Chapter 20

Constructed Wetlands

20.1 BACKGROUND

Wetlands have been recognized as a natural resource throughout human history. Their importance in their natural state is appreciated by such people as the Marsh Arabs around the confluence of the Tigris and Euphrates rivers in southern Iraq, as well as in managed forms (e.g., rice paddies, particularly in Southeast Asia) (Mitsch and Gosselink, 2000).

The water purification capability of wetlands is being recognized as an attractive option in wastewater treatment. For example, the UK Environment Agency spends significant amounts of money on reed bed schemes in England and Wales. Such systems are designed, for example, to clean up mine water from collieries on which the constructed wetlands and associated community parks are being built.

Reed beds provide a useful complement to traditional sewage treatment systems. They are often a cheap alternative to expensive wastewater treatment technologies such as trickling filters and activated sludge processes (Cooper et al., 1996; Kadlec and Knight, 1996). Vertical-flow and horizontal-flow wetlands based on soil, sand, and/or gravel are used to treat domestic and industrial wastewater (Sun et al., 1999). They are also applied for passive treatment of diffuse pollution, including mine drainage (Mungur et al., 1997), as well as urban and motorway runoff after storm events (McNeill and Olley, 1998).

Furthermore, wetlands serve as a wildlife conservation resource and can also be seen as natural recreational areas for the local community (Hawke and José, 1996). The functions of macrophytes within constructed wetlands have been reviewed previously. *Phragmites* spp., *Typha* spp., and other macrophytes typical for swamps are widely used in Europe and North America (Brix, 1999).

20.2 DEFINITIONS

Defining wetlands has long been a problematic task, partly due to the diversity of environments, which are permanently or seasonally influenced by water, but also due to the specific requirements of the diverse groups of people involved with the study and management of these habitats. The Ramsar Convention, which brought wetlands to the attention of the international community,

Wetlands for Water Pollution Control. http://dx.doi.org/10.1016/B978-0-444-63607-2.00020-4

proposed the following definition (Convention on Wetlands of International Importance Especially as Waterfowl Habitat, 1971): "Wetlands are areas of marsh, fen, peatland, or water, whether natural or artificial, permanent or temporary, with water that is static or flowing, fresh, brackish, or salt, including areas of marine water, the depth of which at low tide does not exceed 6 m."

Another, more succinct, definition is as follows (Smith, 1980): "Wetlands are a half-way world between terrestrial and aquatic ecosystems and exhibit some of the characteristics of each." This complements the Ramsar description since wetlands are at the interface between water and land. This concept is particularly important in areas where wetlands may only be "wet" for relatively short periods of time during a year, such as in areas of the tropics with marked wet and dry seasons.

These definitions put emphasis on the ecological importance of wetlands. However, the natural water purification processes occurring within these systems have become increasingly relevant to those people involved with the practical use of constructed or even seminatural wetlands for water and wastewater treatment. There is no single accepted ecological definition of wetlands.

Wetlands are characterized by the following (United States Army Corps of Engineers, 2000):

- The presence of water;
- Unique soils that differ from upland soils; and
- The presence of vegetation adapted to saturated conditions.

Whichever definition is adopted, it can be seen that wetlands encompass a wide range of hydrological and ecological types, from high-altitude river sources (contradiction to United States Army Corps of Engineers (2000)) to shallow coastal regions, in each case being affected by prevailing climatic conditions. For the purpose of this chapter, however, the main emphasis will be upon constructed wetlands in temperate and oceanic climates.

20.3 HYDROLOGY OF WETLANDS

20.3.1 Hydro-Period and Water Budget

The biotic status of a wetland is intrinsically linked to the hydrological factors by which it is affected. These affect the nutrient availability as well as physicochemical variables such as soil and water pH and anaerobiosis within soils. In turn, biotic processes will have an impact upon the hydrological conditions of a wetland.

Water is the hallmark of wetlands. Therefore, it is not surprising that the input and output of water (i.e., water budget) of these systems determine the biochemical processes occurring within them. The net result of the water budget (hydro-period) may show great seasonal variations, but ultimately it delineates wetlands from terrestrial and fully aquatic ecosystems.

From an ecological point of view as well as an engineering one, the importance of hydrology cannot be overstated, as it defines the species diversity, productivity, and nutrient cycling of specific wetlands. That is to say, hydrological conditions must be considered if one is interested in the species richness of flora and fauna or if the interest lies in utilizing wetlands for pollution control.

The stability of particular wetlands is directly related to their hydro-period; that is, the seasonal shift in surface and subsurface water levels. The terms flood duration and flood frequency refer to wetlands that are not permanently flooded and give some indication of the time period involved in which the effects of inundation and soil saturation will be most pronounced.

Of particular relevance to riparian wetlands is the concept of flooding pulses as described by Junk et al. (1989). These pulses cause the greatest difference in high and low water levels and benefit wetlands by the inflow of nutrients and washing out of waste matter. These sudden and high volumes of water can be observed on a periodic or seasonal basis. It is particularly important to appreciate this natural fluctuation and its effects since wetland managers often attempt to control the level by which waters rise and fall. Such manipulation might be due to the overemphasis placed on water and its role in the life cycles of wetland flora and fauna, without considering the fact that such species have evolved in such an unstable environment (Fredrickson and Reid, 1990).

The balance between the input and output of water within a wetland is called the water budget. This budget is summarized by Eq. (20.3.1.1), where the volumetric units could be cubic meters:

$$\Delta V/\Delta t = P_n + S_i + G_i - ET - S_o - G_o \pm T \qquad (20.3.1.1)$$

where:

V = volume of water storage within a wetland;
$\Delta V/\Delta t$ = change in volume of water storage in a wetland per unit time (t);
P_n = net precipitation;
S_i = surface inflows, including flooded streams;
G_i = groundwater inflows;
ET = evapotranspiration;
S_o = surface outflows;
G_o = groundwater outflows; and
T = tidal inflow (+) or outflow (−).

