Wetlands: Water "living filters"?

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ABSTRACT

Human societies have indirectly used natural wetlands as wastewater discharge sites for many centuries. Observations of the wastewater depuration capacity of natural wetlands have led to a greater understanding of the potential of these ecosystems for pollutant assimilation and have stimulated the development of artificial wetlands systems for treatment of wastewaters from a variety of sources. Constructed wetlands, in contrast to natural wetlands, are human-made systems that are designed, built and operated to emulate wetlands or functions of natural wetlands for human desires or needs. Constructed wetlands have recently received considerable attention as low cost, efficient means to clean-up not only municipal wastewaters but also point and non-point wastewaters, such as acid mine drainage, agricultural effluents, landfill leachates, petrochemicals, as well as industrial effluents. Currently, untreated wastewater discharge in the natural wetlands sites is becoming an increasingly abandoned practice whereas the use of constructed wetlands for treatment of wastewater is an emerging technology worldwide. However, natural wetlands still play an important role in the improvement of water quality as they act as buffer zones surrounding water bodies and as a polishing stage for the effluents from conventional municipal wastewater treatment plants, before they reach the receiving water streams. In fact, one of the emerging issues in environmental science has been the inefficiency of wastewater treatment plants to remove several xenobiotic organic compounds such as pesticides and pharmaceutical residues and consequent contamination of the receiving water bodies. Recent studies have shown that wetlands systems were able to efficiently

remove many of these compounds, thus reaffirming the importance of the role which can be played by wetlands in water quality preservation.

The aim of this work is to present a review on the application of wetlands as “living filters” for water purification. Emphasis was focused on the removal of micropollutants, especially xenobiotic organic compounds such as pharmaceuticals residues, which are not efficiently removed by conventional municipal wastewater treatment plants. Furthermore, the role of wetlands as protection zones which contribute to the improvement of the aquatic ecosystems’ quality will be discussed.

1. Introduction

Wetlands have been recognized throughout human history to be a valuable natural resource. Their importance has been appreciated in managed forms, for example rice paddies, particularly in South East Asia, but also in their natural state by such people as the Marsh Arabs around the confluence of the rivers Tigris and Euphrates in southern Iraq (Mitsch and Gosselink J.G., 2000). Benefits provided by wetlands include water supply and control, mining, use of plants, wild-life, integrated systems and aquaculture, erosion control, education and training, recreation and reclamation (USEPA and USDA-NRCS, 1995; Cooper et al., 1996; Vymazal et al., 1998a; USEPA, 2000; Sundaravadivel and Vigneswaran, 2001).

The water purification capability of wetlands, in particular, has for long been recognized. Natural wetlands usually improve the quality of water passing through them, acting as “living filters” and serving as transitional zones or “ecotones” between terrestrial and aquatic systems (Mitsch and Gosselink J.G., 2000; Sundaravadivel and Vigneswaran, 2001). They provide several physical, chemical, and biological processes which allow for the depuration of pollutants resulting from point and non-points source, thereby contributing for an improvement of water quality. In many regions, natural wetlands have been used, for centuries, as convenient wastewater discharge sites and sinks for a wide variety of anthropogenic pollutants including toxic organic compounds (Kadlec and Knight, 1996; Vymazal, 1998).

Despite the many benefits offered by wetlands, some of these areas have also been for long regarded as wasted, useless land, unsuitable for agriculture, and subjected to drainage in order to make them available for cultivation. Since the early 20th century, wetland losses attributed to agriculture have been dramatic. Extensive wetland draining in the 1960s and 1970s led to increased available agricultural production acreage. However, in many places, in parallel with this practice, a decline has been observed in the water quality of the neighboring water bodies. An aggravated potential for damage to the aquatic systems, such as increased sedimentation or fish kills, is expected when rivers, streams, and lakes adjacent to the former wetland areas receive runoff following rainfall events. The functional role of wetlands in improving water quality has been, in recent years, a compelling argument for their preservation and study. The realization of the importance of wetlands, adjacent to other water bodies, has resulted in the fact that drainage of wetlands has ceased in many countries and that even previously drained wetlands are restored.

The water treatment capabilities of wetlands are thus generally recognized but the extent of their treatment capacity is largely unassessed. However, studies have led to both a greater understanding of the potential of natural wetland ecosystems for pollutant assimilation and the design of new natural water treatment systems inspired in these natural systems. There remain, however, concerns over the possibility of harmful effects resulting from toxic compounds and pathogens that may be present in many wastewater sources. Also, there are concerns that there may be a potential for long-term degradation of natural wetlands due to the addition of nutrients and changes in the natural hydrologic conditions influencing these systems. At least in part due to such concerns, there has been a growing interest in the use of constructed wetlands systems (CWS) for wastewater treatment.

Significant advances have been made in the last years in the engineering knowledge of creating artificial wetlands that can closely imitate the treatment functions that occur in the natural wetland ecosystems. These CWS can be defined as man-made systems that have been designed and constructed to utilize the natural processes involving wetland vegetation, soils, and their associated microbial populations to assist in treating wastewater (Hammer and Bastian, 1989; Vymazal, 1998). They are designed to take advantage of many of the same processes that occur in natural wetlands, but do so within a more controlled environment.

While some CWS have been designed and operated with the sole purpose of treating wastewater, others have been implemented with multiple-use objectives in mind, such as using treated wastewater effluent as a water source for the creation and restoration of wetland habitat for wildlife use and environmental enhancement.

The construction of artificial wetlands for the treatment of wastewater has been developing fast over the last decades and it represents now a widely accepted and an increasingly common treatment alternative. The many advantages offered by CWS such as simplicity of design and lower costs of installation, operation, and maintenance make them an appropriate alternative for both developed and developing countries (USEPA and USDA-NRCS, 1995; Vymazal et al., 1998a; USEPA, 2000).

In the following sections of this text the water purification functions of natural wetlands are presented in greater detail and, afterwards, the constructed wetland systems are described. Studies on the removal of several types of pollutants by these systems, as well as the more recent new trends on the use of CWS for pollutants removal are discussed.

2. Natural wetlands

2.1. Definition and characterization

Wetlands encompass a broad range of wet environments, ranging from submerged coastal grass beds to salt marshes, swamp forests and boggy meadows (USEPA and USDA-NRCS, 1995; Kadlec and Knight, 1996; Vymazal et al., 1998a; Sundaravadivel and Vigneswaran, 2001).

A single precise definition and classification for wetlands that can correctly describe them in a comprehensive way for most purposes still has not been developed. In fact, a definition for wetlands has long been the subject of debate, due to the great variety of environments which are, either permanently or seasonally, influenced by water as well as to the specific requirements of the diverse groups of people involved in the study and management of these systems. Terms used in wetlands classification are many and are often confusing. Still, they are important for both the scientific understanding of these systems and for their proper management.

The Ramsar Convention, which in 1971 brought a worldwide attention to wetlands, took a broad approach in its definition in the text of the Convention (Article 1.1) (UNESCO, 1994):

> **"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 six metres".**

In addition, for the purpose of protecting coherent sites, the Article 2.1 stipulates in order to be included in the Ramsar List of internationally important wetlands, they may incorporate:

> **“riparian and coastal zones adjacent to the wetlands, and islands or bodies of marine water deeper than six metres at low tide lying within the wetlands”.**

Another definition of wetlands was proposed by the U.S. Fish and Wildfire Services, which also developed a classification system capable of encompassing and systematically organizing for scientific purposes all types of wetland habitats. According to such view, wetlands are described as the transition areas between terrestrial and aquatic systems, where water is the dominant factor determining soil characteristics and development of associated biological communities. The definition specifies that wetlands need, at least periodically, to fulfill one or more of the following four requirements (Hammer and Bastian, 1989; Cowardin and Golet, 1995; Brady and Weil, 2002):

- areas where the water table is at or near the surface or where the land is covered by shallow water;
- areas supporting predominantly hydrophytes (water-tolerant plant species);
- areas with predominantly undrained hydric soils. Hydric soils are those that are sufficiently wet for long enough to produce anaerobic conditions, thereby limiting the types of plants that can grow on them;
- areas with non-soil substrate (such as rock or gravel) that are saturated or covered by shallow water at some time during the growing season of plants.

The U.S. Fish and Wildlife Service classification system (Cowardin and Golet, 1995) is much like the hierarchical system used by scientists to classify plants and animals, starting out with five large systems and progressively subdividing into a series of subsystems, classes and subclasses, which are then characterized by examples of dominant types of plants and animals. This system thus provides a consistent standard of terminology to be used among scientists and specialists.

Various legislation and agency regulations define wetlands in more general terms. The U.S. Environmental Protection Agency (EPA) and the U.S. Army Corps of Engineers jointly define wetlands as (Environmental Laboratory, 1987):

> **“Those areas that are inundated or saturated by surface or ground water at a frequency and duration sufficient to support, and that under normal circumstances do support, a prevalence of vegetation typically adapted for life in**

> **saturated soil conditions. Wetlands generally include swamps, marshes, bogs, and similar areas".**

One of the most recent definitions has been used by the U.S. National Research Council, which defines wetlands as (National Research Council, 1995; Vymazal et al., 1998a):

> **"an ecosystem that depends on constant or recurrent, shallow inundation or saturation at or near the surface of the substrate".**

Notwithstanding which of the definitions one may use, three major factors are salient in the characterization of a wetland: water (hydrology), substrate (physico-chemical features) and biota (type of vegetation and microbial activity)(National Research Council, 1995).

The characteristics of all these three components are interdependent and conditioned by each other. It is from the complex interactions among them that results the values and functions of wetlands.

2.2. Natural wetlands as natural water "living filters"?

Long regarded as wastelands, wetlands are now recognized as important features in the landscape that provide numerous beneficial functions for people and for fish and wildlife. These services, considered valuable to societies worldwide, are the result of the wetlands' inherent and unique natural characteristics.

Wetlands support a rich diversity of wildlife and fisheries by being stopping-off points and nesting areas for migratory birds and spawning grounds for fish and shellfish. Those wetlands along the coasts, riverbanks and lakeshores have a valuable role in stabilizing shorelands and protecting them from erosion. One of the greatest benefits of inland wetlands is the natural flood control or buffering provided for downstream areas by slowing the flow of floodwater, desynchronizing the peak contributions of tributary streams and reducing peak flows on main rivers (Hammer and Bastian, 1989; USEPA and USDA-NRCS, 1995). Some wetlands may function as discharge areas for groundwaters, allowing stored groundwater to sustain surface base flow in streams during dry periods (Hammer and Bastian, 1989). Additional benefits provided by these natural systems include mining (peat, sand, gravel), use of plants (staple food plants, grazing land, timber, paper production, roofing, agriculture, horticulture, fodder), integrated systems and aquaculture (*e.g.* fish cultivation combined with rice production), energy (hydroelectric, solar energy, heat pumps, gas, solid and liquid fuel) education and training, recreation and reclamation (USEPA and USDA-NRCS, 1995; Vymazal et al., 1998a).

Perhaps one of the most important but least understood functions of wetlands is water quality improvement. These systems may well be considered “natural purifiers of water” as they provide an effective treatment for many kinds of water pollution (Hammer and Bastian, 1989; Kadlec and Knight, 1996). In fact, a capacity has already been recognized in wetlands to efficiently reduce or remove large amounts of pollutants from point sources (e.g. municipal and certain industrial effluents) as well as nonpoint sources (e.g. mining, agricultural and urban runoff) including organic matter, suspended solids, excess of nutrients, pathogens, metals and other micropollutants (Hammer and Bastian, 1989).

This pollutants removal is accomplished by the interdependent action of several physical, chemical and biological processes which include sedimentation, filtration, chemical precipitation, sorption, biodegradation, plants uptake among others. The mechanisms and the interdependences among the wetlands components (water, substrate and biota) are complex and not yet entirely understood, although some progresses have been achieved in the latest years as the awareness to the water depurative functions of wetlands becomes more widespread.

The hydrology of the sites, the soil and the biota (vegetation and microorganisms) are reportedly the main factors influencing water quality in wetlands.

2.3. Factors influencing water quality

The hydrological cycle emerges with an underlying major role as it influences the type of vegetation, microbial activity and biogeochemical cycling of nutrients in soil. Indeed, the biotic status of a wetland is intrinsically linked to the hydrological factors, which affect the nutrient availability as well as physicochemical parameters 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 (Mitsch and Gosselink J.G., 2000; Kivaisi, 2001).

Soil is one of the most important physical components of natural wetlands. Physical and chemical characteristics of the soil can greatly influence the type of wetland plants that will be prevalent over its surface and the microbial populations that will live on the soil phase. In addition, soil characteristics such as acid-base properties, redox potential and sorption capacity will also determine the type of physical-chemical processes occurring within the aqueous medium that can be responsible for the removal of certain types of pollutants, with a major impact in water quality.

Macrophytes are the dominant vegetation in wetlands. These plant species are typically adapted to water saturated conditions and are able to persist in anaerobic soil conditions as a result of high water content. Compared with the vegetation of well-drained soils, wetland plants have a worldwide similarity which overrides climate and is imposed by the common characteristics of a free water supply and the abnormally hostile chemical environment which plant roots must endure. It is not surprising that plants regularly found in wetlands have evolved functional mechanisms to deal with the environmental stresses.

Virtually all wetland plants have elaborate structural mechanisms to avoid root anoxia. Rhizosphere oxygenation is considered essential for active root function, and also enables the plants to counteract the effects of soluble phytotoxins, including sulfides and metals, which may be present at high concentrations in anoxic substrates.

Microorganisms play a central role in the biogeochemical transformations of nutrients (Cooper et al., 1996; Vymazal et al., 1998b; Stottmeister et al., 2003; Vymazal, 2007), and the metabolism of organic compounds including even some xenobiotic compounds (Machate et al., 1997; Stottmeister et al., 2003). There is a close interdependence between microorganisms and vegetation. Much of the plants nutrients are the result of the mineralization of more complex compounds by the microorganisms, whereas the activity of the latter is stimulated by enzymes released in root exudates. The aerobic conditions provided by the plants in their rhizosphere will also be determinant for the type of microbial populations and bioprocesses available in this region.

The conjugation of all these factors and interactions between different wetlands components and their associated processes lead to essentially different abilities to interact with water pollutants by different types of wetlands. An overview of the abilities by different types of natural wetlands to cope with various non-point pollution problems along with a summary of each wetland type characteristics is presented in table 1.

Table 1. Characteristics of different types of natural wetlands and their ability to retain non-point source pollutants (IETC-UNEP, 1999)

Type of Wetland	Characteristics	Ability to retain non-point source pollutants
Wet meadows	Grassland with waterlogged soil; standing water for part of the year	Denitrification only in standing water; removal of nitrogen and phosphorus by harvest
Fresh water marshes	Reed-grass dominated, often with peat accumulation	High potential for denitrification, which is limited by the hydraulic conductivity
Forested wetlands	Dominated by trees, shrubs; standing water, but not always for the entire year	High potential for denitrification and accumulation of pollutants, provided that standing water is present
Salt water marshes	Herbaceous vegetation, usually with mineral soil	Medium potential for denitrification; harvest possible
Bogs	A peat-accumulating wetland with minor flows	High potential for denitrification but limited by small hydraulic conductivity
Shoreline wetlands	Littoral vegetation of significant importance for lakes and reservoirs	High potential for denitrification and accumulation of pollutants, but limited coverage

In spite of the general abilities for water depuration that can be observed for typical wetland configurations, it is very difficult to predict responses to water pollution by natural wetlands and to translate their behavior from one geographical area to another due to the extreme variability of the functional components that characterizes them. Therefore, natural wetlands can not be viewed as a systematic approach to wastewater treatment. Only in a controlled environment provided by constructed wetlands, can such treatment work in a reliable and reproducible manner.

2.3. Natural wetlands preservation through the construction of artificial wetlands

Currently, in many countries, natural wetlands are protected areas, thus meaning that wastewater application is not permitted. Although studies have shown that natural wetlands are able to provide high levels of wastewater treatment (Hammer and Bastian, 1989), there is concern over possible harmful effects of toxic compounds and pathogens in wastewaters and a long term degradation of wetlands due to additional nutrient and hydraulic loadings from wastewater. These potential benefits and concerns have promoted a growing interest in the use of artificial wetlands for wastewater treatment (USEPA and USDA-NRCS, 1995).

