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Key Points:

- We investigated air-water CO_2 fluxes in a vast coastal wetland under contrasting hydrological cycles of extremely high and low flooding
- Aquatic CO_2 fluxes patterns revealed a strong variability and highest emissions from flooded systems occurred under wet hydrological cycles
- Areal air-water C transport was lower than the estimated net primary production, indicating that the ecosystem acted as a large CO_2 sink

Supporting Information:

- Supporting Information S1

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Effect of hydroperiod on CO_2 fluxes at the air-water interface in the Mediterranean coastal wetlands of Doñana

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Abstract Wetlands are productive ecosystems that play an important role in the Earth's carbon cycle and thus global carbon budgets. Climate variability affects amount of material entering and the metabolic balance of wetlands, thereby modifying carbon dynamics. This study presents spatiotemporal changes in air-water CO_2 exchange in the vast wetlands of Doñana (Spain) in relation to different hydrological cycles. Water sources feeding Doñana, including groundwater and streams, ultimately depend on the fluctuating balance between annual precipitation and evapotranspiration. Hence, in order to examine the contribution of the rainfall pattern to the emission/capture of CO_2 by a range of aquatic habitats in Doñana, we took monthly measurements during severely wet, dry, and normal hydrological years (2010–2013). During wet hydrological cycles, CO_2 outgassing from flooded marshes markedly decreased in comparison to that observed during subsequent dry-normal cycles, with mean values of 25.84 ± 19 and 5.2 ± 8 mmol m^{-2} d^{-1}, respectively. Under drier meteorological conditions, air-water CO_2 fluxes also diminished in permanent floodplains and ponds, which even behaved as mild sinks for atmospheric CO_2 during certain periods. Increased inputs of dissolved CO_2 from the underground aquifer and the stream following periods of high rainfall are believed to be behind this pattern. Large lagoons with a managed water supply from an adjacent estuary took up atmospheric CO_2 nearly permanently. Regional air-water carbon transport was 15.2 GgC yr^{-1} under wet and 1.24 GgC yr^{-1} under dry meteorological conditions, well below the estimated net primary production for Doñana wetlands, indicating that the ecosystem acts as a large CO_2 sink.

Plain Language Summary Wetlands are productive ecosystems that play a significant role in the Earth's carbon cycle, representing important contributors to the global carbon budget. Climate variability affects productivity in wetlands, thereby modifying their capacity to act as sink or source for atmospheric CO_2. This study addresses how the hydrological cycle influences the capacity for carbon sequestration in the Mediterranean wetlands of Doñana. Covering a surface of 3560 km^2, Doñana region includes a rich variety of landforms and vegetation types representative of Mediterranean lowlands. Its wetlands are one of the most emblematic protected areas in Europe with a high biotic diversity and unique importance for aquatic wildfowl. The region experiences annual cycles of flooding (October to March) and desiccation (May to June), with the inundation cycles being dependent on rainfall. Our measurements suggest that drier meteorological conditions result in lower CO_2 emissions to the atmosphere from flooded marshes and permanent ponds whereas large lagoons with man-managed water supply from an adjacent estuary behave as carbon sequestrators. Predictions indicate an increasing frequency of droughts over the Mediterranean region due to climate change. These results highlight the importance of water management in Doñana for wetlands conservation and their role in the atmospheric CO_2 exchange.

1. Introduction

Wetlands are among the most highly dynamic and productive of ecosystems and behave as net carbon (C) sinks due to their efficient storage of carbon in water logged soils [*Kayranli et al.* 2010]. This ecosystem service has a major impact on the atmospheric carbon pool and the Earth's radiative balance [*Mitsch et al.*, 2013]. Hence, characterization of carbon dioxide (CO_2) exchange in wetlands has become a key topic in climate change research. However, not all wetlands are equally effective in C withdrawal. In terms of their contribution to the atmospheric CO_2 budget, recent research has established a distinction between coastal wetlands and inland wetlands, as the former behave as significant net CO_2 sinks whereas the latter act as small CO_2 sinks or are nearly neutral [*Lu et al.*, 2016]. Thus, and taking into account the diversity of wetland ecosystems, more studies need be conducted to quantify the atmospheric CO_2 exchange in these regions and determine accurate continental carbon budgets.

Concurrently, wetlands are very sensitive to climate change (prolonged droughts, storm runoff, and sea level rise) [*IIPCC*, 2013] and increasing anthropogenic perturbations (eutrophication, land use conversion, and soil erosion). Both drivers have a large impact on ecosystem hydrology and the concomitant carbon fluxes [*Junk et al.*, 2013].

At present, research on C dynamics within wetlands mostly focuses on the assessment of the net ecosystem productivity (see compilation by *Lu et al.* [2016]), which is measured by quantifying the gas exchange rates in the atmosphere at ecosystem level. Therefore, the contribution of the CO_2 fluxes from the aquatic compartment is incorporated in the measurement, as it is only one component of the net ecosystem CO_2 exchange (NEE). However, air-water CO_2 transference in wetlands presents a large spatiotemporal variability and, particularly, in temperate regions where changes in rainfall frequency and intensity along with evaporation rates significantly alter wetlands hydrology. It is known that the depth of the water level and the length of the inundation period strongly affect wetland CO_2 fluxes, although mixed responses have been found [*Altor and Mitsch*, 2008; *Bubier et al.*, 2003; *Blodau et al.*, 2004; *Jimenez et al.*, 2012; *Han et al.*, 2015]. This is due to the fact that flooding conditions influence directly or indirectly carbon exchange in several different aspects. For instance, upon inundation, some plant leaves are submerged, which reduces aerial photosynthesis [*Schedlbauer et al.*, 2010; *Jimenez et al.*, 2012], and also, as soils become waterlogged, oxygen diffusion into de wetlands becomes limited, which hampers microbial activity and degradation of soil organic matter, causing a decrease in heterotrophic respiration [*Jimenez et al.*, 2012]. On the other hand, inundation favors the inputs of terrestrial organic substrates, which enhances aquatic CO_2 production by respiration [*Mayorga et al.*, 2005]. Therefore, recent studies have established the necessity to distinguish aquatic carbon fluxes in vegetated wetlands and capture C dynamics in both compartments under different climatic conditions, which also allows to explore decouplings [*Matthes et al.*, 2014; *Sturtevant et al.*, 2016; *McNicol et al.*, 2017].

Furthermore, it has been projected that the frequency and intensity of precipitations will vary under future climate change all over the world [*IPCC*, 2013]. Specifically, in large parts of Europe, the frequency of warm spells has already increased over the last 50 years [*Bastos et al.*, 2014; *Ciais et al.*, 2005] and it is anticipated that in the long term, the Mediterranean region will experience an increase in the duration and intensity of droughts with an overall decrease in the precipitation pattern [*IPCC*, 2013]. Hence, further information on the effects of the hydroperiod on CO_2 exchange in Mediterranean wetlands becomes even more important in the context of global climate change. This information is relevant not only to gain insights on the mechanisms that regulate the CO_2 fluxes in wetlands but also for predicting potential impacts of climate change.

In this study, we examined air-water CO_2 fluxes in relation to the characteristics of the hydrological cycle in a range of aquatic systems belonging to the wetlands of Doñana, the largest coastal wetland of South Europe (Figure 1). Located in the Atlantic coast of southwestern Spain, the wetlands are composed by a rich variety of landforms and vegetation types representative of Mediterranean lowlands. In a previous work [*Morris et al.*, 2013], we analyzed the capacity of the system for C sequestration. We reached two main conclusions: (i) spatial variability of aquatic CO_2 fluxes resulted from different biogeochemical conditions and (ii) even though Doñana's water bodies were jointly a net annual source of CO_2, net primary production compensated the outgassing, suggesting that the system as a whole acted as an annual net CO_2 sink. Nevertheless, those first measurements of aquatic fluxes in Doñana wetlands were taken during an extremely wet hydrological cycle (2009–2010). The region subsequently passed a prolonged meteorological dry phase that extended from November 2011 to November 2012, with winter 2012 being one of the driest rainy season's (usually extending from October to April) recorded during the last 40 years (Spanish Meteorological Agency, AEMET). Hence, this study was aimed at evaluating the impact of the annual precipitation pattern on CO_2 exchange from the aquatic systems of Doñana by examining the dynamics of dissolved CO_2 and air-water CO_2 fluxes using high spatiotemporal data. We hypothesized that a prolonged drought might affect the CO_2 exchange patterns by altering the aquatic metabolism in the flooded areas. To our knowledge, no previous assessment on C dynamics in the aquatic compartment of Doñana had been conducted under different climatic conditions. Hence, our objective was also to provide an initial analysis of the sink/source strength of the wetlands under contrasting hydrological cycles.