20.3.2 Precipitation, Interception, Through-Fall, and Stem-Flow

In general terms, wetlands are most widespread in those parts of the world where precipitation exceeds water loss through evapotranspiration and surface runoff. The contribution of precipitation to the hydrology of a wetland is influenced by a number of factors. Precipitation such as rain and snow often passes through a canopy of vegetation before it becomes part of the wetland. The volume of water retained by this canopy is termed interception. Variables such as precipitation intensity and vegetation type will affect interception, for which median values of several studies have been calculated as 13% for deciduous forests and 28% for coniferous woodland (Dunne and Leopold, 1978).

The precipitation that remains to reach the wetland is termed the through-fall. This is added to the stem-flow, which is the water running down vegetation stems and trunks and is generally considered a minor component of a wetland water budget, such as 3% of through-fall in cypress dome wetlands in Florida (Heimburg, 1984). Thus, through-fall and stem-flow form Eq. (20.3.2.1), where the volumetric units could be cubic meters; this is the most commonly used precipitation equation for wetlands:

$$P_n = TF + SF \tag{20.3.2.1}$$

where:

P_n = net precipitation;
TF = through-fall; and
SF = stem-flow.

20.4 WETLAND CHEMISTRY

20.4.1 Oxygen

Because wetlands are associated with waterlogged soils, the concentration of oxygen within sediments and the overlying water is of critical importance. The rate of oxygen diffusion into water and sediment is slow, and this (coupled with microbial and animal respiration) leads to near-anaerobic sediments within many wetlands (Moss, 1998). These conditions favor rapid peat buildup, since decomposition rates and inorganic content of soils are low. Furthermore, the lack of oxygen in such conditions affects the aerobic respiration of plant roots and influences plant nutrient availability. Wetland plants have consequently evolved to be able to exist in anaerobic soils.

While the deeper sediments are generally anoxic, a thin layer of oxidized soil usually exists at the soil—water interface. The oxidized layer is important, since it permits the oxidized forms of prevailing ions to exist. This is in contrast to the reduced forms occurring at deeper levels of soil. The state of reduction or oxidation of iron, manganese, nitrogen, and phosphorus ions determines their role in nutrient availability and also toxicity. The presence of oxidized ferric iron (Fe^{3+}) gives the overlying wetland soil a brown coloration, whereas reduced sediments have undergone glaying, a process by which ferrous iron (Fe^{2+}) gives the sediment a blue-gray tint.

Therefore, the level of reduction of wetland soils is important in understanding the chemical processes that occur most likely in sediment and influence the corresponding above water column. The most practical way to determine the reduction state is by measuring the redox potential, also called the oxidation–reduction potential, of the saturated soil or water. The redox potential quantitatively determines whether a soil or water sample is associated with a reducing or oxidizing environment. Reduction is the release of oxygen and the gain of an electron (or hydrogen), whereas oxidation is the reverse (i.e., the gain of oxygen and loss of an electron). This is shown by Eq. (20.4.1.1) and explained in detail by Mitsch and Gosselink (2000).

$$E_H = E^0 + 2.3[RT/nF]\ \log[\{ox\}/\{red\}] \tag{20.4.1.1}$$

where:

E_H = redox potential (hydrogen ion scale);
E^0 = potential of reference (mV);
R = gas constant = 81.987 cal/deg/mol;
T = temperature (°C);
n = number of moles of electrons transferred; and
F = Faraday constant = 23,061 cal/mole/volt.

Oxidation (and therefore decomposition) of organic matter (very reduced material) occurs in the presence of any electron acceptor, particularly oxygen; although NO^{3-}, Mn^{2+}, Fe^{3+}, and $SO_4{}^{2-}$ are also commonly involved in oxidation, the rate will be slower in comparison with oxygen. A redox potential range between +400 mV and +700 mV is typical for environmental conditions associated with free dissolved oxygen. Below +400 mV, the oxygen concentration will begin to diminish and wetland conditions will become increasingly more reduced (>−400 mV).

Redox potentials are affected by pH and temperature, which influence the range at which particular reactions occur. The following thresholds are therefore not definitive:

- Once wetland soils become anaerobic, the primary reaction at approximately +250 mV is the reduction of nitrate ($NO_3{}^-$) to nitrite ($NO_2{}^-$), and finally to nitrous oxide (N_2O) or free nitrogen gas (N_2).
- At about +225 mV, manganese is reduced to manganous compounds. Under further reduced conditions, ferric iron becomes ferrous iron between approximately +100 mV and −100 mV, and sulfates become sulfides between approximately −100 and −200 mV.
- Under the most reduced conditions (<−200 mV) the organic matter itself and/or carbon dioxide will become the terminal electron acceptor. This results in the formation of low-molecular-weight organic compounds and methane gas ($CH_4\uparrow$).

20.4.2 Carbon

Organic matter within wetlands is usually degraded by aerobic respiration or anaerobic processes (e.g., fermentation and methanogenesis). Anaerobic degradation of organic matter is less efficient than decomposition occurring under aerobic conditions.

Fermentation is the result of organic matter acting as the terminal electron acceptor (instead of oxygen, as in aerobic respiration). This process forms low-molecular-weight acids (e.g., lactic acid), alcohols (e.g., ethanol), and carbon dioxide. Therefore, fermentation is often central in providing further biodegradable substrates for other anaerobic organisms in waterlogged sediments.

