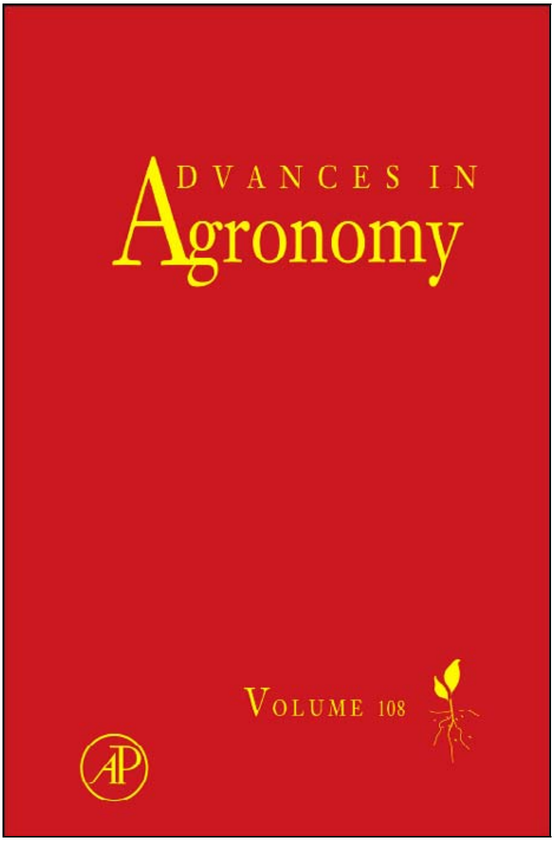

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CHAPTER ONE

Mitigating Nonpoint Source Pollution in Agriculture with Constructed and Restored Wetlands

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Abstract

Nonpoint source pollution (NPSP) from agricultural runoff threatens drinking water quality, aquatic habitats, and a variety of other beneficial uses of water resources. Agricultural runoff often contains a suite of water-quality contaminants, such as nutrients, pesticides, pathogens, sediment, salts, trace metals, and substances, contributing to biological oxygen demand. Increasingly, growers who discharge agricultural runoff must comply with water-quality regulations and implement management practices to reduce NPSP. Constructed and restored wetlands are one of many best management practices that growers can employ to address this problem. This review focuses on the ability of constructed and restored wetlands to mitigate a variety of water-quality contaminants common to most agricultural landscapes. We found that constructed and restored wetlands remove or retain many water-quality contaminants in agricultural runoff if carefully designed and managed. Contaminant removal efficiency generally exceeded 50% for sediment, nitrate, microbial pathogens, particulate phosphorus, hydrophobic pesticides, and selected trace elements when wetlands were placed in the correct settings. There are some potentially adverse effects of constructed and restored wetlands that must be considered, including accumulation of mercury and selenium, increased salinity, mosquito habitat, and greenhouse gas emissions. Proper wetland management and design features are discussed in order to reduce these adverse effects, while optimizing contaminant removal.

1. MITIGATING POLLUTION WITH WETLANDS

An emerging challenge for agriculture is to feed the world without adversely affecting the environment. Global demand for food is growing at an alarming rate. According to FAO predictions, food production must increase 40% by 2030 and 70% by 2050 to sustain the planet's population growth (OECD-FAO, 2009). Today, roughly 1.4 billion hectares of cropland are in production across the planet, yet to sustain this emerging global demand, cropland area would have to more than double (OECD-FAO, 2009). At the same time, prime farmland is being lost to urbanization and other land uses. The loss of this productive farmland has displaced farming into marginal lands that are more erosive and require more inputs than those required for prime farmland (Charbonneau and Kondolf, 1993). Thus, soil and water resources will be subjected to added pressures in the future requiring cost effective, best management practices (BMPs) to ensure environmental protection.

Nonpoint source pollution (NPSP) is a global problem affecting the safety of our drinking water supply and aquatic habitats. According to the 2000 National Water Quality Inventory, agriculturally derived NPSP is the leading cause of water-quality degradation in surface waters (US EPA, 2002). Pollutants originating from agricultural runoff include sediment, nutrients (N and P), pesticides, pathogens, salts, trace elements, dissolved organic carbon (DOC), and substances that contribute to biological oxygen demand (BOD). For example, discharge of nutrients into aquatic ecosystems has lead to dramatic shifts in trophic relationships (Boesch *et al.*, 2001) including hypoxia/anoxia induced "dead zones" in more than 400 locations worldwide (Diaz and Rosenberg, 2008). Thus, new and effective management practices for agriculture must be identified, tested, and monitored in order to reduce the impacts of agriculture on the sustainability of water resources.

Wetlands are widely advertised as critical components of our planet providing a wide variety of ecosystem services: kidneys of the hydrologic cycle by removing pollutants, biodiversity hot spots, habitats of rare and endangered species, ground water recharge zones, localized areas for flood protection, carbon sinks, and aesthetic value (Zedler, 2003). Upon settlement of the United States, the lack of understanding for the role of wetlands and drive for agricultural production resulted in a loss of over 53% of the nation's wetlands (Dahl, 1990). California and Texas, two states leading agricultural production in the United States, have lost more than a combined 5 million hectares of wetlands. Much of this loss was as result of programs in the United States such as Swamp Buster, which encouraged the conversion of marginal land (e.g., wetlands) into agricultural production. Coincident with this landscape conversion was the rise in use of agricultural chemicals. As a result, the filtration effect of wetlands has been uncoupled from riparian environments resulting in severe degradation of the nation's (and the planet's) water resources. Only in the last few decades have wetlands been recognized for their potential role to ameliorate NPSP.

Traditionally, constructed and restored wetlands have been developed in agricultural settings to improve wildlife habitat, mainly through the U.S. Conservation Reserve Program and the Wetlands Reserve Program (WRP). The WRP is an outreach effort administered through the Natural Resource Conservation Service (NRCS) and its partners. It is designed to provide financial and technical assistance to landowners to restore, enhance, and protect wetlands and surrounding surface waters. As of 1999, there were a total of 785,000 ha of marginal farmland that have been enrolled in the WRP (Mitsch and Gosselink, 2000). The conversion of floodplain agroecosystems to wetlands is becoming a popular land-use practice nationwide (Fig. 1), yet little information exists to document how these wetlands filter water-quality contaminants in runoff from agricultural fields.

1.1. Types of anthropogenic wetlands

There are many different definitions of wetlands from a variety of federal agencies and stakeholders. Mitsch and Gosselink (2000) present a definition by NRC (1995) as one of the most comprehensive descriptions of a wetland:

Figure 1 Restored wetland in the San Joaquin Valley, CA. This CW receives irrigation tailwater for approximately 6 months during the growing season. A natural wetland in this setting would be inundated with water during the winter and early spring months.

> "A wetland is an ecosystem that depends on constant or recurrent, shallow inundation or saturation at or near the surface of the substrate. The minimum essential characteristics of a wetland are recurrent, sustained inundation or saturation at or near the surface and the presence of physical, chemical, and biological features reflective of recurrent, sustained inundations or saturation. Common diagnostic features of wetlands are hydric soils and hydrophytic vegetation. These features will be present except where specific physiochemical, biotic, or anthropogenic factors have removed them or prevented their development."

This review will address the ability of two types of wetlands, constructed and restored wetlands (termed CW herein), to improve water quality in agricultural landscapes. Constructed wetlands, also referred to as created wetlands, are developed in areas where natural wetlands did not previously exist. Restored wetlands are enhanced and/or developed wetlands in areas where wetlands were drained or disturbed in some manner (Mitsch, 1992; Van de Valk and Jolly, 1992). There are two main types of CWs, surface flow and subsurface flow (both vertical and horizontal). Subsurface flow wetlands are not common in agricultural settings because of the high maintenance costs associated with the clogging of porous media. Therefore, this review primarily focused on surface flow CWs, where agricultural runoff (surface and/or subsurface) is delivered to and passes through a wetland system ultimately destined for adjacent surface water bodies such as rivers, streams, lakes, and estuaries.

This review addresses the application of CWs to mitigate NPSP in agricultural settings, primarily from field runoff and subsurface drainage. CWs are one of several BMPs for mitigating NPSP. There is a tremendous body of literature on treatment wetlands, which we define as wetlands designed to filter and treat municipal waste water (but also storm runoff, mine waste, and animal waste). Despite the tremendous depth of knowledge on treatment wetlands (e.g., Kadlec and Knight, 1996), there is a paucity of published information addressing the efficacy of CWs for controlling NPSP (Baker, 1992; Woltemade, 2000). Moreover, CWs in agricultural settings differ greatly from treatment wetlands, and direct comparisons between treatment wetlands, which have relatively constant input flows, are not always reliable (Poe *et al.*, 2003; Tanner *et al.*, 2005). Most treatment wetlands that receive municipal or animal waste experience continuous water flow and uniform input loads of waste. For example, in a study of water quality in 244 sewage treatment facilities across the nation, standard deviations of mean values for nutrients were around 10% (Gakstatter *et al.*, 1978). In contrast, the relative standard deviation for irrigation tailwaters in the San Joaquin Valley of California often exceeded 50% for several water-quality parameters (Brauer *et al.*, 2009). Before the early 1990s, most water-quality research on wetlands in agricultural settings has focused on runoff from confined animal operations (Cronk, 1996; Mitsch and Gosselink, 2000; Tanner *et al.*, 1995, 2005). The composition of nitrogen (N) and phosphorus (P) differs between waste water effluent and agricultural cropland runoff. Relative comparisons of the two indicate that wastewater is N limited with a mean N:P ratio of 2.4:1 while agricultural runoff tends to be P limited with a mean N:P ratio of 31:1 (Baker, 1992). Nutrients in treatment wetlands are often immobilized in organic/particulate forms, where as in agriculture, these constituents are commonly in inorganic/dissolved forms making the process of plant uptake more relevant (Baker, 1992).

The goal of this review is to summarize the current state of knowledge regarding the use of CWs in agricultural settings to improve water quality. In this effort we considered benefits of implementing CWs, and discussed dominant wetland processes, contaminant removal efficiencies, wetland management practices, and design and placement considerations. This review focuses on surface flow-through wetlands and does not directly address evaporation ponds, vertical seepage wetlands, treatment wetlands, or natural wetlands. CWs in agricultural settings receive a broad suite of water-quality contaminants, and therefore the potential amplification of some constituents resulting in adverse effects will also be addressed.

1.2. Governing factors influencing CWs

1.2.1. Climate

Temperature is a controlling variable for biogeochemical reaction rates, thus the coincidence of agricultural runoff with seasonal temperatures is a key factor in contaminant removal. Irrigated agriculture represents the best case scenario, where CWs receive inflows from tailwaters during the warmest times of the year. However, many CWs are placed in farmscapes to intercept storm water runoff. These systems often receive highest inflows during winter rains or spring snowmelts, often during the coldest times of the year (Werker *et al.*, 2002).

Solar radiation drives wetland energy balance and ultimately governs all wetland processes. Solar radiation directly affects primary productivity, temperature, and evapotranspiration (Kadlec, 1999). It also contributes to photodegradation of organic compounds. Solar radiation and wind govern evapotranspiration and water loss affecting removal efficiencies calculated on a concentration basis.

1.2.2. Inflow

CWs receiving agricultural runoff witness event-based fluxes of water and materials that correspond with hydrological patterns, irrigation and cultivation practices, and biogeochemical cycles, all of which are governed to a large extent by climate. As such, CWs in these settings experience a high degree of variability (Brauer *et al.*, 2009; Woltemade, 2000). Variability in hydrologic loading depends on wetland design and the origin of source water (e.g., irrigation runoff, tile drainage, surface runoff, stream flow diversion, or in-stream flow). Seasonal patterns in contaminant flux and dilution occur as a result of land use, storm events or snow melt, discharge from tile drainage, and/or irrigation runoff. Concentration pulses may reflect runoff events, fertilization timing, mineralization of soil organic matter, and/or application of soil amendments. Pesticide concentrations vary as a function of application timing, crop rotation, crop mix, and drift patterns. When evaluating the efficacy of CWs for water-quality purposes, or when comparing CWs across regions, it is important to consider the nature of source waters and the timing of their delivery.

CWs receiving irrigation runoff experience seasonal variability governed by the length of the growing season and cropping patterns. In California's Central Valley, it was shown that wetland input water concentrations of nutrients, sediment, and salinity originating from tailwaters were highly variable and showed no relationship with flow when the contributing area was relatively small (<1500 ha) (Brauer *et al.*, 2009). Water-quality contaminant concentrations were less variable, however, in large contributing areas, which supplied constantly high input loads. Contaminant concentrations tend to be more variable when the size of the contributing area is small because pulses are linked to the timing of biogeochemical processes, irrigation, fertilization, and cultivation. Large contributing areas integrate all factors that result in contaminant flux, the end result being a more constant contaminant concentration within input waters (Brauer *et al.*, 2009).

1.3. Contaminant removal processes

In agricultural settings, wetlands serve as filters, sinks, and transformers of water-quality constituents (Jordan *et al.*, 2003). The retention and/or removal of water-quality contaminants in CWs are/is governed by three general processes: additions, transformations, and translocations. Input loading affects the rate and pathway of removal mechanisms. Transformations lead to a change in phase and reactivity of constituents, while translocation processes render contaminants inactive and/or inert, often through burial. In many instances, transformations and translocations work in concert, resulting in a constituent loss. Some specific processes lead to a permanent loss from the system, such as the transformation of nitrate to N_2O and N_2 gas and its diffusion into the atmosphere. Others result in the transfer of contaminants from one compartment of the system (water column) to another (sediment), the latter rendering the contaminant less reactive in the environment.

There are several mechanisms acting in CWs that contribute to the removal of contaminants, including: (1) sedimentation and burial (phosphorus, pesticides, particulate organic carbon, pathogens); (2) biogeochemical transformations (denitrification, methanogenesis, dimethylselinide production); (3) biotic uptake of nutrients and salts; (4) microbial degradation of pesticides and organic matter; (5) redox transformations affecting solubility, sorption, and toxicity (e.g., As, Se, methyl-Hg); (6) predation of pathogens; and (7) photodegradation of pesticides and organic matter. As a result of these processes, it is commonly considered that wetlands have a predominantly beneficial effect on water quality (Jordan *et al.*, 2003; Zedler, 2003). Important factors controlling water purification capacity of wetlands include rate of contaminant inflows, residence time of water in the wetland, availability of organic matter and other substrates for growth of microbes, light intensity and penetration, temperature, and nutrient uptake by plants (Phipps and Crumpton, 1994; Woltemade, 2000).

1.3.1. Redox processes

Redox status of wetland soils dictates many important constituent transformations affecting the chemical phase (aqueous, solid, or gas), mobility of some contaminants, and the reactivity of sorption sites. Reducing conditions arise as soils become saturated. Oxygen rapidly becomes limited in submerged soils because the oxygen diffusion rate is orders of magnitude slower in saturated soil compared with well-drained soils. Anaerobic conditions develop in the absence of O_2, and as a result, other electron acceptors are utilized for microbial respiration. In the presence of oxygen, redox potentials are generally in the range of 400–600 mV. Following oxygen depletion, nitrate is reduced to N_2O and N_2 gas at a threshold redox potential around 250 mV (Mitsch and Gosselink, 2000). Once nitrate (NO_3) is consumed, constituents that affect P cycling are reduced, such as manganese and iron (hydr)oxides, at redox thresholds around 225 and 100 mV, respectively. At low redox potentials, sulfate is reduced to sulfide (-100 mV) and CO_2 is reduced to methane (-200 mV).

Wetland soils are not completely reduced. A thin oxidative layer exists at the soil surface, which ranges in thickness from a few millimeters to several centimeters. This layer forms as a result of mixing between the atmosphere, water column, and soil. Its thickness is mediated by temperature, rate of diffusion, plant and microorganism respiration rates, oxygen production via photosynthesis by aquatic vegetation, and mixing in the water column (Mitsch and Gosselink, 2000). Since some water-quality constituents become less mobile under oxidizing conditions (Mn and Fe), this thin oxidized layer can act as a barrier for translocations from sediment pore water to the water column. Moreover, it also serves as an important area where aerobic biochemical reactions occur, such as mineralization and methane oxidation.

1.3.2. Sedimentation

Sedimentation is the physical process of solid particles settling in water. The rate of sedimentation is governed by particle size, particle density, water velocity and turbulence, salinity, temperature, and water column depth. In wetlands, sedimentation results in many ecosystem benefits. The most dramatic effect is an increase in water clarity, which is important to downstream fish habitat and the aesthetic value of connected water bodies. Sedimentation also contributes to water-quality improvements through the settling of reactive particles that serve as sorption sites for other contaminants such as pesticides, trace metals, phosphorus, ammonium, and pathogens. Carbon sequestration is partially facilitated through sedimentation, where settled particulate organic carbon and carbon associated with sediment is buried and preserved in anaerobic soil environments where decomposition is very slow (Smith *et al.*, 2001, 2002). Removal of particulate organic matter also reduces the BOD, which reduces the potential for hypoxia in aquatic ecosystems.

1.3.3. Sorption

The process where contaminants in the water column are removed from solution and retained on surfaces of solid particles is termed sorption. Sorption leads to contaminant removal by rendering the contaminant less reactive or by removing it from the system through sedimentation and burial. Sorption is limited by the amount of sorptive surfaces and the chemical and mineralogical nature of the particles. The nature of water-quality contaminants is also important to consider. Cations, for example, will be attracted by negatively charged colloids of clay or organic matter via cation exchange reactions. Sorption to particulates coupled with sedimentation and burial is also an important removal process for pathogens and pesticides (Knox *et al.*, 2008; Streets and Holden, 2003). An important process that facilitates phosphorus removal occurs through sorption via inner- and outer-sphere complexes to crystalline and poorly crystalline oxides or clay crystal edges and subsequent sedimentation.

1.3.4. Photochemical processes

Photochemical processes can cause direct or indirect transformation of water-quality contaminants (Miller and Chin, 2005). Organic chemicals and constituents such as pesticides, herbicides, pharmaceuticals, pathogens, and DOC can be remediated in wetlands by photodegradation. While most pathogens can be destroyed directly by UV light, many pesticides decompose as a result of indirect photolysis (Miller and Chin, 2005). For example, humic substances when exposed to photons can yield reactive oxygen species and the photochemically excited states of dissolved organic matter (DOM) may enhance photolysis of organic contaminants. Nitrate has also been shown to be an important photosensitizer in wetlands, producing hydroxyl radicals ($OH^{\cdot}$) when photolyzed (Zepp *et al.*, 1987).