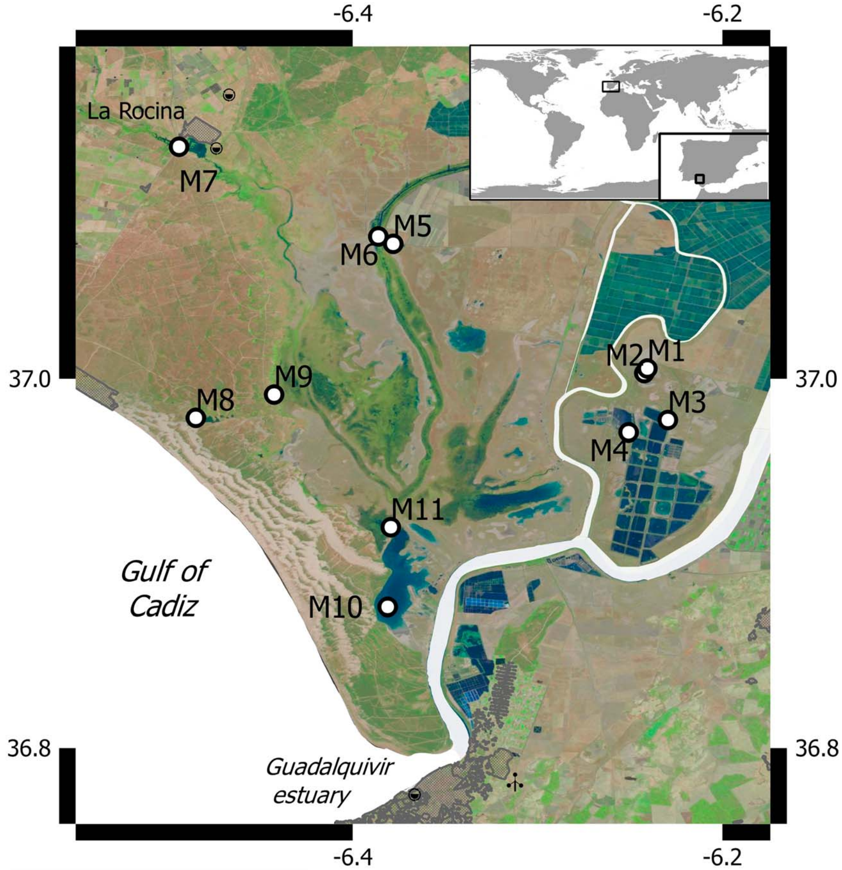

Figure 1. Location of Doñana area and sampling sites. M1–M4: Veta La Palma, M5: Lucio de la F.A.O., M6: Marisma Gallega, M7: La Rocina floodplain, M8: Laguna Dulce-Santa Olalla, M9: Lucio del Bolín, M10: Lucio del Membrillo, M11: Veta Lengua.

2. Methods

2.1. Site Description and Sampling Strategy

Doñana natural area (~100,000 ha of surface) situated at the mouth of the Guadalquivir river (Figure 1) is an ecosystem complex that contains one of the most valuable wetlands in Europe [*Čížková et al.*, 2013]. It harbors a wide variety of aquatic systems, such as river/streams, a vast marshland area, and a large number of temporary and permanent lagoons and ponds [*Serrano et al.*, 2006], jointly covering a surface of 3560 km^2. As it hosts five threatened bird species and one of the largest Mediterranean heronries, and it is the wintering site for more than 500,000 waterfowl each year, the wetlands have various degrees of environmental protection; an area of highly regulated National Park that occupies approximately 54,000 ha and a surrounding region categorized as Natural Park where certain traditional activities are permitted. Some parts of the wetlands were declared a Biosphere Reserve in 1980, a Ramsar Site in 1982, and a UNESCO World Heritage Site in 1995.

The main water inputs to Doñana wetlands are rainfall, the streams situated in the northern side of the National Park (e.g., La Rocina stream, Figure 1), and groundwater from the Almonte-Marismas aquifer [*Olías et al.*, 2008]. Until the late 1990s, the marshes were also flooded by estuarine waters entering from the Guadalquivir River (Figure 1), but as a result of the Aznalcollar mining spill, the Doñana marshland was completely isolated from the estuary using dykes and floodgates in order to prevent the entry of toxic contamination into the Park.

Over the last century the ecosystems of Doñana have experienced severe land use transformations [*Zorrilla-Miras et al.*, 2014], as they are delimited by populous municipalities whose major economic activities are tourism and agriculture, which cause competing water resource demands, especially from the underground aquifer. In conjunction with this range of pressures upon the aquatic resources of Doñana, the projected increase in occurrence and severity of droughts will plausibly exacerbate modifications in quantity and quality of water supply to the wetlands. Presently, the mean annual precipitation in the region is about 550 mm, with rainfall mostly occurring between October and March and absent during the summer months (June–August) [*Serrano et al*., 2008].

In order to encompass the diversity of aquatic systems present in Doñana, 11 water bodies were chosen for our study (Figure 1), as previously considered [*Morris et al*., 2013]. Sites M1:M4 belong to the private aquaculture farm Veta la Palma (11.300 ha) and are situated in the Natural Park. Regularly, the fish farm pumps in water from the Guadalquivir estuary to the ponds to keep the water level required for extensive culture [*Walton et al*., 2015]. Therefore, Veta la Palma lagoons can be classified as permanent ponds that provide a valuable ecosystem service, since during the dry season bird populations can reach 300,000 individuals [*Kloskowski et al*., 2009]. M5 is a depression (*lucio*) fed by rainfall, but it also receives pumped water from the underground aquifer whereas M6 represents a plain connected to the salt marshes that relies on rain and to a lesser extent on groundwater seepage. M7 is a permanent floodplain inundated by La Rocina stream, and M8 site corresponds to a large pond complex located in the extensive sand dune system of Doñana whose hydrology is strongly connected to the local aquifer, sustaining surface water via groundwater inflow [*Gómez-Rodríguez et al*., 2010]. Finally, M9:M11 are also water depressions located in the marshes but inundation in these sites depends exclusively on rainfall. Sampling in the marshland sites (M5, M6, and M9:M11) was conducted when sufficient water level was present (a minimum water height of 0.1 m). In summer 2012 this level was not maintained all season in some sites. Sampling was carried out on foot or a small boat and the exact GPS position at each site only varied slightly depending on the water level. To allow comparisons with the previous study, water bodies have been grouped into four categories: (1) Veta la Palma (sites M1:M4), (2) Doñana wetlands that agglutinate the marshland sites M5, M6, M9:M11, (3)La Rocina floodplain (M7), and (4) the Dune ponds (M8).

Monthly sampling was carried out in two periods: (1) March 2010 to March 2011 that corresponded to the hydrological years (starting 1 September) 2009–2010 and 2010–2011 and (2) November 2011 to May 2013, which corresponded to the hydrological years 2011–2012 and 2012–2013. Sampling occurred approximately every 30 days during daylight hours, and at each site water conductivity, temperature, and pH were measured with a Yellow Spring (YSI Incorporate) portable multiparameter probe YS6820v2, which was followed by water collection to determine carbon system parameters.

2.2. Data

2.2.1. Meteorology and Remote Sensing

Hourly measurements of rainfall (mm), air temperature (°C), and wind speed (m s^{-1}) were provided by a meteorological station located in Lebrija (36°58′35″N, 06°07′34″W) from the Junta de Andalucía network (www.juntadeandalucia.es/agriculturaypesca/ifapa/ria/servlet/FrontController). Atmospheric partial pressure of CO_2 (pCO_{2air}, μatm) was obtained from the NOAA (National Oceanic and Atmospheric Administration, USA) monitoring station in Izaña (Spain) (http://www.esrl.noaa.gov/gmd/dv/site/).

Surface water coverage between 1985 and 2015 was estimated using the Landsat satellite image archive (http://landsat.usgs.gov/). Low cloud (<35%), “top-of-atmosphere” radiometrically corrected images from Landsat 5, 7, and 8 were selected. Individual pixels identified as cloud (using a simple Landsat cloud score of >20) were excluded from analysis and the remaining pixels used to calculate the Midinfrared Normalized Difference Water Index (MNDWI = [green − swir1]/[green + swir1]). A simple threshold (MNDWI > 0) was used to classify the images into “surface water” and “land,” respectively. The total extent of surface water coverage was estimated as the number of pixels classified as surface water multiplied by the pixel area (30 m^2). No validation was undertaken to assess the suitability of the chosen radiometric index or threshold value; however, previous studies [*Bustamante et al*., 2009; *Díaz-Delgado et al*., 2010] provide similar estimates and also suggest MNDWI performs reasonably well in regions with high turbidity and halophyte cover, as is often the case in Doñana wetlands.

