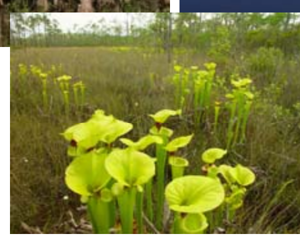
White Paper on

Nutrients in Wetlands: Implications to Water Quality under Changing Climatic Conditions





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1.0 Introduction

Globally, wetlands can be found in all climates ranging from the tropics to the tundra, with the exception of Antarctica. Approximately 6% of Earth's land surface, which equals about 2 billion acres (approximately 800 million hectares), is covered by wetlands. The United States alone contains about 12% of the world's wetlands, or about 274 million acres (111 million hectares) of wetlands. Soil and water quality within a watershed are influenced by agricultural, forested, range, wetland and urban land management. Non-point source pollution of streams, rivers, groundwater, lakes, wetlands, and estuaries is linked to the management practices used in these ecosystems. The question of immediate concern is: *Are the current watershed management practices compatible or adequate to sustain, protect and preserve wetlands and water resources?* While many current practices are compatible, not all are adequate to sustain water resource quality and protect wetland resources.

In conjunction with the U.S. Environmental Protection Agency's (USEPA) National Nutrient Strategy(USEPA, 1998), the USEPA has published technical guidance manuals for developing numeric nutrient criteria for all water bodies including lakes and reservoirs, streams and rivers, estuaries and coastal marine waters and wetlands. Numeric water quality criteria for nutrients are expected to be set at levels that protect aquatic life and recreational uses of waters from undesirable effects of excess nutrients. States, Tribes and Territories must therefore determine appropriate levels of nutrients for these systems over a range of time and conditions that will prevent water quality impairment. Demonstrations of how numeric nutrient criteria can be developed for these ecosystems will help these entities protect their water quality. For wetlands, the USEPA has developed a scientifically defensible guidance manual to assist States, Tribes, and Territories in assessing the nutrient status of their wetlands, and to provide technical assistance for developing regionally-based numeric nutrient criteria (USEPA, 2008a). The development of nutrient criteria is part of an initiative by the USEPA to address the problem of eutrophication caused by human activities. Several strategies have been developed by States, Tribes and Territories to reduce point and non-point source nutrient loads to wetlands and aquatic systems. Many of these strategies have been not adequate in reducing nutrient loads to water bodies, therefore development of numeric nutrient criteria may aid in formulating more effective strategies to control nutrient loads. Furthermore, any numeric nutrient criteria developed should take into consideration changing climatic conditions.

Although wetlands occupy only a small portion of the total landscape, their overall role at landscape, regional, and global scales is much greater than their area. Wetlands exist at the interface between terrestrial and aquatic environments. They serve as sources, sinks, and transformers of materials. Wetlands are divided into two broad categories: freshwater wetlands and coastal wetlands. Freshwater wetlands are situated within interior landscapes, such as floodplains along rivers and streams, wet prairies and hardwood swamps, prairie potholes, pocosin wetlands, and marshy areas around lakes and ponds. Coastal wetlands are linked to estuaries that support coastal marshes and mangroves. The biological productivity of wetlands can often exceed that of terrestrial and aquatic systems. Although there is a wide range of wetland types, they have common characteristics, some structural (water, soils and biota) and others functional (nutrient cycling, water balance, organic matter production and accretion) (Lewis, 1995). Wetlands, as the name implies, are the lands located in wet areas. Three major components constitute wetlands: hydrology (presence of water at or near the surface for a period of time), hydrophytic vegetation (wetland plants adapted to saturated soil conditions) and hydric soils (saturated soil conditions exhibiting temporary or permanent anaerobiosis). Wetlands can be very diverse with very high internal spatial heterogeneity with respect to vegetation, soils, and hydrology. The characteristics and functions of any given wetland can be inferred by its landscape position, climate, hydrology, vegetation and soils.

Since wetlands can serve as sinks, sources, and transformers of nutrients and other chemical contaminants, they have a significant impact on downstream water quality and ecosystem productivity (Figure 1). The primary driver of wetland processes is ecosystem biogeochemistry. Wetland biogeochemical cycles can have global significance (Figure 2). For example, eutrophication of oligotrophic wetlands resulting from increased nutrient loads can enhance the primary productivity. High primary productivity can result in increased rates of organic matter accumulation providing sinks for carbon (increased carbon sequestration). High carbon accumulation rates can enhance microbial activities in soil and the water column. Increased rates of microbial activities can increase production of greenhouse gases, and increased levels of greenhouse gases can result in negative feedback on climate change. Depending on nutrient loads, high rates of organic matter accumulation can also impact the surface water quality. Thus, biogeochemical cycles within wetlands can have both positive and negative feedbacks. Adequate understanding of the roles played by wetland ecosystem functions is critical in determining whether wetlands function as net sinks for carbon

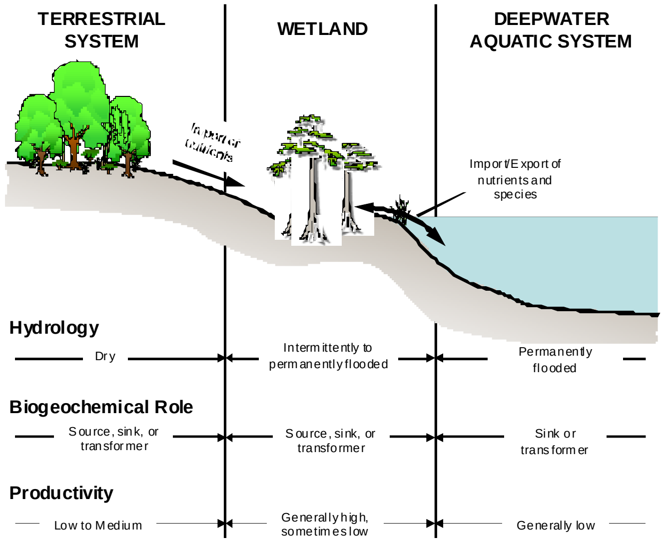


Figure 1. Wetlands shown as a continuum between terrestrial and aquatic systems. (Mitsch and Gosselink, 2007; Reddy and DeLaune, 2008).

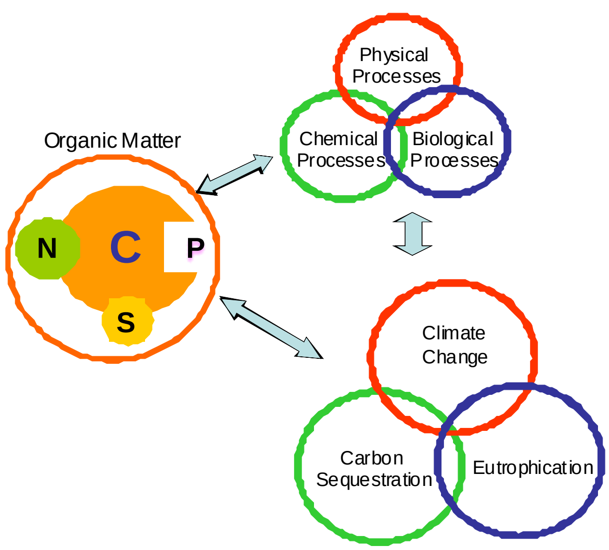


Figure 2. Linkages between physical, chemical, and biological processes and global scale processes in the biosphere (Reddy and DeLaune, 2008).

and associated nutrients. States/Tribes must determine appropriate levels of nutrients in these systems over a range of time and conditions that will prevent water quality impairment, while also serving as net sinks for carbon and associated nutrients.

The overall objective of this white paper is to review the available literature and provide science-based support to better understand key wetland ecosystem functions (water quality improvement, carbon and nutrient sequestration), especially under changing climatic conditions while maintaining water quality. Climatic change may include alterations in temperature and precipitation, global sea level rise, groundwater depletion and water level drawdown, fire, hurricanes and excessive flooding and greenhouse gas emissions. This white paper may provide information to assist the USEPA, States, Tribes and Territories in assessing the nutrient status of their wetlands by considering water, vegetation and soil conditions, and provide technical assistance for developing regionally-based, scientifically defensible numeric nutrient criteria for wetland systems. In this document, the term wetlands or wetland systems pertain to the regulatory definition of wetlands (40 C.F.R.§ 230.3 (t); 40 C.F.R. §122.2; 33 C.F.R. § 328.3 (b)) that are considered as "waters of the United States." However, States and authorized Tribes may, at their discretion, apply this document to wetlands that are considered waters of the state or authorized Tribe.

2.0 Wetland Ecosystem Services and Functions

Wetlands are a key component of the landscape. Although wetlands are one of the most productive ecosystems on the earth, their functions and values have only been recognized by society in the past three decades, resulting in a vast amount of recently published literature (Mitsch and Gosselink, 2007; Reddy and DeLaune, 2008). This heightened activity fosters a better understanding of wetland science, as well as an increased interest in protecting and conserving these ecosystems. The Clean Water Act requires that wetlands be protected from degradation because of their multiple functions, including water quality improvement and wildlife habitat. The values and functions of wetlands are now well recognized, as evidenced by public awareness and implementation of national policy to protect and preserve these fragile ecosystems. Economic analysis of various ecosystems suggests that freshwater wetlands and estuaries are more valuable than other ecosystems of the biosphere (Constanza et al., 1997). Wetlands are valuable resources that provide a number of important functions for the environment and man, including food, fiber (e.g., reeds), clean water, carbon and other nutrient stores/sinks, flood and storm control, ground water recharge and discharge, pollution control, organic matter (sediment) export, routes for animal and plant migration and landscape and waterscape connectivity. Constanza et al. (1997) estimated the total global value of these goods and services provided by coastal areas and inland wetland ecosystems to be $15.5 trillion or some 46% of the estimated total value of goods and services provided by all ecosystems worldwide (Table 1).

Table 1. Estimated economic value of selected ecosystems of the biosphere (Costanza et al., 1997; Batzer and Sharitz, 2006).

Ecosystem	US \$ ha^{-1} yr^{-1}
Estuaries	22,832
Swamps and floodplains	19,580
Coastal sea grass/algae beds	19,004
Tidal marsh/mangroves	9,990
Lakes/rivers	8,498
Coral reefs	6,075
Tropical forests	2,007
Coastal continental shelf	1,610
Temperate/boreal forests	302
Open oceans	252

Some examples of wetland ecosystem services and functions may include the following: (1) sink, source and transformer: depending on wetland type, hydrologic regime, and nutrient/contaminant inputs; (2) hydrologic flux and storage: provides flood control, erosion control, groundwater recharge, and serves as a medium to transport nutrients; (3) biogeochemical cycling: controls sediment and nutrient processing while influencing water quality; (4) biological productivity: affects fisheries as well as timber and shrub crops; (5) major sink for carbon via sequestration in vegetation and soil and detrital production/decomposition; (6) wildlife/community habitat: provides human recreation, animal harvest, as well as wildlife refugia; and (7) source of greenhouse gases: especially methane and nitrous oxide.