1.4. Vegetation

Vegetation plays an important role in filtration of contaminants in wetlands. Assimilation of pollutants including metals and nutrients is an important translocation and transformation mechanism, but is not considered a removal process unless vegetation is harvested and removed or burned in the case of nitrogen. There are, however, a variety of indirect contributions of vegetation toward contaminant removal. Stems and leaves within the water column impede water flow promoting particle settling and preventing sediment resuspension. Wetland vegetation also increases the surface area of substrate for microbial attachment and biofilm communities that are responsible for many transformation processes (Brix, 1997). As plants die and decay organic carbon is supplied, which is needed for many microbial transformations such as denitrification. Organic materials are also important in the sorption of pesticides in CWs. Central to nitrogen transformations (ammonium and organic N), wetland vegetation facilitates the existence of the soil aerobic zone by transferring oxygen from the atmosphere to the rhizosphere via aerenchymous tissues facilitating mineralization, nitrification, and methane oxidation. Another function of plants is to decrease the hydrologic load leaving CWs through transpiration (Carty *et al.*, 2008).

The shading effect of an emergent canopy can have positive and negative impacts on contaminant removal. Canopy interception of solar radiation reduces UV light penetration in the water column, which reduces pathogen attenuation and photodegradation processes. However, light interception results in less phytoplankton algae that could cause high BOD and hypoxia downstream.

Wetland vegetation has been shown to uptake considerable amounts of nutrients. For example, *Schoenoplectus tabernaemontani* was found to uptake 190–390 g N m^{-2} yr^{-1} (Tanner *et al.*, 1998) and *Scirpus*, *Phragmites*, and *Typha* were found to assimilate 90–130 g N m^{-2} yr^{-1} (Debusk *et al.*, 1995; Kadlec, 1999). The effects of plant uptake in a CW are counteracted by litter deposition and mineralization of detritus, and thus, vegetation must be harvested and disposed of annually to facilitate long-term nutrient removal.

2. SUSPENDED SEDIMENT

Out of all the pollutants from irrigated agriculture, CWs are most effective at removing suspended sediment. Sediment adversely affects surface water bodies by decreasing water clarity, and destruction of benthic communities and spawning beds in rivers and streams. Sediment can also be considered indirectly toxic since pollutants (metals, pesticides, pathogens, and nutrients) are often sorbed to particulates. The forms of suspended sediment are organic and mineral. Mineral fractions may include microaggregates, sand, silt, or clay.

The dominant process of suspended solids removal is sedimentation. As high energy input flows are dispersed across the CW environment, the velocity is reduced, resulting in settling of the suspended load. The energy needed to support suspended particles is dissipated by the increase in cross-sectional area and in part by vegetation, which reduces turbulence and decreases water velocity (Barko *et al.*, 1991; Schmid *et al.*, 2005). Several studies, however, have disputed the claim that vegetation directly affects sedimentation (Brueske and Barrett, 1994; Leonard *et al.*, 2002). Instead, it is thought that vegetation reduces resuspension resulting in increased net sediment retention (Braskerud, 2001; Brueske and Barrett, 1994). Other factors in the CW environment that affect sedimentation are degree of particle flocculation, particle diameter, particle density, water temperature, turbulence, and residence time.

The amount of vegetative cover has been shown to affect sediment resuspension. For example, Braskerud (2001) found that a 30% increase in vegetative cover from less than 20% reduced sediment resuspension from 40% to near zero. Wetland depth may also indirectly affect sediment retention. Water levels should be deep enough to reduce water velocity on the soil surface, however, if too deep, vegetation cannot establish resulting in significant resuspension of sediment. Water depths between 20 and 50 cm optimize plant establishment, decrease water velocities, anchor soil, and provide the added benefit of short particle settling distance (Braskerud, 2002a). Some studies contradict this statement, finding higher sedimentation rates in deeper open water environments (Brueske and Barrett, 1994; Fennessy *et al.*, 1994). Preferential flow through unvegetated areas may be responsible for higher sedimentation rates witnessed in these studies, by distributing more material to open areas. Maynard *et al.* (2009) found that fine sediments (silts and clay) were transported along preferential pathways through wetlands with low HRT resulting in a decrease in the retention efficiency for particle bound P. This may also apply to particle-associated pesticides, metals, pathogens, and other chemicals.

Sediment accumulation rates are highly variable when comparing different wetlands. In a review of several freshwater wetlands in the eastern half of the United States, Johnston (1991) found mass sediment accumulation rates to range from 39 to 5200 g m^{-2} yr^{-1} and in some instances no sedimentation occurred. Out of about 39 different wetlands, the average sediment mass accumulation rate among mineral soil wetlands was 1680 g m^{-2} yr^{-1}. Wetlands with the highest accumulation rates received agricultural field runoff (Cooper *et al.*, 1987) or sediment-rich stream and river waters, many of which drained agricultural areas (Johnston, 1991). In a review of nine wetlands receiving stream or river water, Phillips (1989) showed that on average 62% of suspended sediment was retained ranging from 23% to 93%.

Sediment removal by CWs can become a problem for wetland managers. Sediment accumulation eventually reaches a point where CWs need to be dredged or regraded to maintain proper hydrologic functioning. In agricultural settings, sediment traps often need to be cleared 1–2 times per year. The costs associated with removal and disposal of accumulated sediment can be substantial. Moreover, the risks associated with the use of potentially contaminated sediment (e.g., pesticides and trace elements) are unknown.

3. PESTICIDES

Pesticides have been detected in most surface water systems throughout the United States. One or more pesticides have been found in 95% of samples collected from about 1600 streams within the United States (Gilliom *et al.*, 1999). Due to the potential deleterious effects on aquatic organisms, there is a growing need to reduce pesticide contamination in receiving waterways. CWs may cause the removal of contaminants via physical, chemical, and biological processes. The use of CWs as a mitigation strategy is gaining in popularity; however, at the present time, there exist only a small number of studies in the literature on the use of CWs in mitigating pesticide contamination. A total of 26 studies representing 18 different wetland systems were found (Table 1). All wetlands in the following reviewed studies were constructed with the purpose of evaluating their effect on water quality.

Pesticides are a diverse group of chemicals with various physiochemical properties that influence their transport and transformation potentials after being applied in the field. There are several classes of pesticides depending on the target organism, including herbicides, insecticides, fungicides, and nematicides. The majority of research evaluating pesticides in CWs has considered herbicides and organophosphate and pyrethroid insecticides. Owing to their different properties, each class of pesticide presents a unique challenge in the development of mitigation measures.

3.1. Herbicides

Herbicides are an extremely heterogeneous class of chemicals with variable physiochemical properties. The reported octanol–water partition coefficient (log) K_{ow} values range from 0.16 for dicamba to over 5.0 for fluroxypyr, making any generalization on their partitioning behavior impossible. Most herbicides are fairly water soluble, with solubilities reaching the 10^3 ppm range. Some, however, such as the popular trazine herbicide simazine, are relatively insoluble at 5 mg l^{-1}.

Runes *et al.* (2003) evaluated atrazine retention under various frequency and intensity of runoff events in a wetland consisting of five 40-m linked cells. Retention varied between 76% and 84% under the five flow regimes. A sixth experiment resulted in 100% of the applied atrazine recovered at the wetland outlet. The authors noted that treatment was most likely compromised due to internal loading from runoff from adjacent fields (Runes *et al.*, 2003). Atrazine retention was also evaluated by Moore *et al.* (2000). The authors estimated a necessary wetland length of 281 m for effectively mitigating input effluent of 147 μg l^{-1}. Effective removal of another triazine herbicide was noted by Stearman *et al.* (2003), who observed a mean

Table 1 Selected characteristics of constructed wetlands reviewed

Reference	Class*	System characteristics	Flow regime	Size (m)[a]	Flow $(m^3\ h^{-1})$	HRT (d)	R (%)
Rose *et al.* (2006)	H, OC	2 sequential cells, mixed[b]	Ponded	100^2, 200^2	Ponded	~14	0–55 (H), 15–39 (OC)
Sherrard *et al.* (2004)	F, OP	Closed system mesocosm	Ponded	1.85 × 0.63	Ponded	3	98
Blankenberg *et al.* (2006)	H, F	8 parallel cells	S.F.	40 × 24	45	n.r.	3–47
Blankenberg *et al.* (2006), Braskerud and Haarstad (2003), Haarstad and Braskerud (2005)	H, F	Stepped sections in expanded stream	S.F.	100 × 8.4	28–63	n.r.	25–67 (yr. 1), 11–19 (yr. 2)
Budd *et al.* (2009)	OP, P	Sediment basin, 1°, 2° cells	S.F.	450 long	252	0.04 (1°)	52–90 (P), 22–61 (OP)
Budd *et al.* (2009)	OP, P	Sediment basin, 1° cells	S.F.	720 long	72	0.75	64–94 (P), 52–82 (OP)
Kohler *et al.* (2004)	H, OC, OP	Interconnected basins on golf course	S.F.	0.34–1.24 ha	1.8–19.4	n.r.	n.r.
Moore *et al.* (2007a,b, 2009), Bouldin *et al.* (2007)	OP, P	Sediment basin, 1°, 2° cells	S.F.	180 × 22	n.r.	n.r.	~95[c] (P)
Moore *et al.* (2002), Schulz and Peall (2001), Schulz *et al.* (2003a)	OP	Single cell, mixed	S.F.	134 × 36	97–1152	n.r.	77–100[c]
Moore *et al.* (2000, 2002)	H	4 single cells	S.F.	66 × 10	45.4	0.38	66–82[c] (H), 83 (OP)
Moore *et al.* (2006), Schulz *et al.* (2003a,b)	OP	2 single cells	S.F.	50 × 10	31.8	n.r.	100[c]

(continued)

Table 1 (*continued*)

Reference	Class*	System characteristics	Flow regime	Size (m)[a]	Flow ($m^3\ h^{-1}$)	HRT (d)	R (%)
Runes *et al.* (2003)	H	5 sequential cells	S.F.	40 × 3 (each)	15–30	n.r.	0–84
Hunt *et al.* (2008)	OC, OP, P	2 sequential cells	S.F.	27 × 12, 24 × 12	3.6	7.4	n.r.
Hunt *et al.* (2008)	OC, OP, P	1 cell with 4 inlets	S.F.	70 × 12	24.5	2.3	52 (OP)
Matamoros *et al.* (2008)	H	Single cell—mixed	S.F.	1 ha	4.2	30	>79
Cheng *et al.* (2002a,b)	OP, H	Twin small	V/R	1 × 1	0.01	n.r.	100 (OP), 0–36 (H)
Stearman *et al.* (2003)	H	7 subsurface flow cells	S.S.	4.9 × 1.2, 4.9 × 2.4	0.03–0.12	2.3–20.6	59–95
Borges *et al.* (2009)	H	4 parallel cells	S.S.	24 × 1	0.2–0.03	3.8	39

* H, herbicide; F, fungicide; OC, organochlorine; OP, organophosphate; P, pyrethroid; S.F., surface flow; S.S., subsurface flow; V/R, vertical/reverse flow; HRT, hydraulic residence time; R, removal efficiency; n.r., not reported.

[a] Size in meters unless otherwise noted.

[b] Mixed = sections of open water and vegetated.

[c] %R estimated from reported input/outputs.

removal of 65–96% for simazine, and 59–96% for the aniline herbicide metolachlor in vegetated cells over a 2-year period. Other herbicides have proven more recalcitrant to mitigation measures. Only 39% of ametryn was removed within 24 × 1 m subsurface flow CW that had a 3.8 day hydraulic retention time (Borges *et al.*, 2009). The retention of certain chemicals varied substantially between studies. In one study, MCPA and mecoprop were effectively treated (>79% removal) over a 2-year period within a 1-ha wetland receiving effluent from a wastewater treatment plant. Removal of terbutylazine was inconsistent, with only 1% removal in the first year, but reaching 80% in the second year of monitoring (Matamoros *et al.*, 2008). Cheng *et al.* (2002a) found that MCPA concentrations decreased by only 36% in another subsurface wetland, while removal of dicamba was negligible. The discrepancy in MCPA removal was most likely due to system variances, as the latter CW was only 1 m^2 in size.

3.2. Organophosphate insecticides

Organophosphates are comprised of two main groups, thionate triesters (P=S) and oxonates (P=O) (Stangroom *et al.*, 2000a). All organophosphates are acetocholinesterase inhibitors and have toxicity to mammalian species. Although heralded as a better choice than their organochlorine predecessors due to their relatively short half-lives, their acute toxicity to human and aquatic organisms is a serious environmental concern that has contributed to the restricted use of some organophosphate products (Bondarenko and Gan, 2004; Ragnarsdottir, 2000). Organophosphates are generally more soluble than pyrethroids, and therefore partition into the aqueous phase more readily. As with pyrethroids, there is generally a positive correlation between pH and rate of hydrolysis. However, photolytic degradation is much more prevalent for organophosphates in natural water systems (Stangroom *et al.*, 2000b).

Chlorpyrifos and diazinon are often detected in watersheds with agricultural inputs at levels of ecological concern. Concentrations of diazinon in agricultural storm water runoff draining into the San Joaquin River Basin were found to be toxic to some fish and invertebrate species (Werner *et al.*, 2004). A survey study of streams within the Central Valley of California found both diazinon and chlorpyrifos present at levels above those set for water-quality standards in over 80% of samples analyzed (Bailey *et al.*, 2000).

Most research concerning organophosphate insecticides in CWs has focused on chlorpyrifos, diazinon, and methyl-parathion. CWs have proven to be an effective mitigation strategy for reducing chlorpyrifos concentration in the water column. One study conducted in the Central Valley of California showed reductions in chlorpyrifos concentrations between 52% and 61% for two separate systems monitored over the course of a 4-month irrigation season (Budd *et al.*, 2009). Two separate studies evaluated chlorpyrifos concentrations within a wetland located along the Lourens River in South Africa. In the first study, inlet chlorpyrifos concentrations reached a maximum of 1.3 μg l^{-1} during a storm event, but were reduced to 0.03 μg l^{-1} at the outlet (Moore *et al.*, 2002). The inlet concentrations of 0.02 μg l^{-1} after a second storm were reduced to below the detection limit at the outlet (Schulz and Peall, 2001). Chlorpyrifos concentrations in suspended sediment were detected at levels reaching 89.4 μg kg^{-1} at inlets, but decreased to below the detection limit at the wetland outlet in both studies.

Studies have also demonstrated the potential of CWs for removing other organophosphates. Methyl-parathion transport was evaluated within vegetated and nonvegetated wetland cells located at the University of Mississippi Field Station. Two studies evaluating simulated runoff events showed the vegetated cells to be 100% efficient at removing methyl-parathion within 40 m (Moore *et al.*, 2006; Schulz *et al.*, 2003a). Azinphos-methyl retention was also evaluated in the Lourens River wetland. Reductions in concentrations ranged from 77% to 93% after a storm event, and 90% on average after five independent spray drift trials (Schulz and Peall, 2001; Schulz *et al.*, 2003b). Parathion and omethoate were completely removed from the water column within the dual 1 m^2 flow wetland chamber that was previously noted to be ineffective at removing MCPA (Cheng *et al.*, 2002a).

Diazinon, another heavily used organophosphate, appears to be more resilient to translocation and transformation processes within wetlands. Moore *et al.* (2007a) conducted a simulated runoff study in a three-cell wetland located in the Beasley Lake watershed in Mississippi, USA. Less than 41% of the total diazinon mass was retained within the sediment retention basin or primary wetland cell. Although measurements were not reported for the outlet, low retention within the first two cells indicated that there was little mitigation of diazinon within the CW. Budd *et al.* (2009) observed similar behavior for diazinon within two CWs located in the Central Valley of California. Diazinon was only detected on four of the eight sampling dates. During one sampling period, diazinon was detected orders of magnitude higher at the outlet than the corresponding inlet. The authors hypothesized an external loading source to the wetland, but average seasonal removal efficiencies (68% and 92%) suggested less mitigation of diazinon compared to chlorpyrifos and pyrethroids (98–100%) within the same system (Budd *et al.*, 2009). Lower removal efficiency of diazinon may be due to its relatively low hydrophobicity as compared to chlorpyrifos and pyrethroids (Table 2).