2.2.2. Aquatic Biogeochemical Variables

Chlorophyll *a* (Chl *a*) analysis was carried out by filtering known volumes of water through Whatman GF/F glass fiber filters, extracting in 90% acetone overnight in the dark, and measuring by fluorometry with a Turner Designs 10 AU Model fluorometer, which was calibrated using a pure Chl *a* standard from *Anacystis* *nidulans* (Sigma Chemical Company). Accurate dissolved oxygen (DO) concentration was derived by potentiometric titration using a Metrohm 794 Titroprocessor and applying the classical Winkler method. The saturation values of O_2 were calculated with the equation given by Benson and Krause [*United Nations Educational, Scientific and Cultural Organization*, 1986] and the Apparent Oxygen Utilization (AOU) was obtained, defined as the difference between the oxygen concentration at saturation and the observed oxygen concentration. Total Alkalinity (A_T) was also determined by titration and following the protocol described by *Mintrop et al.* [2000]. Samples were collected and stored in borosilicate bottles (500 ml) poisoned with 100 μL of a $HgCl_2$ saturated aqueous solution until their analysis on the laboratory. Accuracy (±2 μmol L^{-1}) was obtained from regular measurements of Certificate Reference Material supplied by Professor Andrew Dickson, Scripps Institution of Oceanography, La Jolla, CA, USA (Batches 85 and 89). Inorganic nutrients (dissolved nitrate, nitrite, phosphate, and silicate) were obtained from filtered (Whatman GF/F glass fiber filters) and frozen (−20°C) water samples (5 mL) using a continuous flow analyzer and following the techniques described by *Grasshoff et al.* [1983]. Concentrations of dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were derived by catalytic oxidation at high temperature (720°C) and chemiluminescence, respectively, with a Shimadzu Total Organic Carbon analyzer, Model TOC-VCPH/CPN [*Álvarez-Salgado and Miller*, 1998]. Dissolved organic nitrogen (DON) was obtained by subtracting the inorganic nitrogen concentration from the TDN. Suspended particulate matter (SPM) and organic (particulate organic matter (POM)) and inorganic (particulate inorganic matter (PIM)) fractions were determined by using the loss on ignition method by filtering 50–100 mL of water through preweighed and precombusted 450°C Whatman GF/F glass fiber filters with a later desiccation of the filter at 60°C during 48 h and finally combusted at 450°C during 5 h.

2.2.3. Statistics

Statistical analyses were performed using R: A Language and Environment for Statistical Computing 3.3.1 (https://www.R-project.org/). Correlations between variables were explored through a principal components analysis (PCA) of the transformed variables ($\log(x + 1)$), considering the monthly averaged wind velocity, total precipitation, and flooding as supplementary quantitative variables.

2.3. Air-Water CO_2 Exchange

The program CO2SYS.xls [*Lewis et al.*, 1998] based on measured alkalinity, pH, and water temperature was used to estimate aqueous pCO_{2water} by using the *Cai and Wang* [1998] and *Dickson* [1990] constants for carbon and sulfate, respectively. Subsequently, air-water CO_2 fluxes (F_{CO_2} in mmol m^{-2} d^{-1}) were calculated according to *Wanninkhof et al.* [2009] by using

$$FCO_2 = k_w k_0 \left([pCO_2]_{water} - [pCO_2]_{air}\right) \tag{1}$$

where k_w (m s^{-1}) is the waterside gas transfer velocity and k_0 (mol m^{-3} atm^{-1}) is the aqueous-phase solubility of CO_2 at the in situ temperature and salinity [*Wanninkhof*, 1992; *Weiss*, 1974]. k_w was calculated using

$$k_w = k_{600}(S_{cw}/600)^{-0.5} \tag{2}$$

where S_{cw} is the Schmidt number interpolated at the in situ temperature and salinity calculated from the diffusivity of CO_2, dynamic viscosity, and density of water [*Johnson*, 2010]. k_{600} is the gas transfer velocity at a Schmidt number of 600 (typical of freshwater at 20°C). k_{600} was predicted from time-ensemble averaged (1 d) horizontal wind velocity at 10 m above the surface (U_{10} m s^{-1}) using the empirical relationships derived for lakes of *Cole and Caraco* [1998].

$$k_{600} = 2.07 + 0.215 \times {U_{10}}^{-1.7} \tag{3}$$

where k_{600} is in cm h^{-1}. U_{10} was calculated from U_z measured at the Lebrija meteorological station according to *Smith* [1988] and spatially averaged to obtain a single value for the region. It can be argued that the empirical relationship selected here to adjust k_{600} values may not be completely suitable to account for by wind enhancement effects in all Doñana aquatic systems, as they are shallow water bodies most of the year but with a marked variation in aquatic cover. In order to check the uncertainty introduced by this particular choice, k_{600} values were also derived by empirical relationships proposed for the global oceans [*Wanninkhof et al.*, 2009] (median k_{600} ~30% higher) and for small water bodies [*Kremer et al.*, 2003] (~30% lower values). In a previous assessment [*Morris et al.*, 2013], an identical analysis was performed and being aware of this caveat, the empirical relationship by *Cole and Caraco* [1998] was finally chosen to allow comparison with former data.

Daily values of $p\mathrm{CO}_{2\mathrm{water}}$, $p\mathrm{CO}_{2\mathrm{air}}$, salinity, and water temperature required to compute S_{cw} and F_{CO_2} were estimated by linear interpolation of the measured monthly values.

Air-water C transport (Mg CO_2 d^{-1}) for the different aquatic regions grouping the sites was calculated in a first approximation by averaging the areal F_{CO_2} values of all sites in each region and multiplying by the inundated area (derived from remote sensing) in specific each region. Transport was calculated over two periods with similar annual precipitation and extent of flooding, but each corresponding to the end and start of a different hydrological year. Hence, values given should be considered representative of wet and dry-normal periods, respectively, rather than specific years.

3. Results

3.1. Meteorology

Monthly air temperatures oscillated between minima of about 8 and maxima of 27°C in the months of January and August, respectively (Figure 2a). Water temperature varied from 7 to 15°C during the winter months and increased to values above 30°C during the summer season (Figure 2a), with the lowest and highest water temperatures being observed in February 2012 and August 2010, respectively. Total annual rainfall was quite variable. Heavy and prolonged rains took place between late autumn 2009 and winter 2010, resulting in a total annual rainfall of 955 mm (Figure 2b). During the subsequent cycle (considered to start in October 2010), annual rainfall slightly decreased but still reached about 700 mm, which was also higher than average for the Doñana area. Therefore, the sampling period comprised between March 2010 and March 2011 was considered to correspond to extremely wet meteorological conditions. In contrast, the 2011–2012 cycle was characterized by an annual precipitation of 377 mm, with isolated rains measured in October–November 2012 (Figure 2b), which is well below the average for the area. This period was followed by a 2013 spring characterized by moderate rains. Hence, sampling between November 2011 and March 2013 reflects the situation encountered under dry-normal meteorological conditions.

The interannual variation in precipitation clearly affected inundation area (Figure 2d). The period of maximum flooding in which 97% of the marshland (sites grouped as Doñana wetlands) was covered by surface water (342 km^2) was found in February 2010. This was one of the largest annual flooding events observed in the Landsat collection (spanning the last 30 years). The maximum extent of flooding was slightly lower during the 2010–2011 cycle (300 km^2, 85%), drastically lower during the dry cycle of 2011–2012 (53 km^2, 15%) and around the 30 year mean values in the subsequent 2012–2013 cycle (212 km^2, 60%). Minimum values observed in summer ranged between 1.7 and 5.8 km^2. In the other regions, flooded surface ranged between 13–88, 0.05–21, and 0.001–1.2 km^2, in Veta la Palma farm, the dune ponds and La Rocina floodplain, respectively (Figure 2d).

Time-ensemble-averaged (daily) horizontal wind velocity at 10 m above the surface (U_{10}) exhibited an oscillating annually pattern, with a median value of the whole series equivalent to 1.9 ± 0.9 m s^{-1} (Figure 2c).