While the application of wastewater to natural wetlands is becoming a deprecated practice worldwide, studies conducted on these systems have led to both a greater understanding of the processes involved in pollutant assimilation and removal as well as suggesting the design of new natural water treatment systems where these water depuration capabilities would be imitated and improved (Vymazal et al., 1998a). Using the knowledge and the experience with the assimilative capacity of natural wetlands, the construction of man-made wetland systems (constructed wetlands) for wastewater treatment has therefore been proposed. The functional role of wetlands in improving water quality, thus, becomes a compelling argument for the preservation of natural wetlands and in recent years the construction of wetlands systems for wastewater treatment.

Constructed wetlands can be built with a much greater degree of control, using a well-defined composition of substrate, type of vegetation, and flow pattern. In addition, constructed wetlands offer several additional advantages compared to natural wetlands including site selection, flexibility in sizing and, most importantly, control over the hydraulic pathways and retention time (Brix, 1993).

3. Constructed wetlands systems

Recent concerns over wetlands losses have generated a need for creation of wetlands, which are intended to emulate the functions and values of natural wetlands that have been destroyed. Such CWS can be defined as a designed and man-made complex of saturated substrates, emergent and/or submergent vegetation, animal life, and water that simulates natural wetlands for human use and benefits (Hammer and Bastian, 1989). Artificial wetlands are engineered or constructed for one or more of the following purposes as indicated by specific descriptive terminology (Kadlec and Knight, 1996; Sundaravadivel and Vigneswaran, 2001):

creation of wetland habitats to compensate for natural wetlands which have been converted for agriculture and urban development (or help offset their rate of conversion) and hence to conserve native flora and fauna including aquatic plants, fish, water birds, reptiles, amphibians and invertebrates (Constructed habitat wetlands)

- flood control facility (Constructed flood control wetland)
- production of food and fiber (Constructed aquaculture wetlands) and
- water quality improvement and wastewater treatment system (Constructed treatment wetlands).

Although CWS are being developed in many parts of the world for various functions, their wastewater treatment capabilities have attracted research efforts for a wide range of treatment applications including domestic wastewaters (Hammer and Bastian, 1989; Cooper et al., 1996; Vymazal et al., 1998a; Kivaisi, 2001; Cooper, 2001; Cameron et al., 2003; Hench et al., 2003; Solano et al., 2004), urban storm-water (Livingston, 1989; USEPA, 1993; Scholes et al., 1998; Carleton et al., 2001; Kohler et al., 2004), agricultural wastewaters (Carty et al., ; Hammer et al., 1989; Cronk, 1996; Knight et al., 2000), landfill leachates (Barr and Robinson, 1999; Nivala et al., 2007), acid mine drainage (Brodie et al., 1989; Ledin and Pedersen, 1996; Sobolewski, 1999) and for polishing advanced treated municipal wastewater for return to freshwater resources. CWS are also used for treating eutrophic lake waters (D'Angelo and Reddy, 1994; Coveney et al., 2002) and for conservation of nature (Hammer and Bastian, 1989; Brix, 1993). For the specific use of wastewater treatment, the systems are also denominated constructed treatment wetland systems (CTWS) and can be defined as engineered systems that have been designed and constructed to utilize the natural processes involving wetland vegetation, soils and their associated microbial assemblages to assist in treating wastewater (Vymazal, 1998; Vymazal, 2005a). CTWS are designed to take advantage of many of the same processes that occur in natural wetlands, but do so within a more controlled environment.

The first experiments aimed at the possibility of wastewater treatment by wetland vegetation were conducted in the 1950’s by Seidel at the Max Planck Institute in Plön, Germany (Seidel, 1955). During the following two decades, in the 1960’s and 1970’s, Seidel proceeded with numerous experiments on the use of wetland plants for treatment of various types of wastewater (Vymazal et al., 1998a). However, it was not before over 20 years of research that the first operational full-scale constructed wetland for municipal wastewater was built in Europe, in Othfresen, Germany (Vymazal et al., 1998a). Meanwhile, research efforts in the U.S. were developing during the 1970’s and 1980’s. Some systems were installed in the 1970’s with an increasing number in the 1980’s. The 1990’s saw a major increase in the number of these systems as the application expanded for use not only to treat municipal wastewater, but also urban stormwater, industrial, mining and agricultural wastewaters. CWS have since been constructed and used all around the world to treat a wide variety of types of wastewater. A list documenting the history of the first uses (both experimental and operational) of macrophytes and/or CWS for the treatment of different types of pollution up until the first half of the 1990’s was compiled and presented by Vymazal (1998a).

The number of CWS in use has very much increased in the most recent years. The use of CWS in the United States, New Zealand and Australia is gaining rapid interest. Most of these systems are used for tertiary treatment from towns and cities, usually using surface-flow systems to remove low concentrations of nutrients (N and P) and suspend solids. Conversely, in European countries, these CWS are usually used to provide secondary treatment of domestic sewage for village populations. These constructed wetland systems have been seen as an economically attractive and energy-efficient way of providing high standards of wastewater treatment.

3.1. Advantages and limitations of CWS

Constructed wetlands systems offer effective and a reliable treatment to wastewater in a simple and inexpensive manner. Its application for wastewater treatment offers many advantages in comparison to more conventional wastewater treatment technologies (USEPA and USDA-NRCS, 1995; USEPA, 2000; Sundaravadivel and Vigneswaran, 2001; Haberl et al., 2003). Constructed wetlands:

- can often be less expensive to build than other treatment options;
- can be built and operated simply;
- utilize natural processes;
- their operation and maintenance expenses (energy and supplies) are low;

- their operation and maintenance require only periodic, rather than continuous, on-site labor;
- are able to tolerate fluctuations in flow, (tolerate fluctuations in flow and pollutant concentrations);
- are able to treat wastewaters with very different constituents and concentration;
- are characterized by a high process stability (buffering capacity);
- are characterized by low excess sludge production;
- facilitate water reuse and recycling.

Additionally, constructed wetlands (USEPA and USDA-NRCS, 1995; USEPA, 2000; Sundaravadivel and Vigneswaran, 2001; Haberl et al., 2003):

- provide habitat for many wetland organisms;
- can be built to fit harmoniously into the landscape;
- provide numerous benefits in addition to water quality improvement, such as wildlife habitat and the aesthetic enhancement of open spaces;
- provide recreational and educational opportunities;
- are an "environmentally sensitive" approach viewed with favor by the general public.

However, there are also some limitations to the use of CWS in treating wastewater (USEPA and USDA-NRCS, 1995; USEPA, 2000; Sundaravadivel and Vigneswaran, 2001):

- they generally require large land area for the same level of treatment by conventional systems making them unsuitable for the treatment for sources that generate large quantities of wastewater, such as large cities;
- they may be relatively slow to provide treatment compared to more conventional treatment technologies;
- performance may be less consistent than in conventional treatment, CW depend on climate and, thus, may have reduce efficiencies during colder seasons;
- they require long period, typically two or three plant growing seasons, for the vegetation before optimal treatment efficiencies are achieved;

- the process dynamics of the CWS are yet to be clearly understood leading to imprecise design and operating criteria;
- these systems typically lie outdoor and spread over large area, their performance is susceptible to storm, wind, and floods;
- they require a base flow of water, they can tolerate temporary water level drawdowns, but not complete drying;
- there may provide breeding grounds for mosquitoes and other pests, though proper design can reduce this problem;
- long-term maintenance may be required;
- the biological components are sensitive to toxic pollutants;
- contaminant accumulation must be monitored to maintain ecological health of the system

3.2. Types of CWS

The basic CWS classification is based on the type of water flow regime. Depending on the level of water column with respect to the substrate bed, two general forms of CWS are used in practice:

- free water surface (FWS) wetlands (also called surface flow (SF) wetlands or aerobic wetlands), and
- subsurface flow (SSF) wetlands (also known as vegetated submerged bed (VSB) systems).

FWS closely resemble natural wetlands in appearance because they contain aquatic plants that are free floating or rooted in a soil layer on the bottom of wetland. In this type of CWS the water flows horizontally through the leaves and stems of the plants, above the substrate (figs. 1A, 1B & 1C). The near-surface layer of water is aerobic while the deeper waters and the substrate are usually anaerobic (USEPA and USDA-NRCS, 1995).

Free water wetlands can further be sub-classified according to the dominant type of macrophytes growing in the system. This type of wetland systems can be (Brix, 1993; USEPA and USDA-NRCS, 1995; Vymazal et al., 1998b; USEPA, 2000):

- a floating macrophyte system – these systems make use both of floating species that are rooted in the substrate (e.g. *Nymphae* spp *Nuphar* spp. (waterlilies), *Potamogeton natans* (pondweed), *Hydrocotyle vulgaris* (pennyworth)) and species which are free floating on water surface (e.g. *Eichhornia crassipes* (water hyacinth), *Lemna* spp., *Spirodella* spp. (duckweed));
- a submerged macrophyte system – the plants used in these systems have their photosynthetic tissue entirely submerged with the flowers being exposed to the atmosphere. Two types of submerged aquatics are usually recognized: the elodeid type (*e.g. Elodea* spp., *Myriophyllum aquaticum* (parrot feather), *Ceratophyllum* spp.) and the isoetid (rosette) type (*e.g. Isoetes*, *Littorella*, *Lobelia)*;
- a rooted emergent macrophyte system – these systems use plants which are the dominating form of life in the natural wetlands. Plants grow at well above the water level, producing aerial stems and an extensive root and rhizome system. These comprise species like the *Phragmites australis* (common reed), *Thypha* spp. (cattails), *Scirpus* spp. (bulrushes), *Iris* spp. (blue and yellow flags) *Juncus* spp. (rush), *Saggitaria latifolia* (duck potato), *Phalaris arundinocea* (reed canary grass), *Carex* spp. (Sedges), *Zizania aquatica* (wild rice), *Eleocharis* spp. (Spikerushes) and *Glyceria* spp. (mannagrasses).

On the contrary, SSF do not resemble natural wetlands because they do not have standing water; they are constructed with a substrate (usually small rocks, gravel, sand or soil) which has been planted with aquatic plants, and the wastewater flows beneath the surface of the support matrix but in contact with the plants roots (USEPA and USDA-NRCS, 1995; Vymazal et al., 1998a). SSF systems (which, by definition, must be planted with emergent macrophytes) can be sub-classified according to their water flow patterns (figs. 1D & 1E). (Cooper et al., 1996; Vymazal et al., 1998a):

- horizontal SSF systems
- vertical SSF systems (upstream or downstream characteristics)
- hybrid systems

In the horizontal SSF (fig. 1 D) the wastewater is fed in at the inlet and flows slowly through the porous medium under the surface of the bed in a more or less horizontal path (the bottom of the bed will actually have a slight slope to induce the liquid flow) until it reaches the outlet zone where it is collected before leaving via level control arrangement at the outlet. During the passage the wastewater will come into contact with a network of aerobic, anoxic and anaerobic zones. The aerobic zones occur around roots and rhizomes that leak oxygen into the substrate.

In vertical SSF (fig. 1 E) wastewater is applied through different arrangements of wastewater feeding and collection mechanisms to maintain a vertical direction of flow, either descending or ascending, through the substrate. This is achieved either by intermittent wastewater application or by burying inlet pipes into the bed at a depth of 60 to 100 cm. Since the wastewater infiltrates through the substrate bed, this type of wetlands are also called “infiltration wetlands”.

Hybrid systems comprise vertical-flow (vertical SSF) and horizontal-flow (horizontal SSF) systems arranged in a staged manner. There are as yet few of these systems in operation and it is perhaps too early to decide which is the best arrangement.

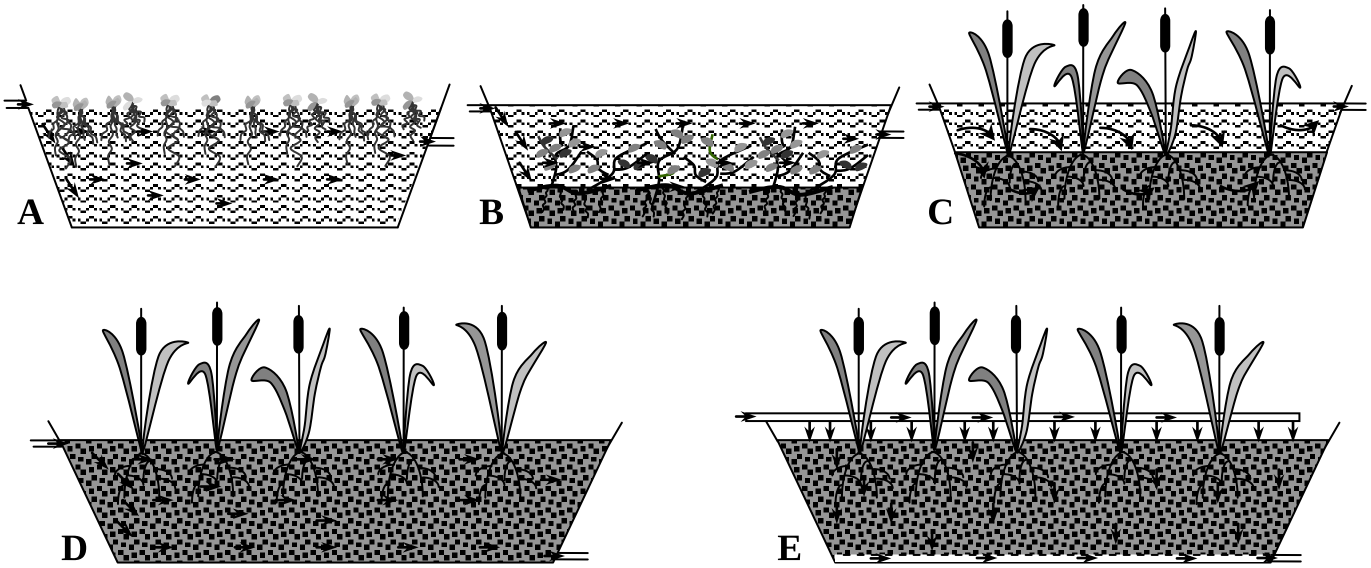

Figure 1. Different types of CWS (**A**, FWS with free-floating plants; **B**, FWS with submerged plants; **C**, FWS with emergent plants; **D**, Horizontal SSF; **E**, Vertical SSF)

The SSF type of wetland is thought to have several advantages over the FWS (USEPA and USDA-NRCS, 1995; USEPA, 2000). SSF wetlands show, in general, higher contaminant removal efficiencies than FWS wetlands per unit area of land occupation. In SSF wetlands the substrate provides more surface area for the development of microorganisms which in part is responsible for its increased efficiency. This may allow a smaller area occupation requirement for SSF wetlands in comparison with FWS, in order to achieve a particular level of treatment. As the water surface in a SSF is below the support matrix surface there is also little risk of odors and insect vectors which are associated with the standing wastewaters of the FWS as well as a minimal risk of public or animal exposure. The accumulation of plant debris in the surface of the SSF can additionally provide some thermal protection in colder climates. Percolation of the wastewater through the substrate in the SSF systems also provides faster depuration with the respect to the organic pollutants and nutrients (USEPA and USDA-NRCS, 1995; USEPA, 2000). In table 2 a comparison of the advantages and disadvantages for each type of constructed wetlands, according to water flow, is presented.