3.3. Pyrethroid insecticides

Most pyrethroid insecticides on the market today are second generation or chemically stable derivatives of pyrethrins, the insecticidal ingredients derived from the chrysanthemum flower. Table 2 lists selected physicochemical

Table 2 Reported pesticide properties and removal efficiency (%R) ranges[a]

Chemical	Class*	log K_{ow}	Solubility (mg L^{-1})	%R	Reference
Ametryn	H	2.63	200	39	Borges *et al.* (2009)
Atrazine	H	2.5	33	0–84[b]	Moore *et al.* (2000), Runes *et al.* (2003)
Bentazone	H	−0.46	570	2	Braskerud and Haarstad (2003)
Dicamba	H	−1.88	6100	0–3	Braskerud and Haarstad (2003), Cheng *et al.* (2002a,b)
Dichlorprop	H	1.77	350	35	Braskerud and Haarstad (2003)
Fenpropimorph	H	4.2	4.3	10–50	Blankenberg *et al.* (2007), Braskerud and Haarstad (2003)
Fluroxypyr	H	−1.24	91	0	Braskerud and Haarstad (2003)
Linuron	H	3	63.8	3–56	Blankenberg *et al.* (2007), Braskerud and Haarstad (2003)
MCPA	H	0.71	273.9	27–93	Braskerud and Haarstad (2003), Cheng *et al.* (2002a,b), Matamoros *et al.* (2008)
Mecoprop	H	0.10	734	23–91	Braskerud and Haarstad (2003), Matamoros *et al.* (2008)
Metalaxyl	H	1.75	8400	0–41	Blankenberg *et al.* (2007), Braskerud and Haarstad (2003)
Metalochlor	H	2.9	1700	57–97	Stearman *et al.* (2003)
Metamitron	H	0.83	488	7–58	Blankenberg *et al.* (2007), Braskerud and Haarstad (2003)
Metribuzin	H	1.58	1050	11–40	Blankenberg *et al.* (2007), Braskerud and Haarstad (2003)
Propachlor	H	1.4–2.3	580	14–67	Blankenberg *et al.* (2007), Braskerud and Haarstad (2003)
Propiconazole	H	3.72	100	13–25	Braskerud and Haarstad (2003)
Simazine	H	2.1	6.2	59–96	Stearman *et al.* (2003)
Terbutylazine	H	3.21	8.5	1–80	Matamoros *et al.* (2008)
Azinphos-methyl	OP	2.96	28	90–100	Schulz and Peall (2001), Schulz *et al.* (2003b)
Chlopyrifos	OP	4.7	1.4	52–100	Budd *et al.* (2009)
Diazinon	OP	3.3	60	0	Budd *et al.* (2009)

(*continued*)

Table 2 (*continued*)

Chemical	Class*	log K_{ow}	Solubility (mg L^{-1})	%R	Reference
Methyl-parathion	OP	3	55	100	Moore *et al.* (2006), Schulz *et al.* (2003a)
Omethoate	OP	-0.74	Miscible	100	Cheng *et al.* (2002a,b)
Parathion	OP	3.83	11	100	Cheng *et al.* (2002a,b)
Prothiofos	OP	5.67	0.7	100	Schulz and Peall (2001)
Bifenthrin	P	>6	<0.001	69–84	Budd *et al.* (2009)
Cyhalothrin	P	6.9	0.005	71–90	Budd *et al.* (2009)
Cypermethrin	P	6.6	0.004	52–64	Budd *et al.* (2009)
Esfenvalerate	P	6.22	0.002	77–87	Budd *et al.* (2009)
Permethrin	P	6.1	0.006	90–94	Budd *et al.* (2009)

[a] Physiochemical properties taken from Tomlin (2000).

[b] The lack of mitigation during one test likely due to external loading, average %R for first five tests = 81%, solubility in mg l^{-1}.

* OP, Organophosphate; P, pyrethroid; H, herbicide.

properties of some pesticides of interest (Laskowski, 2002). As evident from the water solubility and K_{oc} values, pyrethroids are extremely hydrophobic and tend to bind to organic matter, including DOM (Bondarenko *et al.*, 2006; Stangroom *et al.*, 2000a; Zhou *et al.*, 1995). Photolysis has been shown to be a potential degradation pathway for several pyrethroids including esfenvalerate, deltamethrin, and fenpropathrin (Stangroom *et al.*, 2000b). In natural systems, however, binding to DOM will limit photolytic degradation. Hydrolytic degradation will most likely be the primary route of abiotic degradation for pyrethroids in wetland systems. The rate of hydrolysis generally increases with increasing pH, resulting in more polar products (Stangroom *et al.*, 2000b). Sediment toxicity or bioavailability is usually estimated from the organic carbon-based sediment concentration, as evident in application of the Equilibrium Partitioning Theory (Di Toro *et al.*, 1991).

Although pyrethroids are fairly nontoxic to mammalian species, they display acute toxicity to aquatic organisms, especially invertebrates, at very low levels. The OC-normalized LC50 values for the amphipod *Hyalella azteca* have been reported for λ-cyhalothrin (0.45 μg g^{-1} OC), bifenthrin (0.52 μg g^{-1} OC), deltamethrin (0.79 μg g^{-1} OC), cyfluthrin, (1.08 μg g^{-1} OC), esfenvalerate (1.54 μg g^{-1} OC), and permethrin (10.83 μg g^{-1} OC) (Weston *et al.*, 2005). Several monitoring studies have attributed observed aquatic toxicity of benthic invertebrates to sediment contamination by pyrethroids (Amweg *et al.*, 2006; Bay *et al.*, 2004; Werner *et al.*, 2004).

Residue concentrations of pyrethroids in sediments have been detected in watersheds throughout the United States, especially in California (Budd *et al.*, 2007; Kimbrough and Litke, 1996). Agricultural fields are a well-documented source of pyrethroids in downstream sediment beds. Weston *et al.* (2004) detected pyrethroids in 75% of sediment samples collected within the agriculture dominated Central Valley of California (Weston *et al.*, 2004). Pyrethroid residues have been frequently detected in the sediment from a number of urban streams in northern California (Amweg *et al.*, 2006; Bacey *et al.*, 2005; Weston *et al.*, 2005).

A few studies have considered the potential of wetlands for removing pyrethroid insecticides from the water column. Due to the hydrophobic nature of this class of chemicals, the studies have consistently shown the high efficiency for wetlands to remove pyrethroids from input waters. Seasonal average reductions in water concentrations for five pyrethroids ranged from 52% to 94% in one study (Budd *et al.*, 2009). Moore *et al.* (2009) observed λ-cyhalothrin and cyfluthrin concentrations in a three-cell wetland for a 55-day period following a simulated runoff event. While input concentrations were 17 and 64 μg l^{-1}, outlet concentrations peaked at 0.77 and 3.77 μg l^{-1} for λ-cyhalothrin and cyfluthrin, respectively (Moore *et al.*, 2009). In a small on-farm system, Hunt *et al.* (2008) observed that pyrethroid concentrations decreased by $>60\%$ at the outlet.

3.4. Pesticide removal

3.4.1. Pesticide characteristics affecting removal

Pesticide removal by wetlands may be influenced by both properties of the pesticides and the characteristics of the wetlands. Figure 2A is a plot of a pesticide octanol–water partition coefficients (K_{ow}) against the reported removal efficiency. One of the difficulties in the correlation analysis was that there are often several reported chemical K_{ow} values for the same compound in the literature. To reduce uncertainties, all log K_{ow} values in Fig. 2 were derived from two sources. Only studies with calculated reductions in concentrations between two lateral points within the system (e.g., inlet and

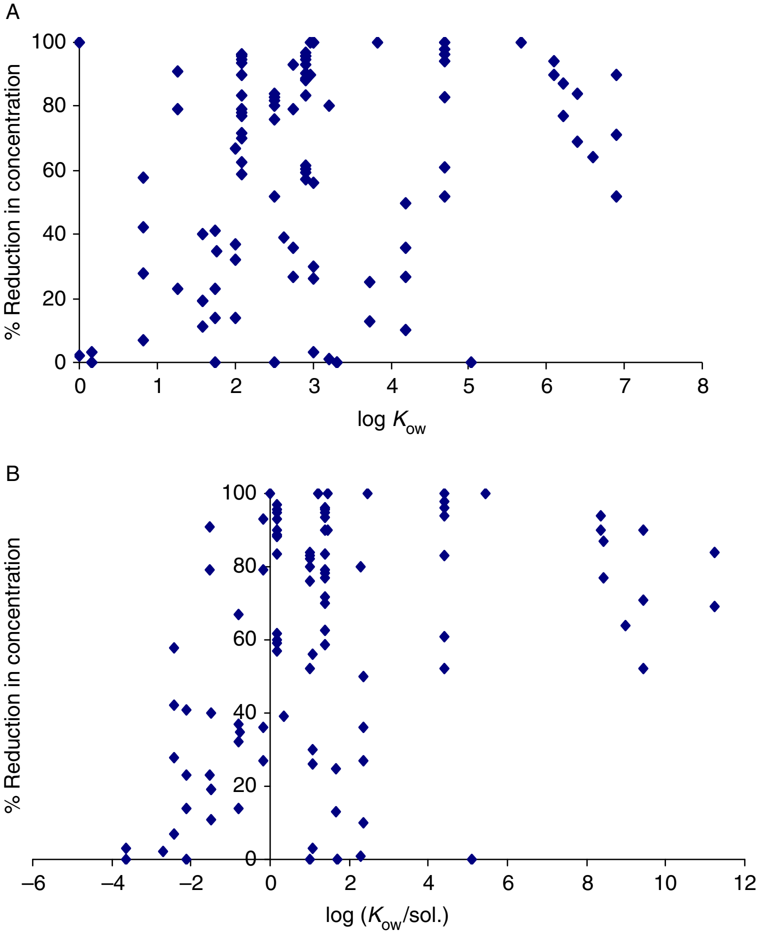

Figure 2 Wetland efficacy in reducing pesticide concentrations (% reduction) in relation to (A) octanol–water partition coefficient (log K_{ow}) and (B) log (K_{ow}/solubility).

outlet) were included. Also, multiple year results were separated and used independently. This resulted in several reduction values (%R) for the same chemical. Negative values were replaced with zero, signifying a lack of mitigation. Although a clear linearity was not observed, a general trend of improved removal was noted with increasing K_{ow} values (Fig. 2A). With one exception, log K_{ow} values >4.2 resulted in $>50\%$ reduction in pesticide concentrations, indicating that for highly hydrophobic chemicals, sorption is the primary driving force of removal. Between log K_{ow} values of 1 and 4, there were large variations in the %R values, indicating that chemicals in this range have the potential for removal by wetlands, but the performance likely depends on system characteristics. Miscible chemicals (log $K_{ow} < 1$) generally had lower %R. This trend was even more pronounced when the K_{ow} was divided by water solubility (Fig. 2B). This suggests that pesticides having high water solubility are not effectively mitigated by wetlands as the primary strategy, independent of system characteristics.

Overall, CWs have shown tremendous promise as a mitigation option for removing insecticides. We found 27 individual %R values reported for 12 organophosphate and pyrethroid insecticides (Table 2). With the exception of diazinon, all %R values were $>52\%$, with several of these compounds completely removed from the water column at the outlet. In comparison, removal of herbicides appears to be much more variable. In some cases, pesticides passed through the system uninhibited, while in others concentrations were effectively reduced.

In addition to the inherent properties of pesticides, the behavior of pesticides in a given wetland is controlled by many environmental variables. Conditions such as hydraulics and hydrology of the wetland are primary external forces affecting pesticide retention and removal. Other important factors include vegetation type and density, availability of organic matter and other substrates for microbial growth, and nutrient uptake demand by plants (Phipps and Crumpton, 1994; Woltemade, 2000). To achieve maximal contaminant removal, it is important to increase retention time within the CW and decrease the persistence of the retained contaminants by providing optimum conditions for biotic and abiotic transformations. Physical removal may be a result of pesticide adsorption by soil and plants, and elimination of the pesticide associated with the suspended particles due to sedimentation and burial, plant filtration, and other physical trapping mechanisms.

3.4.2. Effect of vegetation

Studies have shown a positive correlation between vegetation density and pesticide removal due to increased sorption to macrophytes and organic matter, physical trapping of pesticide-laden particles by plants, or a reduction in hydraulic conductivity (Moore *et al.*, 2002; Schulz *et al.*, 2003c). Sorption to plants has been shown to be the primary sink in highly vegetated agricultural ditches (Bennett *et al.*, 2005). Only a few studies were designed with the intent to directly evaluate the role of vegetation in pesticide removal. Stearman *et al.* (2003) observed herbicide removal over a 2-year period in wetland systems, where half of the cells contained *Scirpus validus* (600 stems m^{-2}) and the other half were absent of vegetation. In the absence of vegetation, average removal efficiencies for metolochlor and simazine were 63% and 64%, respectively. Removal increased to 82% and 77% for metolachlor and simazine, respectively, in vegetated cells. In a similar study, methyl-parathion removal was evaluated in the presence and absence of vegetation. The vegetated cells were planted with both *Juncus effuses* (256 ramets m^{-2}) and *Leersia oryzoides* (43 ramets m^{-2}). Concentrations were below detection limits in semipermeable membrane devices (SPMD) deployed at the outlet of the vegetated cells 96-h postexposure of a simulated storm runoff event. The mean concentration in the SPMD at the outlet of the nonvegetated cells was 8.83 $\mu g\ g^{-1}$, indicating downstream transport of methyl-parathion was minimized in the presence of vegetation (Moore *et al.*, 2006). Rose *et al.* (2006) did not observe a difference in pesticide removal for diuron, aldicarb, or fluometuron between vegetated and open water cells of a CW draining a cotton field during the first monitoring season. During the second season, however, fluometuron removal was 17% higher in the vegetated portion in the beginning of the season, but lower at the end of the season once an algal bloom occurred in the open water section.

Other research has provided indirect evidence for the positive correlation between vegetation and pesticide removal. Moore *et al.* (2002, 2007a, 2009) evaluated phase partitioning of several organophosphate and pyrethroid insecticides in wetland systems after simulated rainfall events. The total chemical mass associated with plants was considerable for chlorpyrifos (25%), diazinon (43%), λ-cyhalothrin (49%), and cyfluthrin (76%) after the events. Budd *et al.* (2009) attributed inefficient mitigation of pyrethroids and organophosphates within a portion of a monitored wetland to a lack of vegetation and subsequent channeling within that section. These studies together indicate the importance of vegetation within a wetland to provide sorption sites and slow down water flow allowing deposition of sorbed pesticides.

3.4.3. Hydrology and hydraulics

The hydrologic and hydraulic properties of a wetland have a dramatic effect on transport of pesticides through CWs (Braskerud and Haarstad, 2003). Pesticide removal efficiency has been shown to decrease considerably with increasing flow (Stearman *et al.*, 2003). Thus, characteristics that control residence time of pesticides in CWs affect attenuation. The rate of sedimentation is often a critical process for pesticide removal from the water column. Sedimentation is dependent on hydrologic residence time, sediment particle size and texture, flocculation of suspended particles, and vegetation (Fennessy *et al.*, 1994). Unfortunately, few studies reported flow rates or estimated residence time of the test systems, making comparative analysis impossible. A comparison of simazine and metolachlor removal in cells with varying hydraulic residence times (HRT) demonstrated removal efficiencies up to $>90\%$ for vegetated cells with HRT >10 days, while for those with HRT <4 days, removal was $<70\%$ on average for both herbicides. The HRT increased by an average of 30% in cells planted with common bulrush (600 stems m^{-2}) as compared to unvegetated cells (Stearman *et al.*, 2003). A HRT of approximately 18 h was found to be sufficient for reducing the concentration of several pyrethroids by 64–94% (Budd *et al.*, 2009).

The HRT of a system should be maximized as much as possible to assure the greatest attenuation due to sorption and degradation. However, in practice, this is often a challenge. Obtaining enough land to achieve long residence time is often economically infeasible. Also, conditions of a particular wetland often change over time as vegetation biomass varies both spatially and temporally, and input flow also changes with time. Dense vegetation has been shown to influence both the flow rate and sedimentation patterns within wetlands (Fennessy *et al.*, 1994). In addition, erosion over time can lead to changes in flow patterns, which can influence HRT. Newly constructed wetlands with a lack of established vegetation are prone to channeling, thereby decreasing the HRT and increasing the potential for downstream transport of pesticides (Budd *et al.*, 2009). In determining an optimal HRT for a system, wetland managers must consider many variables, such as the pesticides of primary interest, the level of desired mitigation, and the range of potential input concentrations. For instance, estimated residence time necessary to achieve a final atrazine concentration of 20 $\mu g\ l^{-1}$ increased from 30–39 days for cells with an initial concentration of 73 $\mu g\ l^{-1}$ to 133–143 days for cells with an initial concentration of 147 $\mu g\ l^{-1}$ (Moore *et al.*, 2000). Maintaining effective mitigation performance to account for varying environmental conditions will be a challenge for wetland managers.

3.4.4. Pesticide sorption and degradation

Pesticide sorption and transformation are important considerations when evaluating wetland performance. Adsorption potential of a pesticide is known to depend on the properties of both the pesticide and the sorbent phase, such as soil or sediment. For hydrophobic chemicals, sorption to soil or sediment is influenced not only by the quantity of organic matter, but also by the binding characteristics of the organic matter (Ahmad *et al.*, 2004; Lee *et al.*, 2003). In addition, pesticides have been shown to become less available to microbial degradation with longer contact time, a concept known as "aging" (Ahmad *et al.*, 2004). The K_d values of several organophosphates were shown to increase dramatically after only 1 month of aging (Bondarenko and Gan, 2004). It is likely to detect higher concentrations associated with sediment further downstream, a phenomenon known as enrichment, because silt and clay settling times are longer and their binding capacity is higher (Gan *et al.*, 2005).

A wetland may be more chemically reactive, due to the presence of favorable conditions, such as pH, temperature, and redox conditions, that can lead to enhanced transformations of the pesticide. Redox potential of a system has been shown to have a dramatic effect on persistence and degradation rates of pesticides in wetlands (Seybold *et al.*, 2001). For example, the persistence of chlorpyrifos in sediments increased significantly under anaerobic conditions ($t_{1/2} = 125$–746 days) in comparison to aerobic soils ($t_{1/2} = 1.8$–4.9 days) (Bondarenko and Gan, 2004). The biotic degradation pathway is dependent on several factors including microbial population, temperature, and the contaminant bioavailability. It is possible that repetitive exposure to the same pesticides over time may cause induction and adaptation of microbes, leading to establishment of organisms capable of rapidly degrading the pesticides in the wetland (Felsot *et al.*, 1981; Racke and Coats, 1988). On the other hand, although pesticide-degrading microbes may become enriched in a wetland, the strong binding capacity of hydrophobic chemicals, such as pyrethroids, has been found to hinder microbial degradation (Lee *et al.*, 2004). The aging of sediment has also been shown to increase the sequestration of hydrophobic chemicals, which further decreases the microbial degradability of sorbed pesticides (Ahmad *et al.*, 2004).

3.4.5. Summary of pesticide removal in CWs

To summarize, CWs are expected to be large sinks for pesticides due to enhanced sediment deposition, plant sorption and uptake, and microbial degradation. A number of studies have demonstrated the potential for CWs to remove pesticides in input flows; however, conditions of CWs as well as pesticide types studied so far are highly variable, preventing a meaningful statistical comparison. In general, pesticide removal efficiencies were shown to vary between chemical, design, hydrology, and vegetation characteristics. Increasing the wetland HRT and maximizing vegetation density help optimize wetland performance. However, there exists a need for more research quantifying the relationship between CW size, HRT, flow, vegetation density, and pesticide removal with chemicals of varying physiochemical properties. This information will be vital to managers for optimizing the performance of CWs within the confines of each system.