3.2. Aquatic Biogeochemistry

Median values of the aquatic biogeochemical parameters are indicated in Table S1 (supporting information). Based on salinity, most aquatic systems could be identified as oligohaline to mesohaline. The highest salinity values were observed in Veta la Palma lagoons (M1:M4), reflecting water pumping from estuary. During the dry-normal hydrological period, salinity sites M3 and M4 increased notably (up to 50 several months), due to increase in the entry of estuarine inputs to compensate water loss by evaporation. This increasing pattern in salinity under drier meteorological conditions was also observed in M6, M8, M9, and M11, as the drought likely favored evapotranspiration. This was not the case in La Rocina floodplain (M7) that is inundated constantly by the stream. Chl *a* concentration also varied considerably among sites, which could be categorized as mesoeutrophic to hypereutrophic systems (Table S1). Overall, chlorophyll levels during the sampling period November 2011 to March 2013 increased in the northern sector of the flooded marshland (M6), in La Rocina floodplain (M7) and in the dune ponds (M8) with respect to those observed during the wet

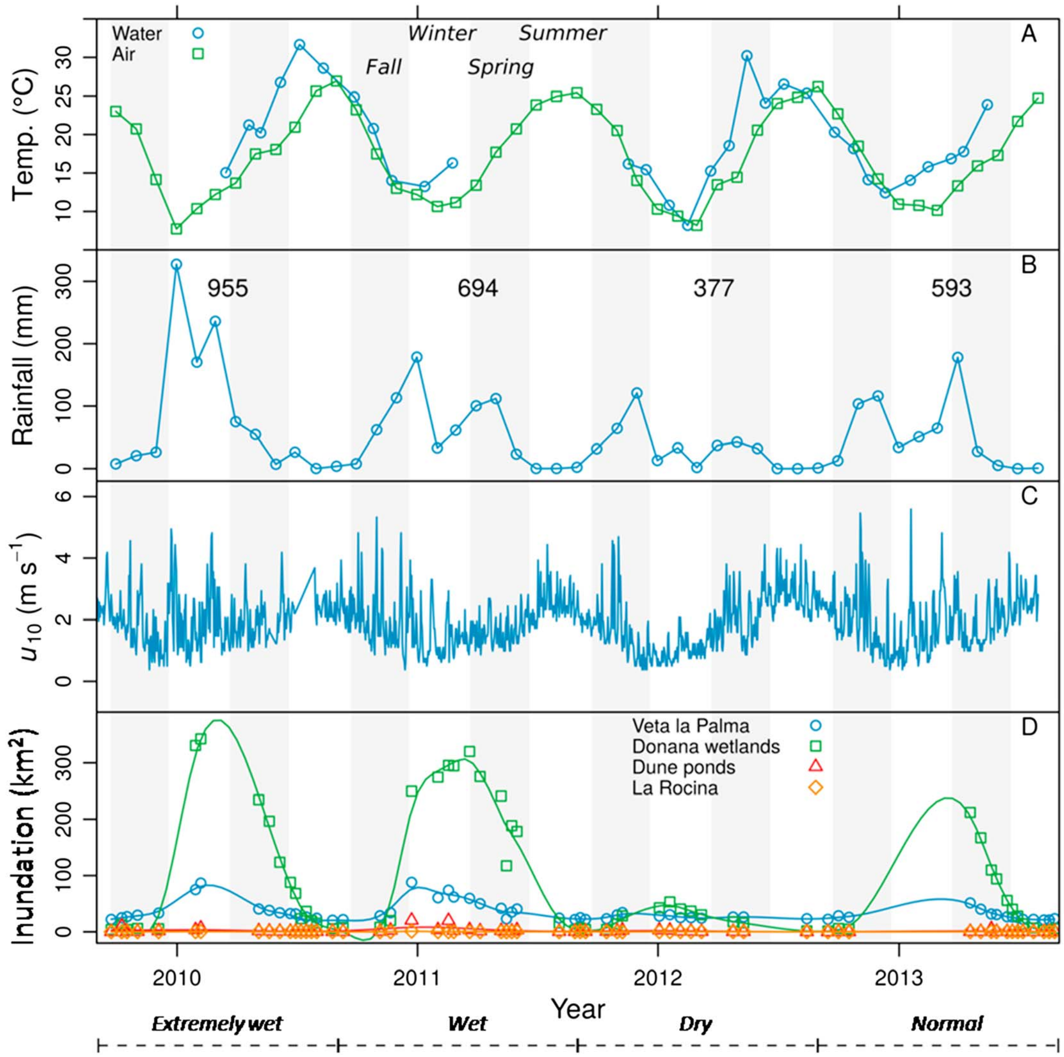

Figure 2. Time series plots of (a) air and water temperature, (b) monthly rainfall, (c) daily mean wind velocity at a height of 10 m, (d) and inundation by regions derived by remote sensing. Light and dark shading represent seasons. Numbers in Figure 1b indicate mean annual rainfall (2010–2013).

sampling period (March 2010 to March 2011) and decreased in the southern sector (M9 and M11) and M5 (*Lucio de la* FAO).

Principle component analysis showed that data could be summarized into five components (with Eigen values >1) that accounted for a cumulative percentage variance of 72%. In order to characterize briefly the aquatic systems only two components that accounted for by 40% of the cumulative variance, PC1 (~23%) and PC2 (~17%) are considered. Examination of biplots of PC1 and PC2 scaled to highlight variable correlations (Figure 3a) and individuals (Figure 3b) underlined strong correlations between most of the variables and suggested general spatiotemporal trends. PC1 exhibited stronger correlations with climatic variables, suggesting seasonality (and hence, extent of flooding), whereas PC2 appeared to mainly represent spatial differences between sampling sites (and hence, origin of the water). Positive values of PC1 were associated with variables linked to phytoplankton biomass and dynamics, such as high concentrations of Chl *a*, dissolved organic compounds (DOC and DON), particulate matter (SPM), and alkalinity and also with high water temperatures and strong wind (Figure 3a). Association between climatic variables and chlorophyll is indicative of the presence of Easterlies that blow frequently in this area over spring-summer and which favored evaporation and phytoplankton concentration. Conversely, negative values correlated with nitrate concentration, precipitations, and flooded area, which can be considered winter-spring events. Positive

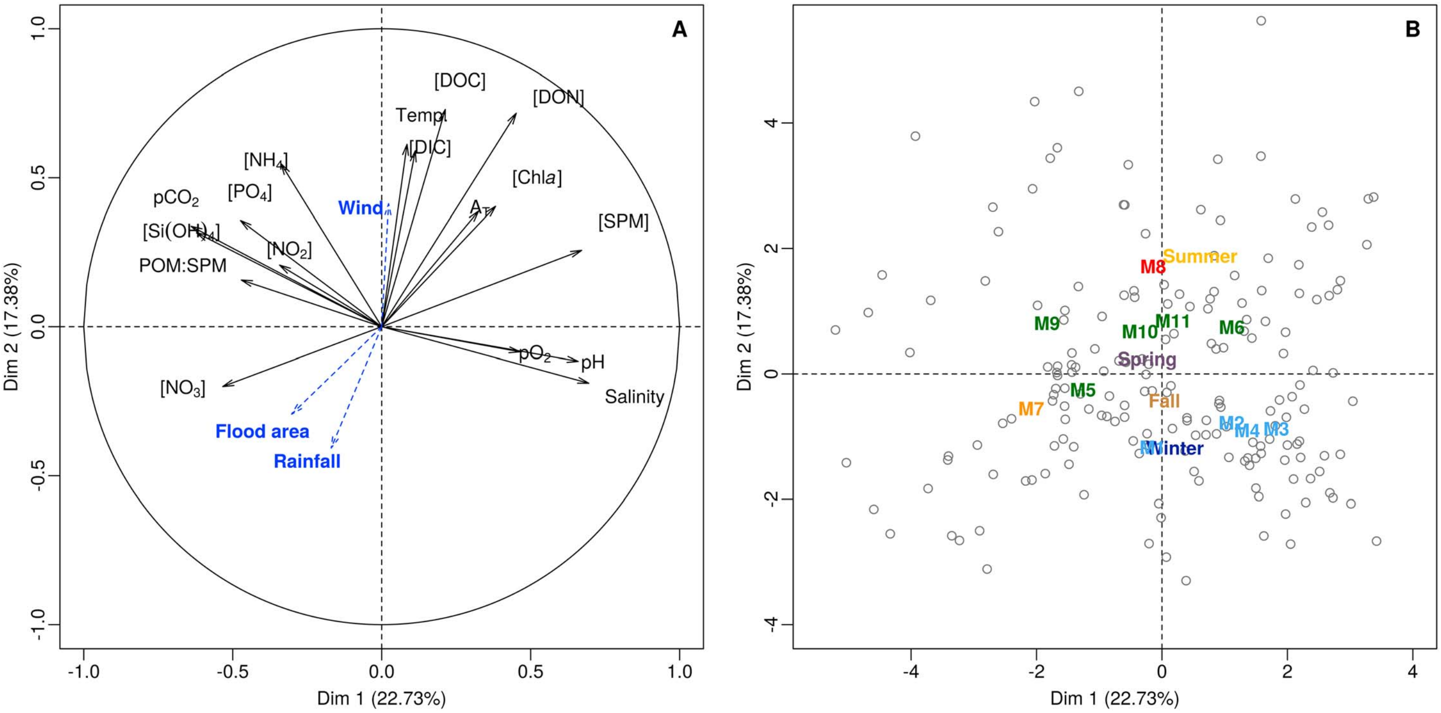

Figure 3. Biplots of water physical and chemical characteristics with (a) scaling highlighting variable correlations and (b) mapping of individual samples. Rainfall, wind velocity, and total flooded surface area are plotted as supplementary variables (blue arrows and text) in Figure 3a. Text representing the centroids for each site and season are shown in Figure 3b. Colors of sites represent regions (Veta la Palma = blue, Doñana wetlands = green, Dune ponds = red, and La Rocina = orange).