3.0 Anticipated Climate Change Effects on Wetlands

Climate change is now seen as one of the major threats to the sustainability and integrity of many ecosystems, including wetlands. Human activities and natural factors have already changed the climate (IPCC, 2007). Climate change is directly linked to global warming and the greenhouse gas effect, primarily due to its effect on temperature. Hansen et al. (2006) reported that global temperatures have increased by 0.6°C over the last three decades, and 0.8°C over the last century. Climate change associated with increased carbon dioxide and other greenhouse gases will alter many of the world's coastal and wetland ecosystems (Hume, 2005; Poff, 2002; Poff et al., 2002). The impact of climate change will vary depending upon the types, magnitudes and rate of changes in temperature, precipitation, nutrient and sediment load, carbon dioxide concentration and other associated factors. Warmer climates, accompanied by changes in precipitation patterns, will affect wetland ecosystem functions through changes in hydrology, biogeochemistry, and primary productivity. Increase in temperatures also may increase the rate of global sea level rise, with projected estimates in the range of two- to five-fold acceleration in sea level rise during the next 100 years. A recent study on Emission Scenarios by IPCC reports that sea level is predicted to rise by 30 to 100 cm by the year 2100 (Meehl et al., 2007). In the absence of increasing sedimentation and vertical accretion (discussed below) this would inundate many low lying areas, especially coastal and freshwater wetlands.

Coastal and estuarine wetland habitats will be severely impacted if sea level rise exceeds the rate of vertical sediment accretion and if inland migration is not possible. Wetlands losses in Louisiana, Maryland, and other parts of the low-lying Gulf of Mexico and Mid-Atlantic coastal margin have been attributed, in part, to sea level rise (Penland and Ramsey, 1997). Prior to human induced impacts, coastal wetlands were sustained because soil accretion from sediment deposition and detritus organic matter kept pace with natural compaction and historical sea level rise (Twilley, 2007). For example, over the past several thousand years, the development of a mosaic of coastal marshes in the Mississippi River delta has been driven by a relatively slow rate of sea level rise. The slow rate of sea level rise allowed coastal wetlands to accumulate organic matter and mineral sediments as the marsh vertically accreted, keeping pace with sea level changes (Nyman et al., 1990). Increasing submergence resulting from a changing climate will initially favor greater methane emission and organic matter accumulation in coastal wetlands. However, over time this may not be the case if marshes cannot maintain the surface elevation with respect to rising sea level or if inland migration is restricted through the construction of levees for the protection of coastal wetlands and developed lands. Sea level rise is not only a threat to coastal marshes by affecting marsh stability, but can also strongly alter biotic communities and freshwater wetland physico-chemical properties. Increased tidal flooding can potentially increase salinity, which will alter the biological diversity of these ecosystems. Sea level rise can lead to the conversion of freshwater wetlands to brackish marshes and finally to salt marshes in response to increased salinity. Acceleration of sea level rise and rapid increase in salinity can create stress on freshwater plant communities and result in eventual plant mortality, especially tidal freshwater floodplain forests. Saltwater intrusion that may accompany sea level rise also may accelerate the release of nitrogen (N) to coastal waters through sorption of ammonium (NH_4) from cation exchange sites and from mineralization of soil organic matter (Weston et al. 2006, C.B. Craft unpublished data). Wetland loss or marsh deterioration can release large amounts of sequestered carbon and other nutrients stored in the soil profile. Due to restrictions such as storm protection levels and human development in many regions there is little area for upland migration of coastal marshes.

Coastal wetland loss has also episodically been impacted by severe storm events. Resulting storm surges from hurricanes can scour and redeposit rooted marsh vegetation. Saltwater, pushed inland by storm surge and tide, can also negatively affect marsh vegetation communities. There is evidence that global warming will result in increased storm frequency and intensity. It has been reported that sea surface temperatures in the tropics have increased by 1^{o}C over the past century, and over this period hurricane intensity has also increased (Emanual, 2005). Hoyos et al. (2006) reported that the increase in the number of category 4 and 5 hurricanes for the period 1970-2004 was linked to the increase in surface water temperature. If this trend continues, Louisiana coastal marshes can expect to be impacted by major hurricanes more frequently in the future. Such increased hurricane activity would likely impact the soil carbon (C) storage in Northern Gulf of Mexico marshes. In coastal Louisiana, it has been estimated that the combined effect of recent hurricanes (Katrina and Rita) in 2005 resulted in a loss of over 200 square miles (518 km^2) of coastal marsh (Barris, 2006). This is approximately equivalent to a loss of 15.4 x 10^6 metric tons C to a depth of 100 cm.

Temperature and precipitation are strong determinants of wetland ecosystem structure and function. Increased mean global temperature of 1 to 3.5°C over the next century (IPCC, 1998) in combination with either stable, reduced or even slightly increased total precipitation would seriously impact freshwater wetlands. Relatively small changes in precipitation, evaporation, or transpiration which alter surface and ground water level by only a few centimeters will be enough to reduce or expand many wetlands in size, convert some wetlands to dry land, or shift one wetland type to another (Burkett and Kusler, 2000).

Vast expansions of tundra, marshes and wet meadows underlain by permafrost (ground material below freezing) may be altered by changes in temperature and hydrology. A warming of 4 to 5^{o}C in Alaska would create a mean annual surface temperature which could melt a significant portion of the subarctic permafrost in the state (Gorham, 1995). The organic soils of bogs, fens and other wetlands in the arctic, sub-arctic and temperate regions are highly vulnerable to changes in groundwater, which plays a crucial role in the accumulation and decay of organic matter. IPCC (1996) climate scenarios for 2020 and 2050 project a temperature increase of 1 to 2^{o}C, and a decrease in soil moisture for areas of boreal and subarctic peatlands. Areas of peat accumulation will move northward if temperature rises as predicted. On the other hand, increases in summer drought, despite overall increasing precipitation, would cause a degradation of southern peatlands (Gorham, 1995) through oxidation of the peat from increased temperatures and frequency of fires. Peatlands are important carbon reservoirs as they store more carbon than other terrestrial ecosystems. Estimates of carbon stored in the world's boreal peatlands range from 20 (IPCC, 1996) to 35 percent of global terrestrial carbon (Patterson, 1999).

Alternations in temperature and precipitation resulting from climate change can affect transport of sediments, nutrients and other constituents from wetlands to downstream aquatic systems. For example, changes in frequency, timing and intensity of rainfall events can not only alter runoff patterns, but can also affect subsequent pollutant loading. Changes in hydroperiod plus hydraulic and pollutant loading rates can significantly affect wetland biotic communities including vegetation, algae and microbial communities, and associated biogeochemical processes. These changes will ultimately have significant effects on water quality and other services provided by wetlands.

4.0 Wetland Biogeochemical Processes

Wetlands serve as sinks, sources and transformers of nutrients and other chemical contaminants, and have a significant impact on water quality and ecosystem productivity. The primary driver of wetland processes is ecosystem biogeochemistry, which involves the exchange or flux of materials between living and non-living components. These fluxes involve interaction of complex processes regulated by physical, chemical and biological processes in various components of the wetland ecosystem. Biotic (plants, microbes, fauna) components can be considered as exchange pools, which are small in size and undergo rapid turnover and cycling (Figure 3).

Abiotic components of wetlands (e.g. soil), which are large in size, undergo slow turnover and provide long-term storage similar to a reservoir. The amount of a given constituent in these pools depends on its residence time, which is simply the amount of material in the reservoir divided by the rate at which the material is removed or added to the reservoir.

Biogeochemical cycles are influenced by various processes that result in exchange of materials between two storage pools. The exchange or cycling pool can encompass up to 20% of the total amount of a given compound of a system and can turnover rapidly, thereby immobilizing and remobilizing compounds in a short time period. The reservoir pool typically contains the majority of a given compound in a system, is less reactive and provides long-term storage. When wetlands are used for wastewater treatment, designs which increase the fraction of contaminants in the reservoir pool are more desirable since this provides long-term removal of the contaminant. Changing climatic conditions will have significant effect on fluxes of materials between living and non-living pools.

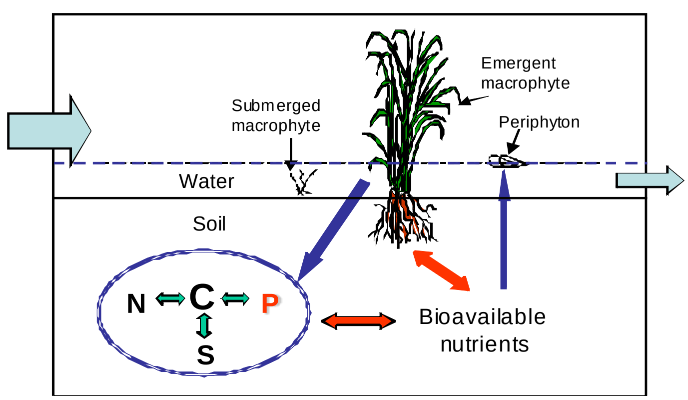


Figure 3. Schematic showing various components of wetland ecosystem

Biogeochemical processes in wetlands involve a host of complex microbial communities, periphyton, vegetation and soil fauna, with interaction and mutual dependency among these communities. Biogeochemical processes quantify exchange and transport of elements or compounds within wetlands including exchange or transport to other systems (e.g. atmosphere). Wetland biogeochemical processes enable one to infer the natural and anthropogenic factors that control or impact functioning at the local, regional and global scale. Nitrogen and carbon cycles are good examples of biogeochemical processes that impact processes (e.g. plant growth, soil accretion) at the local and regional water quality level and global levels (greenhouse gas emissions, carbon storage) (Reddy and D'Angelo, 1994; Megonigal et al., 2004; Reddy and DeLaune, 2008). In this section we present a brief discussion on how and to what extent changing climatic conditions will affect biogeochemical processes and water quality of wetlands (Table 2).