4. NITROGEN (N)

4.1. Environmental impacts

Constructed wetlands have become a popular BMP for treatment of nitrate in waste waters. Nitrate contamination of surface water and groundwater resources is prolific in agricultural regions. Excess nitrogen causes eutrophication in surface waters and is the limiting nutrient responsible for dead zones in estuaries and oceans (Boesch *et al.*, 2001). In agricultural regions, nitrate is a major water-quality constituent of concern in groundwater (Nielsen and Lee, 1987). Nitrate is a human health risk when present in drinking water due to its potential for causing methemoglobinemia in infants. Approximately one-third of the total N loading in the planet's rivers is anthropogenic, originating from agriculture, sewage, urban runoff, and atmospheric deposition (Meybeck, 1982).

4.2. N cycling in CWs

Forms of nitrogen in irrigated agricultural runoff include nitrate, ammonium, and organic N (dissolved and particulate). The type of N in input waters is important because wetlands are not as effective at removing organic N and ammonium, as they are for nitrate (Phipps and Crumpton, 1994). Nitrogen inputs to CWs in cropland settings come from field and surface water runoff, agricultural return flows and tile drains, but can also result from biological fixation, and wet and dry atmospheric deposition (Fig. 3). Unlike treatment wetlands that receive wastewater with high levels of dissolved organic N and ammonium, the dominant form of N in CWs that receive agricultural runoff is nitrate (Baker, 1998). The relative amounts of organic N and ammonium depend on organic matter mineralization rates, soil properties, and agricultural practices such as the use of manures.

The dominant N removal mechanism in CWs is respiratory denitrification, the microbially mediated transformation of nitrate to N_2O and N_2 gasses in the absence of oxygen (Kadlec and Knight, 1996). The low redox potentials in CW soils result in the perfect environment for denitrification. This process is mediated by heterotrophic microbes at redox potentials around 250 mV. Other N removal mechanisms, which account for a fraction of N removal in CWs include: plant assimilation, sedimentation and burial of particulate N (organic N and N adsorbed to particles), and ammonia volatilization (Fig. 3; Tanner *et al.*, 2002). Nitrate leaching can also be considered a removal mechanism, although it clearly does not result in an environmental improvement unless nitrate is denitrified in groundwater.

There are many published studies that have documented denitrification as the primary NO_3 removal mechanism in wetlands (Kadlec and Knight, 1996). Only a handful of studies have directly measured denitrification process in CWs receiving NPSP from agriculture (Hernandez and Mitsch, 2007; Poe *et al.*, 2003; Xue *et al.*, 1999). Comparisons of denitrification rates among studies in CWs is difficult because values vary widely depending on climate, vegetation, source water chemistry, hydrology, and methods used (Seitzinger, 1993). The dominant controlling variables on denitrification rates are dissolved oxygen concentration, nitrate levels, sediment organic

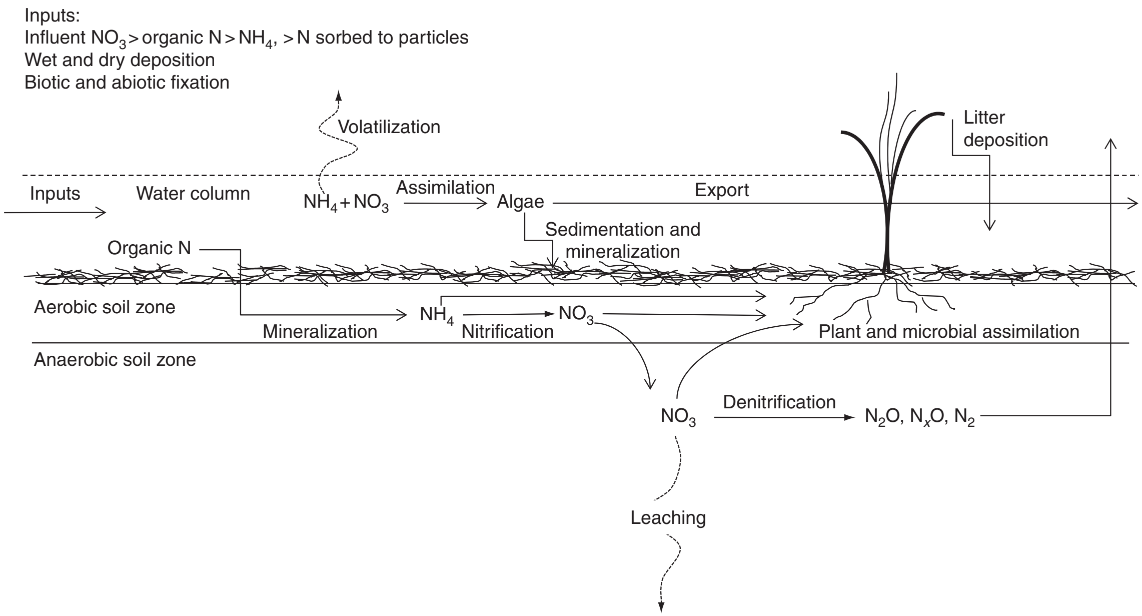

Figure 3 Schematic of the nitrogen cycle in CWs.

matter concentration and quality, temperature, and macrophyte cover (Poe *et al.*, 2003). In surface flow wetlands, the rate of denitrification is also controlled by the degree of mixing between the water column and anoxic soil. Thus, water exchange and nitrate diffusion are important factors.

Studies that have used ^{15}N tracer methods and the acetylene inhibition technique to measure denitrification in CWs in agricultural settings have demonstrated similar findings with rates ranging from 0.02 to 11.8 mg N m^{-2} h^{-1} and average rates around 2 mg N m^{-2} h^{-1} (Fleischer *et al.*, 1994; Poe *et al.*, 2003; Smith *et al.*, 2000; Xue *et al.*, 1999). The range in values represents seasonal temperature effects, differences in nitrate loading, and microbially labile carbon concentrations. Significant correlation between nitrate/nitrite and denitrification rate ($P < 0.01$; $r^2 = 0.98$) have been demonstrated, where pulses in nitrate after storm events stimulated denitrification (Poe *et al.*, 2003). Studies commonly show maximum rates in the summer and minimum rates when temperatures decrease (Poe *et al.*, 2003; Xue *et al.*, 1999). The optimum temperature range for denitrification is 20–25 °C, and the rate decreases below 15 °C as diffusion rates and microbial activity decrease (Beutel *et al.*, 2009; Spieles and Mitsch, 2000). Wetland soil denitrification rates were shown to increase by as much as two orders of magnitude with a 21 °C increase from 4 °C (Sirivedhin and Gray, 2006). Thus, the ability of CWs to transform nitrate from agricultural runoff is compromised in areas where peak runoff and N loadings occur during the cold seasons. In settings where CWs receive input waters from streams or rivers, high N loads are common in fall, winter, and early spring runoff. However, N removal can still occur if a bulk of the N is organic N due to removal by settling and burial (Braskerud, 2002b).

The availability of organic carbon for microbes is an important factor regulating denitrification rates (Beauchamp *et al.*, 1989). Vegetation is the primary carbon source in many CWs and vegetation type affects the availability of carbon, serving as the "parent material" that is used by heterotrophic denitrifiers. Hernandez and Mitsch (2007) observed differences in denitrification potential (DNP) within experimental wetlands that corresponded to differences in vegetation and hydrologic environment. DNP was highest (~0.065 mg N h^{-1} kg^{-1}) in zones where emergent macrophyte communities were dominant and soils were continuously submerged. DNP was lower, around 0.02 mg N h^{-1} kg^{-1}, in open water communities and the forested edge of the wetland. Organic matter quality, as measured by cold water extraction, had a positive linear relationship with DNP. *Typha* spp. was the dominant emergent macrophyte, where labile carbon forms (high levels of cold water extractable C) and DNP rates were highest. Environments with plants that decompose more readily to labile forms of organic matter result in higher denitrification rates (Hernandez and Mitsch, 2007). Denitrification is low in open water bodies where water levels are too high for emergent macrophyte establishment or where woody species are the dominant carbon source (DeLaune *et al.*, 1996; Kadlec, 2005; Westerman and Ahring, 1987). In agricultural settings, there is often large inputs of organic matter from the eroded topsoil or from algae blooms (Maynard, 2009).

A potential adverse effect of nitrogen removal by denitrification in CWs is the production of N_2O. N_2O is a greenhouse gas several times more potent than CO_2. It can be argued, however, that once NO_3 has entered the hydrologic cycle, its ultimate fate is to be denitrified. Thus, the location where denitrification occurs is inconsequential assuming the conversion ratio of nitrate to N_2O is similar in wetlands compared to other large NO_3 sinks (Mitsch *et al.*, 2001).

In settings where organic N or NH_4 are the dominant forms in input waters, such as systems that receive animal waste, mineralization and nitrification must first occur in order to facilitate significant N removal. Nitrification occurs where oxygen is present. In CWs, oxygen is present in the water column and in the soil aerobic zone, a thin interface between the water column and the anaerobic root zone (Fig. 3; Reddy *et al.*, 1989). Since oxygen diffusion rates into flooded soil are very low, the movement of oxygen through aerenchymous tissue of wetland plants into the root zone is an important process that maintains this aerobic layer. In this soil environment, transformations of organic N and NH_4 to nitrate occur in the rhizosphere. Other factors that influence N transformations to NO_3 include chemical oxygen demand, available carbon source, pH, and temperature.

NH_4 is a component in many fertilizers applied to fields, commonly as anhydrous ammonia, ammonium nitrate, or ammonium sulfate. Ammonium can be oxidized via nitrification to NO_3 in agricultural soils. Ammonium can be transported from fields since it is adsorbed to cation exchange sites of soil colloids and fixed by vermiculite clay minerals. However, ammonium tends to build up in anaerobic soil horizons where large soil organic matter pools slowly decompose. Wetland mineralization rates are variable ranging from 4 and 357 mg N m^{-2} day^{-1} with a mean of 111 ± 124 mg N m^{-2} day^{-1} (Martin and Reddy, 1997). A diffusion gradient for NH_4 exists in wetland soils because nitrification occurs in the aerobic zone (Fig. 3). The rate of diffusion of NH_4 into the overlying aerobic soil horizon is very slow, much slower than NO_3. Thus, in settings where NH_4 and organic N dominate, removal rates are first limited by sedimentation and then by mineralization and diffusion into aerobic zones where nitrification can occur followed by translocation of nitrate to anaerobic zones where denitrification occurs.

4.3. N removal efficiency

Studies of CWs for waste water treatment have found that NO_3 removal efficiency decreases with increasing hydraulic load and as wetland surface area decreases (Kadlec and Knight, 1996; Knight *et al.*, 2000; Tanner *et al.*, 1998). Mitsch and Gosselink (2000) have summarized nitrate removal from agricultural runoff as a function of nitrate loading from two wetlands in the Midwest, USA, receiving dilute NO_3 input concentrations. They found that nitrate removal, calculated on an aerial basis (g N m^{-2} yr^{-1}) increased with NO_3 loading. However, when calculated on a mass or concentration basis, NO_3 removal decreased with increased N loading. While mass removal increases with greater N loading calculated on an aerial basis, differences in concentration between input and outputs may be insignificant at high loading rates (Kadlec, 2005). Mitsch and Gosselink (2000) suggest that the tradeoff between percent NO_3 removal and NO_3 export load occurs at input loads of 50 g NO_3–N m^{-2} yr^{-1} in Midwestern climates.

N-loading comparisons are difficult to extrapolate among CWs across the nation or globe because in agricultural settings, flow and nitrogen load vary across a wide range of temporal scales (Table 3). Wetland characteristics (shape, size, depth, age, sediment characteristics, and vegetation) also vary widely. Most studies of CWs receiving NPSP from agriculture report NO_3 removal efficiencies ranging from 30% to as high as 99% (Table 3). Similar studies of NO_3 removal in cold environments, which also tend to have short HRTs, range from being a NO_3 source to up to 15% removal (Table 3; Bastviken *et al.*, 2009; Braskerud, 2002b; Koskiaho *et al.*, 2003). Studies have demonstrated that NO_3 removal responds to N pulses (Phipps and Crumpton, 1994; Poe *et al.*, 2003). This response to N pulses was induced after episodes of little or no nitrate influx suggesting that denitrification in these settings was N limited.

Nitrogen in NPSP is highly variable in agricultural settings. In CWs where contaminants are supplied by runoff from streams, seasonal patterns in total N load exist. High total nitrogen (TN) loading is often associated with high flows in spring and fall runoff. Low TN loads are observed during summer at low stream flow where N removal processes have more time to occur (Hill, 1996). Seasonal trends in N form also affect N removal rates. In a study of CWs in Illinois, Phipps and Crumpton (1994) found that N removal rates were high when nitrate was the dominant form of TN. These wetlands became sources of N in summer months when organic N was the dominant form of TN. In settings where CWs are supplied by tailwaters, the relationship with flow is less clear, and variability in TN and NO_3 is a result of the catchment size, variety of crops grown, timing of fertilization, and crop rotations (Brauer *et al.*, 2009).

In irrigated agriculture, where high runoff events are less frequent, a design that accommodates low to moderate flows is needed. Nitrate removal is greatest in settings where NO_3 makes up a majority of the TN load. In CWs receiving input water from agricultural streams, N removal efficiency was greatest (up to 93%) in seasons when NO_3 comprised most of the TN input load (Phipps and Crumpton, 1994). In contrast, N removal was low (8%) and some CWs were sources of N (-22% to -33%) during seasons where organic N comprised most of the TN load.

Table 3 Reported nitrate removal efficiencies relative to select wetland characteristics

Project	Location	HRT (d)	Area (ha)	Depth (m)	Input (mg l^{-1})	Rem. Eff. (%)	Notes
Hey *et al.* (1994)	Illinois	–	2–3.5	1–1.5	1.22	85.5–98	River water, agricultural watersheds; data from 1991, April–October
Mustafa *et al.* (1996)	Florida	–	49	–	1.69	26	River water; Total N only
Phipps and Crumpton (1994)	Illinois	–	1.9–2.4	0.6–0.7	–	78–95	Same site as Hey *et al.*, 1994. Data from 1991 season, April–November
Comin *et al.* (1997)	NE Spain	–	–	0.1–0.5	–	50–98	Rice field runoff over growing season
Hunt *et al.* (1999)	North Carolina	1–111	3.3	0.3–2	6.6	51	In-stream wetland; removal was a load reduction
Larson *et al.* (2000)	Illinois	–	0.60–0.78	–	0.1–52	37–65	Vertical seepage study
Kovacic *et al.* (2000)	Illinois	11–21	0.3–0.8	0.4–0.9	–	34–44	Spring flow, tile drainage; Removal was lowest in lowest HRT
Woltemade (2000)	Midwest	–	0.03–3.7	–	–	20–80	Comparison of case studies
Borin *et al.* (2001)	NE, Italy	–	0.32	–	–	1	Crop runoff with waste water applied
Braskerud (2002b)	Norway	–	0.035–0.09	0.2–0.8	0.75–2.8	−1 to 9	In-stream wetlands, agricultural watersheds
Koskiaho *et al.* (2003)	Finland	0.25–1.6	0.48–0.6	0.9–2	2.4–7.9	0–36	Removal increased with increase in HRT, no removal at HRT of 0.25 day
Jordan *et al.* (2003)	Maryland	12–19	1.3	>1	0–2	52	Year-round storm runoff from agriculture

Tanner *et al.* (2005)	New Zealand	1.5–51	0.026	0.3	11	11–46	Seasonal mass removal rates from dairy pasture runoff
Kovacic *et al.* (2006)	Illinois	7–12	0.16–0.4	0.4–0.5	1.5–8.9	16–43	Tile drain input water
Moreno *et al.* (2007)	NE Spain	1–4	0.005–0.05	0.1	5.8–20.7	24–43[a]	–
Mustafa *et al.* (2009)	Ireland	–	0.12–0.24	1–1.5	3.81	74	Dairy farm effluent; very little outflow
Bastviken *et al.* (2009)	Sweeden	1–3	0.002	0.4	–	3–15	Compared emergent versus submersed vegetation types
Beutel *et al.* (2009)	Washington	8	0.7–0.8	0.6	1.3–1.4	90–93	Runoff during growing season 10–22 °C
Moreno *et al.* (2010)	NE Spain	2–15	0.005–0.5	0.1	–	34–87	Received runoff during growing season. Compared size and HRT

HRT, hydraulic residence time.

[a] Removal was calculated from total N.

For CWs receiving storm runoff from agricultural fields, the wetland to watershed area is an important consideration. Generally speaking, N removal is highest in larger wetlands (>0.5 ha) where HRTs are around one day or more (Table 3). Most studies agree that N removal efficiencies increase as hydraulic loading rate decreases and HRT increases (Jordan *et al.*, 2003). Some of the highest removal rates reported in the literature for CWs receiving agricultural NPSP are $\geq 90\%$. These sites have in common warm temperatures during runoff, large area, and HRTs ≥ 1 day (Table 3; Beutel *et al.*, 2009; Borin and Tocchetto, 2007; Comin *et al.*, 1997; Hey *et al.*, 1994; Moreno *et al.*, 2007, 2010; Phipps and Crumpton, 1994). Nitrogen removal is lowest in cold climates and/or where wetland area is small relative to its contributing area (Table 3; Bastviken *et al.*, 2009; Braskerud, 2002b; Koskiaho *et al.*, 2003; Mustafa *et al.*, 2009). In such settings, longer water retention times are needed (Kadlec, 2005). The wide range in removal efficiencies observed among CWs in similar environments may also be a result of variability in input flow (Carleton *et al.*, 2001; Jordan *et al.*, 2003).

5. PHOSPHORUS (P)

5.1. Environmental impacts

In many agricultural systems, nutrient management strategies maximize nitrogen availability and uptake, often resulting in phosphorus (P) application rates that exceed crop requirements (Whalen and Chang, 2001). As a result, many agricultural areas have experienced a buildup of soil P above that required for plant growth, with reported excess application rates of 1–9 kg P ha^{-1} yr^{-1} in the United States (Slaton *et al.*, 2004) and 20 kg P ha^{-1} yr^{-1} in Europe (Edwards and Withers, 1998). Phosphorus is relatively immobile in most soils, and generally remains close to the point of application. Consequently, decades of fertilization have resulted in high soil P concentrations, which can be transported from fields primarily as erosion during storm and irrigation events. The discharge of agricultural runoff into surface water bodies has resulted in dramatic shifts in trophic relationships (Jeppesen *et al.*, 2000), resulting in part from elevated P concentrations due to its limiting status in many freshwater ecosystems.