Table 2. Advantages and disadvantages of free water surface and subsurface flow wetlands (adapted from Halverson (2004))

Free water surface wetland	
Advantages	Disadvantages
• Less expensive to construct and operate and simpler to design than SSF wetlands and conventional treatment methods • Can be used for wastewater with higher suspended solids content • Offer greater flow control than SSF wetlands • Offer more diverse wildlife habitat • Provides habitat for plants and wildlife	• Lower rates of contaminant removal per unit of land than SSF wetlands, thus they require more land to achieve a particular level of treatment than SSF wetlands • Requires more land than conventional treatment methods • Risk of ecological or human exposure to surface-flowing wastewater • May be slower to provide treatment than conventional treatment • Odor and insects may be a problem due to the free water surface
Subsurface flow wetland	
Advantages	Disadvantages
• Higher rates of contaminant removal per unit of land than FWS wetlands, thus they require	• Requires more land than conventional treatment methods

less land to achieve a particular level of treatment than FWS wetlands	• May be slower to provide treatment than conventional treatment
• Lower total lifetime costs and capital costs than conventional treatment systems	• More expensive to construct than FWS wetlands on a cost per acre basis
• Less expensive to operate than FWS systems	• Waters containing high suspended solids may cause plugging
• More accessible for maintenance because there is no standing water	
• Odors and insects not a problem because the water level is below the media surface	
• Provides habitat for plants and wildlife	
• Minimal ecological risk due to absence of an exposure pathway	

There are more than twice as many FWS systems in the United States than SSF systems (Halverson, 2004). In Europe SSF systems outnumber FWS systems. In general, FWS wetlands require more land to achieve the same pollution reduction as SSF wetlands, but are easier and cheaper to design and build (USEPA, 1993; USEPA and USDA-NRCS, 1995).

The SSF technology is based on the work of Seidel (Seidel, 1955). Since then the technology has grown in many European countries and is nowadays applied worldwide.

3.3. CWS components

Constructed wetlands are engineered systems of wastewater treatment that are designed and constructed to utilize the natural processes that occur in natural wetlands. A constructed wetland consists of a properly-designed basin that contains soils or other selected substrate, water column, and wetland vegetation, as the main elements. Other important components that assist in the treatment of the wastewater, such as the communities of microorganisms, develop naturally. The concerted action of all these components (substrate, macrophytes and microbial population adapted to the wastewater toxicity) through a variety of chemical, physical and biological processes, is responsible for the depuration of wastewaters achieved in a CWS (fig. 2).

Aquatic plants play a central role in the depuration mechanisms occurring in a CWS as they provide support for and stimulate the microorganisms' growth and, as well, promote the removal of a variety of pollutants by their adsorption, uptake or phytodegradation. Their role in the direct degradation and uptake of organic pollutants, in particular xenobiotics of anthropogenic origin, is not as important as the microorganisms' action, but in many cases is still very significant. Microorganisms have, in fact, the major role in the biodegradation of this type of contaminants, through their metabolic transformations. In addition, they also have a participation in the removal of some inorganic compounds such as in the nitrogen cycle.

In the case of a SSF wetland, the substrate component is also fundamental not only because it provides the physical support for the macrophytes and microorganisms development but also since it can promote a series of chemical and physical processes which additionally contribute to the decontamination the polluted wastewater.

3.4. Pollutant removal processes

A number of physical, chemical and biological processes operate concurrently in constructed and natural wetlands to provide the removal of contaminants (Figure 2).

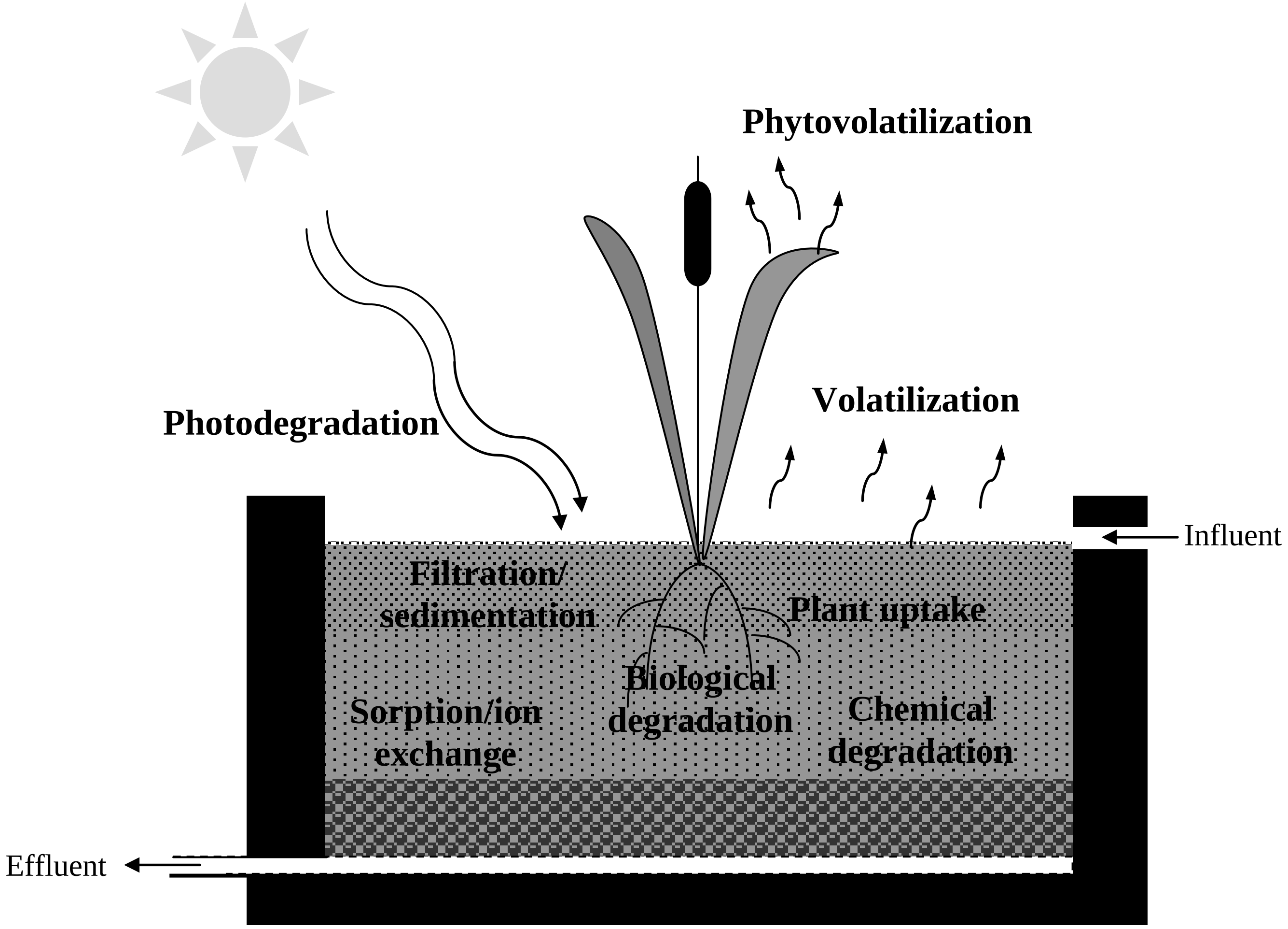

Figure 2. Summary of the major physical, chemical and biological processes controlling pollutant removal in CWS

These processes include, among others, sedimentation, plant uptake, microbial degradation, sorption, precipitation and volatilization. Removal of pollutants from water may be accomplished through storage in the wetland substrate and vegetation, or through losses to the atmosphere. A basic understanding of how these processes operate in wetlands is extremely helpful for assessing the potential applications, benefits and limitations of CWS.

3.4.1. Physical processes

CWS are capable of providing highly efficient physical removal of pollutants associated with particulate matter in the wastewater through sedimentation and filtration. Physical pollutant removal processes in wetland systems occur mainly due to the presence of plant biomass and, in the case of SSF wetlands, also to the substrate media.

Sedimentation of suspended solids is promoted by the low flow velocity and by the fact that the flow is often laminar in wetlands. The pathways of wastewater are retarded in a CWS due to the resistance to flow provided by vegetation, which thereby enhances sedimentation of suspended solids. In addition to serving as sediment traps, a primary role in suspended solids removal by floating plants is also to limit re-suspension of settled particulate matter. On the other hand, the media acts as filter beds, similarly as in filtration processes, and in this manner contribute to the physical removal of suspended solids through straining.

Volatilization, which involves diffusion of a dissolved compound from the water into the atmosphere, is another potential means of contaminant removal in wetlands. Some of the simpler inorganics resulting from mineralization (such as ammonia) and many types of organic compounds are volatile, and are readily lost to the atmosphere from wetlands and other surface waters. Although volatilization can effectively remove certain contaminants from the water, it may prove to be undesirable in some instances, due to the potential for polluting the air with the same contaminants and, subsequently, contaminate neighboring areas through rainfall or dustfall.

3.4.2. Chemical processes

A wide range of chemical processes are involved in the removal of contaminants in wetlands. The most important chemical removal processes in wetland soils are sorption and precipitation. Other chemical processes such as redox reactions, hydrolysis and complexation, can result in transformations of the pollutants which can be accessory to removal either through precipitation or adsorption. Processes such as photolysis and ionic exchange with mineral components of the substrates can also contribute to the removal of some particular classes of pollutants.

Sorption refers simultaneously to both adsorption and absorption phenomena, and the term is used whenever the extent to which each phenomenon is responsible for the compound's removal is not clear or well defined. These chemical processes occur at the surfaces of plants roots and substrate, resulting in a short-term retention or long-term immobilization of the contaminants.

The sorption process is influenced by characteristics of the substrate, such as its texture, content in organic matter and ion exchange properties, by characteristics of the wastewater, such as its dissolved organic matter content, pH and electrolyte composition, and by the properties of the pollutant itself. In the case of pollutants with acid-base properties, the pH in the liquid compartment will determine the form (ionic or neutral) in which they will be present in solution and this aspect may have a strong influence over the extent of sorption to mineral surfaces with ion exchange properties.

Complexation phenomena can also contribute, in some cases, to increase the solubility of some pollutants or, in other cases, to facilitate binding of pollutants to a mineral surface.

Precipitation is also a major process leading to long-term removal of pollutants. The extent of these processes is frequently dependent on pH and redox conditions. Hydrolysis very often leads to the formation of insoluble oxides and hydroxides, while changes in protonation states are a frequent means of converting soluble ionic forms of a compound into a neutral insoluble form. Precursor redox reactions are also commonly associated with precipitation phenomena through the conversion between more soluble oxidation states into oxidation states that easily lead to formation of insoluble compounds. In addition, sorption is a process which, in some cases, also is accessory to co-precipitation phenomena.

3.4.3. Biological processes

CWS are biological systems in which biological processes play a major role in removal of pollutants. Probably the most widely recognized biological process for inorganic pollutant removal in wetlands is plant uptake. Contaminants that are also forms of essential plant nutrients, such as nitrate, ammonium and phosphate, are readily taken up by wetland plants. However, many wetland plant species are also capable of uptake and even significant accumulation of, certain toxic metals such as cadmium and lead. The rate of contaminant removal by plants varies widely, depending on plant growth rate and concentration of the contaminant in plant tissue.

In wetlands, as in many terrestrial ecosystems, when the plants age and die, the dead plant material, known as detritus or litter, is deposited at the substrate surface. Some of the nutrients, metals or other elements previously removed from the water by plant uptake are lost from the plant detritus by leaching and decomposition, and recycled back into the water and solid media. Water-soluble contaminants are leached more rapidly upon the death of the plant or plant tissue, while a more gradual loss of contaminants occurs during decomposition of detritus by bacteria and other organisms. The recycled contaminants may be flushed from the wetland in the surface water, or may be removed again from the water by biological uptake or other means.

Although microorganisms may also provide a measurable amount of contaminant uptake and storage, it is their metabolic processes that play the most significant role in the decomposition of organic compounds through the transformation of complex molecules into simpler ones. This provides an important biological mechanism for removal of a wide variety of organic compounds, including those found in municipal and industrial wastewater. The efficiency and rate of organic C degradation by microorganisms is highly variable for different types of organic compounds.

Microbial metabolism also affords, in wetlands, for the removal of inorganic nitrogen, i.e., nitrate and ammonium, ultimately resulting in the release of nitrogen gas, in the form of N_2, which is subsequently lost to the atmosphere. The coupled processes of nitrification and denitrification are universally important in the cycling and bioavailability of nitrogen in wetland and upland soils (Vymazal, 2007).

An understanding of the basic physical, chemical and biological processes controlling contaminant removal in wetlands will substantially increase the probability of success of treatment wetland applications. Furthermore, a working knowledge of biogeochemical cycling, the movement and transformation of nutrients, metals and organic compounds among the biotic (living) and abiotic (non-living) components of the ecosystem, can provide valuable insight into overall wetland functions and structure. This level of understanding is useful for evaluating the performance of contaminant removal by constructed wetlands and for assessing the functional integrity of human-impacted, restored and mitigation wetlands.

A more detailed discussion follows, describing the mechanisms studied that are involved in contaminant removal by CWS, for each of the most important types of water contaminants.

4. Mechanisms of pollutants removal by CWS

Wetlands have been found to be effective in treating organic matter, suspended solids and nutrients as well as for reducing metals, trace organic pollutants and pathogens. The main pollutants removal mechanisms in CWS include biological processes such as microbial metabolic activity and plant uptake as well as physical and chemical processes such as volatilization, sedimentation, filtration, adsorption and precipitation at the water-substrate, root-substrate and plant-water interfaces.

The following table provides an overview of the major pollutant removal mechanisms that operate in the wetland environment, which are responsible for the removal/reduction of wastewater contaminants.

Table 3. Pollutant removal mechanisms (Brix, 1993; Cooper et al., 1996; Vymazal et al., 1998b; Sundaravadivel and Vigneswaran, 2001)

Wastewater pollutant	Removal mechanism
Total Suspended Solids (TSS)	• Sedimentation

	• Filtration
Soluble Biodegradable Organic Matter (measured as BOD)	• Microbial degradation (aerobic, anoxic and anaerobic) • Adsorption • Plant uptake
Nutrients:	
Nitrogen (N)	• Ammonification (mineralization) • Nitrification/ denitrification • Nitrate-ammonification • Plant/microbial uptake • Media adsorption/ion exchange • Ammonia volatilization • ANAMMOX
Phosphorus (P)	• Media adsorption • Plant and microbial uptake • Sedimentation • Precipitation
Metals	• Adsorption and cation exchange • Complexation • Precipitation/co-precipitation • Oxidation and hydrolysis • Plant uptake • Microbial oxidation/reduction (microbial-mediated processes) • Sedimentation and filtration
Pathogens (microbial population)	• Sedimentation • Filtration • Natural die-off • Predation • UV irradiation • Excretion of antibiotics form roots by roots of macrophytes • Adsorption
Organic xenobiotics	• Sedimentation • Volatilization • Biodegradation • Adsorption • Plant uptake • Photolysis • Chemical reactions

Constructed wetlands should be engineered to maximize the particular removal mechanisms required for the treatment of a given wastewater. A good understanding of the complex mechanisms involved in the removal of the different types of pollutants present in the wastewater is therefore essential for the design and operation of any CWS.

4.1. Suspended solids removal

Municipal and some industrial effluents usually contain large quantities of suspended solids. Excessive amounts of this suspended particulate matter may cause adverse effects such as reducing the light available to photosynthetic organisms. On settling, it may also alter the characteristics of the river bed, potentially making it a less suitable habitat for the local organisms. However, this problem is amongst the most readily solvable ones of wastewater treatment, and is usually very efficiently addressed in a CWS. A brief review of the literature data reveals usually very high values reported for the removal of suspended solids independently of the CWS type, with efficiencies usually above 90% (Vymazal et al., 1998a; Gómez Cerezo et al., 2001; Merlin et al., 2002; Ansola et al., 2003; Cameron et al., 2003; Mantovi et al., 2003).

In a CWS the major mechanisms responsible for removal of settleable suspended solids are sedimentation and filtration. Non-settling/colloidal solids are removed, at least partially, by bacterial growth (which results in the settling of some colloidal solids and the microbial decay of others) and collisions with the adsorption to other solids (Vymazal et al., 1998b).

In FWS systems suspended solids are removed in part by sedimentation, enhanced by very low flow velocities and shallow depths, and in part by filtration through the living vegetation and vegetative litter. Additional removal of solids also occurs at the soil interface (Metcalf and Eddy, 1991).

