# Biogeochemistry of Mediterranean Wetlands: A Review about the Effects of Water-Level Fluctuations on Phosphorus Cycling and Greenhouse Gas Emissions 

Inmaculada de Vicente ${ }^{1,2(D)}$<br>1 Departamento de Ecología, Universidad de Granada, 18071 Granada, Spain; ivicente@ugr.es; Tel.: +34-95-824-9768<br>2 Instituto del Agua, Universidad de Granada, 18071 Granada, Spain

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#### Abstract

Although Mediterranean wetlands are characterized by extreme natural water level fluctuations in response to irregular precipitation patterns, global climate change is expected to amplify this pattern by shortening precipitation seasons and increasing the incidence of summer droughts in this area. As a consequence, a part of the lake sediment will be exposed to air-drying in dry years when the water table becomes low. This periodic sediment exposure to dry/wet cycles will likely affect biogeochemical processes. Unexpectedly, to date, few studies are focused on assessing the effects of water level fluctuations on the biogeochemistry of these ecosystems. In this review, we investigate the potential impacts of water level fluctuations on phosphorus dynamics and on greenhouse gases emissions in Mediterranean wetlands. Major drivers of global change, and specially water level fluctuations, will lead to the degradation of water quality in Mediterranean wetlands by increasing the availability of phosphorus concentration in the water column upon rewetting of dry sediment. $\mathrm{CO}_{2}$ fluxes are likely to be enhanced during desiccation, while inundation is likely to decrease cumulative $\mathrm{CO}_{2}$ emissions, as well as $\mathrm{N}_{2} \mathrm{O}$ emissions, although increasing $\mathrm{CH}_{4}$ emissions. However, there exists a complete gap of knowledge about the net effect of water level fluctuations induced by global change on greenhouse gases emission. Accordingly, further research is needed to assess whether the periodic exposure to dry-wet cycles, considering the extent and frequency of the cycles, will amplify the role of these especial ecosystems as a source of these gases and thereby act as a feedback mechanism for global warming. To conclude, it is pertinent to consider that a better understanding about the effect of water level fluctuations on the biogeochemistry of Mediterranean wetlands will help to predict how other freshwater ecosystems will respond.


Keywords: biogeochemistry; phosphorus; greenhouse gases emissions; sediment; water level fluctuations; Mediterranean wetlands

## 1. Introduction

Wetlands are among the world's most productive and valuable ecosystems [1]. Despite covering only $1.5 \%$ of the Earth's surface, wetlands provide $40 \%$ of ecosystem services worldwide, such as provisioning, regulating, habitat and cultural services [2]. Among them, three regulating services are globally significant [3,4], namely water quality improvement, flood abatement, and carbon management. Wetlands purify water (which is why they are often called 'nature's kidneys') through storing nutrients and other pollutants in their soils and vegetation, and trapping sediments [5]. In particular, nutrients such as phosphorus and nitrogen (as nitrate), commonly associated with agricultural runoff and sewage effluent, are removed or significantly reduced by wetlands [6,7]. As a result, wetlands are traditionally considered as "hotspot" for biogeochemical transformation worldwide [8].

Biogeochemical processes in wetlands are highly dynamic [9,10] and involve complex interactions between hydrological processes, mineralogical transformations, and bacterial and vegetation communities [11,12]. The increasing worldwide affectation of wetlands by
a shift in environmental conditions due to climate change, land use development, resource extraction, urbanization, and sea level rise [13,14], will lastly alter the hydrological regime, impacting the biogeochemical processes. Although some previous reviews have been conducted, both under a global perspective [15-17] and under a regional context [18], the present study is the first review focused on Mediterranean wetlands, which are among the most threatened ecosystems due to climate change and natural habitat loss [19]. Mediterranean wetlands are considered as unique ecosystems exposed to Mediterranean climate forcing, and thus they are located in a more extensive region beyond the Mediterranean basin, including other geographic areas such as parts of California, South Africa, Chile, and Southern Australia [20] (Figure 1). As a result of this climate, they are subjected to a strong seasonality in water supply outside the hot season and they also experience a long vegetation period that makes them quite distinct from the standard limnological paradigm [21]. Apart from these external conditions, several internal features (i.e., shallowness and a typically high catchment area to lake area ratio) make Mediterranean wetlands especially sensitive to water level fluctuations induced by global change.


Figure 1. Geographic locations with a Mediterranean climate.
In this review, after explaining the vulnerability of these ecosystems to global change and the key role played by sediments in their biogeochemistry, we analyze the potential effects of such hydrological changes in both phosphorus dynamics and greenhouse gas emissions. Phosphorus is one of the major nutrients limiting primary production in many freshwater ecosystems [22] and, thus, it is frequently responsible for eutrophication, which is a critical issue for water managers [23]. Our additional interest is to assess the dependence of greenhouse gas emissions under different water level scenarios. This concern is based on the observation that wetlands have the highest carbon density among terrestrial ecosystems and contain around $15 \%$ of the world's organic soil carbon [24], being the dominant natural source of methane emissions [25]. Accordingly, in the context of global change, it is essential to clarify the last effect of hydrological fluctuations in Mediterranean wetlands on the release or retention of sedimentary phosphorus and on their role as a sink or a source of greenhouse gases.

## 2. Sensitivity of Mediterranean Wetlands to Global Change Factors

Climate change is one of the planetary boundaries that has already crossed their limits [26]. It represents a complex amalgam of stressors, including alterations in temperature [27], elevated atmospheric $\mathrm{CO}_{2}$ [28], and increased frequency and intensity of droughts and extreme flow events $[29,30]$. Additionally, synergies with other stressors could amplify the effects of climate change. For instance, summer droughts, as they are projected for future Mediterranean climate, will not only lead to elevated temperatures and habitat fragmentation, but they may also exacerbate the impacts of eutrophication and toxins by increasing pollutant concentrations [31].