Table 2. Climate change effects on wetlands

Variable	Effect
Increased temperature	Accelerated growth, increased rate of biogeochemical processes. Increased rates of greenhouse gas emissions (methane and nitrous oxide).
Change in precipitation patterns	Increased wet periods – increases hydraulic and pollutant (sediments, nutrients, and other chemical constituents) loading rates. Increased dry period – increases rates of decomposition processes and nutrient regeneration. Increased nitrous oxide emissions. Change in diversity of biotic communities.
Sea-level rise	Increased inundation, salinity and stress on plants, decreased productivity, shift from freshwater marshes to brackish marshes. Increased sulfate inputs. Reduced methane emissions. Increased regeneration of bioavailable nutrients. Change in diversity of biotic communities and in some cases wetland loss.
Increased atmospheric carbon dioxide (CO_2)	Increased primary productivity and carbon sequestration in soils. Increased rate of microbial activities.
Hydroperiod and hydraulic loading rates; pollutant loading rates	Degraded water quality.

Wetlands host complex microbial communities, including bacteria, fungi, protozoa and viruses. The size and diversity of microbial communities are directly related to the quality and quantity of resources available in their habitat. Many of these communities may respond rapidly to disturbances resulting from climate change such as hydrologic alternations (water level drawdown), drought, hurricanes, fire and/or external nutrient loading. Wetlands support diverse microbial communities because of the abundance of organic substrates and supply of different types of inorganic and organic electron acceptors that result from wet and dry cycles. For example, wetlands support microbial communities that utilize a wide range of organic substrates and different electron acceptors including oxygen, nitrate, iron and manganese oxides, sulfate, and bicarbonate (Reddy and DeLaune, 2008). Microbial communities derive energy by coupling oxidation of organic and inorganic donors with the reduction of electron acceptors. The aerobic populations are restricted to the plant detritus layer and periphyton mats in the water column at or near the surface and to the surface soil (few millimeters), while anaerobic populations dominate the subsurface soil layers. In addition, the ability of macrophytic vegetation to transport oxygen to the root zone also supports aerobic populations in the rhizosphere. Electron acceptors such as oxygen are added to the soil via a subsiding water-table (draining), while other electron acceptors (such as sulfate) are added through hydraulic loading to the system or by sea level rise.

4.1 Organic matter decomposition

The majority of organic matter in wetlands is composed of complex, high molecular weight compounds, but only small molecular weight compounds dissolved in soil solution can pass through the microbial cell membranes and enter microbial cells from the soil environment. Dissolved organic matter (DOM) consists of proteins, amino acids, polysaccharides, and more refractory compounds of unknown structure. Only a small percentage of DOM is available for microbial uptake. To utilize DOM, heterotrophic bacteria must hydrolyze large compounds through the production of extracellular enzymes. This hydrolysis is the rate limiting step in organic matter decomposition in aquatic environments, thus enzyme activities and microbial biomass often regulate organic matter decomposition in soils.

Microbial biomass in wetland soils is a major component of various transformations and processes including enzyme production, microbial respiration and organic matter degradation (Figure 4). Soil microorganisms derive energy and C from the breakdown

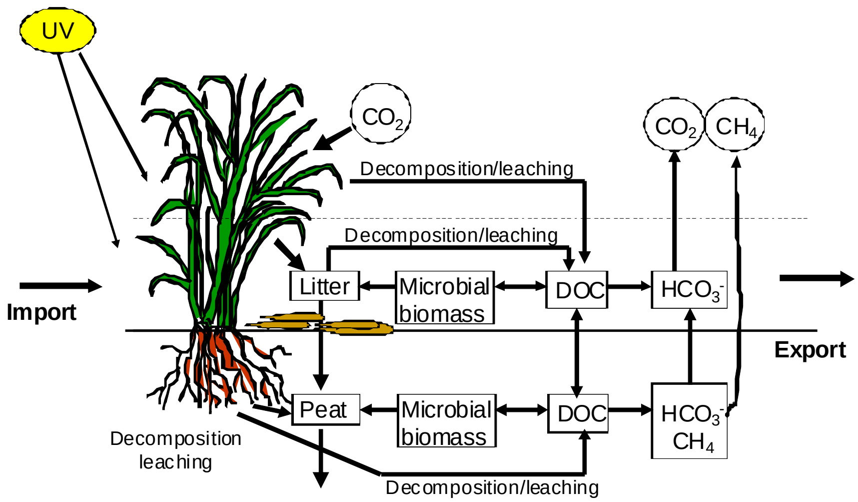


Figure 4. Schematic showing carbon cycle in wetlands (Reddy and DeLaune, 2008).

of detritus and soil organic matter which promotes nutrient cycling in soils. Microbial biomass and organic matter degradation may be limited by available nutrients if sufficient supply is not met through nutrient regeneration, or from soil solution. This may result in the immobilization of nutrients in soil microbial biomass. Biomass is often enhanced under aerobic conditions compared to anaerobic conditions under flooded soils (Wright and Reddy, 2001), which contributes to increases in activity upon drainage of flooded soils.

The shift from flooded to drained conditions leads to a shift from aquatic vegetation to more terrestrial vegetation communities, and a decrease in algal/periphyton contributions to total primary production (Childers et al., 2003). Drainage of wetlands therefore removes a source of net primary production (periphyton) that is important to food webs of aquatic ecosystems. The major effect of drainage in the ecosystem occurs below ground, where organic matter decomposition by heterotrophic microorganisms is significantly greater under drained conditions (Wright and Reddy, 2001). Thus, as wetlands undergo water level withdrawal by drainage, the sequestered C would be released back to the atmosphere. Several carbon cycling processes, therefore, are influenced by changing climatic conditions (Table 3).

Table 3. Carbon cycle in wetlands influenced by changing climatic conditions.

Variable	Effect
Increased temperature	Increased rate of enzyme and microbial activities; rapid turnover of organic matter; increased carbon dioxide and methane production; increased dissolved organic matter (DOM) generation (effect is more pronounced in temperate climates than sub-tropical and tropical climates).
Change in precipitation patterns	Frequent wet and dry cycles can increase organic matter decomposition; increased export of DOM; increased rate of enzyme and microbial activities; increased rate of methane emissions during wet periods and increased rate of carbon dioxide emissions during dry periods
Sea-level rise	Decreased rate of enzyme and microbial activities; slow turnover of organic matter in response to increased submergence, increased turnover of organic matter in response to increased salinity; decreased rate of methane emissions; increased rate of organic matter accumulation in response to submergence, decreased rate of organic matter accumulation in response to salinity; increased rate of anaerobic organic matter decomposition; increased rate of DOM export. Decreased plant production and carbon fixation due to increase stress associated with flood and salt stress. In areas where marshes can not migrate inland there will be marsh deterioration and loss of stored carbon.
Increased atmospheric CO_2	Increased rate of plant productivity; high rate of organic matter accumulation; increased or decreased rate of organic matter turnover; alternation of biotic diversity.

Organic matter decomposition in wetlands is regulated by various external and internal factors (Figure 5). Water-table fluctuation is one of the key regulators of organic matter decomposition in wetlands. Drained peats have been reported to decompose 50 times faster under drained than flooded conditions (Clymo, 1983). Drainage of organic soils also leads to a decline in surface elevation commonly referred to as subsidence (Holden et al., 2004; Snyder, 2005). Initially after drainage, soils subside due to water loss and become more hydrophobic, which retard rewetting of these soils. However, over the long-term, microbial oxidation is the primary driving factor of soil subsidence.

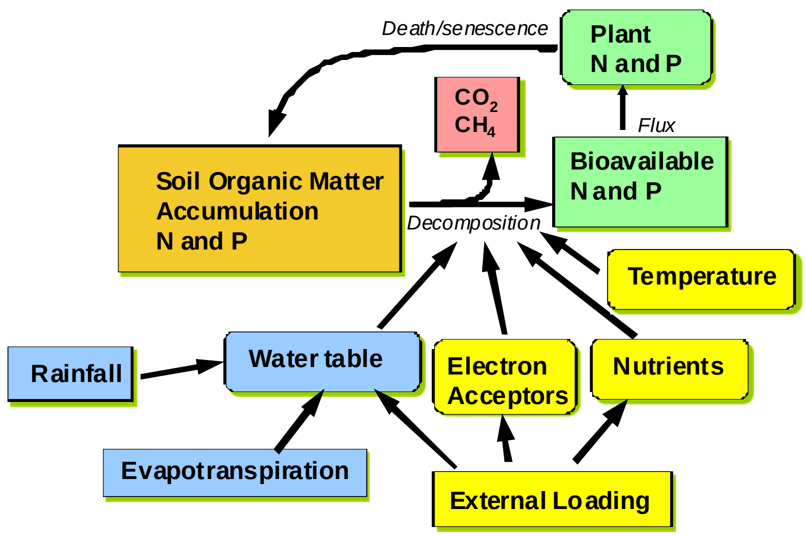


Figure 5. Schematic showing the factors regulating organic matter decomposition in wetlands (Reddy and DeLaune, 2008).

Wetlands around the world are experiencing disturbances such as drainage, eutrophication and problems with heavy metal toxicity which either influence dissolved organic matter, or are influenced by dissolved organic matter. The Florida Everglades present a case in which all three disturbances are important. Nutrients and associated contaminants from the Everglades Agricultural Area have flowed into the northern Everglades for many decades, causing enrichment of certain areas with a growing concern about the transport of nutrients to Florida Bay (Reddy et al., 1999). Mercury (Hg) toxicity is also a major problem, as it is in many wetlands around the world, and is largely transported by dissolved organic carbon (DOC) in the Everglades (Strober et al., 1995). Wetlands also experience relatively high levels of solar ultraviolet (UV) radiation which could increase in the future if stratospheric ozone continues to decline. Solar UV radiation has been shown to alter aquatic DOM (Wetzel, 2002). The concentrations of DOM in wetland waters are a product of inputs (production of new soluble organic matter and imports), exports (microbial decomposition and solar mineralization) and exchanges with the solid organic matter by adsorption and desorption (Wetzel, 1993a,b, 2002; Qualls and Richardson, 2003). The inputs of new DOM which includes DOC, dissolved organic N (DON), and especially dissolved organic P (DOP), are substantially increased by elevated plant productivity associated with phosphorus (P) enrichment. This increase is also caused by a shift in vegetation species from sawgrass (*Cladium jamaicense*) to cattails (*Typha domingensis*), which produces more DOM in newly senesced litter. The concentrations of DOM are also influenced by outputs due to microbial decomposition and mineralization caused by solar radiation. In terms of the eutrophication in the Everglades and other wetlands, it might be considered desirable if the dissolved organic nutrients were not mineralized and simply flowed through the system. The export of dissolved organic matter in water from the various areas of the Everglades has important implications for downstream sections. Not only is most N carried in the form of DON, but also most Hg complexed with DOM (Strober et al., 1995) is transported to downstream waters. Sorption and desorption from the peat acts as a buffer and strongly regulates DOM concentrations. In other wetlands, hydrologic flowthrough, the concentration of DOM in water, the adsorption properties of peat, the solar radiation reaching the water column and plant productivity are likely to influence the relative importance of DOM cycling (Wetzel, 2001; Qualls and Richardson, 2003; Osborne, 2005).