In SSF systems, suspended solids are removed primarily by filtration through the substrate. Thus, there is a tendency for solids to clog or seal the infiltrative surface of the systems. These systems must, then, be designed and operated to minimize loss of infiltrative capacity (Metcalf and Eddy, 1991). In most applications, a sedimentation pond is added upstream of the wetland cells to promote the removal of larger suspended particles and minimize the chance of clogging the wetland cells. The pond can also dilute the raw influent if it is considered too strong. These TSS treatment processes also contribute to a significant portion of the removal of organic matter, nutrients (mostly nitrogen and phosphorus) and pathogens. In SSF systems, the high removal efficiencies of suspended matter have, in some cases, also shown to be less sensitive to seasonal conditions (Merlin et al., 2002).

Frequently, removal of suspended solids is observed to occur mainly within the early stages of treatment (Vymazal et al., 1998a; Gómez Cerezo et al., 2001; Merlin et al., 2002).

4.2. Soluble organic matter

The biochemical oxygen demand (BOD), which indirectly quantifies the amount of biodegradable organic matter, provides a broad measure of the effects of organic pollution on a receiving water body.

In general the origins of organic effluents and their composition are extremely diverse and one can expect a similar diversity in the effects they have on receiving waters. Domestic effluent is the greatest source of organic materials discharged to fresh waters. In urban areas, the run-off from houses, factories and roads can also result in severe pollution, especially in storm conditions after periods of dry weather. Industrial effluents are a further source of organic pollution. These may be routed via the wastewater treatment works or they may be released, with or without treatment, directly into a waterway. Among the industries producing effluents containing substantial amounts of organic wastes are the food processing and brewing industries, dairies, abattoirs and tanneries, textile and paper making factories and farms.

One of the major problems caused by effluents with high BOD loads occurs as organic matter is gradually decomposed by the microorganisms in a much similar way to the processes occurring in biological treatment processes in wastewater treatment plants. This microbial process, in which the more complex organic molecules are broken down into simple inorganic molecules, involves a considerable consumption of dissolved oxygen. When high loads of organic pollution are present, oxygen may be used at a higher rate than it can be replenished from the atmosphere or the photosynthetic activity of aquatic plants, thus causing its depletion with severe consequences for the water stream biota, including reduced fitness and, in extreme cases, asphyxiation (Mason, 2002). The sedimentation of organic waste at the bottom of streams may also alter its characteristics, with potential harmful effects to its biota.

A majority of operating CWS in the world are used for treatment of municipal wastewater in which organic substances constitute the prominent pollutants. Hence, a vast information bank is available on CWS performance of organic matter removal. Wetlands are efficient users of external carbon sources, which is manifested by good reductions in BOD (Hammer and Bastian, 1989; Vymazal et al., 1998b; Sundaravadivel and Vigneswaran, 2001).

Soluble degradable organic matter in wastewater is removed mainly through microbial degradation whereas uptake of degradable organic matter by macrophytes is negligible compared to biological degradation (Metcalf and Eddy, 1991).

The microorganisms responsible for the degradation are generally associated with slimes or films that develop on the surfaces of substrate particles, vegetation and litter (Metcalf and Eddy, 1991; Vymazal et al., 1998b).

Organic compounds may be degraded both aerobically and anaerobically and it is difficult to quantify the ratio between the two types (Ottova et al., 1997). The oxygen required for aerobic degradation is supplied directly from atmosphere by diffusion or oxygen leakage from the macrophyte roots into the rhizosphere.

The efficiency of organic matter removal in CWS is well documented in numerous reports in the literature. In table 4 a sample of some illustrative studies is presented.

Table 4. Organic matter (BOD) removal in several types of CWS

Type of CWS	Reduction rate	References
FWS (pilot-scale)	89%	(Chen et al., 2006)
Hierarchical Mosaic of Aquatic Ecosystems (HMAE®)	80-95%	(Ansola et al., 2003)
HSSF	86.6%	(Vymazal, 1999)
HSSF	≥ 90%	(Merlin et al., 2002)
HSSF	94%	(Mantovi et al., 2003)
HSSF (review)	85%	(Vymazal, 2005c)

SSF	75-79%	(Karathanasis et al., 2003)
Multi-stage system	90%	(Gómez Cerezo et al., 2001)
Set of single-family CW (review)	70%	(Steer et al., 2002)
VSSF	97%	(Haberl et al., 2003)
VSSF	96%	(Meuleman et al., 2003)
VSSF (pilot-scale)	> 98%	(Sleytr et al., 2007)

Soluble organic matter removal efficiency in CWS is generally high, usually exceeding 80%, but the efficiency of organic matter treatment does show some variation according to the CWS type. These differences are revealing of the dependence on several design and operational parameters including the type of CWS/vegetation/substrate, the hydraulic and mass loading rates, flow regime, hydraulic residence time, and BOD decay rate, which in turn is a function of temperature (Vymazal, 1999; Vymazal, 2005c). Because of the complexity of these interdependencies, different studies set up under different conditions are not easily comparable. For example, the role of the substrate and the rhizosphere in FWS systems is quite negligible compared with SSF, where long residence times allow extensive interaction with the wastewater.

While resilient, slow growing species with low seasonal biomass turnover, and high root zone aeration capacity may be suitable for FWSs, high productivity species, tolerant to high levels of pollutants and hypertrophic waterlogged conditions may be functionally superior in SSFs (Tanner et al., 1995).

Indeed, one aspect that has been controversial is the role of vegetation and the effects of different plant species as mono or polycultures in promoting treatment. Although some studies (Soto et al., 1999; Vymazal, 1999; Merlin et al., 2002) have documented that macrophytes can improve BOD removal from wastewaters by: i) enhancing sedimentation, ii) providing mechanical filtration, iii) providing nutrient assimilation, and iv) stimulating the microbial activity and its development; others did not detect any significant difference between planted and unplanted systems (Tanner et al., 1995).

Seasonal variations in BOD removal efficiency by CWS in the presence of various macrophytes species have been reported by several investigators, with consistent treatment deterioration being observed in late winter months (Kuehn and Moore, 1995). It is uncertain, however, whether the poor winter performances are due to cold temperatures alone or the combined effect with increased hydraulic loadings, because several other studies have not shown significant treatment effects between winter and summer (Neralla et al., 2000).

4.3. Nutrients removal

The major sources of nutrients pollution (primarily, sources of nitrogen and phosphorus) in water bodies are derived, in urban areas, from domestic wastewaters, industrial wastewaters and storm drainage whereas rural sources of nutrients include those from agriculture, from forest management and from rural dwellings.

Often, either nitrogen or phosphorus is the limiting factor in an aquatic system, and the addition of excess nutrients may cause eutrophication in rivers, streams, estuaries and coastal waters or other undesirable changes in the ecological community such as ammonia's toxicity to aquatic biota and problems caused by excessive levels of nitrates in drinking water which may be a public health issue.

The problems caused by excess of nutrients can also directly affect human activities and these problems can be summarized into three main areas: those associated with quality of water supply, those affecting aesthetic and recreational activities, and those causing difficulties with the management of water courses and lakes (Mason, 2002).

A wetland system offers excellent ecological possibilities to act as a sink for nutrients. Nutrient cycling in CWS includes pathways of nutrient transformation between several different forms and transfer between the different compartments such as water, substrate, litter, plants, etc.

4.3.1. Nitrogen removal in CWS

Nitrogen is a major component of most wastewaters and all nitrogen forms, including nitrogen gas (N_2), are biochemically interconvertible and are components of the nitrogen cycle. The dominant forms of nitrogen in wetlands that are of importance to wastewater treatment include organic nitrogen, ammonia, ammonium, nitrate, nitrite, and nitrogen gas.

The relative proportion of each depends on the type of wastewater and pre-treatment. Organic forms are present in dissolved and particulate forms, while inorganic N is present in dissolved forms. Particulate forms are removed though settling and burial, while the removal of dissolved forms is regulated by various biogeochemical reactions functioning in the substrate and water column (Fig. 3). Relative rates of these processes are affected by physico-chemical and biological characteristics of substrate, water column and vegetation type.

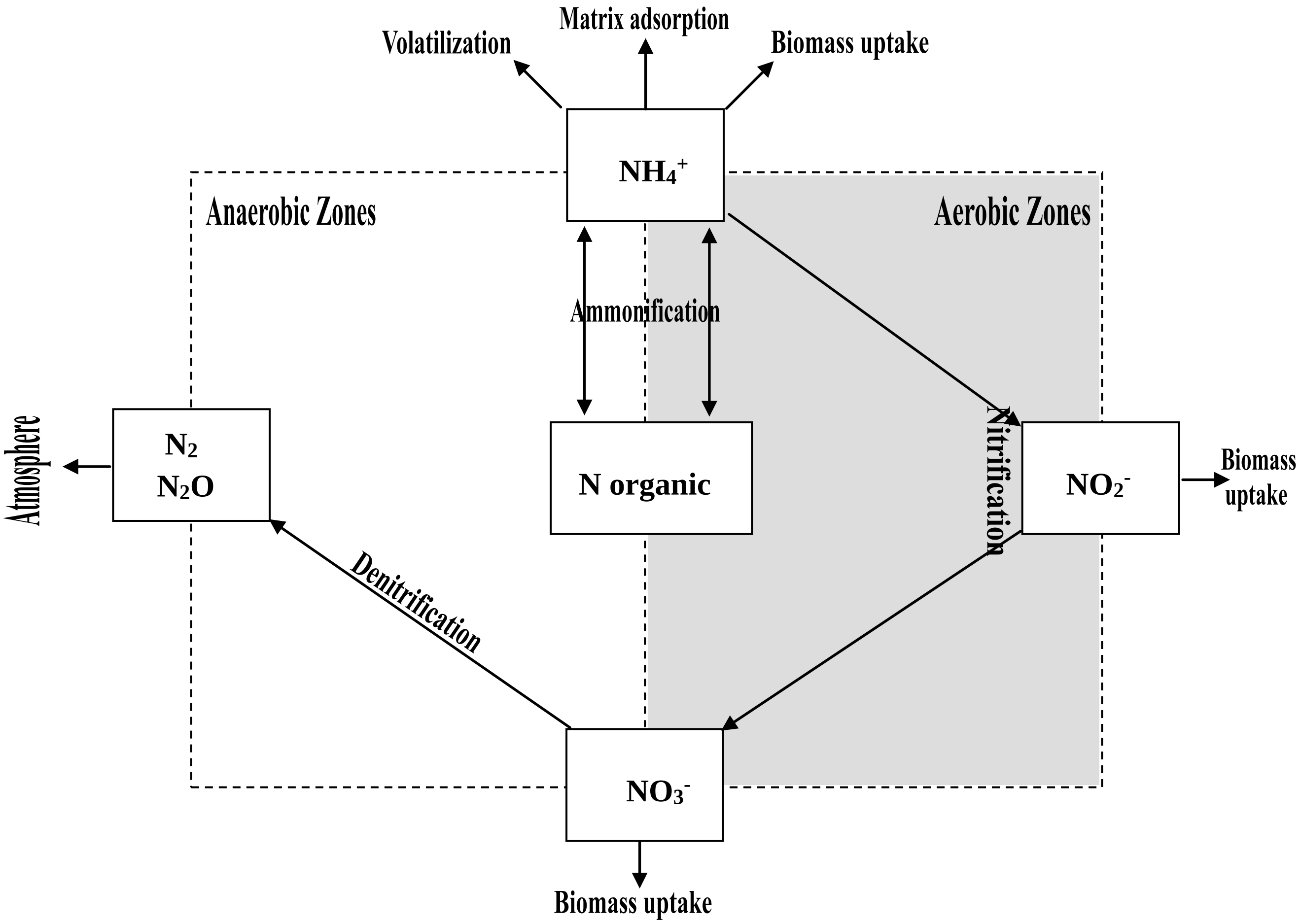

Figure 3. Nitrogen transformation/removal mechanisms in CWS (adapted from Cooper et al. (1996))

The transformation and removal of nitrogen in CWS involves a complex set of physical, chemical and biological processes (fig. 3). The mechanisms involved in the removal of nitrogen from wastewater depend on the major forms in which the nitrogen is present.

Mineralization, biological uptake, nitrification and nitrate reduction to ammonium are processes that transform one form of nitrogen to another (fig. 3). In terms of the nitrogen cycle, these mechanisms are conservative processes and operate to cycle nitrogen within a system. Denitrification and ammonia volatilization are export processes and result in the net loss of nitrogen from the system. Conversely, nitrogen fixation returns nitrogen from the atmosphere to the CWS.

4.3.1.1. Nitrogen conservative transformations

The major processes of nitrogen transformations which do not lead to nitrogen release from the system are enumerated in Table 5. The various forms of nitrogen are continually involved in chemical transformations from inorganic to organic compoundHs and back from organic to inorganic. All of these transformations are necessary for wetland ecosystems to function successfully, and most chemical changes are controlled through the production of enzymes and catalysts by the living organisms they benefit (Vymazal, 2007).

Table 5. The major nitrogen conservative transformations and retention processes in CWS (adapted from Vymazal (2007)).

Process	**Transformation**
Ammonification (mineralisation)	Organic-N → ammonia-N
Nitrification	Ammonia-N → nitrite-N → nitrate-N
Nitrate-ammonification	Nitrate-N → ammonia-N
Plant/microbial uptake (assimilation)	Ammonia-N, nitrite-N, nitrate-N → organic-N
Ammonia adsorption	
Organic nitrogen burial	

Ammonification (mineralization) – is the process where organic nitrogen is biologically converted into inorganic nitrogen, especially ammonium (Vymazal et al., 1998b; Vymazal, 2007). Ammonium is converted from organic forms through a complex biochemical process involving the catabolism of amino acids with a net release of energy (Vymazal, 2007). In some cases, this energy is used by microorganisms for growth, and ammonia is directly incorporated into microbial biomass (Vymazal, 2007).

The process can occur under aerobic or anaerobic conditions but, in comparison to facultative and obligate anaerobic mineralization, the contribution of aerobic mineralization to the overall N mineralization would be very small (Vymazal et al., 1998b).

A wide range of ammonification rates are reported in the literature, with values ranging between 0.004 and 0.53 g N m^{-2} d^{-1} (Reddy and D'Angelo, 1997; Tanner et al., 2002). Net release of NH_4^+ is determined by the balance between ammonification and immobilization (conversion of inorganic nitrogen ions into organic forms) which is controlled by the N requirements of microorganisms involved, nature of organic N, temperature, pH, redox conditions, C/N ratio, available nutrients concentration and substrate conditions such as texture and structure (Vymazal, 2007). The optimal ammonification temperature is reported to be 40–60 °C while optimal pH is between 6.5 and 8.5 (Vymazal et al., 1998b; Vymazal, 2007).

Nitrification – is usually defined as the biological oxidation of ammonium to nitrate with nitrite as an intermediate in the reaction sequence (Vymazal et al., 1998b; Vymazal, 2007). Nitrification is performed primarily by chemoautotrophic bacteria, which derive energy from the oxidation of ammonia and/or nitrite and carbon dioxide is used as a carbon source for synthesis of new cells (Vymazal et al., 1998b; Vymazal, 2007). The process consists of two main sequential steps (Vymazal et al., 1998b):

$$NH_4^+ + 3/2\ O_2 \rightarrow NO_2^- + 2\ H^+ + H_2O \qquad (1)$$

$$NO_2^- + 1/2\ O_2 \rightarrow NO_3^- \qquad (2)$$

$$NH_4^+ + 2\ O_2 \rightarrow NO_3^- + 2\ H^+ + H_2O \qquad (3)$$

The first step, the oxidation of ammonium to nitrite, is executed by strictly chemolithotrophic (strictly aerobic) bacteria which are entirely dependent on the oxidation of ammonia for the generation of energy for growth. In soil, species belonging to the genera *Nitrosospira*, *Nitrosovibrio*, *Nitrosolobus*, *Nitrosococcus* and *Nitrosomonas* have been identified (Vymazal et al., 1998b; Brady and Weil, 2002; Vymazal, 2007).