Climate change is arguably the greatest emerging threat to global biodiversity and to the functioning of local ecosystems [28,32]. Aquatic ecosystems are particularly vulnerable to climate change for the following reasons: (i) many species within these fragmented habitats have limited abilities to disperse as the environment changes; (ii) water temperature and availability are climate-dependent; and (iii) many systems are already exposed to numerous anthropogenic stressors [31]. In these ecosystems, a warmer climate will drastically affect the hydrological cycle and change atmospheric and meteorological properties such as precipitation patterns, atmospheric water vapor and evaporation [28,33], and consequently it will impact water quality by intensifying many forms of water pollution [34,35]. Among aquatic ecosystems, wetlands are particularly sensitive to changes in their water balance, resulting in reduced areal extent, increased vulnerability to fire, and altered rates of exchange of greenhouse gases [36].

From an economical point of view, Costanza et al. [37] emphasized the disproportionate contribution of wetlands to the natural capital provided by world's ecosystems. Later, Balmford et al. [38] reviewed the costs and benefits of converting wild habitats to other uses (e.g., woodland into logs, and mangrove into aquaculture), and concluded that conversion was always harmful in overall economic terms. At this point, it is worth noting that it has been already recognized that the adverse effects of global change, such as sea level rise, and changes in hydrology and in the temperature of water bodies, will lead to a reduction in the services provided by wetlands [39]. For the case of Mediterranean wetlands, it is expected that direct and indirect impacts of global change will particularly affect the biodiversity of Mediterranean wetlands and their related ecosystem services [40,41]. However, not all Mediterranean wetlands are equally affected, with the Eastern and Southern part of the basin already being the most heavily impacted [42]. The Spanish National Ecosystem Assessment [43], inspired by the Millennium Ecosystem Assessment, evaluated, for each ecosystem type, the actual status and trends for the last five decades (1960-2010) of 22 ecosystem services. This report concluded that $60 \%$ of the original areas of wetlands have been degraded and, accordingly, these systems have undergone considerable degradation of most of their services (regulating and provisioning), with the only exception of cultural services. In fact, they are the only ecosystems that have suffered the intense synergistic effect of at least three direct drivers of change: land-use change, pollution, and over-exploitation of water.

In the last twenty years, specific concerns about the impacts of global climate change on aquatic ecosystems, which causes global environmental challenges regarding the management of water resources, have been raised [17,31,35,36,44,45]. However, there exists a knowledge gap regarding Mediterranean wetlands, which is especially striking, as Mediterranean climate ecosystems will likely experience the greatest proportional change in biodiversity [46]. Mediterranean wetland ecosystems are characterized by the presence of extremely high fluctuations in water level, which make this unique biophysical environment a biogeochemical hotspot at the landscape level [47]. As Mitsch and Gosselink [48] noted, hydrology is probably the single most important determinant of the establishment and maintenance of specific types of wetlands and wetland processes. Among wetlands, it is evident that the structure and functioning of Mediterranean wetlands are especially vulnerable to global climate change, as it has been predicted that it will shorten precipitation seasons and increase the rate and length of summer droughts in this area [49].

Among the inherent characteristics of Mediterranean wetlands that make them especially sensitive to global change, we may remark their shallowness and their typically high catchment area to lake area ratio [21]. All these are responsible for a huge proneness to changes in land uses. In this sense, recent studies have found that land uses in wetland catchments are critical factors to consider when evaluating the effects on the diversity and composition of their aquatic communities [50-54]. In the Mediterranean region, agricultural practices are the most important human activity, inducing a drastic transformation of the landscape, with a great loss rate and degradation of wetlands [55-58]. As Gilbert et al. [59] recognized, the source ecosystem (watershed) affects the sink ecosystem (wet-
land), as much as the increment of the edge/volume ratio, making it more exposed to the exchange of substances with the surrounding terrestrial landscapes [60-62].

Lastly, Figure 2 summarizes the impacts of global change on Mediterranean wetlands. In brief, major drivers of global change are: (i) air temperature; (ii) solar radiation, (iii) precipitation, (iv) wind speed, and (v) human activities. As greenhouse gases increase in the atmosphere, the increase in radiative forcing results in higher surface temperatures, increased water-holding capacity of the atmosphere, increased evaporation, and larger water vapor amounts [63]. In fact, larger water vapor content (a greenhouse gas) will also result in a positive feedback $[63,64]$. On the other hand, it has also been reported that global warming and solar radiation have mutual connections [34,65]. In particular, NazariSharabian et al. [34] made a detailed explanation of the connection between both solar radiation and global change and the inherent implications. Climate change is also expected to increase the frequency and intensity of droughts and extreme flow events [28,29] which will reduce freshwater availability and quality. The wind will also be affected by climate change, causing both direct and indirect impacts on water resources [66]. Modeling results for predicting the wind speed in different regions in 2050 have shown that some areas (e.g., Northern Europe and Central and South America) will be affected by stronger surface wind speeds, while decreasing wind speeds have been predicted for Southern Europe and Eastern and Southern Asia [67]. Accordingly, Mediterranean wetlands are expected to present higher water column thermal stabilities, which, otherwise, will likely cause more frequent Cyanobacterial blooms [68-70]. Additionally, and as Nazari-Sharabian et al. [34] suggested, human activities linked to an increasing population, rapid urban development, and lack of land use planning, continually contribute to the degradation of the environment and water resources. More specifically, human activities cause an increase in external nutrient loads to Mediterranean wetlands, both directly (e.g., discharge of treated and untreated wastewaters) and indirectly (e.g., changes in catchment land uses) [71,72]. Furthermore, human activities also generate an over-exploitation of water resources that lastly leads to increased annual and interannual fluctuations of water levels, far beyond natural amplitudes [73]. As a result, the combination of all stressors driven by global change will dramatically impair the water quality of these threatened ecosystems by increasing both internal and external nutrient loads. Next, in this review, we will focus on the effect of changes in water level on phosphorus cycling and greenhouse gas emissions.


Figure 2. Major drivers of global change on Mediterranean wetlands (modified from [34]). The main issues addressed in this review are marked in bold letters.