Dissolved organic C fluxes from precipitation vary with values in the range of 0.3 to 8.9 g C/m^2 year in North America, 1.9 to 3.9 g C/m^2 year in tropical islands, 1.3 to 4.8 g C/m^2 year in South America, 1.4 to 5.8 g C/m^2 year in Europe, 3.4 to 3.5 g C/m^2 year in Australia, and 1.1 g C/m^2 year in Africa (Aitkenhead-Peterson et al., 2003). A wide range of DOC fluxes (1- 84 g C/m^2 year) from terrestrial ecosystems (forests, grasslands, peatlands) have been reported (Aitkenhead-Peterson et al., 2003). In a recent study, Freeman et al. (2004a,b) observed a 65% increase in the DOC concentration of freshwater draining from upland watersheds in the United Kingdom over the past 12 years. These researchers attribute the DOC rise to an increase in the activity of phenol oxidase, an enzyme believed to regulate carbon storage in peatlands. They also showed that increases in temperature had significant effects on phenol oxidase: a 10°C rise in temperature (in the range of 2 to 20°C) resulted in a 36% increase in activity and was also accompanied by an equivalent increase in the amount of DOC released (Freeman et al., 2004a,b).

In water storage reservoirs created on peatlands, autochthonous DOC from algae and macrophyte origin can be an important contributor to the total DOC pool (Reddy, 2005). The relative importance of these two sources (algae and macrophytes) depends on water depth, nutrient status, and physico-chemical environment in the water column. During active growth, both algae and macrophytes release a significant proportion of their primary production as DOC. The DOC produced from these sources consists of low-molecular weight compounds, is biologically labile and readily used as an energy source by microorganisms (Wetzel, 2002). Flooding well drained peat soils results in a flush of DOC release from soil to the overlying water column. Upon flooding, and subsequent anaerobic soil conditions, much of the active aerobic microbial population dies and the metabolic activities shifts to facultative and anaerobic bacteria. As a result, microbial groups that rely on oxygen as their terminal electron acceptor during respiration now depend on alternate electron acceptors. Organic matter decomposition under these conditions is typically slower and results in solubilization of organic matter and accumulation of dissolved organic compounds instead of the C being completely oxidized to CO_2. Thus, flux of DOC from soil to the overlying water column is rapid during the first few months of flooding and decreases with time. Depending on environmental conditions and hydrology, the initial flush of DOC from peat soils may be sustained for a few months to one to two years, as observed in a mesocosm study (Reddy, 2005).

As organic matter decomposes, it is subject to burial, a process which generally results in a shift from aerobic to anaerobic conditions. In wetland soils, decomposition proceeds at significantly slower rates due to predominance of anaerobic conditions where, over time, moderately decomposable organic matter along with lignin and other recalcitrant fractions accumulate. The biodegradability of organic matter decreases with depth, as the material accreted in the deeper depths is much older and more humidified as compared to the material accumulating in the surface layers. Processes regulating the stabilization of organically bound nutrients in wetland soils are intimately linked with the chemical structure of soil organic C. Linking C, N, sulfur (S) and P is therefore considered a key aspect of any effort to understand soil organically bound nutrient stabilization (Gressel et al., 1996). The biological processes that control the turnover of organically bound nutrients gradually change so it is possible that changing nutrient status or hydrologic regime induces shifts in microbial community structure that are responsible for accelerated degradation of organic compounds (i.e., shift towards organisms adapted to access recalcitrant compounds).

4.2 Nitrogen

Several N cycling processes are influenced by changing climatic conditions (Table 4) (see reviews by Hefting et al., 2004; Buresh et al., 2008; White and Reddy, 2009) (Figure 6). Of the many elements necessary to sustain biotic production in wetlands, N presents unique challenges due to its chemical versatility, which is expressed in the various valence states it can occupy, the array of biotic and abiotic transformations in

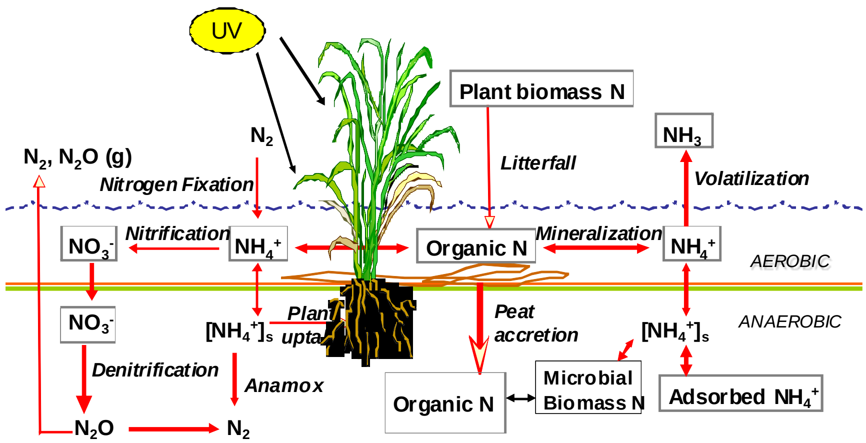


Figure 6. Schematic showing nitrogen cycle in wetlands (Reddy and DeLaune, 2008).

which it participates, and the diversity of states (soluble, gaseous) it exists in. Nitrogen cycling in wetlands is controlled by the same interdependent variables that control wetland formation and development: climate, hydrology, geomorphology and vegetation. The effects of climate are expressed through hydrology and temperature. Temperature, through its effect on biochemical kinetics, controls the rates at which microbes and plants process N. Hydrology, along with geomorphology, controls marsh formation and N cycling. Vegetation, in response to climate, hydrology and geomorphology, also regulates N cycling. Plant growth depends on a readily available supply of mineralizable N, which often limits primary production.

Nutrients bound in living tissues are returned by decomposition in forms that plants can assimilate. Broadly defined, decomposition consists of leaching, net accumulation, and

net mineralization. Leaching refers to the rapid loss of water soluble N compounds such as inorganic NH_4 and nitrate (NO_3), amino acids and high molecular weight organic compounds such as DNA and plant pigments. Mineralization refers to conversion of organic matter to inorganic constituents, especially NH_4, by microbial degradation. Net mineralization is the balance between gross mineralization and microbial immobilization or uptake. Ammonium not taken up by plants or tightly bound to sediments may be nitrified. Factors that limit autotrophic nitrification in wetland environments include lack of available oxygen, acid conditions, competition from plants, allelopaths and lack of available P. Two forms of nitrate reduction, denitrification and dissimilatory reduction of nitrate to ammonia, occur in wetland sediments. Denitrification leads to an export of N as mostly gaseous nitrous oxide (N_2O) and nitrogen gas (N_2) from ecosystems, whereas dissimilatory reduction to ammonia conserves N as ammonia within the system.
Export of N is also related to the hydrology of the wetland, as with the case of tidal or fluctuating water-level marshes, where the import or export of N varies depending on local conditions.

Table 4. Nitrogen cycle in wetlands influenced by changing climatic conditions.

Variable	Effect
Increased temperature	Increased rate of enzyme and microbial activities; rapid turnover of organic nitrogen; increased rate of nitrification; denitrification; and biological nitrogen fixation.
Change in precipitation patterns	Wet and dry cycles promote coupled nitrification and denitrification; dry periods – increased rate of nitrous oxide emission; wet periods – decreased rate of nitrous oxide production; increased benthic nitrogen fluxes from soil to water column.
Sea-level rise	Decreased rate of enzyme and microbial activities; slow turnover of organic matter; decreased rate of nitrous oxide emissions; high ammonium accumulation; increased rate of dissimilatory nitrate reduction to ammonia (DNRA); increased benthic nitrogen fluxes from soil to water column. Decreased N processing (denitrification, accumulation in soil) with increased salinity
Increased atmospheric CO_2	Increased rate of nitrification; denitrification; and biological nitrogen fixation

The amount of N accumulated in wetland soils depends on the balance between plant production and decomposition, and the balance between allochthonous import and particulate export. Atmospheric inputs add 0.5 to 1 g $N/m^2/yr$ as NH_4 and NO_3 (Bowden, 1987). Nitrogen fixation is the process whereby atmospheric N_2 is converted to ammonia by certain types of bacteria and algae, where the N is generally incorporated into cell structures. Most N fixation occurs in the aerobic water column by algae and N-fixing bacteria, although some bacteria can fix N in anaerobic soil, but this process is considered minimal. Nitrogen fixation can represent a major source of N into aquatic and wetland ecosystems. Generally, N fixation contributes an equivalent amount of N to wetlands as atmospheric deposition. Surface and subsurface water inputs of N to wetlands are highly variable, and much of it passes through and is not taken up/assimilated by wetland biota.

Soils form the single largest pool of N in wetland ecosystems followed by plants and available inorganic N (Reddy and D'Angelo, 1994; Bridgham et al., 1998). The slowest turnover in these pools follow a similar trend with turnover in the soil pool (hundreds of years), and the fastest turnover occurs in the inorganic pools (days or hours). Nitrogen fixation is an important supplementary input in some wetlands, but is probably limited by the excess of fixed N usually present in soils of these systems. Soils form through the deposition and slow decay of plant detritus. Initially, N is conserved as microbes immobilize it within their cells. Later, microbes release this N in inorganic forms (NH_4 and NO_3) that plants can re-assimilate. During the internal cycle between available NH_4, microbes and vegetation, some N may be nitrified to NO_3. The NO_3 formed has several fates which may tend to either conserve N (uptake and dissimilatory reduction to NH_4), or lead to its loss (denitrification). Both nitrification and denitrification operate at rates far below their potential, and under proper conditions (e.g. draining or fluctuating water levels) may accelerate.

Drainage of soils will decrease algal populations, and thus limit N fixation and N inputs into the river and wetland ecosystems. As such, water withdrawals may decrease floodwater depth above the soil surface and expose soil to the atmosphere, which will have the effect of minimizing algal N_2 fixation, so bulk N inputs into the wetland system by N_2 fixation should decrease. However, as mentioned earlier, enhanced N mineralization resulting from drainage likely contributes to greater N load from wetlands to the river, which may stimulate algal and microbial populations, and enhance N_2 fixation within wetland ecosystems.

Most of the N in wetland soils is present in the organic form, with a small percentage in inorganic forms such as NH_4 and NO_3. Many of the N cycling processes described above occur simultaneously at the interface of oxic/anoxic conditions, or at the water-table depth. Aerobic soils above the water table would likely experience more oxic conditions leading to organic N mineralization and nitrification of mineralized ammonia into nitrate. Nitrate is readily leached from soils and can contaminate groundwater or surface waters, depending on the direction of water flow. Nitrate is produced primarily in aerobic environments, such as drained soils, which encourage heterotrophic decomposition. Conversely, nitrate is consumed in anaerobic flooded soils.