The second step in the process of nitrification, the oxidation of nitrite to nitrate, is performed by facultative chemolithotrophic bacteria, *Nitrobacter*, which can also use organic compounds, in addition to nitrite, for the generation of energy for growth (Vymazal, 2007).

Nitrification rates in wetlands were reported to be in the range of 0.01–2.15 g N m^{-2} d^{-1} with the mean value of 0.048 g N m^{-2} d^{-1} (Reddy and D'Angelo, 1997; Tanner et al., 2002). Nitrification is influenced by concentrations of ammonium-N, BOD concentration, temperature, pH value, alkalinity of the water, inorganic C source, moisture, microbial population, dissolved oxygen and potential for toxic compounds.

Nitrification is strictly an aerobic process in which the end product is nitrate; this process is limited when anaerobic conditions prevail.

Nitrate-ammonification – refers to a process of anoxic reduction of nitrate to ammonia. This is the first anoxic process to occur after oxygen depletion in the reduction of nitrate to molecular nitrogen or ammonia. This is performed by two different groups of nitrate-reducing bacteria: the denitrifying bacteria which produce N_2O and N_2 as major reduction products (denitrification), and the nitrate-ammonifying bacteria which produce NH_4^+ as the major end product of the reduction of nitrate (Vymazal, 2007).

The nitrate-ammonification rates is influenced by environmental factors such as absence of O_2, redox potential, temperature, pH value, organic matter, etc.

Nitrogen assimilation (plant/microbial uptake) – refers to a variety of biological processes that convert inorganic nitrogen forms into organic compounds that serve as building blocks for cells and tissues. The two forms of nitrogen generally used for assimilation are ammonium and nitrate nitrogen (Vymazal, 2007). Macrophyte growth is not the only potential biological nitrogen assimilation process in wetlands, microorganisms and algae also utilize nitrogen.

The potential rate of nutrient uptake and storage (standing stock) by plant is limited by its net productivity (growth rate) and the concentration of nutrients in the plant tissue. Therefore, desirable traits of a plant used for nutrient assimilation and storage would include rapid growth, high tissue nutrient content, and the capability to attain a high standing crop.

In the literature, there are many reviews on nitrogen concentrations in plant tissue as well as nitrogen standing stocks for plants found in natural stands and constructed wetlands (Mitsch and Gosselink J.G., 2000; Vymazal, 2007). However, if the wetland vegetation is not harvested, the vast majority of the nutrients that have been incorporated into the plant tissue will be returned to the water as result of decomposition processes.

Ammonia adsorption/ionic exchange – the reduced state ammoniacal N is stable but can be adsorbed onto active sites of the substrate. However, the ion exchange of NH_4^+-N on cation exchanging sites of the substrate is not considered to be a long-term sink for NH_4^+-N removal but rather is presumed to be rapidly reversible (Vymazal et al., 1998b).

In a continuous-flow system, under stable conditions, the sorbed NH_4^+-N will be in equilibrium with NH_4^+-N in solution. An intermittently loaded system will display rapid removal of NH_4^+-N by adsorption mechanisms and a gradual release during rest periods.

The rate and extent of these processes are reported to be influenced by several factors, such as nature and amount of clays, nature and amount of soil organic matter, periods of submergence and drying, and presence of vegetation.

Organic nitrogen burial – some fractions of the organic nitrogen incorporated in detritus in a wetland system may eventually become unavailable for additional nutrient cycling through the process of peat formation and burial. The values of organic nitrogen burial have been reported for various natural wetlands, however, in constructed wetlands there are practically no data available (Vymazal, 2007).

4.3.1.2 Removal/retention mechanisms

In addition to the processes just described, some of which actually remove nitrogen from the wastewater into some component of the wetland, further removal may consist of nitrogen release off the system through ammonia volatilization, denitrification and anaerobic ammonium oxidation. Conversely, normal operation of CWS may include the natural incorporation of nitrogen in the system through fixation.

Ammonia volatilization – is a physicochemical process where ammonium-N is in equilibrium with gaseous and hydroxyl forms (Vymazal et al., 1998b; Brady and Weil, 2002; Vymazal, 2007):

$$NH_4^+ + OH^- \rightarrow H_2O + NH_3 \qquad (4)$$

As can be seen, ammonia volatilization will be more pronounced at higher pH levels. These high pH values which facilitate volatilization are created during the day, in wetland, by the photosynthesis of submerged macrophytes and algae.

The volatilization rate is controlled by the NH_4^+ concentration in water, pH values, temperature, wind velocity, solar radiation, the nature and density of vegetation and the capacity of the system to change the pH value in diurnal cycles (absence of CO_2 increases volatilization).

The volatilization of ammonia in CWS can result in nitrogen removal rates as high as 2.2 g N m^{-2} d^{-1} (Stowell et al., 1981).

Denitrification – is a bacterial facilitated anoxic process of nitrate reduction that may ultimately produce molecular nitrogen (N_2) through a series of intermediate gaseous nitrogen oxide products. This respiratory process reduces oxidized forms of nitrogen in response to the oxidation of an electron donor such as organic matter (Brady and Weil, 2002).

The organisms that carry out this process are commonly present in large numbers and are mostly facultative anaerobic bacteria in genera, such as *Pseudomonas*, *Bacillus*, *Micrococcus* and *Achromobacter.* These denitrifying bacteria are chemoheterotrophs, which obtain their energy and carbon from the oxidation of organic compounds. Other organisms are autotrophs, such as *Thiobacillus denitrificans,* which obtain their energy from the oxidation of sulfide. The exact mechanisms vary depending on the conditions and organism involved (Brady and Weil, 2002).

It is generally agreed that the actual sequence of biochemical changes from nitrate to elemental gaseous nitrogen is (Vymazal, 2007):

$2\ NO_3^- \Rightarrow 2\ NO_2^- \Rightarrow 2\ NO \Rightarrow N_2O \Rightarrow N_2$ (5)

Environmental factors known to influence denitrification rates include the absence of O_2, redox potential, substrate moisture, temperature, pH value, presence of denitrifiers, substrate type, organic matter, nitrate concentration and the presence of overlying water (Vymazal, 2007).

The estimation of denitrification rates in CWS varies widely in the literature between 0.003 and 1.02 g N m^{-2} d^{-1} (Reddy and D'Angelo, 1997; Vymazal, 2007).

Denitrification is the predominant microbial process that modifies the chemical composition of nitrogen in a wetland system and the major process whereby elemental nitrogen is returned to the atmosphere.

Anaerobic ammonium oxidation (ANAMMOX) – is the anaerobic conversion of NO_2^- and NH_4^+ to N_2. It was demonstrated that in an ANAMMOX process, nitrate is used as an electron acceptor (Vymazal, 2007).

Not all the transformation/removal processes of nitrogen occur in all types of constructed wetlands and the magnitude of individual processes varies among types of CWS.

Volatilization may be a significant route for nitrogen removal in constructed wetlands with open water surface where algal assemblages can create high pH values during the day through their photosynthetic activity (Vymazal et al., 1998b; Vymazal, 2007).

Nitrification occurs in all types of CWS, however, the extent of this process is determined by oxygen availability. Nitrification takes place when oxygen is present in concentrations high enough to support the growth of strictly aerobic nitrifying bacteria. Nitrification *per se* is a limiting process for nitrogen removal from most types of CWS because ammonia is the dominant species of nitrogen in sewage and many other wastewaters (Vymazal, 2007). On the other hand, denitrification is considered as a major removal mechanism for nitrogen in most types of constructed wetlands (Vymazal, 2007). The concentrations of nitrate, however, are usually very low in wastewater (the exception is drainage water from the agriculture and some industrial wastewaters) which also limits the extent to which this process can occur. However, the coupling between the nitrification and denitrification processes provides the conditions for this to be the major nitrogen removal process in many treatment wetlands. Different requirements for the presence of oxygen for nitrification and denitrification are the major obstacle in many treatment wetlands for achieving higher nitrogen removal.

Nitrate-ammonification occurs under conditions of low redox potential values and, therefore, there is a potential that this process may be important in treatment wetlands where anaerobic conditions do occur, e.g., in treatment wetlands with horizontal sub-surface flow (Vymazal, 2007).

Ammonium adsorption is limited to CWS with sub-surface flow where the contact between substrate and wastewater is efficient.

In Table 6 are displayed the removals of various forms of nitrogen by different types of CWS which can be found in the literature.

The removal efficiency of several nitrogen forms in CWS is well documented in numerous reports in the literature. In table 6 a sample of some illustrative studies is presented.

Table 6 - Nitrogen removal in several types of CWS

Type of CWS	Reduction rate	References
Created wetland	97% (NO_3^-/NO_2^--N) 100% (NH_3-N)	(Kohler et al., 2004)
CWS (pilot scale)	85% (NO_2^--N) 88% (NO_3^--N) 13% (NH_4^+-N)	(Maine et al., 2007)
CWS (Single-family)	56% (NH_4^+-N)	(Steer et al., 2002)
FWS	53% (inorganic-N) 60% (NO_2^--N) 70% (NO_3^--N)	(Maine et al., 2006)
FWS (review)	41.2% (total-N) 55.1% (NH_4^+-N) 60.7% (NO_3^--N)	(Vymazal, 2007)
FWS	3 to 15% (total-N)	(Braskerud, 2002)
FWS (pilot-scale)	56% (NH_3-N)	(Chen et al., 2006)
Hierarchical Mosaic of Aquatic	98% (NH_4^+-N)	(Ansola et al., 2003)

Ecosystems (HMAE®)		
HSSF	50% (total-N) 79% (organic-N)	(Mantovi et al., 2003)
HSSF (review)	42% (total-N) 48% (NH_4^+-N) 35% (NO_3^--N)	(Vymazal, 2005c)
HSSF (review)	42.3% (total-N) 48.3% (NH_4^+-N) 38.5% (NO_3^--N)	(Vymazal, 2007)
Small-scale wetland mesocosms	55%(Kjeldahl-N)	(Hench et al., 2003)
VSSF	30% (total-N)	(Meuleman et al., 2003)
VSSF (review)	44.6% (total-N) 84.2% (NH_4^+-N)	(Vymazal, 2007)
VSSF (pilot-scale)	99.5 % (NH_4^+-N)	(Sleytr et al., 2007)

Due to the varied forms in which nitrogen may be present in a wastewater, several very different mechanisms will be operative in their transformation or removal. Furthermore, the efficiencies of the different mechanisms are very dependent on the particular conditions. As such, comparisons are quite difficult to establish among several studies and the reported total nitrogen removed will vary significantly.

The most effective removal of nitrogen results from volatilization of ammonia and the coupled nitrification-denitrification process with elimination of gaseous nitrogen. The absence of a free water surface in SSF systems is a limiting factor for the efficiency of the volatilization process in this type of systems, and thus the efficiency of this process may be considerable only in FWS. On the other hand, a single-stage system hardly provides both aerobic as well as anoxic zones for adequate nitrification and denitrification in simultaneity. Multi-stage systems have been suggested as possibly being able to improve the conditions for the coupled nitrification-denitrification process.

Some environmental conditions, such as temperature and dissolved oxygen also have a significant influence in the overall efficiencies.

Importance of harvesting in the case of nitrogen removal is not as critical as in other cases, for instance the removal of phosphorus.

4.3.2. Phosphorus removal in CWS

Phosphorus is another nutrient which, when available in excessive amounts, also causes eutrophication in water bodies. Removal of phosphorus tends not to be as high as nitrogen removal in wetlands as no direct metabolic pathway is provided for its biological removal. Phosphorus removal in wetlands is achieved by a variety of physical, chemical and biological processes.

Phosphorus is typically present in wastewaters as organic phosphorus and in inorganic form, predominantly as orthophosphate but also as polyphosphates (Cooper et al., 1996; Vymazal et al., 1998b). Organically-bound phosphorus is present e.g., in phospholipids, nucleic acids, nucleoproteins, phosphorylated sugars or organic condensed polyphosphates (coenzymes, ATP, ADP) (Vymazal, 2007). Organic phosphorus is not readily bioavailable until it undergoes enzyme hydrolysis. Free orthophosphate is the only form of phosphorus believed to be utilized directly by algae and macrophytes and thus represents a major link between organic and inorganic phosphorus cycling in wetlands (Vymazal, 2007). Phosphorus availability from organic phosphorus depends on the rate of mineralization and biodegradability, which increases with the nutrient loading in CWS.

Wetlands provide an environment for the inter-conversion of all forms of phosphorus, which are cycled in the soil-water-plant components.

4.3.2.1 Removal/retention mechanisms

Phosphorus removal in CWS can be described as a combination of both short-term (uptake by plants and microorganisms) and long-term storage processes (burial in peat/soil). Direct assimilation of wastewater phosphorus by macrophytes represents in general only a minor contribution to the overall phosphorus removal. Adsorption and precipitation can initially only be considered as short-term storage. However, once this material is buried within a layer of peat, it becomes part of the long-term “sink” storage. If the settled particulate matters remain insoluble, the phosphorus removal by sedimentation is permanent.

However, if the particulate material is biodegradable organics, after degradation, phosphorus will be released back to the water column.

Phosphorus transformations and removal in CWS, thus, involve a variety of processes which include sedimentation and burial in soil, adsorption, precipitation, mineralization and plant/microbial uptake (Vymazal, 2007).

Sedimentation and burial – most studies on phosphorus cycling in wetlands have shown that soil/peat accumulation is the major long-term phosphorus sink (Richardson and Marshall, 1986). Over long-term periods, significant portions of organic P remain in soil as part of peat build-up and, under anaerobic conditions, these forms of phosphorus are relatively resistant to microbial breakdown. In nutrient-enriched wetlands long-term P peat accretion can reach nearly 1 gm^{-2} yr^{-1} (Craft and Richardson, 1993).

Adsorption – adsorption of phosphorus to the substrate has been recognized as one of the most important removal mechanisms (Vymazal, 2007). Traditionally, locally available materials such as sand and soils have been used as substrate for P-removal. In many cases, these substrates have been used without any knowledge of the P-retaining capacities (Brix et al., 2001) even though greater attention has been given more recently to the use of materials with well-tested P adsorptive qualities, among which light expanded clay aggregates (LECA) is one the most popular choices (Brix et al., 2001). Retention by adsorption is strongly related to the amounts of Fe (oxides), Al and Ca minerals and frequently is associated with posterior longer-term removal by precipitation and co-precipitation. The rate of adsorption is controlled by soil pH and Eh, adsorptive surface area and temperature (Reddy and D'Angelo, 1997; Vymazal et al., 1998b).

Precipitation – in acid soils, inorganic P is adsorbed on oxides and hydroxides of iron and aluminum and may precipitate as insoluble phosphates (Vymazal et al., 1998b). On the other hand, in the alkaline, calcareous soils precipitation by calcium carbonate as insoluble Ca mineral bound-P is the dominant removal process (Vymazal et al., 1998b; Brix et al., 2001). Thus, precipitation can refer to the reaction of phosphate ions with metallic cations, especially Fe, Al, Ca or Mg, forming amorphous or poorly crystalline solids.

In addition to direct chemical reaction, phosphorus can co-precipitate with other minerals, such as ferric oxyhydroxide and the carbonate minerals, such as calcite (calcium carbonate).

Plant uptake – the phosphorus uptake capacity of macrophytes is lower as compared with nitrogen uptake. Thus, phosphorus concentration in plant tissues are much lower than that of nitrogen (Vymazal et al., 1998b; Brix et al., 2001). The concentration of phosphorus in the plant tissue varies among species and sites and also during the seasons. Phosphorus uptake by macrophytes is usually highest during the beginning of the growing season (in most regions during the early spring), before maximum growth rate is attained (Vymazal, 2007).

Most of the phosphorus taken up by the herbaceous vegetation of wetlands is obtained through their roots from the soil porewater and translocated to the aboveground growing tissues (Reddy and D'Angelo, 1997; Vymazal, 2007). Upon maturity and senescence, a substantial portion of the phosphorus in above-ground tissues is translocated and stored into below-ground biomass (roots and rhizomes). Depending on the type of macrophyte, in nutrient-rich systems most of the remaining aboveground-stored phosphorus is released back into the water as detrital tissue either by initial leaching or as result of decomposition.

