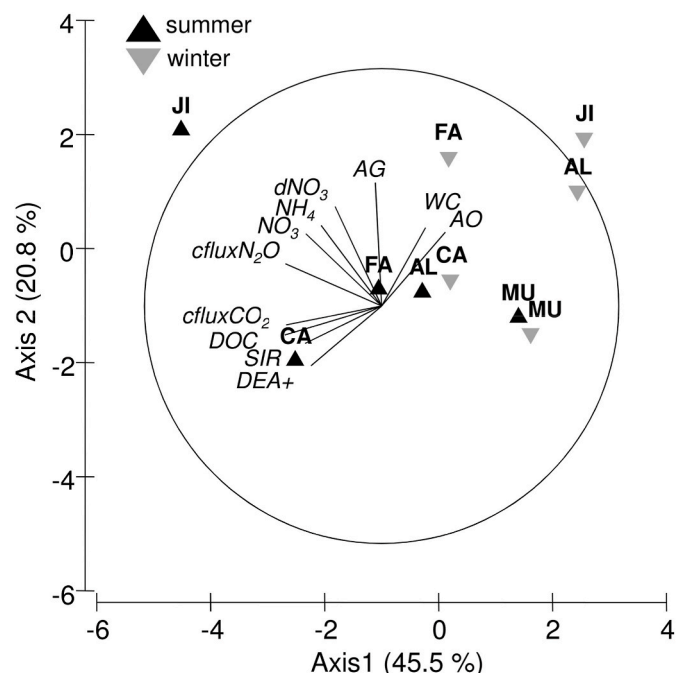
**Fig. 8.** Principal Component Analysis (PCA) of the study variables across rivers and seasons. AG: agriculture; WC: water content; AO: ammonia oxidation; DEA+: denitrifying activity (acetylene blocked); SIR: substrate induced respiration; cfluxCO$_2$ and cfluxN$_2$O: cumulative fluxes of CO$_2$ and N$_2$O, respectively after long-term rewetting; DOC, NO$_3$ and NH$_4$: content of dissolved organic carbon, nitrate and ammonium in sediments, respectively; dNO$_3$: delta value reflecting the net loss of nitrate in sediments after long-term rewetting.

wetting-liberated substrate (Congreves et al., 2019; Fierer and Schimel, 2002). We must note that the high DOC content observed in the sediments in CA and JI, which had the highest CO$_2$ fluxes and SIR during summer, should have a different source; natural vegetation and agricultural exudates (Lugato et al., 2014), respectively, according to their main land use in the watershed This would involve that uncontrolled expansion of agriculture may ultimately drive arid systems to be more heterotrophic by enhancing respiration and CO$_2$ emissions (Gu et al., 2022) beyond rates they could present under unaltered structure (i.e., natural riparian vegetation).

We initially hypothesized that denitrification-derived N$_2$O emissions may require long time to operate as hypoxic conditions develop (Arce et al., 2018). Using the $^{15}$N isotope pairing technique in a microcosm study, Pinto et al. (2022) measured fluxes of N$_2$O derived both from denitrification and nitrification after short and long-term rewetting of river sediments subjected to dry-wet cycles. Although we cannot assure which N-microbial pathway contributed most to N$_2$O emissions, our results provide to support denitrification to be a considerable process contributing to the N$_2$O emissions in dry riverbeds following rewetting conditions that may favor O$_2$ depletion (Zaady et al., 2013). In fact, as PCA reflected, denitrifying enzymatic activity (DEA+) and cumulative N$_2$O emissions appeared correlated across rivers and dates, which reflects the implication of this microbial process for N$_2$O formation upon rewetting, as seen in other agricultural soils (Thilakarathna and Hernandez-Ramirez, 2021a).

Although ammonia oxidation rates measured under dry conditions were generally low in the study rivers, we cannot discard the potential contribution of this process to N$_2$O formation upon rewetting within aerobic microsites (Congreves et al., 2019; Thilakarathna and Hernandez-Ramirez, 2021a) during the development of our experiment in some rivers.

As rewetting progressed in time, we observed that low N$_2$O emission remained stable until the end of the experiment. Like CO$_2$ fluxes,

cumulative N$_2$O fluxes variation across rivers were more linked to DOC than inorganic N availability suggesting the relevance of C availability for denitrification (Congreves et al., 2019; Fierer and Schimel, 2002). The importance of organic C as primary driver for biogeochemical pathways variation is plausible considering the poor vegetation coverage within dry riverbeds where DOC source is limited to inputs of either litter riparian plants or agricultural areas surround.