CWs have become a popular management practice to remove P from agricultural runoff (Jordan *et al.*, 2003; Raisin and Mitchel, 1995; Reinelt and Horner, 1995). However, due to the conservative nature of P in wetlands (i.e., no significant gaseous loss pathway), sustainable long-term P removal has proven to be particularly challenging given that wetland soils provide the only long-term P sink (DeBusk and DeBusk, 2000, DeBusk *et al.*, 2005). Although there has been a tremendous amount of work conducted on the fate of P in freshwater aquatic systems (Reddy *et al.*, 1999; Sharpley, 1999), there is much less known with regards to the mechanisms of P retention in CWs receiving agricultural runoff.

5.2. Phosphorus forms in CWs

In agricultural watersheds, phosphorus entering wetlands is typically present in both organic and inorganic forms that are either dissolved (<0.45 μm) or particulate (>0.45 μm). In most agricultural soils, 50–75% of P is inorganic, with 60–90% of P transported from cultivated fields in the particulate form (Sharpley, 1999). While dissolved inorganic P (DIP) is, for the most part, immediately available for biological uptake, particulate forms of P (PP) must first be transformed before biological utilization can occur. The extent to which the PP fraction becomes bioavailable is dependent upon a range of chemical, physical, and biological processes (Uusitalo and Elknom, 2003), and thus, PP represents a variable but long-term source of P for aquatic biota.

Different fractions of inorganic PP and the relative bioavailability of each fraction are operationally defined based on a chemical extraction scheme, typically consisting of four sequential extractions of increasing recalcitrance (Cooke, 1992; Hieltjes and Lijklema, 1980; Psenner *et al.*, 1988; Reddy *et al.*, 1998). These fractions include: (i) exchangeable P, (ii) Fe and Al bound P, (iii) Ca and Mg bound P, and (iv) residual P. The bioavailable fraction of PP (i.e., exchangeable P) has been reported to range between 5% and 30% for agricultural runoff (DePinto *et al.*, 1981; Dorich *et al.*, 1985; Maynard *et al.*, 2009; Uusitalo *et al.*, 2000) and 15–32% in CWs (Maynard *et al.*, 2009).

In general, wetlands possess conditions conducive for PP transformations to occur including: shallow water depths, short settling times for suspended sediment, anaerobic soils, and fluctuating hydroperiods. Wetlands have been shown to be effective sinks of PP through the retention of sediment and particulate organic material (Braskerud, 2002a; Johnston, 1991; Richardson, 1999), however, deposition of PP may result in its transformation to soluble forms via E_h/pH driven reactions (e.g., iron oxide dissolution) and kinetic processes (e.g., desorption and organic P mineralization) (James *et al.*, 2002). When accounting for these potential transformations, the fraction of PP that is potentially bioavailable has been reported to range from 50% to 70% of PP (Dorich *et al.*, 1985; James *et al.*, 2002; Maynard *et al.*, 2008; Pionke and Kunishi, 1992). Additionally, wetlands are known for their ability to transform inorganic P into organic forms (e.g., plant and microbial assimilation), thus minimizing the immediate impact of P inflows (Brix, 1997; Gächter and Meyer, 1993). Biogeochemical cycling of P in wetlands is complex; therefore, to better assess the efficacy of CWs to attenuate P loads, it is critical to evaluate the mechanisms by which these systems transform and remove different forms of P, with particular emphasis on the bioavailable fractions.

5.3. P transformations

Phosphorus retention in CWs is controlled by a range of physical, chemical, and biological processes, including sedimentation, filtration, chemical sorption and precipitation, redox processes, microbial interactions, and uptake by vegetation (Reddy and DeLaune, 2008). The three dominant retention mechanisms include: storage in biomass (biological), sorption to soil (chemical), and formation and accretion of new mineral and organic soils (physical) (Fig. 4; Kadlec, 1997; Reddy and DeLaune, 2008).

Phosphorus that enters the wetland water column is quickly taken up by bacteria, periphyton, and aquatic plants. However, studies using P radioisotopes have shown that wetland biota provide a small and typically short-term sink for P, while wetland soils serve as larger long-term sinks (Davis, 1982; Richardson and Marshall, 1986). In one study it was found that of the total ^{32}P added to the Everglades water column, macrophytes contained less than 10%, periphyton around 20%, and soils around 60% of P added (Davis, 1982). In a Michigan mesocosm study, 80–90% of added P was located in the soil compartment after 1–2 weeks (Richardson and Marshall, 1986). When wetland plants and microbes decompose, most of the P contained in cellular materials is mineralized and made available for further cycling, while a smaller fraction is stored within refractory organic compounds that contribute to the accretion of new soil (Fig. 4).

The chemical processes of adsorption to particles and settling is considered one of the most important long-term P sequestration mechanisms (Reddy *et al.*, 1995; Richardson, 1985), although rates of P removal by this process can vary significantly due to differences in biogeochemical conditions. Wetland systems with the highest P adsorption capacity are typically neutral to acidic mineral soils with high levels of Fe and Al (hydr)oxides (Richardson, 1985; Sah and Mikkelsen, 1986) or alkaline mineral soils with high concentrations of Ca (Litaor *et al.*, 2003). Iron and aluminum (hydr)oxides occur in soils as mixtures ranging widely in their degree of crystallinity, particle size, surface area, and reactivity (Jones and Bowser, 1978; Schwertmann, 1988). It is widely recognized that poorly crystalline oxides exhibit higher P sorption capacity compared with more crystalline phases, due to their larger surface area per unit volume (Parfitt, 1989; Parfitt and Childs, 1988).

The P sorption capacity of wetland soils is strongly influenced by redox processes involving iron and its potential interaction with sulfur. Phosphorus solubility in wetland soils is directly affected by changes in redox potential (Patrick, 1964). At low E_h values (i.e., 100 to -250 mV) P solubility increases resulting in high P concentration in soil pore water (Ann *et al.*, 2000). The dominant processes controlling phosphorus solubility in anaerobic systems are thought to be the reduction and dissolution of iron and its reprecipitation as ferrous minerals (Reddy and DeLaune, 2008). In many wetland systems, the

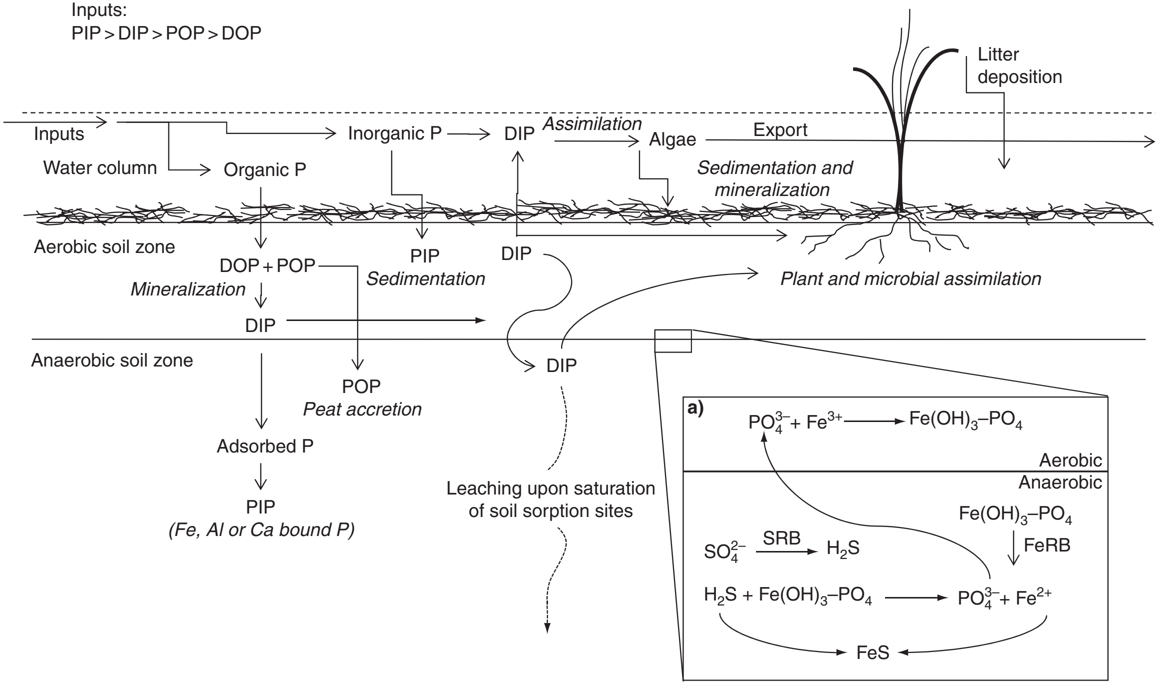

Figure 4 Schematic of phosphorus cycle in constructed wetlands. Phosphorus fractions include particulate inorganic P (PIP), dissolved inorganic P (DIP), particulate organic P (POP), and dissolved organic P (DOP). Magnified insert (A) shows the effects of sulfate reduction on iron–phosphate complexes. SRB, sulfate-reducing bacteria; FeRB, Fe(III)-reducing bacteria; $Fe(OH)_3$, amorphous Fe(III) oxide. $Fe(OH)_3–PO_4$ complexes can be reduced biotically via FeRB or abiotically via H_2S.

presence of a thin oxidized layer at the soil–water column interface is important in regulating P flux between the soil and water column (Chambers and Odum, 1990; Scudlark and Church, 1989). The reduction and dissolution of crystalline Fe and its reformation as poorly crystalline Fe within this oxidized layer provides an important trap for P due to its high P sorption properties (Fig. 4; Chambers and Odum, 1990; Patrick and Henderson, 1981; Richardson, 1985; Scudlark and Church, 1989).

In many agricultural areas, the leaching of SO_4 from fields has been linked to eutrophication in freshwater wetlands due to its effect on P mobility (Bostrom *et al.*, 1982; Caraco *et al.*, 1989; Lamers *et al.*, 1998; Lucassen *et al.*, 2004). In CWs, sulfide produced during sulfate reduction reacts rapidly with dissolved Fe(II) in pore water or Fe(II) sorbed to mineral surfaces (Bostrom *et al.*, 1982; Heijs *et al.*, 1999; Moore and Reddy, 1994; Patrick and Kahlid, 1974; Roden and Edmonds, 1997; Rozan *et al.*, 2002). As dissolved iron availability decreases, sulfide reacts with organic- and mineral-bound iron complexes. This can result in the release of P associated with redox-sensitive iron pools and organo-mineral complexes (Fig. 4; Kleeberg and Dudel, 1997; Lamers *et al.*, 1998; Roden and Edmonds, 1997; Rozan *et al.*, 2002).

The removal of bioavailable P fractions (e.g., DIP and labile PP) via sorption processes is an important mechanism for limiting eutrophication of surface waters. However, the P sorption capacity of wetlands receiving continued exposure to elevated P inputs has been shown to diminish as sorption sites become saturated (Richardson, 1985). For example, high initial rates of P removal were reported in 10 freshwater wetlands in Maryland, followed by large exports of P after a few years, thus suggesting a potential limitation of wetlands to remove P over the long term in watersheds receiving high P loads (Richardson, 1985). In systems that experience high sedimentation rates, however, the influx of new surface material with new sorption sites may prevent P saturation (i.e., saturation of P adsorption sites) in CW soils (Maynard *et al.*, 2009).

The accumulation of new soil, via deposition of exogenous mineral and organic sediments and endogenous organic matter, is the dominant process responsible for sustained long-term P retention (Richardson, 1999), and has been shown to operate over a wide range of climatic and geographic conditions (Craft and Richardson, 1993; Faulkner and Richardson, 1989; Mitsch, 1992). Annual P accumulation rates for selected wetlands with both mineral and organic soils were summarized by Johnston (1991), wherein wetlands with mineral soils accumulated 0.1–8.2 g P m^{-2} yr^{-1} (average = 1.46 g m^{-2} yr^{-1}), compared to 0.04–1.1 g P m^{-2} yr^{-1} (average = 0.26 g m^{-2} yr^{-1}) in wetlands with organic soils. Although the accumulation of P associated with organic and inorganic matter is a relatively slow process, it represents a major sink for P in CWs. Consequently, it is important to understand the composition and stability of newly accreted materials to determine the long-term efficacy of P retention in wetland systems (Reddy and DeLaune, 2008). Additionally, the microenvironmental factors at the soil–water column interface (e.g., redox potential, availability of electron acceptors, pH) and the chemical composition of both water and soil (e.g., iron, aluminum, calcium, and sulfur content) dictate how effectively P associated with settling particles is retained in wetland soils (Richardson, 1999).

5.4. Removal efficiencies of P fractions

There have been numerous studies evaluating the potential of wetlands to retain P, however, the majority of these have examined systems that receive regulated flows from municipal or other waste water sources. Additionally, most studies have focused on inflow and outflow characteristics of water, with very limited information on the internal processes regulating P cycling and retention. Although CWs are capable of removing large quantities of P from inflowing water, the concentration of P in outflow water is dependent upon the mass P loading. Using the North American Wetland Database, Richardson and Qian (1999) developed a statistical model that established a threshold mass P loading value of 1 g m^{-2} yr^{-1} for optimum P removal efficiency with minimal ecosystem change. Additionally, Debusk *et al.* (2005) conducted a review of wetlands from around the world that were used for removing P from agricultural runoff. They concluded that low outflow P concentrations (15–20 $\mu g\, l^{-1}$) were only attainable at low mass P loading rates ($<$1–2 g m^{-2} yr^{-1}). However, reported mass P loads for CWs treating agricultural runoff vary widely, ranging from 1 to over 100 g m^{-2} yr^{-1} (Debusk *et al.*, 2005). Thus, meeting low targeted outflow P concentrations is challenging given the high wetland area requirements per unit mass of P removed.

Newly constructed wetlands are thought to be more effective at removing P than older wetlands due to rapid vegetation growth and associated P uptake, and high availability of P sorption sites (Debusk *et al.*, 2005). In general, an increase in mass P loading will result in an increase in outflow P concentrations, while a decrease in mass P loading will tend to decrease outflow P. However, in older wetlands that experience variable P loading conditions, load reductions do not always result in a decrease in outflow P concentration (Debusk *et al.*, 2005; Jordan *et al.*, 2003). This is due to the release of existing P retained in the soil, also termed "phosphorus memory" or "phosphorus buffering," during periods of low P loading (Reddy and DeLaune, 2008). This was demonstrated in a restored wetland in Maryland, where in the first year of the study 59% of TP was retained, while in the second year there was no significant net removal (Jordan *et al.*, 2003). This was attributed to a decrease in inflow TP concentration in the second year resulting in a release of P stored in wetland sediment.

5.5. Wetland management strategies to improve P removal

Some of the key design parameters effecting wetland P removal include: water flow velocity, water depth, hydraulic retention time, length-to-width ratio, vegetation type and cover, and soil physiochemical properties (Reddy and DeLaune, 2008). Since the dominant form of P transported in agricultural runoff is PP, the design and management of wetlands to maximize retention of suspended sediment is essential in effectively removing P. Wetland vegetation increases sedimentation and trapping of PP by slowing water velocities, providing a substrate for particles to adhere to, and preventing resuspension (Braskerud, 2001). Additionally, designing CWs with optimal length-to-width ratios or flowpaths can dramatically increase hydraulic retention times (Persson *et al.*, 1999).

In addition to initial wetland design features, a number of management techniques have been evaluated for improving long-term P removal performance by CWs, including routine vegetation harvesting, removal of accumulated sediment, and chemical immobilization of P in sediment using amendments (Debusk *et al.*, 2005). While microbial and plant uptake are generally considered short-term transient P pools (De Groot and Fabre, 1993; Richardson and Marshall, 1986), the harvesting of plant biomass may lead to the removal of considerable amounts of P, ranging from 4 to 15 kg P ha^{-1} yr^{-1} (Hoffman *et al.*, 2006; Richardson and Marshall, 1986). Additionally, the removal of accumulated sediment was shown to be effective in reducing P concentration in the overlying water column in a Florida wetland (Debusk *et al.*, 2005). In this study, sediment removal decreased water column P concentrations from 130 $\mu g\ l^{-1}$ before removal, to 62 $\mu g\ l^{-1}$ after sediment removal. However, sediment removal from several shallow lakes was shown to be less successful in reducing TP concentrations (Moss *et al.*, 1996; Ruley and Rusch, 2002). Inorganic chemical amendments, typically alum (aluminum sulfate) and $FeCl_3$ (ferric chloride), have been used effectively to reduce excess dissolved phosphorus from the wetland water column and soil pore water (Reddy and DeLaune, 2008). While these management practices have been shown to work in pilot-scale systems, their technical and economic feasibility for full-scale use remains to be demonstrated.

6. DISSOLVED ORGANIC MATTER

The fate and transport of DOM through wetlands is of great concern due its importance in a multitude of biogeochemical reactions. DOM can be an important component of the microbial food web (Findlay and Sinsabaugh, 2003) and contribute to BOD and hypoxia (Volkmar and

Dahlgren, 2006). Complexation of metals by DOM can contribute to transport and ecological availability of metals (Hirose, 2007) and to enhanced rates of toxic methyl-mercury production (Ravichandran, 2004). Similarly, due to the hydrophobic nature of DOM, it may adsorb pesticides and facilitate their transport (Muller *et al.*, 2007). DOM is of particular concern in waters used as a source of drinking water because it is a precursor for disinfection byproducts (DBPs), such as trihalomethanes, haloacetic acids, and haloacetonitriles (Chow *et al.*, 2005; Richardson *et al.*, 2003; Xie, 2004). Some of these DBPs are suspected to be mutagens, carcinogens, or developmental toxicants if ingested over extended periods of time (Ahmed *et al.*, 2005; Muellner *et al.*, 2007; Villanueva *et al.*, 2004).