Phosphorus storage in vegetation can range from short- to long-term, depending on type of vegetation, litter decomposition rates, leaching of P from detrital tissue, and translocation of P from shoots to roots tissues. Phosphorus storage in aboveground biomass of emergent macrophytes is usually short-term, with a large amount of P being released during the decomposition of litter (Vymazal, 2007). In order to remove phosphorus from CWS it is necessary to harvest macrophyte biomass. This is especially necessary for free-floating plants.

Microbiota uptake – the phosphorus uptake by microbiota (bacteria, fungi, algae, microinvertebrates, etc.) is rapid because these organisms grow and multiply at high rates. It seems that the amount of microbial storage depends also on trophic status of the wetland (Vymazal, 2007). In less enriched sites the microbial uptake may store more phosphorus as compared to more eutrophic sites.

Although bacteria are generally considered decomposers that simply mineralize organic P, they have also been shown to regulate the P flux across the sediment–water interface (Kleeberg and Schlungbaum, 1993)and contribute to terminal P burial through production of refractory organic compounds.

Of importance, and seldom recognized, is the amount of P that can be sequestered by the algal component of wetlands, especially in areas with open water (Vymazal, 2007). Algae and algal assemblages can affect phosphorus cycling either directly (uptake, release) or indirectly through photosynthesis-induced changes in water and soil/water interface (e.g pH, dissolved oxygen). In fact, diurnal fluctuations of pH (increasing during daytime due to photosynthetic activity and decreasing during the night due to respiration) can produce cycles of precipitation and resolubilization.

In the table 7 are presented some results about the reduction rates (%) of phosphorus in different wetland systems found in literature.

Table 7 - Phosphorus removal in several types of CWS

Type of CWS	Reduction rate	References
Created wetland	74%	(Kohler et al., 2004)
CWS (Single-family)	80%	(Steer et al., 2002)
FWS	70%	(Hadad et al., 2006)
FWS	21 – 44%	(Braskerud, 2002)
FWS (pilot-scale)	35%	(Chen et al., 2006)
FWS (review)	48.8%	(Vymazal, 2007)
Hierarchical Mosaic of Aquatic Ecosystems (HMAE®)	93 %	(Ansola et al., 2003)
Hybrid system	89%	(Oovel et al., 2007)
HSSF	60 %	(Mantovi et al., 2003)
HSSF (review)	41.1%	(Vymazal, 2007)
HSSF (review)	32%	(Vymazal, 2005c)
VSSF	>80%	(Brooks et al., 2000)
VSSF	24%	(Meuleman et al., 2003)

VSSF	59.5%	(Vymazal, 2007)
VSSF (pilot-scale)	< 47.4 %	(Sleytr et al., 2007)

Removal of total phosphorus is reported in a range of efficiencies varying between 20% and 90% showing a marked dependence on fundamental aspects such as the CWS type, the vegetation and especially the substrate used, water flow regime, hydraulic and mass loads, hydraulic residence time and environmental conditions.

The CWS generally have a greater potential to remove nitrogen than phosphorus because nitrogen can be converted to nitrogen gas and be emitted to the atmosphere as a consequence of the coupled nitrification-denitrification process. The only sustainable removal mechanism for phosphorus in a CWS is plant uptake and subsequent harvesting and that is an especially important route of phosphorus removal in FWS systems with free-floating macrophytes. However, it is important to develop an efficient harvesting frequency in order to keep macrophytes at the optimum growth stage to ensure optimum phosphorus removal (Vymazal, 2007). Still, the amount of phosphorus that can be removed by harvesting the plant biomass usually constitutes only a small fraction of the amount of phosphorus loaded into the system with the wastewater except in CWS which have low inflow loadings.

Microbial uptake is considered in all treatment systems only as temporary storage of phosphorus with very short turnover rate. Phosphorus which is taken up by microbiota is released back to the water after the decay of the organisms.

Phosphorus may also be bound to the substrate of the SSF mainly as a consequence of adsorption and precipitation reactions with calcium, aluminum and iron in the substrate. The capacity of a CWS to remove phosphorus from wastewaters may then be dependent of substrate characteristics (contents in Al, Fe and Ca ions, grain size distributions, pH and specific area). Various artificial media have been tested in order to improve the P-removal in CWS among which are, for example, light expanded clay aggregates (LECA), wollastonite, vermiculite, diatomaceous earth, blast furnace slag and limestone (Brooks et al., 2000; Johansson and Gustafsson, 2000; Brix et al., 2001; Oovel et al., 2007). The removal of phosphorus through adsorption and precipitation can be significant (Vohla et al., 2005) but it is important to realize that these processes are saturable and adsorption decreases over time (Vymazal, 2007). In addition, daily pH variations due to the respiration/photosynthesis cycles may be responsible for cycles of phosphorus precipitation/resolubilization.

4.4. Pathogen removal

Waterborne diseases remain a major hazard in many parts of the world. The important organisms from a public health point of view are the pathogenic bacteria and viruses. Protozoan pathogens and helminth worms are also of particular importance in tropical and subtropical countries (Rivera et al., 1995; Cooper et al., 1996; Vymazal et al., 1998b).

Wastewater discharges are the major source of contamination by faecal pathogenic microorganisms in rivers and coastal waters posing a risk to public health (Mason, 2002; Sleytr et al., 2007).

The treatment of wastewater pathogens in CWS is essentially a two stage process. Most pathogens are particles ranging from very small viruses to the large eggs and cysts of helminths. One of the stages of pathogen treatment is particle removal. This occurs via the same processes as for removal of suspended solids, namely sedimentation, filtration, surface adhesion and aggregation.

A series of other processes are important in influencing the viability of pathogens as infectious agents which may occur in a stage either before or after pathogenic particles removal. The major mechanisms in this stage are the hostility of the environmental conditions (temperature, pH, dissolved oxygen concentration, redox potential, salinity, turbity), predation by nematodes, protists and zooplankton and infection by other organisms, antibiosis, exposure to UV radiation and natural die-off (Metcalf and Eddy, 1991; Cooper et al., 1996; Kadlec and Knight, 1996; Ottova et al., 1997; Vymazal et al., 1998a).

The efficiency of CWS concerning the removal of microorganisms, especially indicator microorganisms like coliforms and enterococci, is a topic that has been thoroughly investigated (Kadlec and Knight, 1996; Perkins and Hunter, 2000; Langergraber and Haberl, 2001; Hench et al., 2003). In table 8, a small sample of such studies is presented as an illustrative display of the typical efficiencies achieved by several types of CWS.

Table 8. Removal of pathogens by different types of CWS

Indicator microorganisms	Type of CWS	Removal efficiencies	References
Faecal coliform (FC)	Hybrid systems (review)	99.4 %	(Vymazal, 2005b)
	FWS	85 – 94 %	(Perkins and Hunter, 2000)
	FWS	52 %	(Cameron et al., 2003)
	FWS	> 99 %	(García et al., 2008)
	FWS (review)	85.6 %	(Vymazal, 2005b)
	Hierarchical Mosaic of Aquatic Ecosystems (HMAE®)	99.997 %	(Ansola et al., 2003)
	Set of single-family constructed wetland (review)	88 %	(Steer et al., 2002)
	SSF	92 %	(Vymazal, 2005c)
	SSF	91 %	(Mashauri et al., 2000)
	SSF	93 – 98 %	(Karathanasis et al., 2003)
	SSF	99 %	(García et al., 2008)
	SSF	99.999 %	(Soto et al., 1999)
	SSF (review)	91.5 %	(Vymazal, 2005b)
	SSF	> 99 %	(Hench et al., 2003)
Faecal streptococci (FS)	Hybrid systems (review)	97.7 %	(Vymazal, 2005b)
	FWS	82 – 90 %	(Perkins and Hunter, 2000)
	FWS	99 %	(García et al., 2008)
	FWS (review)	84 %	(Vymazal, 2005b)
	SSF	99 %	(García et al., 2008)
	SSF	> 98 %	(Mantovi et al., 2003)
	SSF	93 - 98 %	(Karathanasis et al., 2003)
	SSF	83 – 90 %	(Perkins and Hunter, 2000)

	SSF (review)	92.6 %	(Vymazal, 2005b)
	SSF	99.999 %	(Soto et al., 1999)

Reported faecal bacteria removal efficiency in CWS is generally high, usually exceeding 85%, and is usually higher for faecal coliforms and somewhat lower for faecal streptococci (Vymazal, 2005b). Is should however be noted that, in spite of high removal efficiencies, if the number of bacteria at the inflow is very large, at the outflow bacteria number may still be too high to meet wastewater quality criteria.

Treatment efficiencies depend on several design and operational parameters including the type of CWS, hydraulic regime, type of vegetation, hydraulic residence time, hydraulic and mass loading rate, substrate, and temperature.

The efficiency of pathogens treatment does show some variation according to the CWS type and observed efficiencies can in most cases be ranked in the order: hybrid wetlands > SSF wetlands > FWS wetlands (Vymazal, 2005b). These differences may be related to the larger contact area among water, bacteria and substrate, which is much bigger in SSF constructed wetlands compared to FWS (Sleytr et al., 2007) therefore enhancing the process rates of the system (Langergraber and Haberl, 2001).

Wetland vegetation plays a crucial role in increasing the efficiency removal of pathogen in CWS. Wetland vegetation improves the trapping efficiency for small particles like viruses by increasing the surface area of biofilms in the flow path. Many species can also release exudates having antimicrobial properties or which can enhance the development in the rhizosphere of populations of bacteria with antibiotic activity (e.g. *Pseudomonas*). For example, it has been shown that root excretions of species such as *Scirpus lacustris* and *Phragmites australis* can diminish the populations of faecal indicators and pathogenic bacteria (Vymazal, 2005b). In addition, the presence of oxygen in the water column (produced by photosynthetic activity of submerged plants and algae in FWS, or released in the rhizosphere through the roots of macrophytes in SSF) creates unfavorable life conditions for enteric bacteria which are either facultative or obligate anaerobic.

Effects of the hydraulic retention time are very simple: the longer the wastewater remains in the system, the longer bacteria remains exposed to unfavorable conditions.

4.5. Metals removal

Metals are naturally present in the environment. However, human activities are responsible for a significant increase in their concentration levels up to a point where they begin to pose an environmental and public health problem. Beyond the natural sources, contamination with metals is mainly associated with such activities as soil disturbance, mining, manufacturing, urbanization, burning of fossil fuels and use of manufactured products such as paints, pesticides, sacrificial anodes and anti-foulants.

In small doses some metals are, in fact, essential to some biological processes (e.g. copper, chromium, nickel, zinc). For example, at low concentrations, copper is a micronutrient of plants essential to the photosynthetic electron transport system. However, at higher concentrations, it is marketed as an effective herbicide. In addition to concentration, the chemical form is also associated with a greater metal toxicity. For example, the methylated form of mercury is much more toxic than inorganic mercury (Mitra, 1986).

Toxic effects by metals are varied and sometimes diffuse and difficult to characterize. In some cases, for very high metal concentrations, toxicity may be acute and ultimately lethal. However, usually toxicity by metals will cause chronic effects resulting from a long-term exposure. Examples of chronic health effects include cancer, disruption of the endocrine system, liver and kidney damage, disorders of the nervous system, damage to the immune systems, and birth defects.

Some metals are not easily eliminated by the organisms and, therefore, they have the potential for bioaccumulation and biomagnification. This constitutes one of the major problems with metal contamination, with the potentiation of the metals' chronic toxicity along the food chain.

In CWS a variety of processes may provide routes for metal retention in the CWS components and their elimination from the wastewater. The main mechanisms occurring in each of the compartments (solid medium, aqueous medium and vegetation) are illustrated in figure 4.

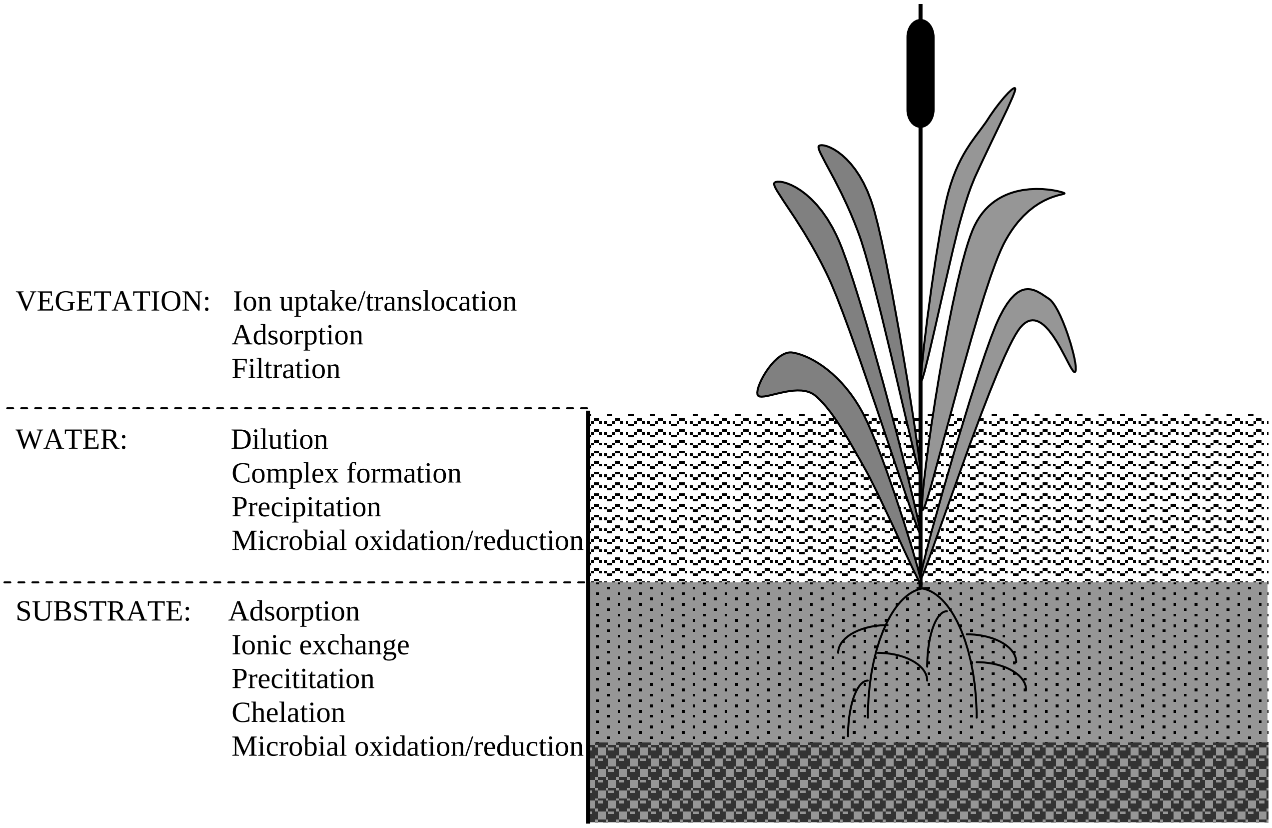

Fig. 4. Metal removal mechanisms in CWS (adapted from Cooper et al. (1996))

The substrate is generally considered to be a sink for metals anthropogenically introduced in the environment. A major fraction of the elements entering the CWS will rapidly be adsorbed onto the solid phase, where a number of physical and chemical processes will determine the strength of metal retention. A small proportion of the metals can, however, remain dissolved and become available for plant uptake.

In CWS another important role in metal removal is played by plants through several processes which include filtration, adsorption, cation exchange, uptake, and root-induced chemical changes in the rhizosphere (Dunbabin and Bowmer, 1992; Chen et al., 2000; Vandecasteele et al., 2005). Long-term metal sequestration by plants depends on the rate of uptake, rates of translocation and retention within individual tissue types, and the rate and mode of tissue decomposition (Kadlec and Knight, 1996). Studies report the highest amounts of metals in the roots, while leaf tissue has the second highest concentrations followed by stems and rhizomes (Burke et al., 2000).