## 3. The Sediment as an Essential Compartment of Mediterranean Wetlands

Traditional limnological research has been especially focused on the pelagic zone [74]; however, in the case of wetlands, as opposed to deep water ecosystems (lakes and reservoirs), the littoral and the benthic zone play an essential role in the overall dynamics of the ecosystem. The essential interest of considering sediment in limnological studies lies in the fact that, as Håkanson [75] points out, this compartment both reflects and affects the characteristics of the water column itself. In the case of Mediterranean wetlands, it is clear that the second aspect (the sediment affects the overlying water column) plays a major role in understanding their functioning compared to other inland ecosystems.

The fact that the sediment reflects the conditions in the water column represents an essential pillar of paleolimnological studies, as sediment can be considered as a bank of environmental information about the processes occurring both in the water column and in the catchment where it sits [76-78]. On a shorter temporal scale, the benthic community is also coupled with the planktonic community through the sedimentation process [79,80]. Therefore, it is possible to say that, in a sense, benthos "exploit" plankton. It is also worth noting that the shallowness of wetlands limits organic matter decomposition in the water column and, therefore, most of the organic matter synthetized in the water column reaches the wetland sediments before being decomposed. Therefore, benthic metabolic activity plays a fundamental role in the global metabolism of this type of systems [81,82]. A last concern related to the fact that sediment reflects overlying water conditions is that sedimentary based indices such as the bioproduction number (BPN, [75]) may represent an appropriate tool for assessing the trophic state of Mediterranean wetlands [83]. The main advantage of using BPN is that, while the application of indices based on water column parameters (see for example $[84,85]$ ) requires repeated seasonal monitoring to obtain the annual mean values, the reproducibility of the BPN method has shown constant BPN values every time, and thus only one sampling representing the spatial heterogeneity of the surface sediment is required [83]. However, some limitations have also been detected when using BPN in Mediterranean wetlands characterized by low sedimentary organic matter content [86]. Secondly, the lake sediment affects the chemical composition of the overlying water column, as it is a dynamic and active compartment where a great diversity of reactions and transformations lead to nutrients mobilization or retention. Indeed, phosphate regeneration, mediated by microbial metabolism and chemical processes such as desorption and dissolution, leads to an accumulation of this nutrient in the dissolved phase (interstitial water), maintaining a continuous flow by diffusion. However, this transport in favor of the concentration gradient is limited by a large number of chemical and biological processes such as adsorption, complexation with cations, precipitation as authigenic minerals and microbial assimilation, which can immobilize the phosphate temporarily or permanently in the sediment [87]. Doubtlessly, this water-sediment interaction reaches its maximum expression in wetlands, where the close and reciprocal connection between both compartments determines that the nutrients reaching the sediment can be again mobilized and transported to the water column, through a wide variety of complex mechanisms [88,89]. In fact, wetland intrinsic characteristics (e.g., shallowness, hydrological regime, morphology, hydraulic residence) are responsible for determining an especially close relationship between the sediment and the water column.

It is precisely this second aspect (sediment affects the chemical composition of the overlying water) that has aroused the greatest interest in recent decades, essentially motivated by the key role that sediment plays in the recovery of eutrophicated aquatic systems. Numerous studies have shown the failure (or delay) of the application of restoration techniques of eutrophicated systems essentially based on the reduction of the external nutrient load [90-96]. The dynamic equilibrium between the solid and liquid sedimentary phase determines that nutrients temporarily retained in the sediment are subsequently mobilized into the water column in response to a decline in its availability in water [87,97]. Accordingly, in order to ensure the successful response of a eutrophicated aquatic ecosystem, in addition to reducing external phosphorus loading, it is recommended to apply in-lake
techniques to decrease internal phosphorus loading and accelerate lake water improvement $[23,98]$. Some of these techniques are based on preventing phosphorus release from sediment by hypolimnetic aeration, nitrate $\left(\mathrm{NO}_{3}{ }^{-}\right)$addition or sediment capping [99]. Some other in-lake techniques are focused on enhancing the phosphorus adsorption capacity of sediment by adding alum, iron, calcium salts, solid phase P-sorbing products (PSPs) from industrial waste, and Phoslock ${ }^{\circledR}$ [100-102]. As Funes et al. [103] recognized, in spite of its widespread application, the main drawback about salt addition is that, although inactivated, phosphorus remains in the sediment and may be released to the water column under changing physicochemical and biological conditions, such as temperature, pH , redox potential, biological activity or resuspension [104-107]. This is a striking point, as sediments from all wetlands, especially from Mediterranean wetlands, are exposed to intense physical and biological processes that eventually lead to uncertain conditions.

## 4. Impact of Sediment Desiccation and Re-Flooding on the Phosphorus Cycle

Even though Mediterranean water bodies are characterized by natural extreme water level fluctuations in response to irregular precipitation patterns [21], global climate change is projected to amplify this pattern by shortening precipitation seasons and increasing the frequency and intensity of summer droughts in this area [49]. The sharpest water level fluctuations linked to climate change occur in closed-basin lakes, where water levels are controlled by the balance between precipitation and evaporation [108]. Apart from a clear effect on lake biota, water level fluctuations drastically affect wetland biogeochemical cycles as the periodic exposure to desiccation and re-flooding cycles drastically modify the physical and chemical properties of the sediment [109,110]. These changes in sediment properties may lead to relevant shifts in phosphorus availability in the overlying water column, as sedimentary phosphorus adsorption and desorption properties may be affected. At this point, it is worth considering that Batzer and Sharitz [109] presented an excellent overview of the relevance of wet/dry cycles for the biogeochemistry of wetlands. These authors recognized that hydrology, biogeochemistry, and microbial ecology are inextricably linked and, thus, they identified some crucial questions to be considered, such as: (i) how long is the wetland dry between wet periods? (ii) how quickly does the water rise? (iii) how deep is the water? (iv) how long does the wetland retain water? (v) how quickly does the water level drop during the dry period? and (vi) in what season does the wetland fill with water?