Among the different sources of DOM within watersheds, wetlands are recognized as one of the most important, contributing a disproportionate amount of DOM relative to their land surface area (Mladenov *et al.*, 2007; Rostad *et al.*, 2000). Wetlands are highly productive and tend to increase DOM concentrations and change its chemical characteristics through internal processing and loading (Pinney *et al.*, 2000). As a result, some studies have found a positive correlation between downstream DOM concentration, expressed by DOC, and the extent of wetland area (Chow *et al.*, 2007; Daley, 2002; Gergel *et al.*, 1999). In any case, wetland performance with respect to DOM dynamics will depend on several wetland design and management factors, such as hydraulic and pollutant loading rate, HRT, vegetation characteristics, nature of sediment, and input water characteristics.

6.1. DOM sources

A major source of DOM in wetlands receiving agricultural runoff is the import of DOM from surrounding croplands (Maynard, 2009). The DOM can consist of readily solubilized materials leaching from plant residues or DOM released from humic substances. These contrasting sources would be expected to have strongly contrasting chemical properties and persistence in the environment. In a study of six wetlands receiving waters from agricultural runoff (primarily irrigation tailwaters) in the Central Valley of California, DOC concentrations in input waters ranged from 1.3 to 12.5 mg l^{-1} (Diaz *et al.*, 2008, 2009). Input waters to wetlands in the Sacramento Valley had significantly higher DOC concentrations (mean = 6.9 mg l^{-1}) compared to those in the San Joaquin Valley (mean = 3.8 mg l^{-1}). DOC concentrations in agricultural drainage waters entering wetlands in the Midwestern USA (surface and tile drain sources) ranged from 2.1 to 3.6 mg l^{-1} in Illinois (Kovacic *et al.*, 2000, 2006) to 18.0 mg l^{-1} in Iowa (Davis *et al.*, 1981). These differences may be attributable to several factors including cropping patterns, tillage and irrigation practices, type of runoff (tile drainage vs. surface runoff) and contrasting soil types and drainage water properties (e.g., ionic strength, pH) (Chow *et al.*, 2006). Thus, DOM inputs appear to be highly variable in time and space.

Within wetlands, DOM can be leached from plants and soils with DOM leaching resulting from a combination of abiotic solubility of plant/sediment organic carbon compounds and microbial degradation of plant residues (Mladenov *et al.*, 2007; Pinney *et al.*, 2000). Therefore, wetlands accumulating high levels of plant biomass and detrital materials in their soils will have a greater potential for internal generation of DOM. Since DOM solubility is a function of water chemistry, factors such as pH, specific conductivity, and divalent versus monovalent cation concentration can strongly affect DOM solubility (Chow *et al.*, 2006). In addition, longer HRTs should result in more DOM leaching due to the longer period for leaching to occur. Wetting and drying cycles have also been shown to enhance DOM production from organic-rich soils (Chow *et al.*, 2006). Reductive dissolution of iron oxides may further contribute to DOM release due to the strong sorption of DOM by iron (hydr)oxides (Reddy and DeLaune, 2008). DOM in wetlands is also subject to concentration by evaporation and dilution due to rainfall events. These factors will largely be determined by the combination of climate (rainfall vs. evapotranspiration), vegetation, and hydrologic characteristics (e.g., HRT). In wetlands having an appreciable infiltration capacity, DOM may be removed from wetland water during subsurface transport. This will result in a decrease in the DOM load leaving the wetland due to the loss of water flux; however, it will not affect the DOM concentration in output waters.

6.2. DOM sinks

Within the wetland environment, DOM can be removed or chemically altered by microbial and photochemical degradation (Engelhaupt *et al.*, 2003; Obernosterer and Benner, 2004; Vahatalo and Wetzel, 2004). Laboratory incubation studies of agricultural drainage waters and wetland waters from the Central Valley, CA, indicate low microbial degradation ranging from less than detection to 8% during 10–14 day incubation periods (Diaz *et al.*, 2008; Engelage *et al.*, 2009). These same studies indicated small changes in the aromatic content of the DOM (as measured by specific ultraviolet absorption at 254 nm) during incubation, which ranged from an increase of 5% to a decrease of 11%. The high molecular weight DOC, which usually comprises the chromophoric DOC fraction, is relatively recalcitrant to bacterial utilization (Engelhaupt *et al.*, 2003; Vahatalo and Wetzel, 2004). Thus, UVA did not significantly change, even though some organic carbon may be utilized by the microorganisms. These studies suggest that the DOM of input and wetland waters is relatively refractory with respect to DOM degradation and alteration by microbial processing.

Photochemical degradation by solar radiation may oxidize DOM to CO_2 or breakdown large molecules into lower molecular weight compounds. Short-term (6–14 days) sun exposure of wetland waters has been shown to decrease UVA by 25–47%, while having a lesser effect on DOM concentration (Diaz *et al.*, 2008; Waiser and Robarts, 2004). These results are consistent with previous studies that showed solar radiation was more effective at converting aromatic carbon into CO_2 and lower molecular weight organic compounds than microbial mineralization (Obernosterer and Benner, 2004; Vahatalo *et al.*, 1999). Other studies suggest that photochemical degradation is the most important mechanism for loss of terrestrially derived humic DOM, while microbial degradation is most important for nonhumic (e.g., algal biomass and plant leachates) and microbially derived, soil humic DOM (Amado *et al.*, 2006; Miller *et al.*, 2009). The effectiveness of photochemical degradation will strongly depend on attenuation of solar radiation by the vegetation canopy and turbidity within the water column. Thus, photochemical degradation would be expected to be highest in open water wetlands having low water column turbidity and long hydrologic residence times.

Sorption of DOM to sediments may result in the loss of DOM from the water column. It is common for a subsurface layer (1–2 cm depth) of poorly crystalline Fe (hydr)oxides to form at the interface between the anoxic and oxic sediments (Reddy and DeLaune, 2008). These poorly crystalline Fe (hydr)oxides have a high surface area and high affinity for DOM sorption.

6.3. DOM input–output budgets from agricultural wetlands

Studies examining wetland DOM/DOC dynamics in a variety of agricultural settings have shown variable results. Illinois wetlands receiving surface and tile drainage showed overall DOC mass retention of 2% (3-year period) (Kovacic *et al.*, 2000) and 9% (21-month period) (Kovacic *et al.*, 2006). In the former study, overall retention was positive in fall, winter, and summer, but negative during the spring (Kovacic *et al.*, 2000). These results contrast with those for an Iowa prairie pothole wetland receiving surface and subsurface drainage from maize/soybean agriculture in which DOC outputs exceeded inputs by 71% (Davis *et al.*, 1981). The large DOC production in the pothole wetland was attributed to very high biomass production as well as pulse flows following a period of drought.

Input–output studies of wetlands in the Central Valley of California indicate a range from net retention to net production of DOC as a result of wetland processing (Diaz *et al.*, 2008, 2009; Maynard, 2009). There was a small reduction (~ 12%) of DOC load between inflow (6437 kg) and outflow (5642 kg) of a sparsely vegetated wetland receiving irrigation tailwaters during the irrigation season (Maynard, 2009). Most studies of DOC dynamics in California agricultural wetlands have examined input and output concentrations rather than loads. Agricultural wetland drainage in California typically has DOC concentrations more than two times higher than agricultural drains and rivers suggesting that some CWs are an appreciable source of DOC (Engelage *et al.*, 2009). Studies by Diaz *et al.* (2008, 2009) have demonstrated that HRT and vegetation density were important factors regulating DOC concentrations. CWs with short HRTs (<2 days) did not produce significant changes in DOC concentration with respect to the irrigation return flow input to CWs. In contrast, CWs with long HRTs (>10 days) increased DOC concentrations by an average factor of 2.4. The increase in DOC was largely attributable to evapoconcentration ($\sim$80% on average) as the electrical conductivity increased by an average factor of 2.0. The remaining DOC concentration increase ($\sim$20% on average) is presumably due to leaching from plants, algae, bacteria, and soil organic materials within the wetlands. Longer HRTs should also allow for higher DOC leaching from organic materials due to the longer contact time between the water and organic materials. In a comparison of four wetlands with contrasting HRTs, DOC concentration consistently increased with increasing HRT with average DOC increases of 0.03, 0.8, 5.2, and 8.8 mg l^{-1} for wetlands with HRTs of 0.9, 1.6, 11.6, and 15–20 days, respectively (Diaz *et al.*, 2009). Importantly, the DOC increase due to evapoconcentration will not impact the DOC load discharged into the rivers as the volume of water will be reduced by a proportional amount. In contrast, the DOC increase related to leaching of organic materials will increase the DOC load to the river. Thus, the higher DOC concentrations found in wetland drainage by Engelage *et al.* (2009), which was a very large CW, may result from evapoconcentration of DOC and may therefore have little effect on DOC load.

CW treatment did not appreciably affect DOC quality (e.g., aromaticity) as assessed by specific ultraviolet absorbance (Diaz *et al.*, 2008, 2009; Engelage *et al.*, 2009). DBP formation potentials were increased in output waters relative to input waters due to the higher DOC concentrations, but the propensity of a given carbon atom to form DBPs was not changed by wetland treatment. The speciation of trihalomethanes in output waters was similar to the input waters (Diaz *et al.*, 2008).

Microcosm studies (14 day incubations) examining microbial degradation (*Escherichia coli* spiked) and photodegradation (natural sun exposure) of wetland waters from the Central Valley of California did not detect significant changes in DOC concentration due to treatment (Diaz *et al.*, 2008). However, there was more than a 25% decrease in UVA_{254} after exposure to sunlight, whereas there was no significant change following the microbial degradation treatment. In terms of trihalomethane formation potential, solar radiation and microbial degradation reduced formation potentials by 24% and 10%, respectively. In contrast, biodegradation studies by Engelage and coworkers for California agricultural wetland drainage waters demonstrated an 8% decrease in DOC and 5% increase in aromatic carbon (as measured by $SUVA_{254}$), but no change in the propensity of DOC to form trihalomethanes in wetland drainage. This suggests that the fraction of DOC most resistant to biodegradation is also the most significant contributor to trihalomethane production in wetland drainage. Based on these studies, we conclude that photodegradation and microbial degradation have variable effects on DBP formation potentials in wetland waters and factors, such as DOM source, HRT, vegetation shading, water temperature, nutrients, etc., will greatly affect the magnitude of their effects.

7. TRACE METALS

Trace metals are naturally occurring and are found at low levels in soil and water. They are typically defined as elements required for life, but can be toxic at elevated concentrations. The United States Environmental Protection Agency (U.S. EPA) has included 13 trace metals on their priority pollutants list. From this list, 10 of them are of concern for agricultural runoff As, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, and Zn; the other three on the list are Ag, Sb, and Tl. The term trace metal is often interchanged with micronutrients, microelements, and heavy metals; although not all trace metals are heavy metals. The terms will be used interchangeably in this review.

The principle factor distinguishing heavy metals from other potential agricultural contaminants, such as nitrogen, phosphorus, pesticides, and pathogens, is the fact they are much less mobile and do not degrade. Annual inputs of trace metals to soil are cumulative and concentrations can increase incrementally each year. The various collective inputs over long time periods should be considered when evaluating trace metals in soils and agricultural runoff. A study modeling the risk of trace element (As, Cd, Cu, Pb, Zn, Se) accumulation in Canadian soils accounting for various inputs (e.g., fertilizers, atmospheric deposition, manures, and biosolids) estimates that trace elements (with the exception of the volatile Se) will be up to threefold higher than present background levels in 100 years (Sheppard *et al.*, 2009). Elevation of trace metals in soils at this level would prove extremely detrimental to agricultural systems and environmental quality. This projection highlights the importance of understanding the mechanisms of trace metal accumulation and transport and should serve as a reminder for the need to develop management strategies to mitigate future trace element additions to soil. Moreover, trace metal buildup is likely to be amplified in CWs, which receive eroded soil from surrounding landscapes.

Due to the strong binding of most trace metals to soil constituents, and their limited transport, trace metals have long residence time in soils (Hesterberg, 1998) and concentrations can become elevated above background levels and threaten plant, animal, and environmental health. Although leaching of metals to groundwater is typically minimal, erosion of metal-rich soil particles via surface runoff can threaten surface water quality, contaminate river sediment, and lead to long-range transport of associated trace metals (He *et al.*, 2004; Quinton and Catt, 2007; Zhang *et al.*, 2003). The presence of elevated trace metal concentrations in soil and water is problematic as they bioaccumulate in the food chain and are resistant to degradation. Plants grown in contaminated soils can uptake metals which are then fed to livestock or directly consumed by humans.

7.1. Sources of trace metals to agricultural soils

Atmospheric deposition and the application of fertilizers, agrochemicals, sewage sludge, soil parent material, irrigation water, and soil amendments with low levels of trace metals can lead to accumulation of a wide range of trace metals in agricultural soils. Of the various inputs by which trace metals enter soils, fertilizers and sewage sludge are considered to be the greatest source for metals to enter agricultural systems (Adriano, 2001).

Phosphate rock (PR) used in the production of inorganic fertilizers is a major source of heavy metals. While the location where PR is mined contributes to its specific composition, heavy metals commonly found in PR include As, Cd, Cr, Pb, Hg, Mo, Ni, and V (Franklin *et al.*, 2005; Mortvedt, 1996; Nziguheba and Smolders, 2008). Of these metals, Cd concentrations are typically of the most concern as Cd is easily incorporated into plant biomass (Basta *et al.*, 2005; McLaughlin *et al.*, 1996) and is potentially the most harmful to human health (Mortvedt, 1996). Average concentrations of trace metals in phosphate fertilizers are given in Table 4. Model simulations examining the risk of As and Cd accumulation in soils from addition of chemical fertilizers reveal that As concentrations will not significantly increase; however, Cd levels could increase over time and pose a risk of transfer to the food chain (Chen *et al.*, 2007).

Historical use of pesticides and application of biosolids, including sewage sludge and animal manures, has increased trace metal content in agricultural soils. The levels of trace metals in sewage sludge are typically higher than animal manures and can vary greatly depending on the source and treatment

Table 4 Mean trace element concentrations (ppm) in various phosphate fertilizers (raw and N–P–K blends)

Phosphate fertilizer	As	Cd	Cr	Cu	Ni	Pb	V	Zn
USA[a] (Franklin *et al.*, 2005)	12.5	37.1	101	36.1	28.3	178	175	235
Europe[b] (Nziguheba and Smolders, 2008)	7.6	7.4	89.5	–	14.8	2.9	–	166

[a] $n = 16$.

[b] $n = 196$, Cu and V not measured.

method. Heavy metals of interest in sewage biosolids include As (1–230 mg kg^{-1}), Cd (1–3410 mg kg^{-1}), Cr (10–99,000 mg kg^{-1}), Cu (84–17,000 mg kg^{-1}), Pb (13–26,000 mg kg^{-1}), Hg (1–56 mg kg^{-1}), Mo (1–214 mg kg^{-1}), Ni (2–5300 mg kg^{-1}), Se (2–17 mg kg^{-1}), and Zn (101–49,000 mg kg^{-1}) (Chaney, 1983). Currently, the application of metal-containing pesticides is not common. Notable exceptions include the foliar application of Cu to prevent disease (e.g., viticulture and citrus industries) (Komárek *et al.*, 2010; Paradelo *et al.*, 2008).

7.2. Trace metal fate and transport in agricultural soils

The fate and toxicity of trace metals in soils is dictated by the chemical form in which they are present within soils. These general forms include water-soluble metals (i.e., free ions, inorganic or organic complexes), exchangeable metals, metals precipitated as inorganic compounds, metals complexed with humic materials, metals bound to hydrous oxides and layer silicate minerals, metals precipitated as insoluble sulfides, and metals bound within the structure of primary minerals (Gambrell, 1994). The two most important factors controlling trace metal speciation in soils, sediments, and wetlands are redox potential and pH (Basta *et al.*, 2005; Du Laing *et al.*, 2009; Gambrell, 1994; Olivie-Lauquet *et al.*, 2001; Schulz-Zunkel and Krueger, 2009). Typically, solubility of trace metals increases under reducing conditions or low pH. In a study examining influence of agricultural practices on trace-element distribution, redox conditions were shown to be the most important factor controlling the movement of Co (Cr, Ni, and Zn influenced to a lesser degree) within the soil profile, primarily due to the reductive dissolution of Fe- and Mn-oxides (Montagne *et al.*, 2007).

Salinity also plays an important role in trace metal transport (Du Laing *et al.*, 2009; Speelmans *et al.*, 2007). High salinity increases heavy metal mobility through complexation with Cl ions (Paalman *et al.*, 1994) and cation exchange (Tam and Wong, 1999). Additionally increasing salinity leads to greater bioavailability of heavy metals (Basta *et al.*, 2005; Speelmans *et al.*, 2007). This is particularly important for semiarid and arid regions, such as the San Joaquin Valley (California), where drainage water, the main water supply for CWs, is often saline and enriched in trace metals, including Se, As, Cu, Mo, and Zn (Herbel *et al.*, 1997). Of these trace metals, the high concentrations of Se have garnered the most attention due to its toxicity to fish and wildlife, most notably waterfowl (Gao *et al.*, 2007; Lemly, 1994; Lemly *et al.*, 1993).

7.3. Trace metals in saturated soils and wetlands

Seasonally submerged soils of CWs fluctuate between oxic and anoxic conditions. Under aerobic conditions, trace metals are typically sorbed or precipitated onto soil constituents including clay minerals, iron, aluminum, and manganese oxides, organic matter, phosphates, and carbonates. Soils saturated for prolonged periods result in reduction of trace metals and Fe- and Mn-oxides to which trace metals are bound (Du Laing *et al.*, 2009; Montagne *et al.*, 2007). Alternatively, the presence of strongly reducing conditions can result in sulfate reduction and heavy metal (e.g., Cd, Cu, Zn) coprecipitation with sulfide minerals facilitating retention in CW soils (Du Laing *et al.*, 2008; O'Sullivan *et al.*, 2004).