Enhanced organic matter decomposition following water-level drawdown will increase inorganic N (NH_4, NO_3), but some of this will then move downward into the anaerobic soil layer, where nitrate will be denitrified. Depending on rainfall and water movement, NH_4 and NO_3 can be transported with water flow from wetlands into rivers where it may promote eutrophication of aquatic and wetland ecosystems downstream.
In coastal wetlands, increased salinity that accompanies sea level rise will lead to reduced denitrification and N sequestration in soil, as soil organic N is mineralized to NH_4 and denitrifiers are inhibited by sulfides produced by sulfate reducing bacteria (Craft et al., 2009).

Nitrous oxide, a greenhouse gas, may be produced in wetland soils during incomplete denitrification. Since drainage of soils increases the aerobic layer, oxygen is preferentially used as an electron acceptor, and as such, denitrification and nitrous oxide emission are reduced. Thus, water withdrawals from wetlands may tend to limit the rate of nitrous oxide production.

4.3 Phosphorus

Phosphorus entering a wetland or stream is typically present in both organic and inorganic forms, and in particulate and dissolved forms (Reddy et al., 1999, 2005) (Figure 7). Several P cycling processes are influenced by changing climatic conditions (Table 5). The relative proportion of each form depends on soil, vegetation and land use characteristics of the drainage basin. To trace the transport and transformations of P, it is convenient to classify forms of P entering into these systems as dissolved inorganic P (DIP), dissolved organic P (DOP), particulate inorganic P (PIP), and particulate organic P (POP). The particulate and soluble organic fractions may be further separated into

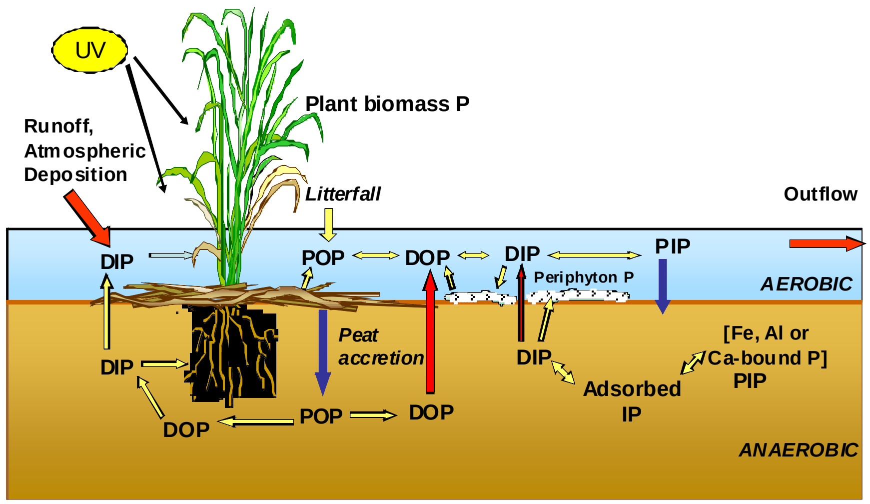


Figure **7**. Schematic showing phosphorus cycle in wetlands (Reddy and DeLaune, 2008).

labile and refractory components. Dissolved inorganic P is considered bioavailable, whereas organic and particulate P forms generally must undergo transformations to inorganic forms before being considered bioavailable. However, these size fractions of P are not necessarily indicative of P bioavailability or chemistry. Both biotic and abiotic mechanisms regulate relative pool sizes and transformations of P compounds within the water column and sediment/soil. Biotic processes include uptake by vegetation, plankton, periphyton, and microorganisms. Abiotic processes include sedimentation, adsorption by sediments/soils, precipitation, and exchange processes between soil/sediment and the overlying water column. Atmospheric inputs of P are relatively low and most P enters from surface flow, either through flooding or runoff from adjacent terrestrial land.

Since productivity and water quality of wetlands to some extent are determined by the bioavailability of limiting nutrients such as P, it is critical to determine their fate in soil and water column of a wetland. Soluble inorganic nutrients generated through biotic and abiotic processes are transformed into organic forms through plant and microbial uptake (Figure 7). In eutrophic wetlands, a significant amount of stored nutrients are in labile pools as low C/N and C/P ratios of detrital tissue favoring rapid decomposition and release. Bioavailability of nutrients such as P decreases with the age of the detrital plant tissue. The lability and the stability of detrital tissue is an important factor as cycling of this material can maintain eutrophic conditions in a wetland, even after external loads are reduced. Prolonged P loading to wetlands can result in distinct gradients in floodwater and soil. This effect is distinct in many subtropical freshwater wetlands receiving nutrient inputs (Davis, 1991; Reddy et al., 1993; DeBusk et al., 1994). In wetlands with spatial nutrient gradients, inorganic P added through external loads is readily utilized near inflow, resulting in increased productivity and release of labile dissolved organic substances associated with DOM. These substances released during mineralization of detrital organic matter can be transported downstream, expanding the impacted area, and can maintain eutrophic conditions even after external loads are curtailed.

Water withdrawals from wetlands will increase P regeneration from wetland sediments, and would likely increase potential for P export to the river. However, P can form stable complexes with minerals which can limit its mobility and potential for export from wetland, so its ultimate fate is dependent on environmental conditions. Thus, P contained within DOM is more prone to export from wetlands, and upon decomposition of DOM, its bioavailability may stimulate microbial and algal productivity in the river.

Phosphorus assimilation and storage in plants depends on its type and growth characteristics. In wetlands, vegetation often plays a significant role in P assimilation and storage. Floating macrophytes usually are present in areas with deep water and absorb P directly from the water column. However, because of rapid turnover, P storage is short-term and much is released back into water after the plants senesce and decompose. Emergent macrophytes have an extensive network of roots and rhizomes with great potential to store P. They have more supportive tissue than floating macrophytes and have a high ratio of below-ground biomass (roots and rhizomes) to above-ground biomass (stem and leaves). Although emergent macrophytes effectively store P, little of the water column P is directly assimilated. Since these plants are rooted in soil, the majority of their P requirements are met from porewater P.

Periphyton play a major role in regulating P concentrations of the water column, as they assimilate both organic and inorganic forms of P. They also induce changes in pH and dissolved oxygen (O_2)concentration of the water column and soil-floodwater interface, thereby influencing the solubility of P. Periphyton are known to mediate the precipitation of calcium carbonate ($CaCO_3$) and to co-precipitate P (Diaz et al., 1997; Scinto and Reddy, 2003).

Table 5. Phosphorus cycle in wetlands influenced by changing climatic conditions

Variable	Effect
Increased temperature	Increased rate of both biotic and abiotic processes regulating phosphorus retention; increased rate of organic phosphorus mineralization.
Change in precipitation patterns	Drought and flooding – increased phosphorus flux to water column; wet periods – increased rate of phosphorus release; dry periods – increased retention of phosphorus; increased phosphorus loads associated with sediments and other particular matter. Increased particulate phosphorus (PP) and dissolved organic phosphorus (DOP) export. Increased benthic phosphorus fluxes from soil to water column.
Sea-level rise	Decreased phosphorus retention as a result of high salinity, sustained anaerobic conditions, and removal of phosphorus binding iron sulfide. Increased DOP export. Increased benthic phosphorus fluxes from soil to water column.
Increased atmospheric CO_2	Increased phosphorus storage in above ground and below ground biomass; increased phosphorus sequestration in organic pools.

Sorption of P onto soil anion exchange sites is a longer term sink for P than vegetation. Sorption is a two-step process, a rapid phase that leads to retention on a surface and a slower phase as surface bound P diffuses and is incorporated into a solid phase. Once the surface exchange sites are saturated with P, sorption potential increases. Solid phase phosphate minerals regulate the solubility of dissolved P in the interstitial waters, soils and sediments. These minerals include apatite, hydroxyapatite, fluorapatite, octocalcium phosphate strengite, vivianite, variscite and wavellite. Because of the complexity involved in mineral formation and solubility of minerals, it is difficult to attribute P retention to any one single mineral. Generally, in acid soil, P is fixed in association with amorphic and poorly crystalline forms of iron (Fe) and aluminum (Al), whereas, in alkaline soils, P fixation is governed by the activities of calcium (Ca) and magnesium (Mg). This P availability generally is greatest in soils and sediments where pH is slightly acidic to neutral.

The mobility of P is governed by P retention capacity and P buffer intensity of wetland soils and stream sediments. Phosphorus retention capacity refers to the maximum available sites, which is determined by physicochemical properties and P already present on a solid phase. Soils and sediments having a large capacity for P sorption are considered to be highly buffered, and sorption in these soils or sediments is irreversible. High buffer intensity reflects in low-solution P concentration. Maximum P retention capacity of soil/sediment is generally reached following saturation of all sorption sites. Phosphorus sorption in soils/sediments is associated with amorphous and poorly crystalline forms of Fe and Al. Iron and Al complexed with organic matter may be responsible for P sorption, suggesting an indirect effect of organic matter. In soils dominated by Fe minerals, reduction of the soluble ferrous oxyhydroxide compounds results in more sorption sites. This reduction is the result of facultative organisms using ferric iron as an electron acceptor during their metabolic process in the absence of oxygen . Although reduction may create larger surface areas for P sorption, the binding energy associated with P sorption is low and desorption potential is high.

Phosphorus retention in soils has received much attention in Florida, especially with regard to the eutrophication of the Everglades wetlands. Phosphorus assimilated by vegetation is deposited as organic matter under flooded conditions. As long as anaerobic conditions exist, the organic matter is fairly stable and does not decompose very quickly. However, drainage promotes rapid aerobic decomposition and organic P mineralization. Phosphorus mineralized from organic matter exists as free phosphate, but this form is very reactive in soils and has potential to form more stable complexes, depending on soil type and environmental conditions. Soil minerals, particularly those containing Ca, Mg, Fe and Al, have a strong influence of P retention and stability. Phosphorus is readily adsorbed or precipitated by these cations, but the stability of these compounds (especially Fe) depends on redox conditions that can fluctuate over time.

In a study of Lake Apopka marsh soils, Olila et al. (1997) showed that P flux can increase by five and ten fold, for three and six weeks drawdown, respectively, followed by reflooding for 30 days. Phosphorus flux was rapid during the first day of reflooding, and values increased by 30 and 300-fold for three and six weeks drawdown and reflooding, respectively (Olila et al., 1997). There is concern that newly accreted peat material during flooded conditions can be oxidized during dry periods, resulting in decreased overall P retention by the wetland. This oxidation results in the conversion of organic P into labile inorganic P, which can be subsequently released into the overlying water column (Olila et al., 1997).