The analysis of the impact of sediment desiccation and re-flooding on the phosphorus cycle is generally based on two different methodological approaches: adsorption experiments with different sediments (wet vs. dry sediment) and re-flooding experiments. Although there are few studies focused on Mediterranean wetlands [110-114], the studies carried out in other types of inland aquatic ecosystems (most of them reservoirs) have shown contradictory results (Table 1) that range from an increase in the phosphorus adsorption capacity after desiccation periods [115-117] to eutrophication events of the water column after sediment re-flooding as a result of a reduction in the phosphorus adsorption capacity [118]. The absence of a clear pattern reflects the complexity of the chemical, physical, and biological transformations involved [110].

There are three main types of mechanisms regulating the uptake and release of phosphorus in hydrologically dynamic wetlands: (i) chemical reactions dominated by sorption-desorption processes and controlled by pH and redox conditions; (ii) physical transformations such as changes in particle size distribution; and (iii) biological processes dominated by microbial activity.

Regarding purely chemical processes, and due to the close phosphorus-iron coupling, most studies have been focused on the transformations of iron oxides as a consequence of the increase in oxygen availability during desiccation [119]. During wetland re-flooding, the dominance of anoxic conditions, because of the intense organic matter decomposition and the low oxygen diffusivity in water relative to air, is responsible for determining phosphorus release from lake sediment. Indeed, the redox potential is one of the drivers of
sedimentary phosphorus retention. Briefly, when the redox potential is lower than +120 mV , the reduction of $\mathrm{Fe}^{+3}$ to $\mathrm{Fe}^{+2}$ takes place, leading to the release of adsorbed phosphorus on iron oxyhydroxides $[120,121]$. However, this paradigm of phosphorus retention under oxic conditions and release under anoxic conditions has been questioned by researchers such as Gätcher and Müller [122] and Golterman [97]. In his book, Golterman [97] recognized that, although in Mortimer's experiment there was a release of both $\mathrm{Fe}^{2+}$ and phosphate in the anoxic tank, the Fe/P ratio showed drastic changes (increase) of nearly an order of magnitude. In this sense, Golterman [97] also summarized some arguments against the release of phosphate bound to iron oxyhydroxides by oxyhydroxides reduction. Then, he noted that a constant stoichiometric release of iron and phosphate around 10 was the only one consistent with the iron-reduction hypothesis. Moreover, Rothe et al. [123,124] demonstrated the existence of long-term retention of phosphorus under anoxic conditions due to the formation of reduced iron phosphate minerals such as vivianite $\left[\mathrm{Fe}_{3}\left(\mathrm{PO}_{4}\right)_{2} \cdot 8 \mathrm{H}_{2} \mathrm{O}\right]$. Later, when wet sediment becomes dry, a sequence of events occurs in which the ferrous iron salts (sulfides, carbonate, and phosphate) previously present in the anoxic zones are rapidly oxidized to ferric oxyhydroxides, with a high affinity for phosphate ion [111] (Figure 3). On the contrary, a prolonged exposure to desiccation conditions would lead to an opposite effect where amorphous iron oxides age and transform into more crystalline forms of iron oxide $[118,119,125]$ and therefore, with a lower phosphorus adsorption capacity. Additionally, it is worth highlighting that, during sediment desiccation, translocation of sedimentary phosphorus fractions can occur. Indeed, Attygalla et al. [114] observed, by running a laboratory experiment with wet sediment exposed to progressively more severe drying (at 30,50 , and $85^{\circ} \mathrm{C}$ ), that drying led to an increase in bioavailable, easily exchangeable phosphorus. These authors concluded that the shifts in phosphorus speciation and the decline in phosphorus adsorption capacity upon drying contribute to the Birch effect-the initial pulse of phosphorus upon inundation of dried soils or sediments. Apart from iron-linked reactions, Golterman [97] pointed out that drying can also result in phosphate precipitating with $\mathrm{CaCO}_{3}$ as calcium concentration increases.


Figure 3. Time-dependent effects of sediment drying on iron chemical transformation.
Furthermore, and as was recognized by de Vicente et al. [110], a variety of physical changes due to sediment drying have been described in the literature. Barrow and Shaw [115] concluded that drying may decrease hydration of iron hydroxide gels in soils, which may increase the specific surface area of iron oxide particles, resulting in increasing phosphate adsorption capacity. However, opposite results have been described by some other authors [126,127], who found that particle size distribution in the dried sediment shifts toward larger particles, leading to a reduction in sediment affinity for phosphate as most of the phosphorus is accumulated in the finer fraction [128]. Indeed, the relevance of physical changes along sediment desiccation has also been described in two oligotrophic high mountain Mediterranean wetlands [110]. These authors found a decrease in phosphate sorption properties in transects from the littoral zone to dry land (up to the upland water mark) concomitantly with loss of amorphous oxides of iron and aluminum as revealed by oxalate and dithionite extractions. They also observed that X-ray diffraction did not indicate increased amounts of crystalline metal oxides, but there was a loss of
fine particles ( $<20 \mu \mathrm{~m}$ ) with the increasing distance from the shore, probably due to wind erosion. Accordingly, the reduction in phosphate adsorption capacity when sediment dries was explained by the loss of amorphous metal oxides, as they are often enriched in the fine sediment fraction.

Lastly, apart from chemical and physical transformations, biological processes are likely to occur when wetland sediment becomes dry. In fact, Batzer and Sharitz [109] recognized that one of the main mechanisms regulating the uptake and release of phosphate in hydrologically dynamic wetlands is a biological process dominated by microbial activity. In this context, it is surprising that, up to date, most studies focused on analyzing the effect of drying and wetting on phosphorus sorption have mainly considered abiotic processes (physical and chemical reactions). Contrarily, Gilbert et al. [113] found that chemical processes, such as those mediated by reduction of iron hydroxides, play a secondary role during sediment desiccation in two countryside Mediterranean wetlands, while organic matter decomposition was the main driver determining sedimentary phosphate retention vs. release upon desiccation. Specifically, these authors observed that desiccation had an overall negative effect on organic matter concentration. Indeed, it is well known that, as organic matter decomposition drastically depends on environmental conditions such as oxygen, drying may cause a notable reduction in organic matter concentration. In fact, oxygen diffusion is 10,000 times slower in water than in the air [16]. Additionally, in both countryside Mediterranean wetlands was found a much lower content in organic phosphorus pools in dried compared to wet sediments. The more plausible explanations for the positive correlation between sediment organic matter content and phosphate adsorption capacity in those study wetlands were the increase in amorphous minerals stabilization [129] and in caption bridging with compounds such as calcium and magnesium [130-132]. Moreover, Darke and Walbridge [129] found that sediment organic matter can also inhibit re-crystallization of both iron and aluminum compounds, thus indirectly assisting phosphate sorption.