Wetland soils are generally characterized as having reducing conditions and high levels of organic matter; serving as a source of ligands to bind trace metals. These two conditions exert a large influence on chemical speciation and transport processes of trace metals in wetlands. Sedimentation is recognized as the primary process responsible for the removal of metals from the aqueous phase in natural and constructed wetlands (Sheoran and Sheoran, 2006). Sedimentation requires aggregation and sorption (including precipitation) to occur for metals to settle and become sequestered in soils. Trace metals readily bind to a wide range of clay minerals, metal (hydr)oxides, and organic matter fractions. Precipitation and sorption of trace metals in wetlands depend on the pH, redox potential, solubility product (K_{sp}) of the metal, trace metal concentration, ionic strength, and background electrolyte composition (Fox and Doner, 2003; O'Sullivan *et al.*, 2004; Sheoran and Sheoran, 2006). The redox status of wetlands can strongly influence the mobility of trace metals, although prediction of mobility is not always straight forward. While increased transport of many metal species is observed under reducing conditions (Du Laing *et al.*, 2009; Montagne *et al.*, 2007), there are cases where strongly reducing conditions lead to increased sediment retention of trace metals. For example, As, Mo, and V accumulation in sediment was highest under more reducing conditions and lowest under more oxidizing conditions (Fox and Doner, 2003). Under moderately reducing conditions both As and V can become mobilized, possibly due to a sequence of simultaneous processes including dissolution, desorption, precipitation, and adsorption. Upon drying of sediments, 73% of Mo became water soluble, having strong implications for the effect of drying wetlands on Mo mobility.

Sorption of trace metals to dissolved and solid-phase organic matter is an important mechanism for metal removal in wetlands, particularly for Cu, Ni, and U (Sobolewski, 1996). Ionizable functional groups within organic matter fractions, such as carboxyl and phenolic moieties, serve as sites for metal binding (Tipping and Hurley, 1992). Once bound to organic matter metals can be sequestered in aggregated forms or on mineral-bound organic matter; alternatively binding to soluble, low molecular weight organic matter can promote transport in the aqueous phase. The release of trace metals within wetlands occurs primarily via organic matter decomposition or microbially catalyzed reduction of Mn and Fe-oxides (Tarutis and Unz, 1995).

Microbial driven redox processes play an important role in the speciation of trace metals in soils and aquatic environments. A study examining the influence of wetland seasonal variability on trace element release revealed that the initiation of trace element release occurs simultaneously with increasing water temperature, a decline of redox potential, and increase in organic carbon content (Olivie-Lauquet *et al.*, 2001). The research hypothesized that Fe- and Mn-reducing soil microorganisms catalyze this change in redox potential and subsequent increase of DOC as microorganisms degrade trace-element-rich organic compounds. The increased DOC serves as a source of organic ligands for transport of trace elements (Olivie-Lauquet *et al.*, 2001). Another example of how microorganisms influence metal concentrations in wetlands is by examining the unique way in which sulfate-reducing bacteria (SRB) contribute to metal sequestration in wetlands. In anaerobic environments, SRB generate H_2S initiating the precipitation of metals from the aqueous phases as metal sulfides (Amacher *et al.*, 1993; Webb *et al.*, 1998).

While reduced aqueous concentrations of trace metals in wetlands is observed, due largely to binding to sediment and organic matter, removal of trace metals from wetlands requires an anthropogenic influence such as harvesting of metal accumulating wetland plants. The use of hyperaccumulating plants (e.g., *Typha latifolia*, *Phragmites australis*, *Glyceria fluitans*, *Eriophorum angustifolium*) has been demonstrated as an effective method for removing a range of metals (e.g., Cd, Cu, Pb, Zn, Hg, Se) from wetland ecosystems (Cheng *et al.*, 2002b; LeDuc and Terry, 2005; Liu *et al.*, 2007; Matthews *et al.*, 2005; Rai, 2009; Williams, 2002).

A number of strategies have been explored to manage CWs containing trace metals. The acidification of evaporation ponds has been proposed to discourage habitation by water fowl and other animals (Herbel *et al.*, 1996, 1997). Acidification of treatment ponds is effective on reducing concentrations of As, Mo, and Se with an increase in Fe and Mn concentrations; however, the high cost for initial acidification limits the implementation of this management strategy (Herbel *et al.*, 1996). Treatment options currently employed include a series of drainage ponds with algal–bacterial selenium removal (ABSR) (Quinn *et al.*, 2000), the use of flow-through wetlands to bind Se to sediment (Gao *et al.*, 2000, 2003a,b), and the use of wetland plants (e.g., *Eichornia crassipes*, *Typha angusfolia*, *Polypogon monspeliensis*) to phytoaccumulate Se (Rai, 2009; Thompson *et al.*, 2003).

Anaerobic bacteria in CW soils facilitate the conversion of inorganic mercury into methylmercury, which is a strong neurotoxin. The existence of low redox potentials and labile organic carbon are CW characteristics that support this transformation. Moreover, DOC is thought to play an important role in the mobility of mercury in wetlands. Hall *et al.* (2008) found that the aromatic reactive fraction of DOC was positively correlated with total mercury and methylmercury in wetland water samples.

Relatively low levels of inorganic mercury can bioaccumulate in tissues of organisms that reside in CWs, especially those at the top of the food chain (Ackerman *et al.*, 2010; Hall *et al.*, 2008). A study of invertebrates in wetlands and rice fields in California demonstrated that mercury bioaccumulation was greater in wetlands that were permanently saturated compared to seasonally saturated rice fields. Since mercury bioaccumulates through the food chain, translocation mechanisms within CWs and its biota are extremely complex and are exceedingly difficult to identify. CWs should be closely monitored if developed in regions with high background levels of mercury, such as those surrounding coal-fired energy plants, waste incineration facilities, and gold mining/extraction sites (Ackerman *et al.*, 2010; Hall *et al.*, 2008).

Trace metals in agriculture will likely become of increasing concern as concentrations continue to slowly increase, threatening food safety, water quality, and human health. To date the use of constructed wetlands for remediation of agricultural drainage water is not prevalent. However, engineered approaches, in conjunction with phytoremediation strategies, may be necessary to protect our agricultural soils, water supplies, and ensure increased production of crops for human and animal consumption.

8. PATHOGENS

Microbial pathogens are considered one of the leading causes of water-quality impairment in agricultural watersheds worldwide (Collins, 2004; Cooley *et al.*, 2007; Rosen, 2000; United Nations Environment Programme, 2004; Wilkes *et al.*, 2009). Microbial pathogens of particular concern for public health include protozoa such as *Cryptosporidium parvum* and *Giardia duodenalis*, as well as bacteria such as *Salmonella* and *E. coli* O157:H7. Watershed sources of these pathogens are diverse as they are shed in the feces of wildlife, humans, livestock, and pets (Simpson *et al.*, 2002). With improvements in wastewater treatment technologies in recent decades, nonpoint sources have become the primary source of microbial pathogens in waterways, with agricultural activities being the single largest contributor. In addition to drinking water and recreational body contact concerns, the use of surface waters for irrigation of fresh produce and vegetables leads to food safety concerns for pathogen contamination (e.g., *E. coli* O157:H7 on spinach) (Cooley *et al.*, 2007).

8.1. Pathogen removal

The use of constructed wetlands as a management practice to reduce microbial contaminant loads represents a potentially effective mechanism to economically treat agricultural runoff prior to discharge into waterways (Rosen, 2000). Retentions of 80–99% have been seen for pathogen indicators such as *E. coli* and fecal coliforms in surface flow CWs treating municipal and livestock wastewater (Gerba *et al.*, 1999; Hill, 2003; Quinonez-Diaz *et al.*, 2001). In contrast to the large literature base available for wastewater treatment wetlands, very few studies have addressed microbial pathogen treatment of agricultural runoff using wetlands (Kadlec and Knight, 1996). Given several differences between agricultural and wastewater treatment wetlands (e.g., pulsed-flow, pollutant loading levels, low hydrologic residence times), it is difficult to extrapolate the microbial pathogen retention efficiencies between these wetland types.

A range of physical, chemical, and biological removal mechanisms affect microbial pathogen fate during wetland treatment (Stottmeister *et al.*, 2003). Physical removal mechanisms include filtration, sedimentation, soil and biofilm adsorption, and aggregation. Biological elimination mechanisms include predation (protozoan and/or viral), bacteriophage activity, lytic bacteria, release of antibiotics by plants and other microbes, and natural death. Chemical elimination mechanisms include oxidative damage, UV irradiation, and toxins excreted by other bacteria and plants. Environmental factors such as pH, sunlight, temperature, vegetation type and density, and redox potential play a role in pathogen survival and elimination (Kristian Stevik *et al.*, 2004). The effectiveness of microbial pathogen removal is also coupled to the HRT with removal modeled by first-order kinetics (Vymazal, 2005).

Differences in performance observed within a given CW in time (diurnally, seasonally, or degree of maturation) or between wetlands (distinct in location) cannot be adequately understood without regard to their dynamic living components (Werker *et al.*, 2002). Since wetlands can take a number of years to achieve a fully developed vegetation community and root zone, the manner in which these systems are allowed to mature may be critical to their long-term performance. The presence of plants has been observed to exhibit highly variable effects on the removal of microbial contaminants in CWs with the type of vegetation often having a large impact on removal efficiency (Stottmeister *et al.*, 2003). Several studies have shown that plants provide for higher rates of pathogen removal when compared to unplanted beds (Decamp and Warren, 2000; Hatano *et al.*, 1993; Soto *et al.*, 1999). Wetland plants and their associated biofilm communities can enhance filtration, adsorption, and inactivation by competition with other microorganisms. In subsurface flow wetlands, the roots of plants are of particular importance and may enhance bacterial inactivation by increasing the variety of microorganisms present in the wetland environment and therefore creating more competition and bacterial reduction (Hench *et al.*, 2003; Werker *et al.*, 2002). In contrast, shading of the water column in surface flow wetlands can significantly reduce *E. coli* retention (MacIntyre *et al.*, 2006). Maximum removal of *E. coli* occurs under high solar radiation and high temperature (Boutilier *et al.*, 2009; Chapra, 1997; Crane and Moore, 1986; Whitman *et al.*, 2004; Zdragas *et al.*, 2002). Thus, shading by vegetation can greatly reduce UV radiation and maximum water temperatures leading to lower removal efficiencies. While vegetation may provide favorable attachment sites for *E. coli*, dense canopies can hinder free exchange of oxygen between the water column and the atmosphere. This vegetative-induced barrier limits dissolved oxygen levels and decreases predator zooplankton populations, which decreases microbial pathogen retention (MacIntyre *et al.*, 2006).

The reduction of *E. coli* by sedimentation is dependent on whether the bacteria are "free floating" or associated with particles (Boutilier *et al.*, 2009). Microbial contaminants associated with particles, especially dense inorganic particles, settle out of the water column faster than those in the free-floating form (Characklis *et al.*, 2005). Quinonez-Diaz *et al.* (2001) found a strong correlation between *Giardia* cyst removal and turbidity suggesting that cysts and turbidity (suspended sediments) were removed simultaneously in wetland systems, possibly due to cyst–particle association. Bacteria have also been shown to survive longer within sediments than within the water column (Howell *et al.*, 1996), and therefore, microbial partitioning between the sediment and water column will affect bacteria fate, transport, and inactivation (Characklis *et al.*, 2005). High water flow pulses into wetlands or channelization may result in resuspension and entrainment of sediment that could mobilize previously retained microbial pollutants during high flow events (Collins, 2004; Jamieson *et al.*, 2005; Wilkes *et al.*, 2009).

A negative collateral effect of constructed wetlands is that they often become an attractive wildlife habitat for possible disease vectors, such as birds, livestock, deer, pigs, rodents, etc. These animals can increase the presence of pathogens in the water by depositing their excreta within the wetland, thus replacing pathogens removed by wetland treatment (Collins, 2004; Cooley *et al.*, 2007).

8.2. Case study: Agricultural wetlands treatment of irrigation tailwaters

There are few studies addressing the fate of pathogens in CWs that focus on field runoff. Therefore, the following case study is presented to document the performance of wetlands treating tailwaters from flood and furrow irrigation from croplands in California to highlight microbial dynamics in agricultural wetland systems. Four constructed surface flow-through wetlands located in the San Joaquin Valley, California and discharging into the San Joaquin River were monitored for their effectiveness in removing *E. coli* from irrigation tailwaters. Characteristics of the wetlands including design, age, catchment area, vegetation coverage, and hydrologic residence time can be found in Diaz *et al.* (2009). The main crops in the study area were tomatoes, alfalfa, melons, nuts, and stone fruits. All wetlands were continuous flow-through wetlands with HRTs ranging from about 0.9 to 11.6 days. Due to the expense and technical challenges in the measurement of human pathogenic organisms, an indicator of pathogen removal, *E. coli*, was monitored (Dufour, 1977; World Health Organization, 2003).

Approximately 47% of water samples collected from irrigation return flows exceeded the *E. coli* standard of 126 cfu per 100 ml (range: 13–1400 cfu per 100 ml). In contrast, *E. coli* concentration in wetland outflows ranged from 0 to 300 cfu per 100 ml. Based on paired input–output concentrations in the four wetlands, mean *E. coli* concentrations were reduced from 69% to 95%. Removal efficiencies in terms of *E. coli* load were even higher, 98–99%, due to water losses (seepage and evapotranspiration) within the wetland. Following wetland treatment, 93% of wetland outflows met the California water-quality standard for *E. coli* (126 cfu per 100 ml). *E. coli* concentration was strongly correlated with total suspended solids, suggesting sedimentation of suspended sediments as a potential mechanism for *E. coli* removal. In spite of several differences among the four wetlands, HRT was a good predictor of *E. coli* removal efficiencies. Mean removal efficiency was 69%, 79%, 82%, and 95% for wetlands having mean HRTs of 0.9, 1.6, 2.5, and 11.6 days, respectively. The importance of HRT was explained by the fact that longer HRTs increase bacteria exposure to removal processes, such as sedimentation, adsorption, predation, impact of toxins from microorganisms or plants, and UV radiation (Stottmeister *et al.*, 2003).

Hourly sampling of *E. coli* concentrations in wetland inputs and outputs showed no consistent diel patterns. On an hourly time scale (during a 24 h period on three different days), *E. coli* fluctuation at the input sites varied from 120 to 792 cfu per 100 ml, while at the output locations ranged from 17 to 60 cfu per 100 ml. Results from this study indicate that passing irrigation tailwaters through wetlands can significantly reduce *E. coli* concentration and load. Of all the parameters considered, HRT appeared to be the factor having the greatest effect on the efficiency of *E. coli* removal. Remarkably, a HRT of less than a day can achieve considerable *E. coli* retention (~70%), which allows for relatively small wetland areas being able to treat runoff from large agricultural areas (up to 360 ha of contributing farmland runoff per 1 ha of wetland in this study).

9. OTHER WATER-QUALITY CONSTITUENTS

9.1. Salinity

Salinity is a common water-quality concern affecting freshwater resources, especially in the western United States. In many arid and semiarid regions, the combination of soil parent materials rich in salts, high evapotranspiration rates, and incomplete deep percolation has resulted in saline agricultural drainage waters. There are no wetland processes that can reduce salinity levels in CWs except blending of input waters with higher quality waters. In most CWs, salinity tends to increase through evapoconcentration if HRTs are long enough. For example, in California, electrical conductivity in output waters increased by a factor of 2 compared to input waters in CWs with residence times >10 days (Diaz *et al.*, 2008, 2009). The intolerance for salinity by most freshwater aquatic life and the need to preserve water quality for downstream users have resulted in the establishment of salinity Total Daily Maximum Loads (TMDL) in surface water bodies throughout the west and southwestern United States. In these settings, using CWs as BMPs to address nutrients and pesticides may be in conflict with established salinity TMDLs.

9.2. Biological oxygen demand

BOD is a water-quality parameter that can be a problem in agriculture discharge (Volkmar and Dahlgren, 2006). Substances such as DOM, algae, and ammonium consume dissolved oxygen through biogeochemical reactions. BOD is an important water-quality parameter because high BOD results in low dissolved oxygen in water, which can kill aquatic life or serve as a barrier for migrating fish. Wetlands have the potential to become either a sink or source of BOD. Studies of treatment wetlands have shown that these systems can reduce BOD; however, there are few studies that focus on CWs in agricultural settings, which tend to receive higher quality runoff compared to treatment wetlands (Stringfellow *et al.*, 2008; Sundaravadivel and Vigneswaran, 2001). While CWs have effectively decreased volatile suspended solids (i.e., organic matter) in output waters (O'Geen *et al.*, 2006) some wetlands receiving agricultural drainage have been identified as a source of BOD (Stringfellow *et al.*, 2008). The component of BOD from these wetlands was mainly organic carbon, with algae being a major contributor.

CWs have the potential to serve as bioreactors for algae when HRTs are long and nutrient levels are high, and can serve as a seed source for algae growth in downstream environments. Maynard (2009) observed a decrease in chlorophyll-*a* concentration (a bioindicator of algae) in CW output waters with a corresponding increase in emergent canopy of macrophytes. It was suggested that the reduction in algae production was caused by canopy interception of sunlight causing a light limitation in the water column. Conversely, wetlands with a large amount of vegetation and long residence times could be a source of organic carbon contributing to BOD. More research is needed to understand the origin of constituents contributing to BOD in wetlands, especially between organic carbon supplied by algae versus vegetation residue.

10. DESIGN AND MANAGEMENT

CWs can be designed for a variety of ecosystem services that contribute to biological habitat and diversity, hydrologic buffering, and water filtration. The placement of CWs for water-quality improvement of agricultural runoff involves many considerations including the nature of runoff (hydrologic loading, constituent loading, and temporal patterns), soil properties, location within a watershed, the amount of space available, and landscape and infrastructure constraints on its development. Ideally, CWs should be developed for multiple ecosystem services and their design should have input from many disciplines including engineers, biologists, ecologists, soil scientists, biogeochemists, and hydrologists. Design considerations for CWs should include: (1) low maintenance of biota, hydrology, and structures; (2) a hydrological infrastructure that utilizes the potential energy of source waters; (3) a system compatible with the surrounding landscape; and (4) a system with multiple environmental objectives (e.g., pollution control, biodiversity, flood prevention) (Mitsch, 1992).