Drainage of wetlands would increase organic P mineralization and increase soluble reactive P (SRP) concentrations in the floodwater. Similarly to N, the P soluble in water or in particulate form would follow drainage patterns toward the river. However, SRP in water would likely decrease due to its precipitation with Fe, Al and/or Ca, which decreases SRP and P availability in water. Thus, not all P produced by water withdrawals would reach the river.

Water withdrawals from wetlands will increase P regeneration from wetland sediments, and would likely increase potential for P export to the river. However, P can form stable complexes with minerals which can limit its mobility and potential for export from wetlands. Thus, P bound to DOM is more prone to export, and as DOM decomposes, the P released may stimulate microbial and algal productivity in aquatic ecosystem downstream.

4.4 Sulfur

Sulfur is important in global biogeochemical cycles, as it is involved in physical and biological transformations between soil, water, and the atmosphere (Figure 8). Several sulfur cycling processes are influenced by changing climatic conditions (Table 6). Sulfur is readily oxidized and reduced in soil depending on hydrologic conditions and drainage greatly influences S transformations and related processes. In wetland soils, sulfate serves as an electron acceptor, especially in coastal wetlands, for decomposition of organic matter, and as such is reduced to sulfides. Sulfides are either released into the atmosphere as hydrogen sulfide (H_2S) in low pH soils or react with metals, such as Fe to form metal sulfides. Metal sulfides formed in flooded soil are unstable when these soils are drained, resulting in acidification from dissolution and oxidation of metal sulfides. Non-reduced sulfate is soluble in water, and thus prone to export as leaching or runoff. During dry periods, sulfate reduction is replaced by aerobic decomposition where oxygen serves as the electron acceptor, leading to greater rates of carbon dioxide production. In freshwater wetlands, sulfur cycling has been less studied than other elemental cycles, and most research is focused on saline coastal environments where sulfate concentrations are higher and mediated by the seawater salinity.

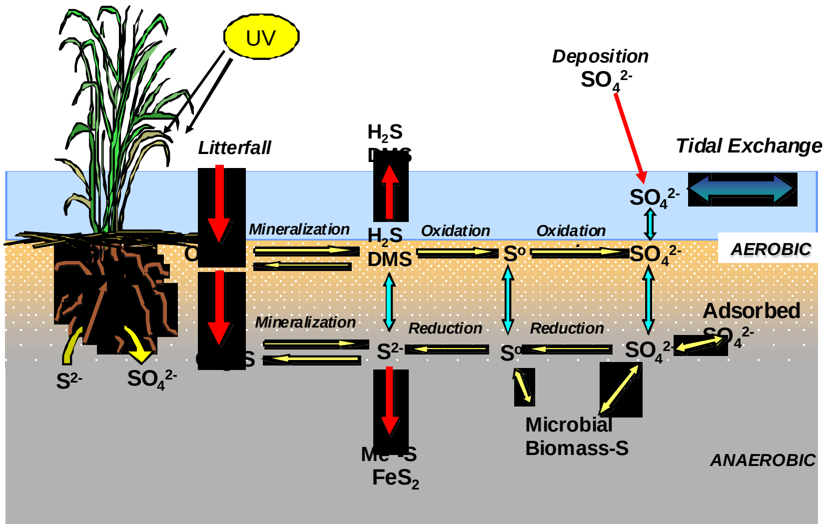


Figure 8. Schematic showing sulfur cycle in wetlands (Reddy and DeLaune, 2008).

Table 6. Sulfur cycle in wetlands influenced by changing climatic conditions

Variable	Effect
Increased temperature	Increased rate of both biotic and abiotic processes regulating sulfur oxidation and reduction; increased rate of organic sulfur mineralization.
Change in precipitation patterns	Wet and dry cycles promote coupled sulfate reduction and sulfide oxidation; dry periods – sulfide oxidation can result in acidification and potential solubilization metals; wet periods – increased rate of sulfate reduction and precipitation of sulfides with metals; increased benthic sulfur fluxes between soil to water column.
Sea-level rise	Increased sulfate input in brackish and freshwater marshes; increased sulfate reduction; potential sulfide toxicity to vegetation; removal of metals through sulfide precipitation; enhanced mercury methylation.
Increased atmospheric CO_2	Increased rates of sulfide oxidation; sulfate reduction; organic sulfur mineralization.

Methanogenesis and sulfate reduction are normally the primary terminal decomposition processes in wetlands. In wetlands, sulfate reduction accounts for up to 50% of the organic C mineralization, and roughly 95% of the sulfide produced is re-oxidized in the aerobic layer in the sediment surface (Jorgensen and Bak, 1991). Drainage of soils would increase the depth of the aerobic layer and decrease emissions of reduced S gases and methane (CH_4). If soluble sulfides accumulate, they may be toxic to plants at certain concentrations.

Mineral S in wetland soils is generally as pyrite or marcasite that forms from the reaction of elemental S, or hydrogen sulfide (HS), with iron monosulfide. In saline soils, pyrite formation is a more common and rapid process than in freshwater soils. Pyrite forms in reduced environments that are subjected to occasional oxidizing conditions. Oxidation of pyrite back to sulfate completes the S cycle. Mineral S formation is faster than mineral S dissolution. Drainage of soils containing large amounts of pyrite or other metal sulfides would result in a long-term dissolution of acid-forming sulfides.

Fractionation of soil S allows for the determination of oxidized and reduced S forms (Pezeshki et al., 1991; Krairapanond et al., 1992). This fractionation delineates different pools: acid volatile S (AVS), hydrochloric acid soluble S (HAS), pyrite-S, elemental S, ester bound S, and C bound S. The sum of these six groups is termed total soil S. Acid volatile S consists of hydrogen sulfide (pH dependent) and iron monosulfide. These two S forms are considered to be very reactive. Hydrochloric acid soluble S consists of the oxidized forms of S such as sulfate (SO_4). HAS is closely linked to porewater S. Ferrous iron reacts with hydrogen sulfide forming iron monosulfide, which then reacts with elemental S to form pyrite. Pyrite-S is generally less prevalent in wetlands compared to other forms of S, possibly due to the slow rate of pyrite formation under reducing conditions. Elemental S is often negatively correlated with AVS since the oxidation of AVS results in formation of elemental S. Ester bound S consists of compounds containing S bound to oxygen in an ester form, or S bound to N atom or another S atom. Ester bound S accounts for 20-30% of the total soil S. Ester bound S can be converted to C bound S by plants and microorganisms and is more labile than C bound S. Carbon bonded S consists of compounds where C and S are bonded, such as in proteins, and accounts for 50-60% of the total S. This fraction is derived from degradation of plant tissue, organic matter, or microbial biomass. Approximately 90% of plant and microbial S is found in amino acids, which suggests the importance of C bound S in wetland S cycling. Carbon bound S can be formed by oxidation of hydrogen sulfide to elemental S and reaction of elemental S with carbonaceous compounds.

The stability of S fractions and pools in soil are dependent on environmental conditions, such as oxidation status of the soil. Carbon bonded S, particularly when part of soil organic matter, lignin or plant litter, is fairly stable. Ester bound S is less stable than C bound S, but is fairly stable when incorporated in soil organic matter. Acid volatile and soluble S, elemental S and S gases are much less stable and are readily cycled among biota, soils and air.

Emissions of reduced S gases, bi-products of sulfate (SO_4) reduction and organic matter decomposition, occur in flooded soils (DeLaune et al., 2002). Drainage of these soils increases the oxidized soil layer, which in turn increases oxidation potential of reduced S gases decreasing their emission rates. Inorganic gases include sulfur dioxide and various species of hydrogen sulfide, whose concentration depends on pH and other factors. Concentrations of gaseous S in porewater are mostly regulated by inorganic oxidized S, especially water soluble SO_4. Reduced S gases, generally organic forms, are often oxidized in the plant rhizosphere and are not emitted to the atmosphere.

Mercury methylation in wetlands is stimulated by elevated sulfate concentrations and sulfate reducers. Maximum mercury methylation was observed at moderate concentrations of sulfate. In addition to external imports of sulfate into wetlands, sulfate can be generated during dry periods via organic matter decomposition by microorganisms. Organic S is transformed to sulfate, which is soluble in water and is readily transported within and downstream of wetlands.

4.5 Reactivity and mobility of metals

Metals which are toxic to aquatic plants and animals can enter wetlands from several sources (Gambrell, 1994). Toxic metals in wetland soils exist in various forms and may undergo numerous transport and transformation processes when they enter wetlands. Dissolved metals may be taken up by biota or sorbed to particle surfaces. Metals may dissolve, precipitate, desorb or be involved in redox reactions. The chemical properties, concentrations and availability determine their fate and toxicity. In wetlands soils the amount of organic matter, clay mineral, soil acidity (pH) and soil oxidation/reduction status determines the solubility and mobility of toxic metals.

Processes affecting trace and toxic metal mobility and bioavailability are different in flooded versus drained wetlands. When changes occur in the oxidation-reduction status of soils, transformations of metals between chemical forms may occur affecting their mobility and availability to organisms. Oxidation-reduction conditions also affect soil pH, a major factor influencing metal chemistry. As oxidized soils are flooded and become anaerobic, the pH tends toward neutrality, regardless of whether the soil was acid or alkaline initially. Thus, the range of pH in typical wetland soils is much smaller than found for upland soils and the near neutral pH of wetland soils favors metal immobilization.

All soils and sediments contain some generally low concentration of trace and toxic metals from natural sources. These background levels can vary widely depending on type of parent material, sedimentation and other factors. Human activities cause metal concentrations to increase in soils to the point they present potential human health or ecological risks. However, elevated concentrations of metals do not necessarily result in releases to water.

The speciation of metal forms found in wetland soil includes metals that are: 1) water soluble including soluble free ions and complexes with DOM; 2) exchangeable; 3) precipitated as inorganic compounds; 4) complexed with large molecular weight humic materials; 5) precipitated as insoluble sulfides or carbonates; and 6) bound in crystalline lattice of clay and parent sediment matter.

Water-soluble metals are the most mobile and available to plants. Exchangeable metals are those bound to soil surfaces by cation exchange processes. Metals in this form are considered weakly bound and may be displaced relatively easily to the water-soluble form. Together, metals in the soluble and exchangeable form are considered readily mobilized and bioavailable. On the other extreme are metals bound within the crystalline lattice structure of clay minerals by isomorphous substitution. Most of these metals are unavailable. Metals precipitated as inorganic compounds normally include metal oxides, hydroxides, and carbonates. The stability of these inorganic metal compounds is controlled primarily by pH. At near-neutral to somewhat alkaline pH levels, metals tend to be immobilized. If pH becomes moderately to strongly alkaline, sediments become oxidized and these metals may be released. Metals bound to large molecular weight organics tend to be effectively immobilized.