When attempting to predict the effect of water level fluctuations on the phosphorus cycle, it is important to assess not only changes in phosphate adsorption capacity, by running batch adsorption experiments, but also the consequence of sediment re-flooding on phosphate availability in the overlying water column. To test it, re-flooding experiments by using different dry sediment (e.g., fresh vs. dried sediment for different times) can be run. Table 2 summarizes results from laboratory and field experiments carried out in different study sites, most of them reservoirs. The foremost result is that, for all study sites, drying events led to phosphorus release upon rewetting, which would thereby contribute to the eutrophication of the aquatic ecosystem. As Watts [133] recognized, biological processes may be of paramount importance and can account for up to $100 \%$ of the phosphorus release. In fact, wetland microbes mediate phosphorus dynamics by assimilating and releasing inorganic phosphorus as part of their growth cycles, excreting extracellular enzymes to hydrolyze organic phosphorus to inorganic forms, and creating the anoxic conditions that favor the reduction of ferric to ferrous iron [109]. Furthermore, they are critical in the uptake of any phosphorus leached from leaves that fall into the wetland [127]. To date, it has been found that, when reinundated, dry sediments release the phosphorus from dead microbial cells [134-136], and that drying can stimulate the decomposition of organic matter, which will increase the phosphorus available for release on rewetting sediments [135].

Table 1. Effects of sediment air drying on phosphorus dynamics reported by the literature in inland aquatic ecosystems.

|  | Mechanism | Consequence | References |
| :---: | :---: | :---: | :---: |
| Chemical | Increase in ferric oxyhydroxides concentration | Increase of phosphorus adsorption capacity | [111] |
|  | Transformation of amorphous iron oxides into more crystalline forms of iron oxides | Decrease of phosphorus adsorption capacity | [118,125] |
|  | Increase in iron crystallinity | Decrease of phosphorus adsorption capacity | [114] |
|  | Phosphate precipitation with $\mathrm{CaCO}_{3}$ as calcium concentration increases | Increase in sedimentary phosphorus concentration | [97] |
| Physical | Increase of specific surface area Shifts towards larger particles | Increase of phosphorus adsorption capacity Decrease of phosphorus adsorption capacity | $\begin{gathered} {[115]} \\ {[110,126,127,135]} \end{gathered}$ |
| Biological | A reduction in organic matter concentration inferring a more intense mineralization | Decrease of phosphorus adsorption capacity | [110,113] |

More specifically, for the case of the two abovementioned oligotrophic high mountain Mediterranean wetlands, de Vicente et al. [110] found that the loss of adsorption capacity for phosphate upon re-wetting was associated with loss of amorphous iron oxides, and the changes appear to be non-reversible. Therefore, in these phosphorus-limited wetlands, both desiccation and re-wetting lead to a decrease in sediment phosphate sorption capacity and increased water level fluctuations, a possible scenario of global change, may therefore increase phosphorus availability in the water column of these oligotrophic systems.

A striking point is that the magnitude of internal phosphorus loading upon re-wetting was shown to rise with the degree of sediment dehydration: the longer the intermittent drying period lasted, the higher was the rise in phosphorus release compared to previous wetting events [137]. Moreover, the effect of desiccation will be much greater for systems that are rarely dried (if ever) compared to water-bodies that are dried out on a regular basis as repeated wetting/drying cycles select for bacteria that are tolerant to periods of desiccation and/or oxidation [112]. It is evident that these results have decisive management implications for the case of Mediterranean reservoirs, where littoral sediments are exposed and desiccated during summer. To some extent, management can influence some of the factors affecting drying and rewetting (i.e., the type of drawdown, severity of drying and conditions of refilling) by modifying the drawdown of water [133]. As this author suggested, if the desired outcome is the repression of the phosphorus flush from the sediment into the water column that typically occurs during refilling, then ideally water levels should be maintained at as high a level as possible with a reduction of drawdown in the summer. However, from a practical point of view, the likelihood of being able to modify drawdown in most of reservoirs so that summer water levels are maximized is remote [133].

Table 2. Mechanisms responsible for phosphorus release upon re-flooding of dry sediment reported by the literature in inland aquatic ecosystems.

| Mechanism | References |
| :---: | :---: |
| Sediment resuspension | [138] |
| Breakdown of sedimentary organic phosphorus | [126] |
| Breakdown of sedimentary bacterial phosphorus | [127] |
| Shifts in bacterial communities, C-limitation as a result of the air exposure and ageing of minerals adsorbing phosphorus | [139] |
| Aging of $\mathrm{Fe}(\mathrm{OOH})$ decrease phosphorus affinity. Biological processes such as organic matter decomposition | [133] |
| Immobilized bacterial phosphorus upon desiccation is released | [140] |
| Loss of amorphous iron oxides upon desiccation | [110] |
| Enhanced mineralization rates, enhanced reduction of iron hydroxides and a general loss in sorption capacity due to increased crystallinity of iron hydroxides | [137] |
| Loss of organic matter upon desiccation | [113] |