Microorganisms may also play a relevant role in heavy metal removal. Such contribution may occur through their metabolism with the modification of the oxidation states of metals which in turn may lead to other transformations, such as precipitation, that effectively remove them from the wastewater.

A more detailed account follows of the several physical, chemical and biological processes which concur for heavy metal removal in a CWS.

4.5.1. Physical removal processes

Sedimentation – this has long been recognized as one of the main processes in removal of heavy metals from wastewater in natural and constructed wetlands (Kadlec and Knight, 1996; Hammer, 1997; ITRC, 2003). Sedimentation is a physical process which follows other mechanisms (precipitation/co-precipitation and flocculation) whereby heavy metals aggregate into particles large enough to sink (Walker and Hurl, 2002). In this way heavy metals are removed from wastewater and trapped in the wetland sediments, thus protecting the ultimate receiving water bodies, i.e. aquatic ecosystem (Sheoran and Sheoran, 2006). Efficiency of sedimentation is proportional to the particle settling velocity and the length of wetland.

4.5.2. Chemical removal processes

In addition to physical removal processes a wide range of chemical processes are involved in the removal of heavy metals in the wetlands:

Sorption – among the chemical processes, sorption is one of the most important removal processes in wetlands, which results in the transfer of ions from water to the soil/sediments and a short-term retention or long-term immobilization of several classes of contaminants (Sheoran and Sheoran, 2006).

In sediments heavy metals are adsorbed by either cation exchange or chemisorption (Sheoran and Sheoran, 2006). In the former process the metal cation will exchange with other small cations (such as, Na^+, K^+, NH_4^+, etc) in their positions in the mineral structures of clays and negatively charged groups of humic acids. Therefore the capacity of soils for retention of metal cations, expressed as cation exchange capacity (CEC) increases with increasing content in clay and organic matter. Chemisorption is a process which involves the formation of chemical bonds with the surface, frequently through complexation/chelation phenomena.

The adsorption capacity by cation exchange or non-specific adsorption depends upon the physico-chemical environment of the medium (e.g. pH, the properties of the metals concerned and the concentration and properties of other metals and soluble ligands present) (Debusk et al., 1996; Sheoran and Sheoran, 2006). Therefore, heavy metals speciation may change with time as the sediment conditions change (Groudev et al., 1999; Wiebner et al., 2005; Sheoran and Sheoran, 2006).

Much of the heavy metals can be easily adsorbed onto particulate matter in the wetland and subsequently be removed from the water by sedimentation. Lead and copper in general tends to be adsorbed most strongly while zinc, nickel and cadmium are usually held weakly which implies that these metals are likely to be more labile and bio-available (Sheoran and Sheoran, 2006).The adsorption of metals varies with the fluctuation of pH in the outflow water (Machemer and Wildeman, 1992). Precipitated hydroxides may also act as adsorption sites for phytotoxic metals present in the water compartment of the wetland (Wood, 1990).

Oxidation and hydrolysis of metals – The states of oxidation of a metal will have a marked influence in its chemical behavior in water. In particular, under some oxidation states a metal may typically hydrolyze to form insoluble oxides or hydroxides whereas in other oxidation states it can be more soluble. Such is the case, for example, of iron, aluminum and manganese which can form insoluble compounds through hydrolysis (sometimes following oxidation processes). This leads to the formation of a variety of oxides, hydroxides and oxyhydroxides (Woulds and Ngwenya, 2004; Sheoran and Sheoran, 2006)

Iron removal depends on pH, redox potential and the presence of various anions. In alkaline conditions Fe^{2+} is a highly soluble cation in water with low content of dissolved oxygen. On the other hand, the form Fe^{3+} is insoluble except in very acid conditions ($pH < 3.5$).
Manganese removal is the most difficult to be achieved because its oxidation takes place at a pH close to 8 (Stumm and Morgan, 1981). In this case bacteria play an important role in the oxidation of Mn by catalyzing the oxidation of Mn^{2+} to Mn^{4+}.
On the other hand, aluminum removal is purely governed by pH. Aluminum hydroxides will precipitate at pH above 5.0-6.0.

Precipitation and co-precipitation – is a major process of heavy metals removal in wetland sediments. The formation of insoluble metal precipitates is one of many factors limiting the bioavailability of heavy metals to many aquatic ecosystems. Precipitation depends on the solubility product (K_s) of the metal involved, pH of the wetland and concentration of metal ions and relevant anions (Brady and Weil, 2002).
Co-precipitation is an adsorptive phenomenon also frequent in wetland sediments. Heavy metals commonly co-precipitate with secondary minerals. Copper, nickel, manganese, and other metals are co-precipitated in Fe oxides and cobalt, iron and nickel are co-precipitated in manganese oxides (Stumm and Morgan, 1981). In addition arsenic and zinc were reported to be retained on iron plaques at the surface of plant roots (Otte et al., 1995). Oxiferric hydroxide surfaces are positively charged under acidic pH conditions and negatively charged under alkaline pH conditions. Thus, adsorption and removal of oxyanions such as arsenic, antimony and selenium, through iron co-precipitation, is favored under acidic pH conditions (Brix, 1993). Alkaline conditions are favorable for co-precipitation of cationic metals such as copper, zinc, nickel and cadmium. Thus metals may become associated with iron and manganese oxides as a result of co-precipitation and adsorption phenomena (Stumm and Morgan, 1981). The process is presumed not to be very important in long-term removal and retention of metals because iron and manganese oxides, being redox sensitive, many re-dissolve following changes in oxygen concentration (Sheoran and Sheoran, 2006).
In addition to oxides, hydroxides and oxihydroxides resulting from hydrolysis, other typical insoluble metal compounds include carbonates and sulfides. Conditions exist for

precipitation of heavy metal carbonates when the bicarbonate concentration in water is high. Carbonate formation can take place when bacterial production of bicarbonate alkalinity in wetland sediments is substantial (ITRC, 2003). Carbonate precipitation is especially effective for the removal of lead and nickel (Lin, 1995), but Sobolewski (1999) some authors reports significant quantities of copper and manganese carbonates accumulated in some natural wetlands.

Wetlands with appropriate substrate may promote the growth of sulfate reducing bacteria in anaerobic conditions. These bacteria will generate hydrogen sulfide which reacts with most heavy metals leading to formation of highly insoluble metal sulfides (Stumm and Morgan, 1981). These provide for long-term metal removal, remaining permanently in wetland sediments as long as they are not re-oxidized (Sobolewski, 1999). Metals such as copper, lead, zinc, cadmium, and arsenic may form highly insoluble sulfides in contact with low concentration of H_2S (ITRC, 2003).

Field results suggest that upon start up of a constructed wetland, the adsorption of dissolved metals onto organic sites in the substrate material will be an important process but over time sulfide precipitation becomes the dominant process for metal removal (Machemer and Wildeman, 1992).

4.5.3. Biological removal processes

Biological removal is perhaps the most important pathway for heavy metal removal in the wetlands where plant uptake plays probably the most widely recognized role. While sediments of wetlands form primary sinks for heavy metals (Gray et al., 2000), macrophytes may absorb heavy metals through roots and also shoots.

It has been proposed that the processes used by plants are not necessarily the same for different species and for different metals. Submerged rooted plants may have high potential for the metals phytoextraction from sediments as well as water, while floating plants can extract metals only from water (Sriyaraj and Shutes, 2001). Among such processes can be mentioned: sorption by roots (a combination of physical and chemical processes such as chelation, ion exchange and chemical precipitation), and the biological processes including translocation to the aerial part and precipitation induced by root exudates or by microorganisms.

The rate of metal removal by plants varies widely, depending on plant growth rate and concentration of the heavy metals in plant tissue. The rate of metal uptake per unit area of the wetland is often much higher for herbaceous plants, or macrophytes such as duckweed (*Lemna minor*) (Zayed et al., 1998), salix (Stoltz & Greger, 2002), cattail (*Typha latifolia*) and common reed (*Phragmites australis*) (Sheoran and Sheoran, 2006). Some of these species can tolerate high concentrations of several metals in their body mass without showing negative effects on the growth (Sheoran and Sheoran, 2006).

There are also some examples in the literature indicating that some species may have the ability to accumulate only specific heavy metals, e.g. the *Spirodela polyrhiza* for Zn (Markert, 1993). Constructed wetlands with well grown *Cyperus alternifolius* and *Vallarsia exaltata* have been reported to be an effective tool in phytoremediation of cadmium, copper, manganese, zinc and lead (Cheng et al., 2002).

Microorganisms also provide a measurable amount of heavy metal uptake and storage; it is their metabolic processes that play the most significant role in removal of heavy metals (Ledin and Pedersen, 1996; Russell et al., 2003; Hallberg and Johnson, 2005; Sheoran and Sheoran, 2006).

Reduction of metals to non-mobile forms by microbial activity in wetlands has been reported by Sobolewski (1999). Metals like chromium and uranium become immobilized when reduced through processes biologically catalyzed by microorganisms (Fude et al., 1994).

In the table 9 are presented illustrative results found in the literature concerning the removal efficiencies for several heavy metals obtained in different constructed wetlands systems.

Table 9. Heavy metals removal efficiencies in different types of CWS

Pollutant	Type of CWS	Reduction rate	References
Lead	CWS (small-scale plot)	≥ 90%	(Liu et al., 2007)
	HSSF	≥ 70%	(Mantovi et al., 2003)
Nickel	FWS	67 %	(Maine et al., 2006)

	FWS	48 %	(Maine et al., 2007)
	Grenhouse experiment	> 43 %	(Hadad et al., 2007)
	HSSF	59 %	(Mantovi et al., 2003)
	HSSF	49 %	(Lesage et al., 2007)
	VSSF	≥ 80%	(Lee and Scholz, 2007)
Copper	HSSF	79 %	(Mantovi et al., 2003)
	VSSF	≥ 95 %	(Lee and Scholz, 2007)
Iron	FWS	95 %	(Maine et al., 2006)
Aluminum	HSSF	93%	(Lesage et al., 2007)
Chromium	FWS	58 %	(Maine et al., 2007)
	FWS	86 %	(Maine et al., 2006)
	Grenhouse experiment	100%	(Hadad et al., 2007)
	HSSF	52%	(Mantovi et al., 2003)
Zinc	CWS (small-scale plot)	≥ 90%	(Liu et al., 2007)
	Grenhouse experiment	≥ 35%	(Hadad et al., 2007)
	HSSF	86 %	(Mantovi et al., 2003)
Cadmium	CWS (small-scale plot)	≥ 90%	(Liu et al., 2007)
	HSSF	24 %	(Mantovi et al., 2003)

Removal efficiencies reported in CWS studies present some variation, from quite low values (~ 25%) to nearly complete removal of some metals. In general, however, the efficiencies are high (> 70%) but these will depend, as usual, on varied factors such as the influent metal loads, the type of vegetation used, the CWS type and on environmental conditions. Obviously, better removals will be achieved when the systems are specifically designed and optimized to solve well-defined metal contamination problems such as mine drainage, where well-known metal accumulator plants will be used preferably, in comparison with systems designed for broader treatment targets where metals are only possibly one among several types of pollutants to remove from wastewaters.

As elemental substances, metal cations are naturally non-biodegradable and, for their permanent elimination from the system, the portion of metals removed by plant uptake will require a periodic plant harvesting. For CWS designed to treat high loads of metal inputs, the harvested plant biomass should afterwards be disposed as hazardous waste and receive appropriate treatment.

4.6. Organic xenobiotics removal

Organic xenobiotics include a large range of synthetic organic compounds, such as phthalates, polychlorinated biphenyls (PCBs), dioxins, polycyclic aromatic hydrocarbons (PAHs), pesticides, sulfonated azo dyes, alkylphenols, bisphenols and pharmaceuticals and personal care products (PPCPs) (Wu, 1999; Mason, 2002; Fent et al., 2006). Several of these substances have been released in increasing amounts in the environment since decades, and, due to the low degradation rate of many of these compounds, a significant increase of their background concentrations has been observed in the different environmental compartments (Tyler et al., 1998; Skakkebaeck et al., 2000).

A growing environmental concern has been emerging in recent years, because of the high toxicity and high persistence of most of these substances in the environment and in biological systems. Even though they occur only at very low concentrations in the environment, and their threats to aquatic life and public health are still not completely understood, nevertheless, sub-lethal effects of these compounds over long-term exposure may cause significant damage to aquatic life, particularly considering that some of these compounds may cause significant endocrine disruption, impair reproduction functions of animals or even be carcinogenic, mutagenic or teratogenic (Wu, 1999; Mason, 2002). Furthermore, the high lipophilicity of many of these xenobiotics greatly enhances their biomagnification, thereby posing potential health hazards on predators at higher trophic levels (including human beings).

The major ecological concern of xenobiotics is their ability to impair reproductive functions and subsequently threaten survival of the species. In fact, there is growing evidence from laboratory and field studies showing that exposure to trace amounts (µg/L – ng/L level) of certain xenobiotic organic compounds (e.g. halogenated hydrocarbons, PCBs, DDT, TBT) may cause reduced gonad development, disruption of normal metabolism of sex hormones (including gonadotropins), arrest of sperm maturation and block a variety of “oestrogen-like” effects on female reproductive systems in fish, birds, reptiles and mammals. This in turn, may lead to reproductive dysfunction such as delayed sex maturity, reduced fertility and hatch rate, depression in secondary sexual characteristics, alternation of sex behavior and viability of offspring (Wu, 1999).

Due to long environmental and biological half lives, recovery from the effects of many xenobiotic compounds is expected to be slow. Indeed, it has been shown that some 15 years were required to remove the negative effects of DDT on reproduction of the white tail eagles in the Baltics, and another 10 years for the population to recover (HELCOM, 1996). Furthermore, despite a decrease in environmental concentrations, the adverse effects may remain in the ecosystem for a much longer period. In the Baltics, DDE decline to 10% of the original levels in 1984, but increased again afterwards, and the egg shells of fish eating birds, which had begun to return to normal, have recently become thinner again. Thus, the downward trend was halted after the ban, and may be due to the recycling of persistent chemicals in sediment (HELCOM, 1996).

A variety of sources may be the origin for the presence of organic xenobiotics in water bodies. A number of xenobiotics classes (phthalates, pesticides, PCBs and bisphenols) are industrial products, used worldwide in several applications and are therefore ubiquitous pollutants (Safe, 1994; Stales et al., 1997; Mason, 2002). Other kinds of compounds (dioxins and PAHs) are not commercial products, but are formed as by-products of various industrial and combustion processes; they are transported from atmosphere to soil and water bodies by the atmospheric runoff or deposited on the soil during the dry period and then go through the water cycle by land runoff (Birkett and Lester, 2003).

Several studies have shown that a vast range of these xenobiotics are present in the effluents from domestic and industrial conventional wastewater treatment plants (WWTPs) (Birkett and Lester, 2003) which indicates that they resist removal by conventional wastewater treatment processes and may persist in the environment even after going through WWTPs. These are designed to deal with bulk substances that arrive regularly in large quantities (TSS, organic matter and nutrients) and many of these organic xenobiotics show a different chemical behavior for which the conventional processes are not wellsuited. The different studies show that the WWTPs removal rates vary according to compound nature, WWTPs overall performance, and environmental conditions.

This is also of potential concern about treated wastewater reuse for non industrial applications, such as irrigation of crops and aquaculture, since these pollutants may become a source of contamination of the food chain.

4.6.1. Removal processes in CWS

Organic xenobiotics removal by CWS involves several interdependent processes which may be classified as abiotic (physical or chemical) or biotic (microbial or phytological).

The primary abiotic and biotic processes that participate in removing organic xenobiotics from contaminated water in a CWS are described in table 10 (Evans and Furlong, 2003; Pilon-Smits, 2005).