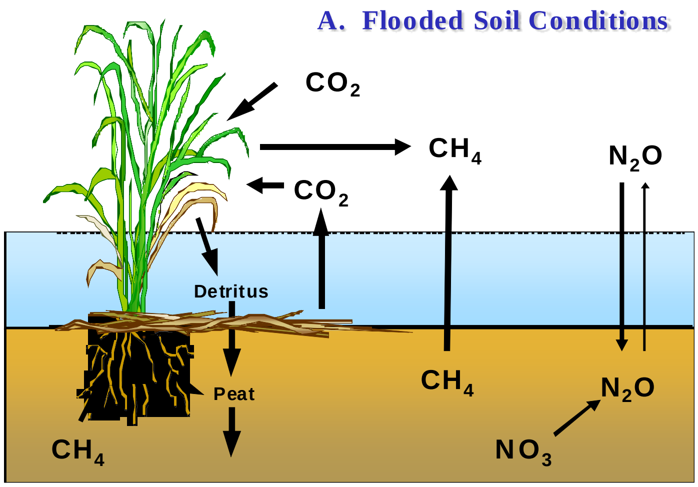
Many metals such as Mg, copper (Cu), zinc (Zn), cadmium (Cd), lead (Pb) and nickel (Ni) are not subject to changes in oxidation state as a consequence of soil oxidation/ reduction conditions. Chemical mobility of metals not subject to valence state changes, however, are affected by changes in pH. For example, Cd and Zn are released from recalcitrant to more mobile forms under oxidizing conditions as pH declines. Drainage of coastal wetland soils re-oxidizes metal sulfides to sulfate. Also, insoluble humic matter in reduced soils held metals more tightly than did humic matter under oxidized conditions.

Metals are more strongly immobilized in wetlands compared to upland soil conditions. Plant uptake, leaching losses and surface runoff losses have all been shown to be a significant migration pathway for metals under oxidized upland conditions as compared to reduced wetland conditions. Metal immobilization in wetland soils should favor the retention of metals released into wetlands from point and non-point sources. At slow flow rates, adsorptive surfaces of clays and humic materials should effectively scavenge and retain trace and toxic metals. Considering the importance of soil pH to metal mobility and plant availability, more attention should be given to seasonal changes in pH due to changing water levels and redox conditions in transition zones between wetlands and uplands.

Since metal cycling in wetlands is dependent on pH and redox potential, drainage of wetland soils increases redox potential and potentially decreases pH, thereby changing the solubility of metals. Likewise, metal complexes with organic matter are released upon decomposition, thereby increasing bioavailability following drainage. The complex nature of metal chemistry in aquatic systems makes it difficult to assess their response to changing climate.

4.6 Greenhouse gases

Wetlands serve as both sources and sink for greenhouse gases (see reviews by Freeman et al., 1993 and Kasimir-Klemedtsson et al., 1997) (Figure 9a, b and c) and drained wetlands are a major source of carbon dioxide. Flooded organic soils emit large amounts of CH_4 and only minor amounts of N_2O. In contrast, drained wetland soils emit low amounts of CH_4 and some N_2O to the atmosphere. Thus, drainage and soil cultivation induce profound shifts in the emissions of N_2O and CH_4. The Global Warming Potentials of these two gases are much higher than that of CO_2, as CH_4 has 25 times higher impact on climatic warming than CO_2, and N_2O has 320 times more impact over a 100 years



perspective (Freeman et al., 1993).

Figure 9a. Schematic showing potential greenhouse gas emissions under changing climatic conditions.

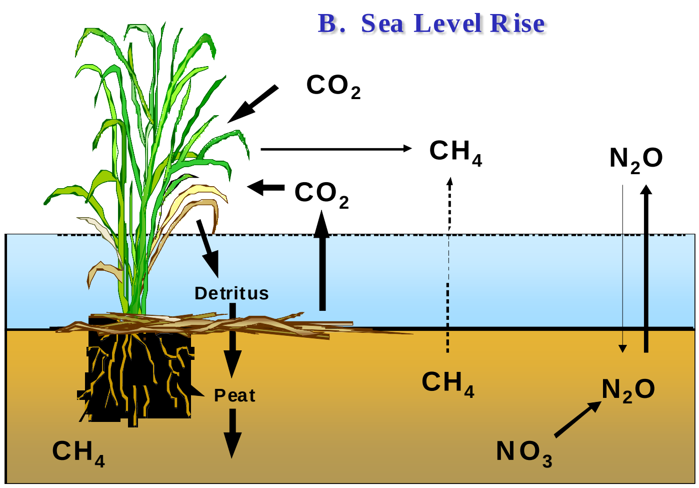


Figure 9b. Schematic showing potential greenhouse gas emissions under changing climatic conditions.

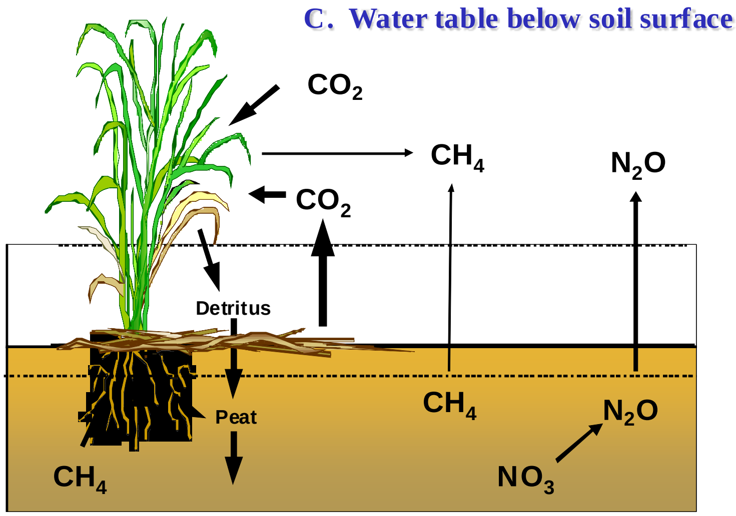


Figure 9c. Schematic showing potential greenhouse gas emissions under changing climatic conditions.

Under drained conditions, gaseous end products are primarily CO_2, but under flooded conditions, reduced-S gases and CH_4 are also released. Sulfate reduction and methanogenesis are greatest in continuously flooded wetland soils, but their contribution to total metabolism decreases with drainage. In flooded soils, CH_4 and reduced-S gases are emitted, but these often oxidize as they flux upward toward the soil surface. Methane oxidation is especially efficient with methane oxidizing bacteria, consuming approximately 90% of the CH_4 flux (King et al., 1990). The presence of thick layers of drained peat may limit CH_4 emissions even when underlying anaerobic peat may be producing CH_4 and reduced-S gases.

Drainage and cultivation of peat soils increase soil aeration and reverse the C flux from a net sink via peat accretion, to a net source of C as the peat is oxidized and CO_2 is emitted into the atmosphere. Drainage and oxidation of the peat leads to soil subsidence and a lowering of the surface soil elevation.

The significance of the N_2O release from drained organic soils to the global greenhouse gas budget is probably even more important than that of CO_2. Nitrous oxide is produced under suboxic conditions in soils as a byproduct of the two microbiological processes, nitrification and denitrification. Nitrous oxide production and emission in organic soil depends on drainage and soil moisture content, with the highest flux at intermediate soil moisture content. There are large uncertainties in N_2O emission estimates, primarily due to the high spatial and temporal variability of N_2O fluxes from soil.

Seasonal fluctuations of greenhouse gas emissions also occur due to bursts of substrate availability following perturbations such as drying/wetting and freeze/thaw events. One example of these fluctuations is evident from relationship of NO_2 with soil moisture content. The depth of the groundwater table and the soil density, parameters influencing the gas conductivity in the soil, may also be important.

Wetlands are a major source of CH_4 to the atmosphere. The main factors proposed to regulate CH_4 emissions from undrained wetland soil are temperature, groundwater level and the type of vegetation. Plants are important because of their net primary productivity coupled with heterotrophic respiration and to the transport of CH_4 (and O_2) via their stems. Land use also has an effect on methane production. When organic soils are drained, oxygen concentrations increase, methane production decreases and methane oxidation increases. Overall, there is a net decline in methane emissions in response to drainage. Methane and nitrous oxide formation is regulated by soil redox potential, with positive Eh (redox potential) values reflecting drained soil conditions (Eh $\geq$300 mv) and values $<$300 mv reflect flooded soil conditions (Figure 10).

Sulfate level also influences methane emission. In coastal regions, sea level increases and associated salt water intrusion into brackish and freshwater marshes will likely result in reduced methane emissions from coastal wetlands.

4.7 Carbon sequestration

Wetlands are sensitive to global climate change and play an important role in the global carbon cycle (Choi and Wang, 2004). However, the dynamics of C cycling in coastal wetlands and their response to global warming is poorly understood. A number of approaches have been proposed to reduce CO_2 concentrations in the atmosphere. One ecological approach is to take advantage of the ability of terrestrial ecosystems to fix and sequester atmospheric C in the soil (Armentano and Menges, 1986). The potential of soil C storage, including coastal wetland soils, is enormous (Rabenhorst, 1995; Eswaran et al., 1995).

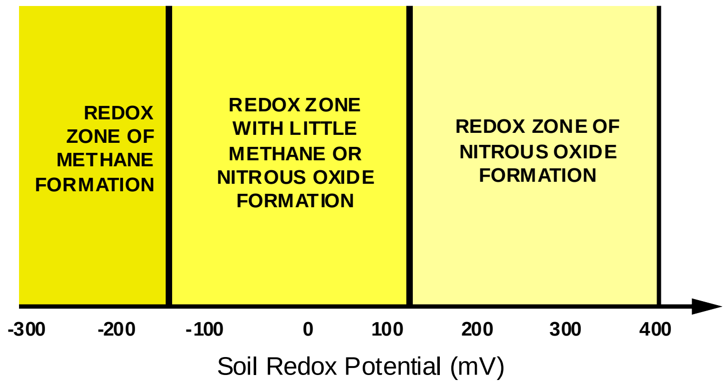


Figure 10. Soil redox zones where methane and nitrous oxide are produced (Reddy and DeLaune, 2008).

The estimated C sequestration, through management of world soils alone, could range between 1.2 and 2.6 Pg C yr^{-1}. (Lal, 2001). Globally, wetlands cover about 7% of the total land surface (Keddy, 2000). Prior to settlement in the U.S., there were an estimated 87 million ha of wetlands, and almost 50% of these wetlands have been lost or converted to other uses (e.g., crop and grazing). Currently, there are approximately 40 million ha of wetlands in the conterminous U.S., and nearly 95% are freshwater wetlands.