## 5. Consequence of Sediment Desiccation and Re-Flooding on Greenhouse Gases Emissions

Carbon dioxide $\left(\mathrm{CO}_{2}\right)$, methane $\left(\mathrm{CH}_{4}\right)$, and nitrous oxide $\left(\mathrm{N}_{2} \mathrm{O}\right)$ are the three main long-lived greenhouse gases in the troposphere, and they have increased by $147 \%, 259 \%$, and $123 \%$ since the preindustrial era, respectively [141-143]. $\mathrm{CO}_{2}$ is the most important anthropogenic greenhouse gas in the atmosphere, representing approximately $66 \%$ of the increase in the global radiative forcing, by 2018, since pre-industrial times. $\mathrm{CH}_{4}$ and $\mathrm{N}_{2} \mathrm{O}$ are the second and third anthropogenic greenhouse gases in relevance, and they represent $17 \%$ and $6 \%$, respectively [144]. Despite their lower concentrations in the atmosphere, $\mathrm{CH}_{4}$ and $\mathrm{N}_{2} \mathrm{O}$ absorb infrared radiation more intensely than $\mathrm{CO}_{2}$ [145], and they present a global warming potential (GWP) of 34 and 298 times, respectively, that of $\mathrm{CO}_{2}$ for a 100-year timescale [141]. Therefore, there is a need for a comprehensive knowledge of global sinks and sources of $\mathrm{CO}_{2}, \mathrm{CH}_{4}$, and $\mathrm{N}_{2} \mathrm{O}$ as well as their environmental drivers.

Briefly, regarding $\mathrm{CO}_{2}$, lakes and reservoirs are usually supersaturated [146], and they release $0.32 \mathrm{Pg} \mathrm{C} \mathrm{yr}^{-1}$ to the atmosphere [147]. In fact, these systems are often heterotrophic as the $\mathrm{CO}_{2}$ production by microbial mineralization of dissolved organic carbon exceeds the $\mathrm{CO}_{2}$ uptake by photosynthesis. On the other hand, rivers, lakes, and reservoirs are also supersaturated in $\mathrm{CH}_{4}$, and they emit up to $77.5-134.4 \mathrm{Tg} \mathrm{C} \mathrm{yr}^{-1}$ [148-150]. Such emission from inland waters represents more $\mathrm{CH}_{4}$ than that emitted from the ocean surface [151]. Traditionally, methanogenesis is considered as the formation of methane during the microbial decomposition of organic matter under anoxic conditions, such as lake sediments. In fact, anoxic sediments are a primary source of $\mathrm{CH}_{4}$ in inland waters [152]. The methane produced in the anoxic sediment diffuses up to the water overlying the sediment, and it is rapidly oxidized by methanotrophs to $\mathrm{CO}_{2}$ in the presence of oxygen [153-157]. Therefore, the net production of $\mathrm{CH}_{4}$ is determined by archaeal methanogenesis in anoxic conditions, and by methanotrophs, which consume $\mathrm{CH}_{4}$ under oxic conditions [156].
$\mathrm{N}_{2} \mathrm{O}$ is produced by two main biological processes: nitrification and denitrification. In soils and sediments, $\mathrm{N}_{2} \mathrm{O}$ is produced as a by-product of nitrification during the microbial transformation of $\mathrm{NH}_{4}{ }^{+}$to $\mathrm{NO}_{3}{ }^{-}$by ammonia oxidizing bacteria under aerobic conditions. However, during denitrification, $\mathrm{N}_{2} \mathrm{O}$ is produced as an intermediate product in the microbial transformation of $\mathrm{NO}_{3}{ }^{-}$to $\mathrm{N}_{2}$ by denitrifying bacteria under anaerobic soil conditions [158,159]. Previous studies have shown that mineral $\mathrm{N}\left(\mathrm{NH}_{4}{ }^{+}\right.$and $\left.\mathrm{NO}_{3}{ }^{-}\right)$ promotes $\mathrm{N}_{2} \mathrm{O}$ emissions, since it can be metabolized by both nitrifiers and denitrifiers in soils [160-162]. The dominance of nitrification or denitrification as the main source of $\mathrm{N}_{2} \mathrm{O}$ depends on whether the soils are aerobic or anerobic and on the availability of mineral $\mathrm{N}[163,164]$. In addition to the biological production of $\mathrm{N}_{2} \mathrm{O}$, some studies have also focused on the abiotic production of $\mathrm{N}_{2} \mathrm{O}$, which may occur by two main pathways: (i) decomposition of $\mathrm{NH}_{2} \mathrm{OH}$ to $\mathrm{N}_{2} \mathrm{O}$, and (ii) chemodenitrification to $\mathrm{N}_{2} \mathrm{O}$ [165-169].

From this outline, it is clear that all processes involved in $\mathrm{CO}_{2}, \mathrm{CH}_{4}$ and $\mathrm{N}_{2} \mathrm{O}$ production are oxygen-dependent and, thus, the hydrology (shifts in the dry-wet cycle) may play a key role in their final function as a sink or as a source. In fact, oxygenation is assured in desiccated sediments, while anaerobiosis depends on a number of factors, such as the sediment structure, temperature and the presence of bioavailable carbon to support metabolic activity [119]. Furthermore, greenhouse gas production is directly connected to changes in organic matter concentration in sediments (discussed earlier in this review).