The sulfur cycle is linked with the oxidation of organic carbon in some wetlands, particularly in sulfur-rich coastal systems. Low-molecular-weight organic compounds that result from fermentation (e.g., ethanol) are utilized as organic substrates by sulfur-reducing bacteria during the conversion of sulfate to sulfide (Mitsch and Gosselink, 2000).

Previous work suggests that methanogenesis is the principal carbon pathway in freshwater. Between 30% and 50% of the total benthic carbon flux has been attributed to methanogenesis (Boon and Mitchell, 1995).

20.4.3 Nitrogen

The prevalence of anoxic conditions in most wetlands has led to them playing a particularly important role in the release of gaseous nitrogen from the lithosphere and hydrosphere to the atmosphere through denitrification (Mitsch and Gosselink, 2000). However, the various oxidation states of nitrogen within wetlands are also important to the biogeochemistry of these environments.

Nitrates are important terminal electron acceptors after oxygen, making them relevant in the process of oxidation of organic matter. The transformation of nitrogen within wetlands is strongly associated with bacterial action. The activity of particular bacterial groups is dependent on whether the corresponding zone within a wetland is aerobic or anaerobic.

Within flooded wetland soils, mineralized nitrogen occurs primarily as ammonium (NH_4^+), which is formed through ammonification, the process by which organically bound nitrogen is converted to ammonium under aerobic or anaerobic conditions. Soil-bound ammonium can be absorbed through rhizome and root systems of macrophytes and be reconverted to organic matter, a process that can also be performed by anaerobic microorganisms.

The oxidized top layer present in many wetland sediments is crucial in preventing the excessive buildup of ammonium. A concentration gradient will be established between the high concentration of ammonium in the lower reduced sediments and the low concentration in the oxidized top layer. This may cause a passive flow of ammonium from the anaerobic to the aerobic layer, where microbiological processes convert the ion into further forms of nitrogen.

Within the aerobic sediment layer, nitrification of ammonium, firstly to nitrite (NO_2^-) and subsequently to nitrate (NO_3^-), is shown in Eqs. (20.4.3.1) and (20.4.3.2), preceded by the genus of bacteria predominantly involved in each process step. Nitrification may also take place in the oxidized rhizosphere of wetland plants.

$$\textit{Nitrosomonas}: \quad 2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+ + \text{energy} \tag{20.4.3.1}$$

$$\textit{Nitrobacter}: \quad 2NO_2^- + O_2 \rightarrow 2NO_3^- + \text{energy} \tag{20.4.3.2}$$

A study in southern California indicated that denitrification was the most likely pathway for nitrate loss from experimental macrocosms and larger constructed wetlands (Bachand and Horne, 1999). Very high rates of nitrate–nitrogen removal were reported (2800 mg N/m^2/day). Furthermore, nitrate removal from inflow wastewater is generally lower in constructed wetlands compared to natural systems (Spieles and Mitsch, 2000). There is considerable interest in enhancing bacterial denitrification in constructed wetlands in order to reduce the level of eutrophication in receiving waters such as rivers and lakes (Bachand and Horne, 1999).

An investigation into the seasonal variation of nitrate removal showed maximum efficiency to occur during summer. This study also indicated a seasonal relationship in the pattern of nitrate retention, in which nitrate assimilation and denitrification are temperature dependent (Spieles and Mitsch, 2000).

Further evidence supporting the importance of denitrification was presented by Lund et al. (2000). The proportion of nitrogen removed by denitrification from a wetland in southern California was estimated by analyzing the increase in the proportion of the nitrogen isotope ^{15}N found in the outflow water. This method is based on the tendency of the lighter isotope ^{14}N to be favored by the biochemical thermodynamics of denitrification, thus reducing its proportion in water flowing out of wetlands in which denitrification is prevalent. Denitrification seems to be the favored pathway of nitrate loss from a treatment wetland, as this permanently removes nitrogen from the system, compared to sequestration within algal and macrophyte biomass.

In some wetlands, nitrogen may be derived through nitrogen fixation. In the presence of the enzyme nitrogenase, nitrogen gas is converted to organic nitrogen by organisms such as aerobic or anaerobic bacteria and cyanobacteria (blue-green algae). Wetland nitrogen fixation can occur in the anaerobic or aerobic soil layer, overlying water, in the rhizosphere of plant roots, and on leaf or stem surfaces. Cyanobacteria may contribute significantly to nitrogen fixation.

In northern bogs, which are often too acidic for large bacterial populations, nitrogen fixation by cyanobacteria is particularly important (Etherington, 1983). However, it should be noted that while cyanobacteria are adaptable organisms, they are affected by environmental stresses. For example, cyanobacteria are particularly susceptible to ultraviolet radiation, whereby their nitrogen metabolism (along with other functions) is impaired (Donkor and Häder, 1996).

20.4.4 Phosphorus

In wetland soils, phosphorus occurs as soluble or insoluble and organic or inorganic complexes. The phosphorus cycle is sedimentary rather than gaseous (as with nitrogen) and predominantly forms complexes within organic matter in peatlands or inorganic sediments in mineral soil wetlands. Over 90% of the phosphorus load in streams and rivers may be present in particulate inorganic form (Overbeck, 1988).

Soluble reactive phosphorus is the analytical term given to biologically available ortho-phosphate, which is the primary inorganic form. The availability of phosphorus to plants and microconsumers is limited due to the following main effects:

- Under aerobic conditions, insoluble phosphates are precipitated with ferric iron, calcium, and aluminum.
- Phosphates are adsorbed onto clay particles, organic peat, and ferric and aluminum hydroxides and oxides.
- Phosphorus is bound up in organic matter through incorporation into bacteria, algae, and vascular macrophytes.