values of PC2 denoted high $p\mathrm{CO}_{2\mathrm{water}}$ levels, and high concentrations of phosphate, silicate, nitrate, and ammonia, along with an elevated POM:SPM ratio (Figure 3a) in the flooded marshland sites (M6, M9:M11) and the dune ponds (M8) and predominantly in spring (Figure 3b). Negative PC2 values were associated with higher salinity and DO, particularly in the mesohaline Veta la Palma lagoons (M1:M4), mainly during the dry-normal hydrological period (Figures 3a and 3b). La Rocina floodplain (M7) and the water depression M5 seemed to fall between these two extremes.

3.3. Air-Water CO_2 Exchange

Dissolved carbon dioxide partial pressure ($p\mathrm{CO}_{2\mathrm{water}}$) varied markedly in time and space (Table S1 and Figure 4). Minimum levels of $p\mathrm{CO}_{2\mathrm{water}}$ always occurred in the fish-farm lagoons (M1:M4) that remained mostly undersaturated with respect to atmospheric CO_2 (ranging from 389 μatm in 2010 to 396 μatm in 2013). Maxima in $p\mathrm{CO}_{2\mathrm{water}}$ were observed during the extremely wet sampling period in the dune ponds (M8) and the flooded marshland sites (M6, M9: M11), reaching values higher than 3000 μatm (Figure 4). In these sites, aqueous CO_2 concentrations diminished over the dry-normal 2011–2013 sampling period. The oligohaline sites (M5, M7, and M8) exhibited very large seasonal $p\mathrm{CO}_{2\mathrm{water}}$ variations during the wet period (Table S1), with low values (>100 μatm) in early spring and autumn and high values (>3500 μatm) in summer and winter. During dry-normal hydrological cycles this seasonality was still observed in La Rocina floodplain (M7), although with lower $p\mathrm{CO}_{2\mathrm{water}}$ levels, which was not the case in the dune ponds (M8) where undersaturation (relative to $p\mathrm{CO}_{2\mathrm{air}}$) was the most common finding (Figure 4 and Table S1), except for a pronounced outgassing occurring in spring 2012 coinciding with some isolated rains (Figure 2b). M5 also experienced a notable decrease in $p\mathrm{CO}_{2\mathrm{water}}$ during drought (Figure 4).

Air-water CO_2 fluxes calculated for both sampling periods reflected variability in dissolved CO_2 in the different aquatic systems. Overall, daily fluxes in La Rocina floodplain (M7) were higher and positive under wet hydrological cycles, indicating a continuous release of CO_2 to the atmosphere (Figure 5 and Table 1). During the dry-normal hydrological cycles, F_{CO_2} values at this site oscillated between 86.4 and −7.2 mmol m^{-2} d^{-1} in fall 2011 and winter 2012, respectively, (Table 1) and negative fluxes were also

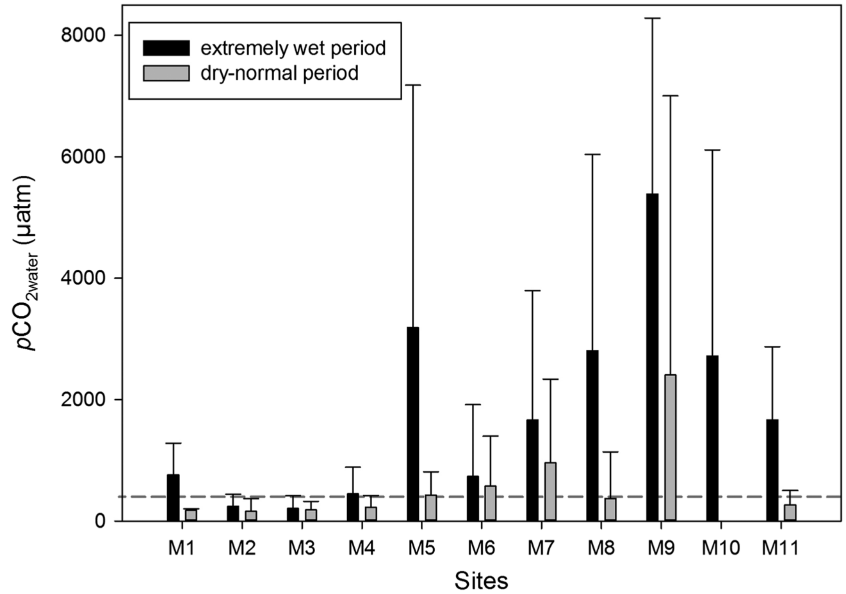

Figure 4. Average (±standard deviation) dissolved concentration of CO_2 (pCO_{2water}) in all sites during both sampling periods. Broken line represents the average atmospheric CO_2 level (~392 µatm) during the years of study.

observed during the winter months of 2013 (Figure 5), indicating an uptake of atmospheric CO_2. In the dune ponds (M8), the dominance of large positive values was clearly observable during the extremely wet period March 2010 to March 2011, with the exception of neutral fluxes detected in fall 2010 (Figure 5 and Table 1). Drier meteorological conditions resulted a clear diminution in the outgassing from the ponds, which mostly took up atmospheric CO_2 over the second sampling period (Figure 5), apart from a noticeable CO_2 emission episode (184.7 mmol m^{-2} d^{-1}, Table 1) registered in June 2012. This massive CO_2 efflux affected the value of the average air-water exchange, although the mean F_{CO_2} from November 2011 to March 2013 was nearly twofold lower (13.1 mmol m^{-2} d^{-1}) than that measured during the previous wet period (23.2 mmol m^{-2} d^{-1}, Table 1). In the flooded marshland (Doñana wetlands sites), CO_2 fluxes experienced a marked temporal variability, with median daily values of 35.2, 3.6, 52.8, 23.5, and 14.1 mmol m^{-2} d^{-1} in M5, M6, M9, M10, and M11 during the wet cycles that drastically decreased during the dry-normal cycles to values of −0.2, −1, 16.3, and 5.6 mmol m^{-2} d^{-1} in M5, M6, M9, and M11, respectively (Table 1). In fact, from November 2011 to March 2013, M5, M6, and M11 behaved as mild CO_2 sinks or were nearly neutral with respect to atmospheric CO_2, with sporadic small effluxes in fall 2012 and spring 2013 (Figure 5). Similarly, negative CO_2 fluxes of small magnitude were dominant in Veta la Palma lagoons (sites M1:M4) over the extremely dry-normal sampling period, indicating a continuous moderate withdrawal of atmospheric CO_2 (Table 1 and Figure 5). Copious rains during the previous March 2010 to March 2011 period resulted in slight sporadic emissions (Figure 5), although on average, they jointly acted as a CO_2 sink or were in neutral equilibrium with the atmosphere, with mean values of 0.3 ± 3.8 and −1.65 ± 3.9 mmol m^{-2} d^{-1} during wet and dry-normal hydrological cycles, respectively (Table 1).

When the respective surface of inundation within each region (Figures 2d and 5) was considered and daily areal fluxes were upscaled, the relevance of flooding on C dynamics in Doñana area was evidenced (Figure 6). During wet hydrological cycles, estimates of regional annual air-water C transport were 15, 0.35, 0.014, and −0.16 GgC yr^{-1} in Doñana wetlands (marshland sites), the dune ponds (M8), La Rocina floodplain (M7), and Veta la Palma permanent lagoons (M1:M4), respectively. These estimates markedly decreased over the extremely dry-normal hydrological cycles (sampling period November 2011 to March 2013), with values of 1.66, 0.03, 0.005, and −0.45 GgC yr^{-1} in the same respective areas. Combined together, the total annual air-water C transport in the Doñana natural area was 15.2 GgC yr^{-1} and 1.24 GgC yr^{-1} under wet and dry meteorological conditions, respectively, indicating that the role of Doñana wetlands in the carbon budget is heavily controlled by the characteristics of the annual hydrological cycle.