Before discussing the potential effect of water-level fluctuations on greenhouse gases emissions, we will first try to assemble the most relevant studies carried out in freshwater ecosystems. Given the inverse relationship between $\mathrm{CH}_{4}$ concentration and lake area $[170,171]$, it is expected that Mediterranean wetlands, characterized by their reduced dimensions, may act as notable sources of this gas to the atmosphere. Probably, one of the most complete overviews about estimations of greenhouse gases flux from different inland waters (including wetlands) compared with those of other anthropogenic activities is the one reported by Deemer et al. [148]. As those authors noted, from a greenhouse gases management perspective, it is crucial to understand the relative role of $\mathrm{CO}_{2}, \mathrm{CH}_{4}$, and $\mathrm{N}_{2} \mathrm{O}$
emissions as $\mathrm{CH}_{4}$ and $\mathrm{N}_{2} \mathrm{O}$ are more powerful greenhouse gases than $\mathrm{CO}_{2}$ (34 and 298 times the global warming potential on a 100-year timescale, respectively [172]). To describe the relative contribution of various greenhouse gas emissions to global warming, emissions were converted to $\mathrm{CO}_{2}$ equivalents, a metric that relates the radiative forcing caused by 1 mass unit of trace greenhouse gas to that caused by the emission of 1 mass unit of $\mathrm{CO}_{2}$ over a given time span. Among all inland waters, it was noted that wetlands exhibited the highest value for the annual $\mathrm{CO}_{2}$ equivalent for $\mathrm{CO}_{2}, \mathrm{CH}_{4}$, and $\mathrm{N}_{2} \mathrm{O}$, and they also concluded that $\mathrm{CH}_{4}$ emissions (4805-8976 $\mathrm{Tg} \mathrm{CO}_{2} \mathrm{Eq}^{\text {year }}{ }^{-1}$ ) were the highest contribution to the radiative forcing. Similar results confirming the role of wetlands as a major natural source of $\mathrm{CH}_{4}$ ( 30 and $40 \%$ to the total emissions) were reported by Kayranli et al. [25] and Koffi et al. [172]. At this point, it is worth mentioning the complete study made by Melton et al. [173], who compiled data of global and peatland wetlands, in the context of the Wetland and Wetland $\mathrm{CH}_{4}$ Inter-comparison of Models Project (WETCHIMP), with the aim of simulating large-scale wetland characteristics and corresponding $\mathrm{CH}_{4}$ emissions from surface waters. Although these authors paid special attention to some regional patterns, due to their inherent characteristics, we would have expected a much more profound consideration of Mediterranean wetlands. Contrarily to these studies, Whiting and Chanton [174] reported annual measurements of the relationship between $\mathrm{CH}_{4}$ emission and net C fixation in three wetland ecosystems (ranging from the boreal zone to the near-subtropics) and found that, considering a 500-year time horizon, these wetlands can be regarded as sinks for greenhouse gas warming potential, and thus attenuate the greenhouse warming of the atmosphere. One likely explanation for the apparent contradiction is the different time scale, since, on a longer timescale, $\mathrm{CO}_{2}$ is higher weighted than other greenhouse gases such as $\mathrm{N}_{2} \mathrm{O}$ and $\mathrm{CH}_{4}$, which have a much shorter lifespan.

Forecast hydrological variations will have profound effects on the processes responsible for nutrient cycling in wetlands [119]. More specifically, Fennesy et al. [175] recognized that wetlands' capacity to sequester carbon is a function of factors that interact across multiple scales and hydrologic disturbances, such as drainage and shortened hydroperiods, which tend to increase soil drying and organic carbon oxidation, resulting in the release of carbon dioxide to the atmosphere [24]. In fact, drying-rewetting cycles may represent a significant physiological stress for soil biota, which can undergo an osmotic shock with possible cell lyses and release of intracellular solutes [176]. Soil and sediment drying promotes the release of bioavailable N due to (i) enhanced aerobic mineralization of organic matter (accumulation of ammonium- N in the sediment) and the (ii) release of cell-bound N and C from sediment bacteria killed during drying [177]. Consequently, an increase in C and N mineralization is generally expected in soils exposed to drying-rewetting events [178]. Rapid changes in water potential may also result in the destruction of soil aggregates, exposing organic matter that had previously been physically protected [179].

Temporarily flooded wetlands are widely distributed in regions with alternating drywet seasons such as Mediterranean climates. Unexpectedly, few studies are focused on assessing the effect of water level fluctuations on greenhouse gases emissions in Mediterranean wetlands $[163,178]$, while most studies have been carried out in Mediterranean reservoirs [180] and in coastal wetlands [181,182]. Although reservoirs, which are aquatic ecosystems especially abundant in the Mediterranean area, are often thought of as "green" or carbon-neutral sources of energy, a growing body of work has documented their role as greenhouse gas sources [148,183,184]. Reservoirs and Mediterranean wetlands share some similarities, such as the high frequency of water level fluctuations and the typically high catchment area to surface area ratio, which are likely to stimulate the role of these ecosystems in the emission of greenhouse gases. Therefore, in reservoirs, it has been documented that drops in hydrostatic pressure during water level drawdowns can enhance $\mathrm{CH}_{4}$ bubbling (e.g., ebullition) rates at least in the short term [185]. This enhanced ebullition may then decrease the fraction of $\mathrm{CH}_{4}$ that is oxidized to $\mathrm{CO}_{2}$ by methane oxidizing microbes [186]. Furthermore, the high catchment area to surface area ratios and close proximity to human activities [187] characteristic of many reservoirs are likely to increase
the delivery of organic matter and nutrients from land to water (relative to natural lakes), potentially fueling additional decomposition [148]. A recent study performed in a set of 12 Mediterranean reservoirs has shown that some reservoirs were sinks (influx rates $<0$ ), and others were sources (outflux rates $>0$ ) for $\mathrm{CO}_{2}$ and $\mathrm{N}_{2} \mathrm{O}$ fluxes, but all reservoirs were $\mathrm{CH}_{4}$ sources [183]. In fact, to determine the net C footprint considering these three greenhouse gases, authors converted the $\mathrm{CH}_{4}$ and $\mathrm{N}_{2} \mathrm{O}$ fluxes to $\mathrm{CO}_{2}$ equivalents using their warming potentials [141] and summed the $\mathrm{CO}_{2}, \mathrm{CH}_{4}$, and $\mathrm{N}_{2} \mathrm{O}$ fluxes in this unit. As a result, they observed that most of the study reservoirs had a positive C footprint in the study time (i.e., acted as greenhouse gases sources).