There are three general conclusions about the tendency of phosphorus to precipitate with selected ions (Reddy et al., 1999):

1. In acid soils, phosphorus is fixed as aluminum and iron phosphates.
2. In alkaline soils, phosphorus is bound by calcium and magnesium.
3. The bioavailability of phosphorus is greatest at neutral to slightly acid pH.

The phosphorus availability is altered under anaerobic wetland soil conditions. The reducing conditions that are typical of flooded soils do not directly affect phosphorus. However, the association of phosphorus with other elements that undergo reduction has an indirect effect upon the phosphorus in the environment. For example, as ferric iron is reduced to the more soluble ferrous form, phosphorus as ferric phosphate is released into solution (Faulkner and Richardson, 1989; Gambrell and Patrick, 1978). Phosphorus may also be released into solution by a pH change brought about by organic, nitric, or sulfuric acids produced by chemosynthetic bacteria. Phosphorus sorption to clay particles is greatest under strongly acidic to slightly acidic conditions (Stumm and Morgan, 1996).

Great temporal variability in phosphorus concentrations of wetland influent in Ohio has been reported (Nairn and Mitsch, 2000). However, no seasonal pattern in phosphorus concentration was observed. This was explained by precipitation events and river flow conditions. Dissolved reactive phosphorus levels peaked during floods and on isolated occasions in late fall. Furthermore, sedimentation of suspended solids appears to be important in phosphorus retention within wetlands (Fennessy et al., 1994).

The physical, chemical, and biological characteristics of a wetland system affect the solubility and reactivity of different forms of phosphorus. Phosphate solubility is regulated by temperature (Holdren and Armstrong, 1980), pH (Mayer and Kramer, 1986), redox potential (Moore and Reddy, 1994), the interstitial soluble phosphorus level (Kamp-Nielson, 1974), and microbial activity (Gächter and Meyer, 1993; Gächter et al., 1988).

Where agricultural land has been converted to wetlands, there can be a tendency toward the solubilization of residual fertilizer phosphorus, which results in a rise of the soluble phosphorus concentration in floodwater. This effect can be reduced by physicochemical amendment, that is, by applying chemicals such as alum and calcium carbonate to stabilize the phosphorus in the sediment of these new wetlands (Ann et al., 1999a,b).

The redox potential has a significant impact on dissolved reactive phosphorus of chemically amended soils (Ann et al., 1999a,b). The redox potential can alter with fluctuating water table levels and hydraulic loading rates. Dissolved phosphorus concentrations are relatively high under reduced conditions, and they decrease with increasing redox potential. Iron compounds (e.g., $FeCl_3$) are particularly sensitive to the redox potential, resulting in the chemical amendment of wetland soils. Furthermore, alum and calcium carbonate are suitable to bind phosphorus even during fluctuating redox potentials.

Macrophytes assimilate phosphorus predominantly from deep sediments, thereby acting as nutrient pumps (Carignan and Kaill, 1980; Mitsch and Gosselink, 2000; Smith and Adams, 1986). The most important phosphorus retention pathway in wetlands is via physical sedimentation (Wang and Mitsch, 2000).

Model simulations on constructed wetlands in northeastern Illinois (USA) showed an increase in total phosphorus in the water column in the presence of macrophytes mainly during the nongrowing period, with little effect during the growing season. Most phosphorus taken from sediments by macrophytes is reincorporated into the sediment as dead plant material and therefore remains in the wetland indefinitely. Macrophytes can be harvested as a means to enhance phosphorus removal in wetlands. By harvesting macrophytes at the end of the growing season, phosphorus can be removed from the internal nutrient cycle within wetlands (Wang and Mitsch, 2000).

Moreover, the model showed a phosphorus removal potential of three-quarters of that of the phosphorus inflow. Therefore, harvesting would reduce phosphorus levels in upper sediment layers and drive phosphorus movement into deeper layers, particularly the root zone. In deep layers of sediment, the phosphorus sorption capacity increases along with a lower desorption rate (Wang and Mitsch, 2000).

20.4.5 Sulfur

In wetlands, sulfur is transformed by microbiological processes and occurs in several oxidation stages. Reduction may occur if the redox potential is between −100 and −200 mV. Sulfides provide the characteristic "bad egg" odor of wetland soils.

Assimilatory sulfate reduction is accomplished by obligate anaerobes such as *Desulfovibrio* spp. Bacteria may use sulfates as terminal electron acceptors (Eq. (20.4.5.1)) in anaerobic respiration at a wide pH range, but usage is highest around neutral pH (Mitsch and Gosselink, 2000).

$$4H_2 + SO_4^{2-} \rightarrow H_2S\uparrow + 2H_2O + 2OH^- \tag{20.4.5.1}$$

The greatest loss of sulfur from freshwater wetland systems to the atmosphere is via hydrogen sulfide ($H_2S\uparrow$). In oceans, however, this is through the production of dimethyl-sulfide from decomposing phytoplankton (Schlesinger, 1991).

Oxidation of sulfides to elemental sulfur and sulfates can occur in the aerobic layer of some soils and is carried out by chemoautotrophic (e.g., *Thiobacillus* spp.) and photosynthetic microorganisms. *Thiobacillus* spp. may gain energy from the oxidation of hydrogen sulfide to sulfur, and further, by certain other species of the genus, from sulfur to sulfate (Eqs. (20.4.5.2) and (20.4.5.3)).

$$2H_2S + O_2 \rightarrow 2S + 2H_2O + \text{energy} \tag{20.4.5.2}$$

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4 + \text{energy} \tag{20.4.5.3}$$

In the presence of light, photosynthetic bacteria, such as the purple sulfur bacteria of salt marshes and mud flats, produce organic matter as indicated in Eq. (20.4.5.4). This is similar to the familiar photosynthesis process, except that hydrogen sulfide is used as the electron donor instead of water.

$$CO_2 + H_2S + \text{light} \rightarrow CH_2O + S \tag{20.4.5.4}$$

Direct toxicity of free sulfide in contact with plant roots has been noted. There is a reduced toxicity and availability of sulfur for plant growth if it precipitates with trace metals. For example, the immobilization of zinc and copper by sulfide precipitation is well known.