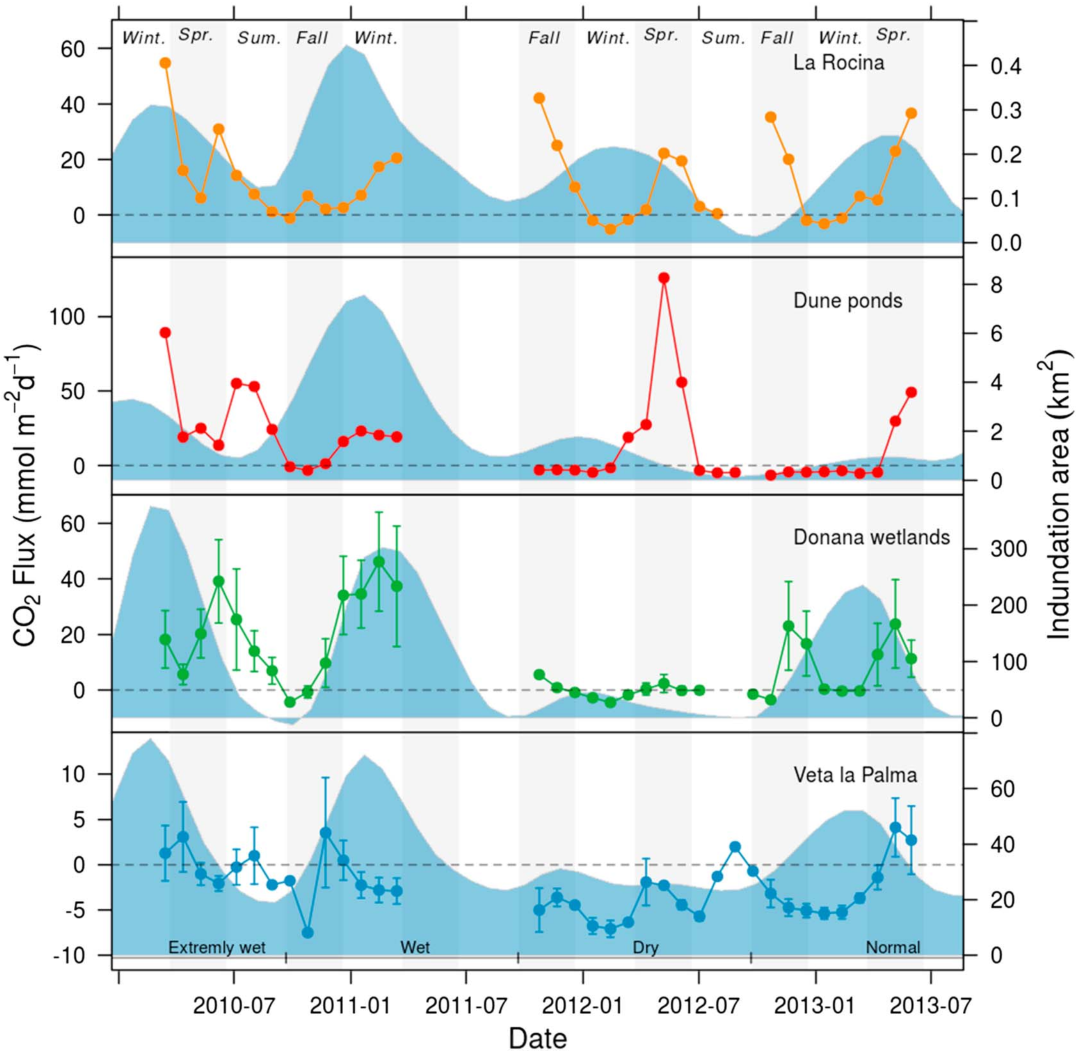

Figure 5. Monthly air-water CO_2 exchange in Doñana aquatic habitats (grouped by regions) during both sampling periods. Characteristics of hydrological cycles are indicated within the graph. Inundation area in each region is also shown (blue shading). Grey shading represents seasons.

4. Discussion

Our key observation is that the annual precipitation pattern clearly influenced the exchange of CO_2 with the atmosphere in the aquatic habitats of Doñana wetlands. Hydrological years marked by prolonged and heavy rains during the rainy season, such as the 2009–2010 and 2010–2011 cycles, caused large emissions of CO_2 from the water systems, particularly from the marshes, whereas drought (2011–2012 cycle) resulted in a

Table 1. Minimum (Min), Mean, and Maximum (Max) Values of Air-Water CO_2 Exchange (F_{CO_2}, in mmol m^{-2} d^{-1}) in Doñana Aquatic Systems During Contrasting Hydrological Cycles

	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11
	Extremely Wet Cycles (Sampling Period March 2010 to March 2011)										
Min	5.1	−5.7	−18.6	−5.0	−3.2	−9.2	−3.9	−7.1	−0.7	−2.7	−2.8
Mean	5.0	−1.5	−3.9	1.6	35.2	3.6	11.7	23.2	52.8	23.5	14.1
Max	22.4	1.3	7.7	20.3	134.4	41.1	80.5	109.8	131.0	149.8	48.4
	Dry-Normal Cycles (Sampling Period November 2011 to May 2013)										
Min	−4.9	−10.1	−14.8	−12.2	−6.1	−7.3	−7.2	−9.5	−7.9	-	−2.9
Mean	4.3	−3.5	−4.1	−3.3	−0.2	−1	9.7	13.1	16.3	-	5.6
Max	19.0	2.2	4.7	14.5	11.2	14.7	86.4	184.7	140.1	-	37.6

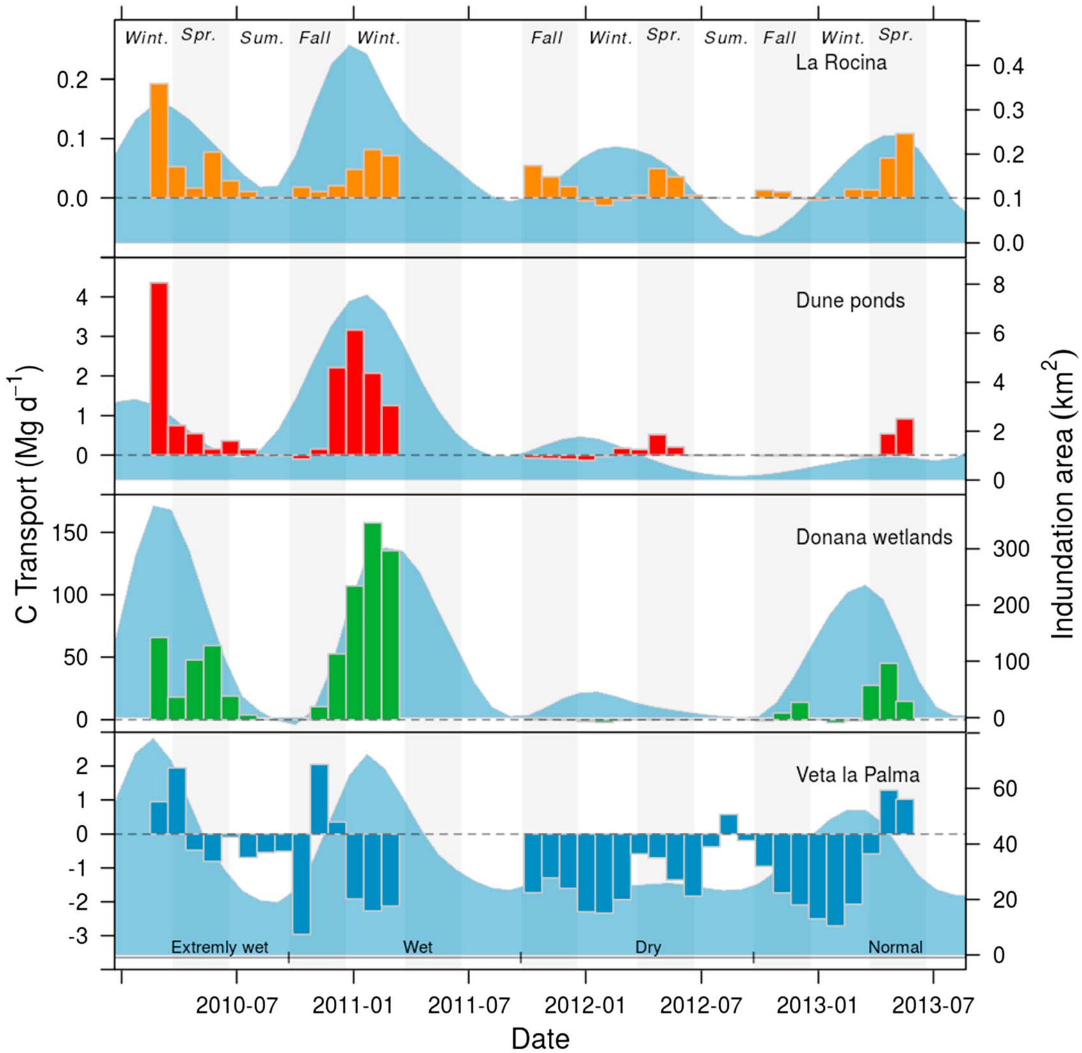

Figure 6. Areal air-water CO_2 transport in Doñana aquatic regions grouping the sampling sites. Inundation area in each region is also shown (blue shading). Characteristics of hydrological cycles are indicated within the graph. Grey shading represents seasons.