The emissions of N$_2$O detected in the study rivers were not high and the comparison between DEA(+) and DEA(-) suggested complete denitrification in most cases. However, this cannot be seen as a conclusive result since these findings can vary in space and time. Recognizing that dry watercourses close to human activities can emit or not considerable amounts of N$_2$O will depend on i) how far denitrification operates (N$_2$O or N$_2$) and its potential limitation by DOC ii) the implication of other mechanisms, such as nitrification. Further experiments which examine the different N$_2$O - microbial routes triggered after different rewetting events (of variable intensity) would help to disentangle mechanistic responses to rewetting and to know to what extent dry watercourses may act as net sources of N$_2$O over different hydrological conditions that take place in space and time.

Far from discerning the relative importance of microbial sources, our experiment allowed to visualize how certain rewetting phenomena can convert dry riverbeds in transitory sources of N$_2$O to atmosphere. While the role of dry inland waters to global CO$_2$ fluxes is being extensively assessed in the last years (Keller et al., 2020; Koschorreck et al., 2022; Marcé et al., 2019), the significance of these ecosystems as potential N$_2$O sources is still unknown and ignored from the global estimations (Yao et al., 2020). Thus, these rewetting events may be considered as an increasing key component of the dry riverbeds ecosystems when considered in their contribution to fluvial emissions of N$_2$O at larger scale.

### 4.3. NO$_3^-$ processing variation following an agricultural impact gradient

Anthropogenic disturbances to ephemeral rivers in arid regions are mainly associated with agriculture, grazing, urbanization, and energy development (Field and Lichvar, 2007). These types of landscape disturbances involve surface grading, vegetation removal, soil compaction, and groundwater withdrawals. These alterations/changes have both direct and indirect impacts on C and N biogeochemistry due to the inherent linkages among riparian vegetation, soil characteristics, surface water-groundwater interactions, and channel morphology in arid ecosystems (Levick et al., 2008; Shaw and Cooper, 2008). The intense irrigated agriculture in the study area, Campo de Cartagena watershed, has led to critical high concentrations of inorganic N in soils, which ends reaching dry watercourses included in the network drainage (Álvarez-Rogel et al., 2020).

In the summer study, the selected rivers showed in fact an increased content in NO$_3^-$ linked to a higher AG% landuse in the watershed. In this context we would expect higher potential denitrification activity in sediments of the most impacted sites when moisture limitation is removed. However, as shown by PCA results, the dentrification activity (DEA+) observed across the different sites and dates did not match with AG% landuse. In fact, the least impacted site in our selected gradient (that is CA, Fig. 1) showed denitrification and N$_2$O production rates upon rewetting (included cumulative N$_2$O emissions) similar to the most impacted and NO$_3^-$ rich-sites (that is, FA and JI, Fig. 1). We must note that with the exception of one of the less impacted sites, MU, the study rivers exhibited low and undetected DEA+ in winter denoting the sensitiveness of the process to low temperature though water limitation is removed. As a result, the vulnerability of the ecosystems to large inputs of NO$_3^-$ in cold seasons would increase whether denitrification operates at low rates despite rewetting events, which is particularly critical in the most impacted sites.

Interestingly, we found that the variation of denitrifying activity across rivers and dates appeared better related with DOC content in

sediments, rather than with $NO_3^-$ availability. As nitrate is usually plentiful in agricultural ecosystems, organic C availability may mediate denitrification variation (Arango et al., 2007). As we observed in the case $CO_2$ fluxes, sediment DOC either from native vegetation or from agricultural exudates also promoted $NO_3^-$ removal by denitrification which re-inforced the importance of C for microbial activity in the study rivers, regardless of the source.

The long-term rewetting experiment allowed us to estimate a final balance of $NO_3^-$ concentration in sediments to assess for the dynamics of N budgets within the riverbeds following active periods of rewetting. The largest positive $\Delta NO_3^-$, reflecting a net loss of $NO_3^-$, was found in the most impacted site (JI) in summer. In other agricultural sites, however, (AL and FA, Fig. 1), negative $\Delta NO_3^-$ indicated net formation of this nutrient during rewetting, thus supporting N-source processes (ammonification and nitrification) over N-sink pathways (denitrification and assimilation). In the case of JI, high $NO_3^-$ content could promote high $\Delta NO_3^-$, probably in response of favored denitrification. It seems that agriculturally affected sites may adjust their response to excess N by enhancing denitrification, (Weitzman et al., 2021), however, chronic $NO_3^-$ inputs to rivers minimize ultimately the effect of this mechanism in controlling the high $NO_3^-$ load.