The input of sulfates to freshwater wetlands, in the form of Aeolian dust or as anthropogenic acid rain, can be significant. Sulfate deposited on wetland soils may undergo dissimulator sulfate reduction by reaction with organic substrates (Eq. (20.4.5.5)).

$$2CH_2O + SO_4^{2-} + H^+ \rightarrow 2CO_2 + HS^- + 2H_2O \tag{20.4.5.5}$$

Protons consumed during this reaction (Eq. (20.4.5.5)) generate alkalinity. This is illustrated by the increase in pH with depth in wetland sediments (Morgan and Mandernack, 1996). It has been suggested that this alkalinity effect can act as a buffer in acid rain-affected lakes and streams (Rudd et al., 1986; Spratt and Morgan, 1990).

The sulfur cycle can vary greatly within different zones of a particular wetland. The stable isotope $\delta^{34}S$ within peat, the $^{35}SO_4^{2-}:Cl^-$ ratio, and the stable isotopes $\delta^{18}O$ and $\delta^{34}S$ of sulfate within different waters were analyzed by Mandernack et al. (2000). The variability in the sulfur cycle within the watershed can affect the distribution of reduced sulfur stored in soil. This change in local sulfur availability can have marked effects upon stream water over short distances.

The estimation of generated alkalinity may be complicated due to the potential problems associated with the use of the $^{35}SO_4^{2-}:Cl^-$ ratio and/or the $\delta^{34}S$ value, which are used to estimate the net sulfur retention. These problems may exist because ester sulfate pools can be a source of sulfate availability for sulfate reduction, and as a $\delta^{34}S$ sulfate buffer within stream water.

20.5 WETLAND ECOSYSTEM MASS BALANCE

The general mass balance for a wetland system, in terms of chemical pathways, uses the following main pathways: inflows, intrasystem cycling, and outflows. The inflows are mainly through hydrologic pathways such as precipitation, (particularly urban) surface runoff and groundwater. The photosynthetic fixation of both atmospheric carbon and nitrogen comprises important biological pathways. Intrasystem cycling is the movement of chemicals in standing stocks within wetlands, such as litter production and remineralization. Translocation of minerals within plants is an example of the physical movement of chemicals. Outflows involve hydrologic pathways but also include the loss of chemicals to deeper sediment layers, beyond the influence of internal cycling (although the depth at which this threshold occurs is not certain). Furthermore, the nitrogen cycle plays an important role in outflows, such as nitrogen gas lost as a result of denitrification. However, respiratory loss of carbon is also an important biotic outflow.

There is great variation in the chemical balance from one wetland to another, but the following generalizations can be made:

- Wetlands act as sources, sinks, or transformers of chemicals depending on wetland type, hydrological conditions, and length of time the wetland has received chemical inputs. As sinks, the long-term sustainability of this function is associated with hydrologic and geomorphic conditions as well as the spatial and temporal distribution of chemicals within wetlands.
- Particularly in temperate climates, seasonal variation in nutrient uptake and release is expected. Chemical retention will be greatest in the growing seasons (spring and summer) due to higher rates of microbial activity and macrophyte productivity.
- The ecosystems connected to wetlands affect and are affected by the adjacent wetland. Upstream ecosystems are sources of chemicals, while

those downstream may benefit from the export of certain nutrients or the retention of particular chemicals.
- Nutrient cycling in wetlands differs from that in terrestrial and aquatic systems. More nutrients are associated with wetland sediments than with most terrestrial soils, whereas benthic aquatic systems have autotrophic activity, which relies more on nutrients in the water column than in the sediments.
- The ability of wetland systems to remove anthropogenic waste is not limitless.

Equation (20.5.1) indicates a general mass balance for a pollutant within a treatment wetland. Within this equation, transformations and accretion are long-term sustainable removal processes, whereas storage does not result in long-term average removal but can lessen or accentuate the cyclic activity.

$$\begin{aligned} \text{In} - \text{Out} = {} & \text{Transformation} + \text{Accretion} + \text{Biomass Storage} \\ & + \text{Water/Soil Storage} \end{aligned} \tag{20.5.1}$$

20.6 MACROPHYTES IN WETLANDS

20.6.1 Background

Wetland plants are often central to wastewater treatment wetlands. The following requirements of plants should be considered for use in such systems (Tanner, 1996):

- Ecological adaptability (no disease or weed risk to the surrounding natural ecosystems);
- Tolerance of local conditions in terms of climate, pests, and diseases;
- Tolerance of pollutants and hypertrophic waterlogged conditions;
- Ready propagation and rapid establishment, spread, and growth; and
- High pollutant removal capacity through direct assimilation or indirect enhancement of nitrification, denitrification, and other microbial processes.

Interest in macrophyte systems for sewage treatment by the UK water industry dates back to 1985 (Parr, 1990). The ability of different macrophyte species and their assemblages within systems to most efficiently treat wastewater has been examined previously (Kuehn and Moore, 1995). The dominant species of macrophyte varies from locality to locality. The number of genera (e.g., *Phragmites* spp., *Typha* spp., and *Scirpus* spp.) common to all temperate locations is great.

The improvement of water quality with respect to key water quality variables, including BOD, COD, total SS, nitrates, and phosphates, has been studied by Turner (1995). Relatively little work has been conducted on the enteric bacteria removal capability of macrophyte systems (Perkins and Hunter, 2000).