drastic diminution of the aquatic fluxes (Figures 5 and 6). Hence, our findings tend to suggest that meteorology regulates the role of the aquatic compartment of Doñana as sink or source of atmospheric CO_2.

It is important to point out, however, that our study only considers fluxes from systems that are permanently inundated, even though the water level may significantly fluctuate form 1 year to another (Figures 2d and 5). Fluxes coming from previously waterlogged soils once exposed to the atmosphere are neglected. These areas, especially in the vast marshland, may act as CO_2 emitters upon desiccation, as an additional efflux due to aerobic decomposition of a large amount of organic sediment deposited during flooding could occur, as it has been observed in Mediterranean dry streambeds [*Gómez-Gener et al.*, 2016]. Still, if those areas were rapidly colonized by vascular plants, these might take up a fair amount of CO_2 from the atmosphere, markedly contributing to the CO_2 absorption during drought. Hence, measurements of CO_2 exchange in zones with emergent vegetation and no standing water should be a future priority in Doñana. This would also lead to accurate estimates of the net ecosystem exchange, as specific data are not presently available for Doñana. The assessment of the NEE would require additional technology (an eddy flux tower) and measurements of carbon inputs/outputs from each ecosystem compartment.

Using data from previous physiological studies, *Morris et al.* [2013] estimated an initial potential net primary production of the surrounding forests, marshes, heath, and scrubland of Doñana equivalent to

75 + 50 GgC yr^{-1}. This amount greatly exceeds the maximum annual aquatic air-water C transport found here during extremely wet years (15.5 GgC yr^{-1}), which would give a high negative NEE for Doñana natural area and even more negative under drier hydrological cycles, when the aquatic C transport markedly decreases (1.24 GgC yr^{-1}). Measurements of annual NEE in coastal wetlands indicate that they are sinks for CO_2 [*Lu et al.*, 2016]. Therefore, while the rough estimate of net primary production in Doñana requires improvement, our results support the notion that coastal wetlands have a high C sequestration capacity.

Studies dealing with changes in NEE between wet and dry years report contrasting conclusions [*Han et al.*, 2015] although generally, drier conditions lead to a reduction in ecosystem C uptake because of enhanced respiration and reduced rates of photosynthesis [*Strack et al.*, 2006, and references therein]. In this study, we only rely on one estimate of net primary production, which hinders predictions about the response of Doñana wetlands to different ecohydrological conditions and climate change.

Moreover, we only focused on CO_2 exchange, and CH_4 should not be ignored in Doñana aquatic habitats, as inland and coastal waters are known to be important sources of methane to the atmosphere [*Barbosa et al.*, 2016; *Borges et al.*, 2016; *Chuang et al.*, 2017; *Upstill-Goddard and Barnes*, 2016; *Panneer-Selvam et al.*, 2014]. CH_4 emissions could indeed turn this productive ecosystem into a net C source, as already shown in freshwater marshes [*Chu et al.*, 2014] and in the Sacramento delta wetlands [*McNicol et al.*, 2017]. Furthermore, a restoration program has been recently implemented to allow connectivity between the Guadalquivir estuary and the marshland to ensure flooding during dry periods. First measurements of methane in the highly heterotrophic Guadalquivir river [*Flecha et al.*, 2015] indicate that the estuary acts as a significant CH_4 source *Huertas et al.*, [2017], in agreement with the patterns found in other European estuaries [*Borges and Abril*, 2011; *Upstill-Goddard and Barnes*, 2016]. Therefore, a thorough investigation of CO_2 and CH_4 transport is still necessary in Doñana natural area under the current habitat conditions.

Nevertheless, our study is foundational because it underlines the possible drivers for controlling the CO_2 dynamics in Doñana water systems. As a general trend, as flooding occurs, dissolved oxygen becomes limiting due to respiration of organic carbon, resulting in increased pCO_{2water} levels. In fact, respiration of contemporary organic matter is the dominant source of excess carbon dioxide that drives outgassing in medium and large rivers [*Mayorga et al.*, 2005]. Particularly, in semiarid terrestrial ecosystems, respiration rates from biological processes markedly increase shortly after flush flooding of dry soils, resulting in substantial CO_2 effluxes to the atmosphere [*Huxman et al.*, 2004]. These CO_2 releases often outweigh the subsequent photosynthetic CO_2 accumulation, resulting in a net loss of C from an ecosystem through a rainy period [*Emmerich*, 2003]. When anaerobic conditions prevails, methanogenesis proceeds and pCO_2 from microbial activity decreases. However, CH_4 can also be respired and converted to CO_2, as evidenced by *Corbett et al.* [2013], enhancing ultimately dissolved CO_2 concentration. This could have been the situation encountered in Doñana marshes. As shown by the PCA (Figure 3), pCO_{2water} was negatively correlated to DO in the marshland sites. Examination of pCO_{2water} levels in relation to the AOU (Figure 7) yielded significant relationships in these sites during both the extremely wet period (r^2 = 0.32, p value < 0.05) and the dry-moderate period (r^2 = 0.30, p value < 0.05). These associations suggest that remineralization of organic matter was responsible of the CO_2 generation from the marshes and rainfall possibly led to increased pCO_{2water} due to the increase in terrestrial organic substrates that were degraded to CO_2. The effluxes registered during spring 2013 coinciding with the seasonal rains would support this association (Figure 5). Furthermore, retention of the rain water within the marshland over an extended period of time during cycle 2009–2010 [*Urdiales Alonso et al.*, 2010] might favor anaerobic conditions and methanogenesis, also driving the large CO_2 outgassing detected over this period (Figures 4 and 5).

It is interesting to note that in M5 the high levels of pCO_{2water} (Figure 4) also appeared associated with high nutrient loads (Figure 3 and Table S1). Although located in the marshland, M5 receives regularly pumped groundwater from the aquifer to keep an appreciable water level needed for bird breeding [*Santoro et al.*, 2010]. Aquifers transporting high concentrations of dissolved C have been identified over the world [*Cruz and Amaral*, 2004; *Marrero et al.*, 2008; *Evans et al.*, 2009; *Kampman et al.*, 2014; *Yamada et al.*, 2011; *Genereux et al.*, 2013; *Rivé et al.*, 2013; *Kuchari*č *et al.*, 2015]. It has been also shown that groundwater discharge from aquifers represents a significant source of atmospheric CO_2 to stream waters [*Crawford et al.*, 2014; *Dinsmore et al.*, 2010; *Oviedo-Vargas et al.*, 2015] and coastal wetlands [*Cai et al.*, 2003; *Atkins*