On the other hand, we must not overlook the role of ammonia oxidation as an internal source of $NO_3^-$. As we previously discussed, following rainfalls, significant production of $NO_3^-$ may evolve (Congreves et al., 2019; Thilakarathna and Hernandez-Ramirez, 2021a) if well oxygenated conditions and no other competitive sinks of $NH_4^+$ co-occur in favor of a net ammonia oxidation. In Campo de Cartagena, organic fertilizers are commonly used in the agricultural soils and organic-N substances can reach rivers where are mineralized to ammonium, as observed in FA in winter (that is a negative net ammonia oxidation). Then, if a newly formed $NO_3^-$ from $NH_4^+$ appears during rewetting events it may contribute to saturate riverbeds sediments whether nitrate is not rapidly utilized through microbial routes, included denitrification (Thilakarathna and Hernandez-Ramirez, 2021b).

Finally, our results provide to support the notion that native vegetation may comprise a labile organic C source to support denitrification as seen in sediments from CA and MU, the least impacted sites. Even though agriculture can potentially support denitrification of $NO_3^-$ through C supply, its influence is temporal and may cease in response to harvesting periods. Avoiding removal of riparian vegetation of these river ecosystems would favor a steady input of organic matter which can fuel permanent N-processing and copes with the potential $NO_3^-$ pollution. Besides, the presence of riparian plants would also buffer the N-fertilizers inputs to the channel by biological assimilation and ultimately reduces the anthropogenic denitrification rates and potential emissions of $N_2O$.

## 5. Conclusions and implications

Our study supports early literature of dry inland waters seen as active spots in terms of C since we found that dry watercourses, impacted or not, are potential sources of $CO_2$ to atmosphere despite lack of surface flow. In terms of N, these rivers could act as transitory $N_2O$ sources when long rainfall-induced rewetting allows conditions to support microbial N-processing. The gas emission values observed in our study indicate that the relevance of dry watercourses is not as high as in other agricultural ecosystems and climates where water or organic matter availability is not limiting microbial activity. In fact, in our study DOC content was most important at explaining the variation of denitrification and $N_2O$ fluxes across the study gradient rather than the agriculture-associate nitrate. Elevated organic C also from agricultural exudates also seemed to drive large rates of respiration and $CO_2$ fluxes in some impacted sites, thus we must not overlook the negative effect of expanded agriculture to lead the nearby riverbeds to be considerable anthropogenic sources of greenhouse gases.

From a management perspective of nitrate pollution, if denitrification is activated upon rewetting as we observed, these events may contribute to reduce high $NO_3^-$ levels at small-local scale within riverbeds in the most impacted areas. Our results also show, however, that this capability could not be efficient in winter when microbial activity, particularly denitrification, is low, and rivers are therefore prone to be more vulnerable to any nitrate input. The study region, Campo de Cartagena watershed, drains towards one of the most vulnerable saline coastal lagoons in Europe, The Mar Menor, which currently suffers from punctuated eutrophication phenomena associated to agriculture. Although the examined impacted sites seem to "acclimate" themselves to excess of nitrate by increasing denitrification, the lack of any other factor limiting the process will ultimately drive to nitrate accumulation in the sediments and its potential leaching following intense floods. The permanence of native vegetation may represent a stable fuel for river N processing. In this sense, management tools in favor of implementation of native vegetation in riparian areas which gradually settle the river channel could revert potential DOC limitation for denitrification. Currently most impacted rivers present unidirectional flows that are directly transported to coastal waters with minimum processing after rainfalls. Vegetation may create water transient storage zones within-channel and increases the opportunity of N-cycling processes to impact nitrogen budgets. Besides, plants are a sink of $CO_2$, thus, if a well developed primary producer community is promoted, the side effects of increased emissions of greenhouse gases in most disturbed sites could be counteracted.

Instead of being considered as simple pipes, we propose that the study watercourses provide potential intervention elements to mitigate nitrate concerns if management actions increase their ecological functions. Nonetheless, although our current results show complete denitrification in most rivers, potential emissions of $N_2O$ upon rewetting derived from an active anthropogenic denitrification should be better assessed *in situ* across the most impacted rivers (from up to down) over year.

## Credit author statement

M.I.Arce was responsible for the conception and design of the study, collection and processing of samples and data and development of the manuscript. M. Sánchez-García contributed to the collection and processing of samples. J. Martínez-López was responsible of the watershed delineation, landuse characterization and the production of Fig. 1. M.L. Cayuela and M.A. Sanchez-Monedero contributed to the conception and design of the study. All coauthors contributed to drafting the manuscript and to provide the final version to be published.

## Declaration of competing interest

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.

## Data availability

Data will be made available on request.

## Acknowledgements

# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2023.117462.

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