20.6.2 Primary Productivity

There have been many studies to determine the primary productivity of wetland macrophytes, although estimates have generally tended to be fairly high (Mitsch and Gosselink, 2000). The estimated dry mass production for *Phragmites australis* (Cav.) Trin. ex Steud. (common reed) is between 1000 and 6000 g/m^2/year in the Czech Republic (Kvet and Husak, 1978), between 2040 and 2210 g/m^2/year for *Typha latifolia* L. (cattail) in Oregon, USA (McNaughton, 1966), and 943 g/m^2/year for *Scirpus fluviatilis* (Torr.) A. Gray [JPM][H&C] (river bulrush) in Iowa, USA (van der Valk and Davis, 1978).

Little of aquatic plant biomass is consumed as live tissue; rather, it enters the pool of particulate organic matter following tissue death. The breakdown of this material is consequently an important process in wetlands and other shallow aquatic habitats (Gessner, 2000). Litter breakdown has been studied along with intensive work on *P. australis*, one of the most widespread aquatic macrophytes (Wrubleski et al., 1997).

There has been an emphasis on studying the breakdown of aquatic macrophytes in such a way that most closely resembles natural plant death and decomposition, principally by not removing plant tissue from macrophyte stands. Many species of freshwater plants exhibit the so-called standing-dead decay, which describes the observation of leaves remaining attached to their stems after senescence and death (Kuehn et al., 1999). Different fractions (leaf blades, leaf sheaths, and culms) of *P. australis* differ greatly in structure and chemical composition and may exhibit different breakdown rates, patterns, and nutrient dynamics (Gessner, 2000).

20.6.3 *Phragmites australis*

Phragmites australis (Cav.) Trin. ex Steud. (common reed, formerly known as *Phragmites communis* (Norfolk reed)) is a member of the large family Poaceae (roughly 8000 species within 785 genera). Common reed occurs throughout Europe to 70° North and is distributed worldwide. It may be found in permanently flooded soils of still or slowly flowing water. This emergent plant is usually firmly rooted in wet sediment but may form lightly anchored rafts of "hover reed."

It tends to be replaced by other species at drier sites. The density of this macrophyte is reduced by grazing (e.g., consumption by waterfowl) and may then be replaced by other emergent species such as *Phalaris arundinacea* L. (reed canary grass).

Phragmites australis is a perennial, and its shoots emerge in spring. Hard frost kills these shoots, illustrating the tendency for reduced vigor toward the northern end of its distribution. The hollow stems of the dead shoots in winter are important in transporting oxygen to the relatively deep rhizosphere (Brix, 1989).

Reproduction in closed stands of this species is mainly by vegetative spread, although seed germination enables the colonization of open habitats. Detached shoots often survive and regenerate away from the main stand (Preston and Croft, 1997).

Common reed is most frequently found in nutrient-rich sites, and it is absent from the most oligotrophic zones. However, the stems of this species may be weakened by nitrogen-rich water and are subsequently more prone to wind and wave damage, leading to an apparent reduction in density of this species in Norfolk (England) and elsewhere in Europe (Boar et al., 1989; Ostendorp, 1989).

20.6.4 *Typha latifolia*

Typha latifolia L. (cattail, reedmace, or bulrush) is a species belonging to the small family Typhaceae. This species is widespread in temperate parts of the northern hemisphere but extends to South Africa, Madagascar, Central America, and the West Indies and has been naturalized in Australia (Preston and Croft, 1997). *Typha latifolia* is typically found in shallow water or on exposed mud at the edge of lakes, ponds, canals, and ditches and less frequently near fast-flowing water. This species rarely grows at water depths >0.3 m, where it is frequently replaced by *P. australis*.

Reedmace is a shallow-rooted perennial producing shoots throughout the growing season, which subsequently die in fall. Colonies of this species expand by rhizomatous growth at rates of 4 m/year, whereas detached portions of rhizome may float and establish new colonies. In contrast, colony growth by seeds is less likely. Seeds require moisture, light, and relatively high temperatures to germinate, although this may occur in anaerobic conditions. Where light intensity is low, germination is stimulated by temperature fluctuation (Hammer, 1989).

20.7 PHYSICAL AND BIOCHEMICAL PARAMETERS

The key physicochemical parameters relevant for wetland systems include the BOD, turbidity, and the redox potential. The BOD is an empirical test to determine the molecular oxygen used during a specified incubation period (usually 5 days) for the biochemical degradation of organic matter (carbonaceous demand) and the oxygen used to oxidize inorganic matter (e.g., sulfides and ferrous iron). An extended test (up to 25 days) may also measure the amount of oxygen used to oxidize reduced forms of nitrogen (nitrogenous demand), unless this is prevented by an inhibitor chemical (Scholz, 2004a). Inhibiting the nitrogenous oxygen demand is recommended for secondary effluent samples (Clesceri et al., 1998).

Upper BOD limits of around 3 mg/l for salmonid rivers and about 6 mg/l for coarse fisheries are traditionally set by fishery agencies. A river is deemed polluted if the BOD exceeds 5 mg/l. Municipal wastewater values are usually between approximately 150 and 1000 mg/l (Kiely, 1997).

Turbidity is a measure of the cloudiness of water, caused predominantly by suspended material such as clay, silt, organic and inorganic matter, plankton and other microscopic organisms, and scattering and absorbing light. Turbidity in wetlands and lakes is often due to colloidal or fine suspensions, whereas in fast-flowing waters the particles are larger and turbid conditions are prevalent predominantly during floods (Kiely, 1997).