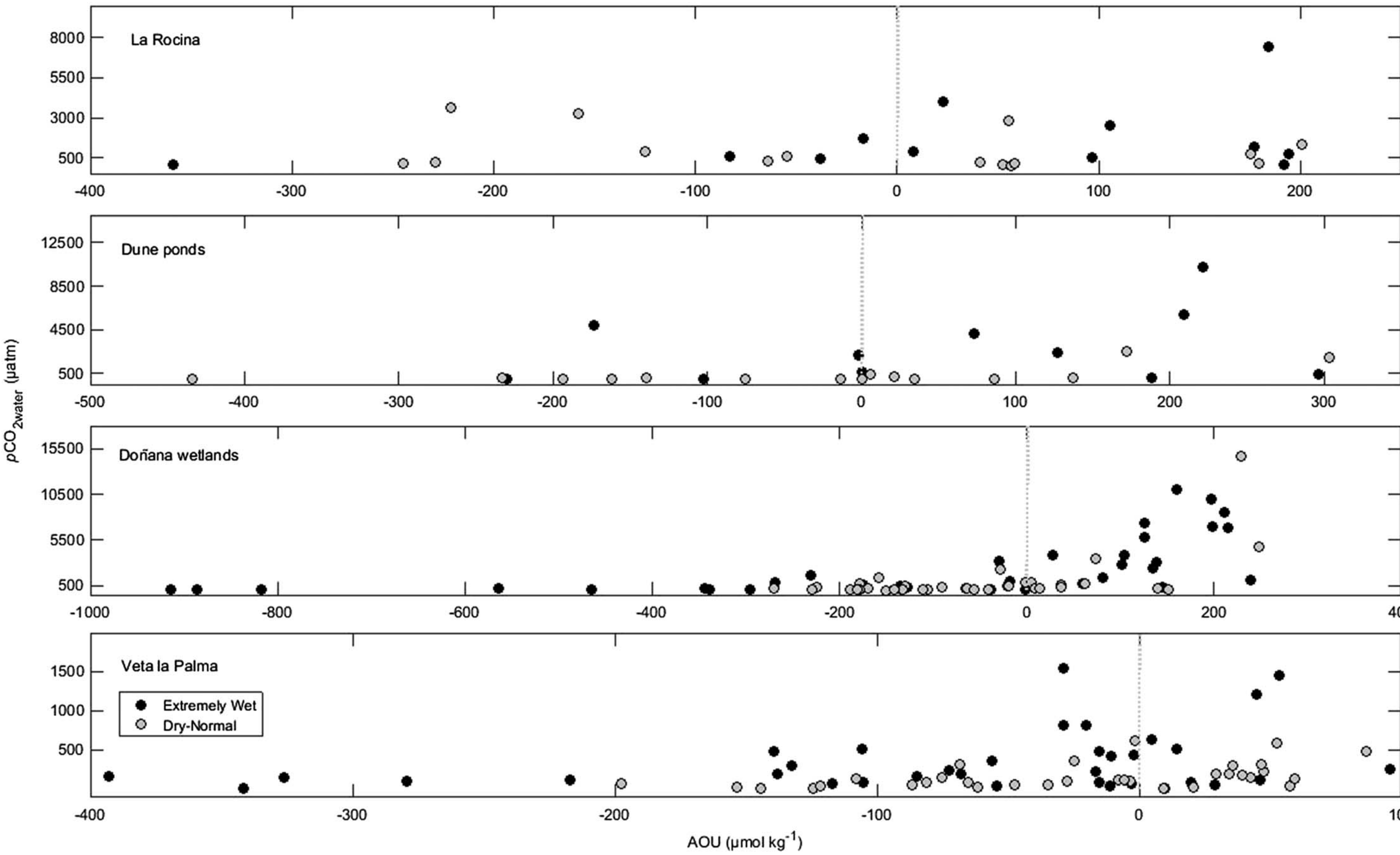

Figure 7. Dissolved CO_2 concentration (pCO_{2water}) in relation to apparent oxygen utilization (AOU) in Doñana aquatic habitats grouped by sites during the contrasting hydrological cycles considered in this work. Note that axis scales are not the same in all plots.

et al., 2013]. In this case, water composition of the Doñana aquifer has been found to be similar to that of precipitation water although more concentrated due to the effect of evapotranspiration in the soil, being also characterized by a slightly acid pH and with high concentrations of nitrates of agricultural origin [*Olías et al.*, 2008]. Hence, the pattern observed in M5 may reflect that input of groundwater was a major factor driving CO_2 evasion from this water depression, which would also accumulate additional nitrogen sources because of the birds nesting.

Similarly, influence of the underground inflows seems to be behind the air-water CO_2 exchange variability in the dune ponds (M8) (Figure 5). In this site, the average emission of CO_2 over the dry-normal period was threefold lower than during the previous wet 2010–2011 period but a large outgassing was found under the episodic 2012 spring rains. Changes in pCO_{2water} and AOU did not correlate well under wet meteorological conditions, but correlation between both variables was significant under dry-normal conditions (Figure 7, $r^2 = 0.32$, p value < 0.05, Figure 7). This trend is similar to that found in Brazilian coastal lakes, where periods of high rainfall caused a tenfold increase in pCO_{2water}, which was attributed to increased inputs of pCO_{2water} from groundwaters to the lakes [*Marotta et al.*, 2010]. Therefore, the alternation in the behavior of the dune ponds as sink or source for atmospheric CO_2 appears to be directly connected to C enriched inputs from the underground aquifer that naturally feeds the dune ponds system [*Gómez-Rodríguez et al.*, 2010].

Similarly, C dynamics in La Rocina floodplain (M7) did not seem to be exclusively modulated by metabolic processes, as no significant correlation was found between pCO_{2water} and AOU regardless of the sampling period (Figure 7). The PCA suggested that high levels of pCO_{2water} appeared associated with high nutrient loads (Figure 3). Large concentrations of nitrate from chemical fertilizers have been measured upstream [*Tortosa et al.*, 2011], which would explain the continuous high levels of dissolved inorganic nitrogen and

DON in this site (Table S1). Discharge from the stream would also provide CO_2, keeping high levels of pCO_{2water} (Figure 4), in agreement with observations indicating that permanent watercourses are important sources of CO_2 [*Raymond et al.*, 2013, *Li and Bush*, 2015]. Nevertheless, it is interesting to note that during wet periods, a constant oversaturation (and emission) occurred (Figure 5) whereas during the subsequent 2011–2012 dry cycle, a certain seasonality in the CO_2 fluxes could be observed with periods (early spring) of low atmospheric absorption (Figure 5 and Table 1). CO_2 evasion from streams and rivers in North America has been highly and positive correlated with the annual precipitation due to the climatic regulation of the stream surface area, and the flushing of carbon dioxide from soils [*Butman and Raymond*, 2011]. Even though La Rocina is a small catchment stream, the pattern of CO_2 fluxes found in its floodplain seems to respond to this association with the rainfall, as the extent of inundation seemed to influence the outgassing. However, large emissions were also measured over summer (regardless of the cycle), suggesting that the seasonal temperature cycle and the balance between degradation of organic matter versus photosynthesis may play some role in regulating pCO_{2water} levels.

In contrast, the mesohaline lagoons of Veta la Palma (M1:M4) behaved almost permanently as mild sinks or were nearly neutral with respect to atmospheric CO_2 (Figure 5 and Table 1). High concentrations of suspended and dissolved matter were regularly present in the ponds (Table S1), which may have both and autochthonous and allochthonous origin due to the production activity and water pumping from the estuary [*Walton et al.*, 2015]. The regular water renewal aimed at maintaining a sustained primary production in the lagoons most likely contributed toward reducing the buildup of dissolved CO_2, thus favoring the uptake of atmospheric CO_2. Anaerobic conditions were impeded and thereby, methanogenesis was unlikely, also due to the higher salinity of the estuarine waters (Table S1). These conditions prevented ultimately CO_2 formation from an alternative pathway. The moderate outgassings registered over winter-spring 2010 and January 2011 (Figure 5) possibly reflected rainfall pCO_2 inputs rather than enhancement of organic matter degradation, as correlation between pCO_{2water} and AOU (Figure 7) was not significant. During the dry-normal period, sporadic and very small CO_2 releases were observed over summer-spring (Figure 5), perhaps attributable to oversaturation due to the thermal effect on gas solubility [*Weiss*, 1974].

C dynamics and their magnitude in response to hydrology had not been previously examined in Doñana wetlands. Hydrological cycles in the region are characterized by a large variability, but climate change is likely to exacerbate it as, for the Mediterranean climatic region, higher minimum temperatures, more extreme high temperature events in summer, and less precipitation have been projected to occur [*Giorgi and Lionello*, 2008; *Roiz et al.*, 2014]. Detailed modeling of groundwater flows indicates that this will result in a decreases in groundwater discharge to the surface water basins [*Guardiola-Albert and Jackson*, 2011]. According to our analysis, these climatic changes will affect aquatic metabolism and carbon fluxes but it is presumable that the entire ecosystem C balance will be altered, potentially in complicated ways, highlighting the need for a multidisciplinary, holistic approach. In the light of the recent Doñana wetlands restoration program, our study also suggests that allowing connectivity between the Guadalquivir estuary and Doñana marshland may result in diminution of aquatic CO_2 fluxes from the marshes due to the effective flush out of large volumes of suspended and organic material during wet years and through impeding desiccation during a prolonged drought. The benefits of this interaction is clearly exemplified in the fish farm lagoons, where pumping of estuarine water contributes ultimately to the withdrawal of atmospheric CO_2.

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