Histosols (peat soils) form within wetland environments and have the highest C content of all soil orders. This high C content is due to the fact that wetland ecosystems have the highest net primary production rate of all terrestrial ecosystems (Amthor and Huston, 1998; Keddy, 2000). In addition, the rate of organic matter (OM) decomposition in wetland soils is slow due to prevailing anaerobic conditions in the flooded soils (Stevenson and Cole, 1999; White and Reddy, 2001). Therefore, wetland soils create an important sink for atmospheric CO_2 as a result of high OM input along with a slow decomposition rate.

Wetland soils are estimated to contain about 20-25% of the terrestrial soil C, despite comprising a relatively small proportion of the total land area occupied (Amthor and

Huston, 1998). Current wetland restoration and conservation goals worldwide provide a critical opportunity to incorporate C sequestration as part of future wetland ecosystem services. Although soil C in wetland soils has been recognized as being an important component of global C budgets and future climate change scenarios, very little work has been done on the role of wetland ecosystems management on increasing C sequestration (Amthor and Huston, 1998; Lal, 2001). Considerable research quantifying C sequestration rates coupled with global change scenarios is needed to provide for sound resource management decisions.

Studies on soil accretion in coastal wetland ecosystems have been conducted worldwide with accretion rates ranging from 0 to 42 mm per year reported (Hatton et al., 1983; Salinas et al., 1986; DeLaune et al., 1990; Twilley et al. 1992; Parkinson et al., 1994; Chmura et al., 2003; Callaway et al., 1996, 1997; Nyman et al., 2006). Research conducted in the Mississippi River deltaic plain has concluded that organic matter accumulation was the main determinant in the vertical growth rate of marshes (DeLaune et al., 1978; Hatton et al., 1983; DeLaune et al., 1994)

Coastal peat deposits are impacted by a variety of threats associated with global climate change and land use management (Henman and Poulter, 2008). These threats include shoreline erosion (Young, 1995), salt water intrusion (Hackney and Yelverton, 1990) and submergence (Pearsall and Poulter, 2005). All of these factors can reduce C sequestration. Response of coastal wetlands to climate change factors also include changes in elevation, boundary or edge distribution, areal extent (wetland:water area) and mineral/organic matter composition of soil or sediment (Day et al., 2008). These physical changes strongly impact biological processes including above and below-ground plant productivity and C sequestration.

It has been estimated that saline wetland soils including salt marshes and mangrove swamps store more than 10,000 Tg of C (Twilley et al., 1992, Chmura et al., 2003, Bouillon et al., 2008). There is a great deal of uncertainty regarding the specific ecological and physical changes in coastal wetlands resulting from increased rates of sea level rise driven by global climate change.

The rise in sea level associated with global warming can only be expected to magnify the effects of natural and anthropogenic stresses on coastal marshes. Despite the enormous number of studies worldwide on wetland accretion rates, very little analysis has been conducted to determine potential decreases in the C sequestration potential of coastal wetlands as related to predicted increase in sea level rise.

4.8 Water quality

Global climate change will have several adverse impacts on ecosystem services provided by natural systems, including wetlands. Wetlands provide a range of ecosystem services, including water quality improvement and reduction of contaminant loads to adjacent or downstream aquatic ecosystems. Climate change is expected to cause an increase in air and water temperature, irregular precipitation patterns, increased storm intensity, and sea level rise which will have an adverse effect on the quantity and quality of water in wetlands. In wetlands, climate change effects can disrupt hydrology and hydroperiod, biogeochemical cycling, and species composition of biotic communities (vegetation, periphyton and microbes), internal fluxes, and storage and stability of carbon, nutrients, metals and organic contaminants.

Alterations in basic functions of wetlands can result in degraded water quality and increased nutrient and contaminant loads to adjacent aquatic systems. Some examples of these effects on water quality were discussed in previous sections. Managers and scientists working with wetlands and water quality monitoring programs should take into account how climate change affects their ability to develop assessment programs and meet nutrient criteria goals. A recent preliminary analysis of the data for streams and rivers by the USEPA (2008b) suggests that climate change effects will decrease the ability of states to discriminate between reference sites and impaired sites.

5.0 Long-term Data

- Conduct review of current information on wetlands as related to key ecological services, especially those pertaining to water quality and the potential effects of climate change on them. Although the primary focus will be on wetlands in different eco-regions of the U.S., any pertinent information on other pertinent global wetlands should also be reviewed.
- Identify key wetlands projects with long-term data to evaluate wetland ecological services and climate change impacts.

- Review the wetlands technical guidance manual and methods module, and, as needed, solicit the assistance of experts who helped to develop these documents.
- Identify long-term data sets to determine the evidence of climate change effects on wetland ecosystem functions.

6.0 Synthesis Workshop

Wetlands are vulnerable to changing climatic conditions, resulting in impacts to biotic communities (vegetation, algae and microbial communities) and ultimately to water quality. The wetlands nutrient criteria technical guidance manual prepared by USEPA (2008a) provides a conceptual model and detailed list of candidate variables to be measured to establish nutrient criteria. The wetlands conceptual model, however, should also include climate change variables and their effect on various physical, chemical, and biological parameters. Current recommended causal and response variables are used to determine nutrient condition of wetlands and to help identify appropriate nutrient criteria. In addition, these variables provide information useful in normalizing causal and response variables and for categorizing wetlands. Causal variables are intended to characterize nutrient availability (or assimilation) in wetlands and could include nutrient loading rates and soil and vegetation nutrient concentrations. Response variables are intended to characterize biotic response and could include community structure and composition of macrophytes and algae (USEPA, 2008a). Thus, a modified monitoring program should be developed after peer review of the current technical guidance manual and methods manuals to evaluate wetland condition under a changing climate.

We propose that USEPA organize a 3-day workshop to determine the roles of wetland ecosystem functions in the context of changing climatic conditions, with emphasis on water quality. A list of key experts will be developed upon consultation with USEPA staff. The goal of this workshop is identify the major data gaps and availability of long-term data sets to evaluate the evidence of climate change effects on wetland functions.

7.0 Conclusions

Changing climatic conditions may stimulate/alter rates, fluxes and storage pools of key elements (carbon, nitrogen phosphorus, and sulfur) involved in biogeochemical processes and services provided by wetlands. For example, accelerated decomposition of organic matter can potentially increase nutrient generation, which may lead to increased nutrient/contaminant loading to adjacent water bodies. Important inorganic elements in wetlands are mobile and thus their concentrations may increase upon flooding and drained cycles, water withdrawals, sea level rise, and increases in temperature. Many inorganic elements required by life and biological processes (e.g., plant growth and decomposition) are bioavailable and will respond to these increases. Drainage also increases enzyme and microbial activities, which facilitates oxidation of organic matter, leading to subsidence and loss of organic soils. Many studies have shown that oxidation of organic matter in wetlands is dependent on water-table depth, temperature, nutrient loading, vegetation communities and release of nutrients. Greenhouse gas emissions will be higher under drained soils as a result of higher microbial metabolism, with different end products than flooded soils. Drained peats emit CO_2 as the end product of microbial activity, while flooding may increase the proportion of CH_4 and reduced-S gases emitted relative to CO_2. Export of DOM and nutrients from wetlands to aquatic ecosystems downstream will likely occur after drainage and water withdrawals.

Changes in **precipitation and alternation in water table or drained wetland conditions** resulting from climate change influences biogeochemical processes and water quality. Below are a few examples:

– Increased aerobic portion of the soil profile
– Increased rates of organic matter decomposition
– Decreased methane emissions
– Enhanced nitrification-denitrification process
– Increased nitrous oxide emissions
– Inhibited dissimilatory reduction of iron and manganese compounds
– Inhibited sulfate reduction
– Decreased soil pH
– Enhanced precipitation of phosphorus
– Decreased internal load of nutrients
– Increased pulsed loading and export of nutrients

Changes in **temperature** resulting from climate change influences biogeochemical processes and water quality in wetlands. Below are a few examples:

- Increased primary productivity
- Alteration of vegetation, periphyton and microbial community composition

- Increased rate of organic matter decomposition
- Accelerated growth, increased rate of biogeochemical processes
- Increased rates of greenhouse gas emissions (methane and nitrous oxide)
- Increased rates of nutrient release
- Increased production of dissolved organic matter

Sea level rise from climate change and **influx of salt water** into freshwater wetlands influences biogeochemical processes and water quality. Below are a few examples:

- Alteration of vegetation, periphyton and microbial community composition
- Increased conductivity of surface water and soil porewaters
- Increased sulfate input and sulfate reduction
- Increased rate of organic matter decomposition
- Sulfide toxicity to biotic communities
- Decreased methane emissions
- Increased production of dissolved organic matter and associated nutrients and other contaminants
- Decreased phosphorus retention by soils
- Increased rate of metal precipitation with sulfides

Increases in **carbon dioxide levels in the atmosphere** resulting from climate change influences biogeochemical processes and water quality. Below are a few examples:

- Increased in primary productivity of biotic community
- Increased rate of organic matter accumulation
- Increased rate of biogeochemical processes
- Increased nutrient storage in above and below-ground biomass
- Increased rates of nutrient and other contaminant release from soils
- Increased rate of methane emissions

Future research needs quantifying the impact of climate change effects on ecosystem functions in wetlands include, but are not limited to:

- Conduct research through pilot studies (in key eco-regions) to determine the best hydrologic, biogeochemical and biological response indicators to determine climate change effects.

- Quantify shifts in wetland vegetation, periphyton and microbial species diversity and distribution in response to change in moisture and rainfall patterns, temperature, sea level rise and increased atmospheric CO_2 levels.
- Quantify storages, rates and fluxes of C, nutrients and contaminants influenced by change in moisture and rainfall patterns, temperature, sea level rise and increased atmospheric CO_2 levels.
- Determine influence of temperature and moisture changes on the C, N and S cycles in wetlands.
- Determine impact of increased sea level rise on carbon gas emissions and carbon sequestration in coastal marsh soils.
- Determine impact on delivery of ecosystems services (nutrient processing capacity, water retention and storage, etc.).
- Determine interactive effects of climate change variables on various biogeochemical processes involved in regulating water quality.
- Conduct in-depth analysis of climate change effects on wetlands and potential influence on adjacent aquatic systems in different regions of the U.S.
- Taking climate change effects into consideration, develop wetland assessment indicators for various wetland types in different regions of the U.S.
- Revise current wetlands nutrient criteria technical guidance manual (USEPA, 2008a) to reflect the climate change effects.

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