The redox potential is another key parameter for monitoring wetlands. The reactivities and mobilities of elements such as iron, sulfur, nitrogen, carbon, and a number of metallic elements depend strongly on the redox potential conditions. Reactions involving electrons and protons are pH- and redox-potential-dependent. Chemical reactions in aqueous media can often be characterized by pH and the redox potential together with the activity of dissolved chemical species. The redox potential is a measure of intensity and does not represent the capacity of the system for oxidation or reduction (American Public Health Association, 1995). The interpretation of the redox potential values measured in the field is limited by a number of factors, including irreversible reactions, electrode poisoning, and multiple redox couples.

20.8 EXAMPLES FOR NATURAL AND CONSTRUCTED WETLANDS

20.8.1 Riparian Wetlands

Riparian wetlands are ecosystems under the influence of adjacent streams or rivers (Scholz and Trepel, 2004). A succinct definition is as follows (Gregory et al., 1991): "Riparian zones are the interface between terrestrial and aquatic ecosystems. As ecotones, they encompass sharp gradients of environmental factors, ecological processes and plant communities. Riparian zones are not easily delineated, but are composed of mosaics of landforms, communities and environments within the larger landscape." There are four main reasons as to why periodic flooding, which is typical of riparian wetlands, contributes to the observed higher productivity compared to adjacent upland ecosystems:

1. There is an adequate water supply for vegetation.
2. Nutrients are supplied and coupled with a favorable change in soil chemistry (e.g., nitrification, sulfate reduction, and nutrient mineralization).
3. In comparison to stagnant water conditions, a more oxygenated root zone follows flooding.
4. Waste products (e.g., carbon dioxide and methane) are removed by periodic flushing.

Nutrient cycles in riparian wetlands can be described as follows:

- Nutrient cycles are "open" due to the effect of river flooding, runoff from upslope environments, or both (depending on season and inflow stream or river type).
- Riparian forests have a great effect on the biotic interactions within intrasystem nutrient cycles. The seasonal pattern of growth and decay often matches available nutrients.
- Water in contact with the forest floor leads to important nutrient transformations. Therefore, riparian wetlands can act as sinks for nutrients.
- Riparian wetlands have often appeared to be nutrient transformers, changing a net input of inorganic nutrients to a net output of their corresponding organic forms.

The nitrogen cycle within a temperate stream—floodplain environment is of particular interest to ecological engineers. During winter, flooding contributes to the accumulation of dissolved and particulate organic nitrogen that is not assimilated by the trees due to their dormancy. This fraction of nitrogen is retained by filamentous algae and through immobilization by detritivores on the forest floor.

As the water of a wetland gets warmer in spring, nitrogen is released by decomposition and by shading of the filamentous algae by the developing tree canopy. Nitrate is then assumed to be immobilized in the decaying litter and gradually made available to plants. As vegetation increases, the plants take up more nitrogen, and water levels fall subsequently due to evapotranspiration. Ammonification and nitrification rates increase with exposure of the sediments to the atmosphere. Nitrates produced during nitrification are lost when denitrification becomes prevalent as flooding later in the year creates anaerobic conditions.

In terms of reducing the effects of eutrophication on open water by urban runoff, the use of riparian buffer zones, particularly of *Alnus incana* (Gray Alder) and *Salix* spp. (Willow) in conjunction with perennial grasses, has been recommended (Mander et al., 1995). Riparian zones are also termed riparian forest buffer systems (Lowrance et al., 1979). Such zones were found to reduce the nutrient flux into streams.

The role of riparian ecosystems in nutrient transformations is specifically important in relation to the production of the greenhouse gas nitrous oxide (N_2O). Due to the inflow of excess agricultural nitrogen into wetland systems, the riparian zones in particular are likely hot spots for nitrous oxide production (Groffman, 2000).

The control of nonpoint source pollution can be successfully achieved by riparian forest buffers in some agricultural watersheds and, most effectively, if excess precipitation moves across, in, or near the root zone of the riparian forest buffers. For example, between 50% and 90% retention of total nitrate loading in both shallow groundwater and sediment subject to surface runoff within the Chesapeake Bay watershed (USA) was observed. In comparison, phosphorus retention was found to be generally less than nitrate retention (Lowrance et al., 1979).

20.8.2 Constructed Treatment Wetlands

Natural wetlands usually improve the quality of water passing through them, acting effectively as ecosystem filters. In comparison, most constructed wetlands are artificially created wetlands used to treat water pollution in its variety of forms. Therefore, they fall into the category of constructed treatment wetlands. Treatment wetlands are solar-powered ecosystems. Solar radiation varies diurnally, as well as on an annual basis (Kadlec, 1999).

Constructed wetlands have the purpose to remove bacteria, enteric viruses, SS, BOD, nitrogen (predominantly as ammonia and nitrate), metals, and phosphorus (Pinney et al., 2000). Two general types of constructed wetlands are usually commissioned in practice: surface-flow (i.e., horizontal-flow) and subsurface-flow (e.g., vertical-flow). Surface-flow constructed wetlands most closely mimic natural environments and are usually more suitable for wetland species because of permanent standing water. In subsurface-flow wetlands, water passes laterally through a porous medium (usually sand and gravel) with a limited number of macrophyte species. These systems often have no standing water.

Constructed treatment wetlands can be built at, above, or below the existing land surface, if an external water source is supplied (e.g., wastewater). The grading of a particular wetland in relation to the appropriate elevation is important for the optimal use of the wetland area in terms of water distribution. Soil type and groundwater level must also be considered if long-term water shortage is to be avoided. Liners can prevent excessive desiccation, particularly where soils have a high permeability (e.g., sand and gravel) or where there is limited or periodic flow.

Rooting substrate is also an important consideration for the most vigorous growth of macrophytes. A loamy or sandy topsoil layer between 0.2 and 0.3 m in depth is ideal for most wetland macrophyte species in a surface-flow wetland. A subsurface-flow wetland will require coarser material such as gravel and/or coarse sand (Kadlec and Knight, 1996).