Next, we will focus on the effect of water level fluctuations on the emission of greenhouse gases. All data reported in the literature reflect that desiccation favors global $\mathrm{CO}_{2}$ fluxes while re-flooding of dry sediments increases $\mathrm{CH}_{4}$ emissions (Figure 4). More specifically, in a Mediterranean wetland, Fromin et al. [178] noted, by using eddy covariance measurements, that global $\mathrm{CO}_{2}$ fluxes were enhanced during early desiccation, decreased under dry conditions, and finally re-enhanced after a rainfall. More recently, Zhao et al. [182] studied the effect of changes in water table level on $\mathrm{CO}_{2}$ and $\mathrm{CH}_{4}$ emissions in a coastal wetland in the Yellow River Delta. They found that water level rise decreased soil $\mathrm{CO}_{2}$ emissions, while increasing soil $\mathrm{CH}_{4}$ emissions. As expected, water table level rise significantly altered soil physical and chemical properties in the uppermost soil layer ( $0-10 \mathrm{~cm}$ ), particularly soil moisture and salinity, which probably jointly affected soil $\mathrm{CO}_{2}$ and $\mathrm{CH}_{4}$ emissions. Furthermore, the cumulative soil $\mathrm{CH}_{4}$ emission was positively significantly correlated to soil organic carbon and total carbon, suggesting that the carbon component can supply energy and nutrients and benefit for soil $\mathrm{CH}_{4}$ production. Similarly, Xu et al. [163] found, in a coastal Mediterranean wetland, that inundation decreased cumulative $\mathrm{CO}_{2}$ emissions, and $\mathrm{N}_{2} \mathrm{O}$ emissions, but increased $\mathrm{CH}_{4}$ emissions. In the same way, Shao et al. [181] demonstrated, in the restored reed wetland of Hangzhou Bay, that water level was related to $\mathrm{CH}_{4}$ production and $\mathrm{CH}_{4}$ flux, and that controlling the hydrological environment in restored wetlands has important implications for the maintenance of their function as carbon sinks.


Figure 4. Changes in greenhouse gases emissions as a function of water level. The size of the arrow represents the relative magnitude of each flux.

Baldwin and Mitchell [119] identified the sequence of several steps that occurs in lowland river-floodplain systems along the wetting-drying regime: (i) partial drying of wet (previously inundated) sediments will produce a zone for coupled nitrificationdenitrification, and thus partial drying may result in a reduction in N availability; (ii) complete desiccation of sediments may lead to a decrease in microbial activity and to the cessation of all anaerobic bacterial processes (e.g., denitrification); (iii) re-wetting of desiccated sediments will result in an initial flush of available N and P coupled with the increase in aerobic bacterial activity, particularly nitrification; and (iv) inundation of floodplain soils will result in the release of $\mathrm{C}, \mathrm{N}$ and P , increasing the productivity and the later onset of anoxia, consequently promoting denitrification. As those authors recognized, clearly the timing of flooding and drying events is critical.

Another key question is the net effect of repeated wetting-drying cycles. In fact, the impact of repeated wetting-drying perturbations on N cycling processes is difficult to predict [119]. While denitrifiers are facultative anaerobic organisms, and thus they should survive this perturbation relatively well, the growth and activity of nitrifiers in soils have been reported to be severely inhibited by wetting-drying cycles [188]. Therefore, coupled nitrification-denitrification may be severely limited as a result of this type of perturbation [119]. However, and contrarily to what was expected, Mitchell and Baldwin [180] reported, in an Australian reservoir, that neither nitrification nor denitrification were notably affected by sediment desiccation reflecting the complexity of the mechanisms that are involved.

## 6. Concluding Remarks

Despite wetlands covering only $1.5 \%$ of the Earth's surface, they provide $40 \%$ of ecosystem services worldwide, such as provisioning, regulating, habitat, and cultural services. Wetlands purify water (which is why they are often called 'nature's kidneys'), being traditionally considered as "hotspot" for biogeochemical transformation worldwide. Globally, and particularly in the Mediterranean basin, they are threatened by climate change and natural habitat loss, and it is expected that direct and indirect impacts of global change will particularly affect their biodiversity and their related ecosystem services. However, not all Mediterranean wetlands are equally affected, with the Eastern and Southern part of the basin being most heavily impacted already. In Spain, $60 \%$ of the original areas of wetlands have been degraded and, accordingly, these systems have undergone considerable degradation of most of their services. Although Mediterranean wetlands are characterized by extreme natural water level fluctuations in response to irregular precipitation patterns, global climate change is projected to amplify this pattern by shortening precipitation seasons and increasing the frequency and intensity of summer droughts in this area. Consequently, a part of the lake sediment will be exposed to air-drying in dry years when the water table becomes low. Doubtlessly, this periodic sediment exposure to dry/wet cycles will likely affect biogeochemical processes, such as phosphorus exchange across the sediment and water interface, as well as the greenhouse gas emission. Furthermore, wetlands' water quality is strongly coupled to sediment biogeochemistry, as this watersediment interaction is maximal. This review shows the inherent difficulties of predicting the ultimate effect of periodic sediment desiccation and re-flooding conditions on the phosphorus cycle, as it depends on the exposure time to dry conditions, the frequency of dry/wet cycles and the sediment's chemical composition. Therefore, it is necessary to generate much more knowledge about Mediterranean wetlands by performing ad hoc studies. Despite these limitations, it is likely that, based on results from re-flooding experiments, water level fluctuations induced by global change enhance phosphorus release from sediments to the overlying water, impairing water quality. In relation to greenhouse gas emissions, although the expected effects of low and high water levels on $\mathrm{CO}_{2}, \mathrm{CH}_{4}$, and $\mathrm{N}_{2} \mathrm{O}$ fluxes are well known, to date, there exists a gap of knowledge about the net effect of alternating water level fluctuations induced by global change on greenhouse gases emissions. Accordingly, further research is needed to assess whether the periodic exposure of dry-wet cycles will amplify the role of these especial ecosystems as a source of these gases and, therefore, will act as a feedback mechanism for global warming. Another special issue to be considered is the effect of the extent and frequency of the wet and dry phases on these fluxes. Lastly, these results suggest that the management, if possible, of Mediterranean wetlands can influence $\mathrm{CO}_{2}, \mathrm{CH}_{4}$, and $\mathrm{N}_{2} \mathrm{O}$ emissions, and that some precautions in such management (limitation of dry-wet alternations and duration of emptying) could help reduce greenhouse gas emissions. To conclude, it is pertinent to consider that a better understanding about the effect of water level fluctuations on the biogeochemistry of Mediterranean wetlands will help to predict how other freshwater ecosystems will respond.

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