10.1. Hydrology

Hydrology is the most important design parameter for successful removal of water-quality contaminants. The efficiency of treatment is largely controlled by the extent to which water is evenly distributed across the wetland area. CW treatment capacity is diminished by designs that result in stagnant zones, which reduce the effective treatment area, or short-circuit flowpaths that decrease water residence time (Kadlec, 2005). It is difficult to optimize hydrologic characteristics of CWs receiving agricultural runoff because flows are not continuous and they can originate from many sources, such as surface runoff, stream and river runoff, tile drainage, or irrigation return flows. Thus, consideration of the seasonality, velocity, volume, and duration of flow is important and will differ greatly among agricultural watersheds. Some key considerations largely instigated from the treatment wetland literature are hydroperiod, hydraulic loading rate, residence time, flowpath design and CW dimensions and morphology (Mitsch and Gosselink, 2000).

10.1.1. Hydroperiod

The temporal pattern of water depth and saturation describes wetland hydroperiod (Mitsch and Gosselink, 2000). Hydroperiod is governed by inflow, ouflow, and storage capacity and is one of the most important hydrologic design considerations because hydroperieod affects wetland surface area, vegetation, particle settling and resuspension, biodiversity, soil redox status, soil mineralogy, and ultimately, pollutant removal. CWs that receive water from irrigated agriculture often have stable hydroperiods during the growing season, but highly variable in the off season due to flooding or dry down. In contrast, CWs that receive water via surface runoff or tile drainage have hydroperiods dependent on rainfall distribution. Those that receive pumped water from adjacent streams or rivers may experience pulse events.

CWs with highly variable hydroperiods experience fluctuations in wetted surface area and depth, which facilitates a diversity of biological and biogeochemical conditions that optimize wetland function (Mitsch and Gosselink, 2000). Episodes of flooding and drying have been linked to improved nutrient removal efficiency. Fluctuating hydroperiod facilitates aerobic and anaerobic conditions and the coupling of nutrient removal processes such as nitrification with denitrification (Wijler and Delwiche, 1954) and poorly crystalline (hydr)oxide formation with P sorption (Busnardo *et al.*, 1992; Maynard *et al.*, 2008, 2009). For example, a comparison of a CW experiencing different hydroperiods over 2 years, one year being consistently wet and the consecutive year having a dry period showed that TN, TP, and organic carbon removal efficiencies were significantly higher when dry down occurred (Jordan *et al.*, 2003). An evaluation of mesocosms subjected to different hydroperiods showed that P removal efficiency was more responsive to fluctuating hydroperiods compared to N (Busnardo *et al.*, 1992).

Similar to hydroperiod, water depth affects plant habitat, light penetration, particle settling, and resuspension. Studies suggest that depth should range from 15 to 50 cm. If shallower, the wetland floor becomes more susceptible to sediment resuspension, channelization, and recruitment of less desirable plants (Braskerud, 2002a; Carty *et al.*, 2008). CWs commonly have deeper depths than the above (Table 3). Deeper depths discourage emergent macrophyte establishment (Kadlec, 2005). Although, localized areas of deeper water promote greater habitat diversity and cooler water temperatures (Knight, 1992).

10.1.2. Hydraulic residence time

HRT is widely recognized as an important design consideration for maximizing pollutant removal. Many wetland studies have identified HRT as one of the main factors affecting contaminant removal efficiency (Blahnik and Day, 2000; Greenway and Woolley, 1999; Jordan *et al.*, 2003; Knox *et al.*, 2008; Toet *et al.*, 2005). HRT can be estimated by dividing the wetland volume by the flow rate or tracer addition studies. Variability in agricultural runoff received by CWs makes it difficult to maintain constant HRT (Woltemade, 2000). Inefficient pollutant removal by CWs is often a result of short HRT due to high hydraulic loading rates or insufficient storage capacity. Since HRT is most often calculated using the wetland volume, values can be somewhat misleading because of wetland depth. For example, a small, deep wetland may have a HRT similar to a larger but shallow system. For most pollutants, removal efficiencies will be higher for shallower systems despite similar HRT because more wetland surface area is available, and more plant and microbial biomass is present. Thus, studies suggest that aerial loading rate is a more accurate design criterion. Designing large wetland areas is the best way to maintain long HRT in agricultural settings, where input flows may be highly variable. Alternatively, HRT can also be managed by decreasing input or output flow, but this process can be costly or impractical to implement. Overly long HRT can have adverse effects by increasing the export of DOC and associated DBPs or by increasing salinity via evapoconcentration effects in semiarid regions (Diaz *et al.*, 2008).

Most studies demonstrate that HRT of 2 days or more is necessary for significant nitrate removal (Beutel *et al.*, 2009; Hey *et al.*, 1994; Kovacic *et al.*, 2000, 2006; Moreno *et al.*, 2007; Phipps and Crumpton, 1994).

10.1.3. Hydrologic loading rate

Hydrologic loading rate, calculated by dividing the flow rate by the wetland surface area, is a way to size a CW relative to its input water flow. Treatment wetland literature suggests that hydrologic loading rates should be between 0.025 and 0.05 m day^{-1} (Mitsch and Gosselink, 2000). Hydrologic loading rate is difficult to design for in agricultural environments, which can receive highly variable inflows originating from expansive land areas. In most agricultural settings, loading rate is partly predetermined by the input flow rate, and therefore, design considerations should manipulate wetland area to optimize hydrologic loading rate. A general rule of thumb is that CWs size should be from 3% to 6% of its contributing watershed area although this depends on the climate and nature of runoff. If the wetland is too small, excessive loading rates will limit the HRT. If the CW is too big, the hydroperiod may be overly variable resulting in expansive dry regions. This guideline may be difficult to implement in irrigated areas, where flows can vary from year to year as a result of crop rotations, changes in technology, and availability of irrigation water.

If surface runoff is the main water supply, hydrologic loading rate can be estimated by watershed modeling with knowledge of the drainage area, climate, and the runoff curve number (Millhollon *et al.*, 2009; USDA-NRCS, 2008). Hydrologic loading rate can also be managed if input waters are pumped into the CW. Braskerud (2002b) reported low removal rates ($<15\%$) in CWs with hydraulic loads ranging from 0.7 to 1.8 m day^{-1}. It was reported that a 2-day residence time was necessary for significant annual N removal in CWs with hydrologic loading rates ranging from 0.26 to 6.8 m day^{-1} (Arheimer and Wittgren, 2002).

10.2. Dimensions and design

Efficient CWs can have a variety of shapes and sizes. In general, the larger the wetland, the greater the potential for contaminant removal. CWs should be wide enough to allow sufficient trapping of sediment and other particulate materials, and long enough to generate adequate residence time for nutrient removal. However, some investigators suggest that long narrow wetlands are less efficient at removing contaminants compared to square or round CWs (Carty *et al.*, 2008; Scholz *et al.*, 2007), most researchers agree that the CW surface area should be as large as possible in order to maximize HRT and storage capacity.

10.2.1. Hydraulic efficiency

The evenness of dispersion of water across the wetland, termed hydraulic efficiency, is largely defined by wetland dimensions and relative position of input and output locations. High hydraulic efficiency maximizes contaminant removal. Hammer (1992) reported the optimum design should have a 3–5:1 length-to-width ratio in order to avoid excessive contaminant loading near the input, even though designs with this ratio may not have optimum hydraulic efficiencies (Persson *et al.*, 1999).

CW designs with good hydraulic efficiency have shapes and/or barriers to facilitate complete mixing throughout the wetland without the persistence of stagnant zones. All CW designs with good hydraulic efficiency have input and output locations positioned on opposite ends of the wetland. Some examples of efficient CW designs include: (1) CWs with multiple input locations across the width of the wetland, (2) upland barriers constructed to create a sinous path across the length of the wetland, (3) an island obstructing and diverting input flow to both sides of the CW, (4) a submerged berm across the width of the CW near the input to encourage vertical mixing, and (5) very long and narrow design (Braskerud, 2002a; Persson *et al.*, 1999). Designs with multiple inlets and outlets are needed for large wetlands to encourage parallel flowpaths to minimize stagnant zones (Fig. 5; Kadlec, 2005).

10.2.2. Sediment traps

Sediment traps are an important design feature in settings where input waters have high levels of suspended solids (Knight, 1992). Sediment traps consist of small swales or ponds positioned between the input and the main

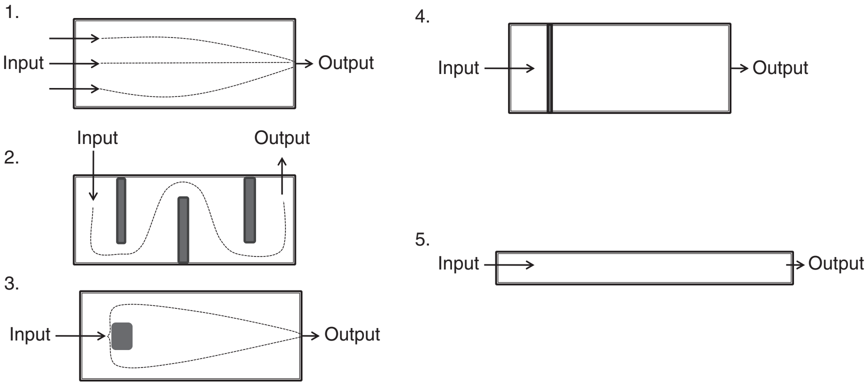

Figure 5 Theoretical designs to optimize hydraulic efficiency in CWs. Examples 2 and 3 depict micro-uplands that expand the active flowpath across the wetland. Example 4 depicts a submerged berm to encourage water mixing. Figure was redrawn in part from Persson *et al.*, 1999.

wetland to promote coarse particle settling before water is distributed across the wetland. Sediment traps should be located at easily accessible positions where sediment can be removed on a regular basis. This design feature decreases sedimentation within the wetland, which lengthens the time between dredging, prevents burial of germinating seedlings, and helps limit channelization and short-circuiting of flowpaths.

CWs often require time to mature in order to reach peak removal efficiency. The time needed ranges from 1 to 3 years depending on the rate of vegetative and microbial establishment. Most CWs have a fixed lifespan depending on sedimentation rates. In agricultural settings, sedimentation rates are highly variable and can be as high as 85 kg m^{-2} yr^{-1} (Maynard *et al.*, 2009). Therefore, to maximize CW lifetime, design specifications should consider sedimentation rates when designing sediment traps, heights of water control structures, and dikes (Hammer, 1992).

10.3. Placement

There are two general options to reduce NPSP from agriculture: (1) management practices implemented on site that limit application and losses from farmlands and (2) off-site practices that intercept NPSP before reaching major water supplies. CWs can be used within a farmscape as an on-site farm practice or as an off-site tool where downstream flood plains are converted to wetlands to mitigate NPSP at watershed scales (Van de Valk and Jolly, 1992).

10.3.1. Watershed to wetland area ratio

Placement of a CW is ultimately a site-specific consideration addressing contaminants of concern, nature of input flows, and desired community goals. The size of the contributing area, hence placement within a watershed, should be considered with the goal of having a low watershed to wetland area ratio (Kovacic *et al.*, 2000). This is especially important for CWs that receive field runoff or stream flow. To maximize particle trapping, Braskerud (2002a) suggests that the placement of CWs should be near the sediment source in low order watersheds. This minimizes travel distance and increases the likelihood for the CW to receive intact aggregates, which have greater settling velocities than smaller particles. Braskerud (2002a) suggested that a CW area of at least 0.1% of the watershed area for optimum sediment trapping, however, this study was conducted at wetland sites that received high particulate loads. To realize effective N and P removal, studies in the Midwestern United States suggested that the watershed to wetland area ratios should be around 15–20:1, which corresponded to 3–6% of the watershed area (Kovacic *et al.*, 2000). In irrigated agriculture, the size of the contributing area is indirectly relevant, and it is more important to consider placement of the CW relative to the magnitude of inflow volume and its variability.

10.3.2. Sociopolitical considerations

There are scientific, social, political, and economic issues that require consideration in order to implement CWs with the intent of having a watershed scale effect on water quality. For example, locating a CW in downstream sites near the watershed output (off-site practices) may be considered an efficient way to implement BMPs at the watershed scale. This approach, however, requires the conversion of a large land area to accommodate the hydrologic load and has the potential to be overwhelmed during extreme events (Knight, 1992). The technological investment needed to develop large CWs capable of handling outflows from an entire watershed is much higher than what would be needed if CWs are distributed throughout the watershed. Distributing CWs within headwater environments (on-site practices), however, can lead to more sporadic inflows and prolonged dry periods, and potentially less efficient systems. More importantly, it requires participation by all (or most) dischargers in order to realize a watershed effect. Other factors to consider for the placement of CWs include the value of land being converted, support of neighboring land owners, the long-term availability of water, presence of adjacent CWs, and the partners that may be financially involved (Jia and Luo, 2009; Van de Valk and Jolly, 1992).

10.3.3. Cost

It is also important to consider the costs associated with CWs. Maintenance costs are mainly associated with sediment removal, vegetation harvest, and/or control and management of water control structures. Development costs are primarily associated with grading, dike construction, and flow distribution, much of which can be subsidized by government programs, such as USDA EQIP and WRP. Knight (1992) estimated project costs for construction of CWs over 100 ha at $10,000 per ha, whereas for smaller CWs, costs can be as high as $50,000 per ha (Knight, 1992). Larger wetlands tend to be more cost effective on an area basis because most costs are associated with the development of berms and input–output structures.

It may be important to consider the visual appeal of CWs to gain support of local stakeholders. Wetlands with a more natural appearance tend to be more attractive and those CWs with sinuous or wavy lines, and level embankments, tend to be most pleasing to the eye. Adding microtopography to create islands or peninsulas for establishment of trees and deeper water areas may also be a good idea to promote texture and biodiversity (Carty *et al.*, 2008).

10.4. Managing vegetation

When choosing vegetation for CWs, the suitability of plants for specific-site conditions, including hydrology, climate, food for wildlife, and water quality, should be considered. Ideally the vegetation should have a high pollutant tolerance and assimilation capacity (Scholz and Lee, 2005). In agricultural settings, planting native species can often fail due to the large seedbank of exotic species within input waters, thus planting with native species is often not supported by the Wetland Reserve Program (Kovacic *et al.*, 2006).

Vegetation provides a variety of benefits but can also become a problem. Vegetation should be encouraged in a way that there is enough biomass for nutrient uptake, sorptive surface area, and plant residue supply. It also needs to be managed to promote light penetration for photodegradative processes and to limit residue accumulation to avoid DOC export. One way to promote this balance is to create areas of deeper water to limit emergent macrophyte establishment intermixed with shallow zones that encourage plant establishment.

10.5. Design features for mosquito control

Mosquitoes are undesirable pests and can be vectors for disease. Design features that promote water-quality improvements are often at odds with mosquito control measures. A variety of mosquito abatement methods can be used including: (1) chemical treatments; (2) biological treatments, such as *Bacillus thuringiensis* variety *israelensis* (*Bti*) and *Bacillus sphaericus* (*Bs*); (3) larvivorous fish such as *Gambusia affinis*; and (4) CW design features that discourage habitat and/or facilitate access by predators. Mosquitoes proliferate in densely vegetated wet areas, a CW condition that is preferred for optimizing many contaminant removal processes. Dense stands of vegetation protect mosquito larvae from predators and inhibit biological control efforts (Knight *et al.*, 2003). CW design features to control mosquito larvae attempt to discourage vegetation by preventing stagnant areas, and encourage mosquito fish habitat (Thullen *et al.*, 2002). These include creation of steep walled basin margins, maintaining episodes of water depths greater than 80–150 cm to discourage establishment of emergent macrophytes and creation of deeper areas for fish with access to shallow areas where larvae proliferate.

11. SUMMARY

NPSP from agricultural activities is a global problem affecting the quality of our waters for drinking, recreation, and aquatic ecosystems. The agricultural community requires cost effective and practical options to attenuate NPSP. CWs are an appealing option because they are effective contaminant removal systems that are relatively inexpensive to develop and maintain (Hammer, 1992; Larson *et al.*, 2000).

NPSP pollutants from agriculture have the potential to be successfully mitigated if CWs are carefully designed and managed. Differences in performance observed within a given CW in time (diurnally, seasonally, or degree of maturation) or between wetlands (distinct in location) result from complex interactions between wetland design (e.g., watershed contributing area to wetland area, placement in watershed, hydrologic efficiency) and management (e.g., hydrologic residence time, hydrologic and pollutant loading rates, vegetation characteristics). CWs efficiently remove (generally $>50\%$ removal efficiency) sediment, nitrate, microbial pathogens, particulate phosphorus, hydrophobic pesticides, and selected trace elements when designed appropriately and placed in the correct settings. Additional ecological services provided by CWs include wildlife habitat and biodiversity, hydrologic buffering of surface waters, ground water recharge zones, and aesthetic value. Many CW systems sequester eroded carbon and endogenous carbon demonstrating that CWs have potential as a climate-change mitigation strategy for agriculture (Maynard, 2009).

There are some potentially adverse effects of CWs that must be considered in certain regions. Areas with high background levels of mercury or selenium are of concern due to bioaccumulation and biomagnification of toxic metals within the food chain. CWs may also be a source of DOC that acts as precursors for formation of carcinogenic disinfection by-products during drinking water purification. CWs with long HRTs can increase salinity in output waters due to evapoconcentration of salts and should be designed with short HRTS (~ 1 day) in areas with high salinity. CWs have the potential to emit potent greenhouse gasses, such as methane and N_2O, thus contributing to global climate change. CWs may also provide breeding grounds for disease-carrying mosquitoes. Proper wetland management can greatly reduce these potentially adverse effects. However, additional site-specific studies are necessary to determine optimum management strategies to maximize contaminant removal and minimize adverse effects across a variety of environmental conditions (i.e., climate, soil, cropping practices).

CWs can be employed as on-site or off-site BMPs to filter agricultural runoff. To realize optimal water-quality improvements at the watershed scale, CWs should be included as part of a combination of management techniques, such as conservation tillage, improved irrigation and fertilization techniques, and vegetated filter strips. Further research evaluating the effects of wetland design and management options on NPSP water-quality concerns will continue to lead to enhanced wetland performance. When considering all of the ecological services provided by wetlands, CWs should be promoted as an integral component of the farmscape.

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