Furthermore, the use of flue-gas-desulfurization by-products from coal-fired electric power plants in wetland liner material was researched (Ahn et al., 2001). These by-products are usually sent to landfill sites. This is now recognized as an increasingly unsuitable and impractical waste disposal method. Although the study was short (2 years), no detrimental impact on macrophyte biomass production was reported. Moreover, flue-gas-desulfurization material may be a good liner and substrate for phosphorus retention in constructed wetlands.

The following conclusions with implications for treatment wetland design were made by Pinney et al. (2000):

- High levels of dissolved organic carbon may enter water supplies where soil aquifer treatment is used for groundwater recharge, as the influent for this method is likely to come from long-hydraulic-retention-time wetlands. Consequently, there is a greater potential for the formation of disinfection by-products.
- A shorter hydraulic retention time will result in less dissolved organic carbon leaching from plant material compared to a longer hydraulic retention time in a wetland.
- Dissolved organic carbon leaching is likely to be most significant in wetlands designed for the removal of ammonia, which requires a long hydraulic retention time.

20.8.3 Wetlands for Stormwater Treatment

Most constructed wetlands in the USA and Europe are soil- or gravel-based horizontal-flow systems planted with *T. latifolia* and/or *P. australis*. They are used to treat urban runoff and domestic and industrial wastewater (Cooper et al., 1996; Kadlec and Knight, 1996; Scholz, 2003; Scholz et al., 2005), and they have also been applied for passive treatment of mine wastewater drainage (Mays and Edwards, 2001; Mungur et al., 1997).

Storm runoff from urban areas has been recognized as a major contributor to pollution of the corresponding receiving urban watercourses. The principal pollutants in urban runoff are BOD, SS, heavy metals, deicing salts, hydrocarbons, and fecal coliforms (Scholz and Martin, 1998a; Scholz, 2004b).

Although various conventional methods have been applied to treat stormwater, most technologies are not cost-effective or are too complex. Constructed wetlands integrated into a best management practice concept are a sustainable means of treating stormwater and prove to be more economic (e.g., construction and maintenance) and energy efficient than traditional centralized treatment systems (Kadlec et al., 2000; Scholz et al., 2005). Furthermore, wetlands enhance biodiversity and are less susceptible to variations of loading rates (Cooper et al., 1996; Scholz and Trepel, 2004).

Contrary to standard domestic wastewater treatment technologies, stormwater (e.g., gully pot liquor) treatment systems have to be robust to highly variable flow rates and water quality variations. The stormwater quality depends on the load of pollutants present on the road and the corresponding dilution by each storm event (Scholz, 2003; Scholz and Trepel, 2004).

In contrast to standard horizontal-flow constructed treatment wetlands, vertical-flow wetlands are flat and intermittently flooded and drained, allowing air to refill the soil pores within the bed (Cooper et al., 1996; Gervin and Brix, 2001; Green et al., 1998). While it has been recognized that vertical-flow constructed wetlands have usually higher removal efficiencies with respect to organic pollutants and nutrients in comparison to horizontal-flow wetlands, denitrification is less efficient in vertical-flow systems (Luederits et al., 2001). When the wetland is dry, oxygen (as part of the air) can enter the top layer of debris and sand. The following incoming flow of runoff will absorb the gas and transport it to the anaerobic bottom of the wetland.

Furthermore, aquatic plants such as macrophytes transport oxygen to the rhizosphere. However, this natural process of oxygen enrichment is not as effective as the previously explained engineering method (Kadlec and Knight, 1996; Karathanasis et al., 2003).

Heavy metals within stormwater are associated with fuel additives, car body corrosion, and tire and brake wear. Common metal pollutants from cars include copper, nickel, lead, zinc, chromium, and cadmium. Freshwater quality standards are most likely to be exceeded by copper (Cooper et al., 1996; Scholz et al., 2002; Tchobanoglous et al., 2003).

Metals occur in soluble, colloidal, or particulate forms. Heavy metals are most bioavailable when they are soluble, in either ionic or weakly complexed form (Cooper et al., 1996; Cheng et al., 2002; Wood and Shelley, 1999).

There have been many studies on the specific filter media within constructed wetlands to treat heavy metals economically. Media used include limestone, lignite, activated carbon (Scholz and Martin, 1998a), peat, and leaves. Metal bioavailability and reduction are controlled by chemical processes including acid volatile sulfide formation and organic carbon binding and sorption in reduced sediments of constructed wetlands (Kadlec, 2002; Obarska-Pempkowiak and Klimkowska, 1999; Wood and Shelley, 1999). It follows that metals usually accumulate in the top layer (fine aggregates, sediment, and litter) of vertical-flow and near the inlet of horizontal-flow constructed treatment wetlands (Cheng et al., 2002; Scholz and Xu, 2002; Vymazal and Krasa, 2003).

Physical and chemical properties of the wetland soil and aggregates affecting metal mobilization include particle size distribution (texture), redox potential, pH, organic matter, salinity, and the presence of inorganic matter such as sulfides and carbonates (Backstrom et al., 2004). The cation exchange capacity of maturing wetland soils and sediments tends to increase as texture becomes finer because more negatively charged binding sites are available. Organic matter has a relatively high proportion of negatively charged binding sites. Salinity and pH can influence the effectiveness of the cation exchange capacity of soils and sediments because the negatively charged binding sites will be occupied by a high number of sodium or hydrogen cations (Knight et al., 1999).

Sulfides and carbonates may combine with metals to form relatively insoluble compounds. Particularly the formation of metal sulfide compounds may provide long-term heavy metal removal because these sulfides will remain permanently in the wetland sediments as long as they are not reoxidized (Cooper et al., 1996; Kadlec and Knight, 1996).