Table 10. Abiotic and biotic processes involved in xenobiotics removal in CWS

Processes		Description
Abiotic		
	Sorption	Including adsorption and absorption, the chemical processes occurring at the surfaces of plants and substrate that result in a short-term retention or long-term immobilization of xenobiotics
	Hydrolysis	The chemical breakdown of organics by the action of water, a process which frequently is pH-dependent
	Photodegradation/ oxidation	Degradation/oxidation of organic xenobiotics by the action of sunlight
	Oxidation/reduction	Modification, which sometimes may be quite substantial, of the xenobiotics due to the action of oxidizing (frequently dissolved oxygen) or reducing agents. Sometimes a redox reaction is a first step leading to removal by other processes, such as precipitation or volatilization. Redox reactions are also frequently brought about by biotic agents such as bacteria, or enzymatically catalyzed
	Precipitation	Many organic compounds have low water solubility and, especially those exhibiting acid-base properties, may convert into insoluble forms by pH changes
	Settling and sedimentation	Removal of particulate matter and suspended solids
	Volatilization	Release of some organic xenobiotics, as vapors, which occurs when these compounds have significant vapor pressures
Biotic		

Aerobic/anaerobic biodegradation	Metabolic processes of microorganisms, which play a significant role in organic xenobiotics removal in CWS
Phytodegradation	Breakdown of organic xenobiotic, either internally, having first been taken up by the plants, or externally, using enzymes excreted by them
Rhizodegradation	Plants provide root exudates that enhance microbial degradation of some organic xenobiotics
Phytovolatilization/ evapotranspiration	Uptake and transpiration of volatile organic xenobiotics through the leaves

The contribution of each process to the overall efficiency of the system will be very dependent on a wide variety of factors relative not only to each CWS component characteristics but also to the properties of the organic xenobiotics, the characteristics of the wastewater and the environmental conditions.

4.6.1.1. Factors affecting organic xenobiotics removal efficiency in a CWS

The degree to which each process will contribute to the overall removal of the organic xenobiotics from contaminated waters in CWS is in turn dependent on the physico-chemical properties of these compounds (e.g., water solubility, sorptive affinity), characteristics of the substrate (e.g., pH, organic matter content, redox status), the plants species, effluent characteristics (e.g., pH, dissolved organic matter, electrolyte composition) as well as other environmental conditions (e.g., temperature, moisture).

Some of the most important organic xenobiotics properties that affect their behavior and removal in CWS are its molecular structure, polarity, ionization constant (pKa), water solubility, sorption coefficient (K_d), octanol-water partition coefficient (K_{ow}), volatility and chemical stability.

The texture of a soil or substrate is an extremely important characteristic in the sorption process. If the substrate is made up of mostly clay and organic matter a significant amount of sorption will take place. Clay, especially intermixed with organic particles, by far adsorbs the most out of the main types of texture (e.g. silt and sand) because of its small particle size, high surface area and high surface charge.

The content in organic matter also has a strong influence in the sorptive properties of the mineral media, mainly due to the presence of humic acids which form a large portion of their composition (Brady and Weil, 2002). These huge organic molecules are characterized by hydrophobic regions suitable for the adsorption of non-polar or weakly polar hydrophobic xenobiotics. However, they also contain numerous chemically active functional groups some of which confer or enrich the ion exchange properties, both cationic and anionic, and surface charge to the substrate which makes it also suitable for the adsorption of polar compounds (Brady and Weil, 2002). The sorption of polar or ionic xenobiotics is also very significant on some silicate clay minerals having substantial surface charge and ion exchange properties. In these materials the pH-changes can affect the sorption processes due to impacts on the pH-dependent ion exchange capacities of these variable charge components (humic organic matter included).

Some of the wastewater characteristics which will strongly influence how the organic xenobiotics will distribute between the aqueous medium and the matrix include the dissolved organic matter (DOM) content, the wastewater's pH and its electrolyte composition. The amount and composition of the DOM may have an important influence on the compound's solubility, and conversely on its sorption by the matrix. DOM may form complexes with the xenobiotic and enhance to its water affinity or it can compete for sorption sites in the substrate's surface (Muller et al., 2007).

In the case of organic xenobiotics with acid-base properties, the pH of the wastewater will determine the form in which they will be present in solution (either ionic or neutral) which, in turn, will affect its water solubility and sorptive affinity for the substrate. The importance of the wastewater's pH is not restricted to the influence it has on the protonation state of the organic xenobiotics but it will also affect the surface charge of the substrate and, thus, influence the electrostatics-based sorption of ionic forms of the compounds.

The presence in the wastewater of certain inorganic ions may introduce additional enhancement or disfavor of the organic xenobiotics sorption onto the matrix. Certain inorganic ions such as phosphate will frequently compete for ion exchange sorption sites in the mineral matrix. On the other hand, complexation phenomena can either contribute, in some cases, to increase the solubility of some xenobiotics or, in other cases, to facilitate binding of the compounds to a mineral surface.

4.6.1.2. Organic xenobiotics removal by the substrate

Many phenomena relevant for organic xenobiotics removal occur within the substrate compartment or is influenced by the media characteristics. However, only in sorption processes does the substrate play an actually active role.

Latest research on CW systems has been focusing on its ability for removing xenobiotic compounds like which are, in general, not very efficiently removed in the conventional treatment processes of the wastewater treatment plants (Moore et al., 2000; Schulz and Peall, 2001; Hannink et al., 2002; Cheng et al., 2002; Stearman et al., 2003; Haberl et al., 2003; Schulz, 2004; Matamoros et al., 2007). However, the media used have been mainly gravel, sand or local soils (Schulz and Peall, 2001; Stearman et al., 2003; Matamoros et al., 2007) and little importance has been given to the selection of more appropriate materials which can enhance the removal of this type of compounds by sorption.

Nevertheless, some materials like LECA, which is being increasingly used as substrate in CWs have already been tested with success for its sorption capacity of some organic xenobiotics like MCPA, clofibric acid, ibuprofen and carbamazepine (Dordio et al., 2007; Dordio et al., 2008a).

Clay minerals and organic matter are generally identified as the two most important solid matrix constituents that confer the xenobiotics retention properties to the substrate. However, substantially different sorption mechanisms are responsible for the sorption of non-polar and polar/ionic xenobiotics.

4.6.1.3. Organic xenobiotics removal by the microorganisms

Biological removal of organic pollutants in a CWS depends on their bioavailability, which depends on their chemical properties, the CWS physico-chemical characteristics and the environmental conditions (Pilon-Smits, 2005; Collins et al., 2006).

Microorganisms usually play an important role in the removal mechanisms of some organic xenobiotics in the CWS The degradation rate of organic xenobiotic and the extent of microbial growth during degradation is highly influenced by the xenobiotic chemical structure (Dua et al., 2002). Structurally simple compounds with high water solubility and low adsorptivity are usually more similar to the naturally occurring substances which are usually used as energy sources by the microorganisms and are easily degraded. In contrast, xenobiotics with chemical structures very different from the naturally occurring compounds are often degraded slowly since microorganisms do not possess suitable degrading genes. In these cases degradation by non-specific enzymes may still occur but at a slow rate by non-specific reactions which do not support microbial growth (co-metabolism) (Seffernick and Wackett, 2001).

Microbial xenobiotic degradation is also strongly influenced by the support medium where the microorganisms are. Temperature, pH, oxygen, presence of toxic substances and nutrients available within the CWS are expected to play a very important role in the removal efficiency.

Microorganisms with the ability to degrade a wide variety of compounds, like benzene, phenol, naphthalene, atrazine, nitroaromatics, biphenyls, polychlorinated biphenyls (PCBs) and chlorobenzoates, have been isolated and characterized (Dua et al., 2002). Although simple aromatic compounds are biodegradable by a variety of degradative pathways, their halogenated counterparts are more resistant to bacterial attacks and often necessitate the evolution of novel pathways (Dua et al., 2002). Among the halogenated compounds, the chlorinated compounds are the most extensively studied (Dua et al., 2002). The presence of chlorine atoms on the aromatic nucleus is known to greatly retard the rate of degradation.

Most of the information available on the biodegradation of chlorinated compounds is on oxidative degradation, since aerobic culture techniques are relatively simple, compared with anaerobic culture methods. Also, aerobic processes are considered the most efficient and generally applicable (Dua et al., 2002). Aerobic degradation is dependent on the presence of molecular oxygen and is catalyzed by enzymes that have evolved for the catabolism of natural substrates and exhibit low specificities.

4.6.1.4. Organic xenobiotics removal by the plants

Plants have an important role in the biotic processes of organics removal in CWS, involving numerous biological processes of which many details still remain to be known or understood. Depending on the pollutant properties, organics may be degraded in the roots zone through the plant’s stimulation of microbial activity or by direct uptake by the plant, followed by degradation, sequestration or volatilization (Evans and Furlong, 2003; Pilon-Smits, 2005).

Plants action in pollutant removal takes different names depending on where the processes predominantly take place. If the organic pollutants are degraded by the microorganisms within the plants’ rhizosphere (and under its influence) the process is called phytostimulation or rhizodegradation. If the plants degrade the organic pollutants directly within their tissues via their own enzymatic activities, then the process is called phytodegradation; other pollutants can leave the plant in a volatile form, and this is called phytovolatilization (Evans and Furlong, 2003; Pilon-Smits, 2005).

Many organic pollutants can be readily taken up by plants but, as consequence of many of them being xenobiotic, there are no specific transporters for these compounds in plant membranes. Therefore, organic xenobiotic move into and within plant tissues via diffusion (passive uptake) through cell walls and membranes (Dietz and Schnoor, 2001; Pilon-Smits, 2005). The flux is driven by the water potential gradient created throughout the plant during transpiration, which depends on the plants characteristics and the CWS environmental conditions. Translocation of the compounds is highly dependent on their water solubility and hydrophobicity. There may exist an optimal hydrophobicity that allows the organic compound to bind to the lipid bilayer of the membrane but not too strongly so that transport can still be facilitated.

Direct uptake is usually an efficient removal mechanism for moderately hydrophobic organic chemicals (log K_{ow} = 0.5 – 3). These include most chlorinated solvents, BTEX (benzene, toluene, ethylbenzene and xylene), many pesticides, and short-chain aliphatic chemicals. Hydrophobic chemicals (log $K_{ow} > 3$) are bound so strongly to the surface of roots and soils that they cannot be translocated easily within the plant, and chemicals that are quite water soluble (log $K_{ow} < 0.5$) are not sufficiently sorbed to roots nor actively transported through plant membranes (Dietz and Schnoor, 2001; Pilon-Smits, 2005). Hydrophobic chemicals (log $K_{ow} > 3$) are candidates for phytostabilization and/or rhizosphere bioremediation by virtue of their long residence times in the root zone (Dietz and Schnoor, 2001; Pilon-Smits, 2005).

Organic compounds which are sorbed to roots can be translocated to other plant tissues and, subsequently, they may be volatilized, they may undergo partial/complete degradation, or they may be transformed to less toxic, especially less phytotoxic, compounds and bound in plant tissues. In general, most organics appear to undergo some degree of transformation in plant cells before being sequestered in vacuoles or bound to insoluble cellular structures such as lignin. Metabolism of pesticides was extensively studied many years ago. More recently, the metabolism of nonagricultural xenobiotics such as trichloroethylene (TCE), TNT, glyceroltrinitrate (GTN), PAHs, PCBs and other chlorinated compounds has also been studied. It was shown that most of these compounds are metabolized but only a few chemicals appear to be fully mineralized. Some plant metabolites of pollutants may be more toxic than the original compounds, making plants less attractive compared with bacteria, which totally degrade organic pollutants.

In the rhizosphere take place important physiological and biochemical processes involved in the removal of contaminants which are induced by the interaction between plants, microorganisms and the solid matrix. Plants sustain large microbial populations in the rhizosphere by secreting a variety of products (exudates, mucigels, dead cell material, etc), which is known as rhizodeposition (Stottmeister et al., 2003). Consequently, favorable plant characteristics for phytoremediation are large and dense root systems which also have high levels of degrading enzymes.

The chemical composition of the exudates is very diverse and varies with the plant species, but they normally include sugars, organic acids and vitamins. It has been shown that this availability of nutrient in the immediate proximity of the roots makes the microbial population much larger in the rhizosphere than in the bulk soil, and that these larger populations increase the degradation of organic compounds (Yu et al., 2003; Sun et al., 2004). Classes of organic compounds that are more rapidly degraded in the rhizosphere than in bulk soil include polycyclic aromatic hydrocarbons (PAHs), total petroleum hydrocarbons, chlorinated pesticides as well as other chlorinated compounds like polychlorinated biphenyls (PCBs), explosives such as TNT and RDX, organophosphate insecticides, and surfactants.

One of the most important characteristics of the macrophyte plants is their ability to supply their root system with oxygen from the atmosphere. The oxygen is released mainly around the root tips promoting detoxification of harmful organic pollutants by oxidation. While these oxidative reactions take place in the immediate surroundings of the plants roots, anaerobic reactions are taking place just a few microns away (Sundaravadivel and Vigneswaran, 2001). The oxidative protective film formed on the root surface protects these sensitive areas from being damaged by toxic wastewater components in the anoxic, usually extremely reduced, rhizosphere (Stottmeister et al., 2003).

For the purpose of phytoremediation, plant species have to be selected based on the criteria of their tolerance to the pollutants toxicity and their capacity to lower the pollutants concentration in water through the variety of the processes which have been described above. Aquatic macrophytes seem to be especially resistant to a great variety of these substances in concentrations normally encountered in typical wastewater compositions. In addition, in numerous studies did these plant species exhibit the capability to reduce the concentrations of various xenobiotics in water. For example, the uptake of explosives such as RDX and TNT from the environment has been observed in several macrophytes (*Typha* spp., *Carex* spp., *Scirpus* spp., *Myriophyllum aquaticum*, *Phalaris* spp.) in numerous studies (Best et al., 1997; Best et al., 1999). *Typha* spp. and *Phragmites* spp. are also known to uptake petroleum hydrocarbons (Haberl et al., 2003) and extensive studies have been conducted on pesticides uptake (Dordio et al., 2008b).

4.6.1.5. CWS developed for organic xenobiotics removal

Many constructed wetlands applications have been consisting of domestic wastewater treatment where the BOD and COD parameters have been used as a cumulative measure of the amounts of organic compounds. However, a more specialized use for the removal of specific organic compounds or classes of compounds has been developing as a growing type of CWS applications.

A significant experience already exists with wastewater from the petroleum industry, food processing industry, pesticide contaminated agricultural runoff, landfill leachates, and waters containing surfactants, solvents, and mineral oils. Specific compounds which have received successful treatment in CWS include a range of petroleum hydrocarbons, among which are BTEX and PAHs, organic solvents (in particular the more problematic chlorinated compounds), explosives such as TNT and RDX, PCBs and textile dyes.

In table 11, an overview of recently published studies using fully assembled CWS serves to show the vitality and diversity of work that is currently being done in this field.

Table 11. Several classes of organic xenobiotics removal in CWS

Organic xenobiotic	Type of CW	Vegetation	References
Petroleum hydrocarbons/ PAHs			
Benzene	VSSF	Phragmites australis	(Eke and Scholz, 2008)
BTEX	FWS	Typha latifolia	(Haberl et al., 2003)
	VSSF	Emergent plants	(Bedessem et al., 2007)
PAHs	HSSF	Phragmites australis	(Giraud et al., 2001)
	Hybrid system	Typha spp., Scirpus lacustris	(Machate et al., 1997)
Petroleum hydrocarbons	FWS	Typha latifolia, Schoenoplectus tabernaemontani	(Gessner et al., 2005)
	VSSF (pilot-scale)	Salix spp. , Scirpus spp., Juncus spp., Phragmites australis	(Haberl et al., 2003)
Chlorinated solvents			
Monochlorobenzene	HSSF	Phragmites australis	(Braeckevelt et al., 2007)
TCE and PCE	VSSF	Common fen plants, winter-tolerant sedges and rushes	(Amon et al., 2007)
TCE	Wetland microcosms	Populus deltoides, Typha latifolia	(Bankston et al., 2002)
Explosives			
RDX	SSF mesocosms	Typha laxmanil	(Low et al., 2008)
TNT	FWS	Submergent and emergent plants	(Best et al., 2001)
	HSSF (pilot-scale)	Phragmites australis	(Haberl et al., 2003)
Pesticides			
Alachlor	SSF	Phragmites australis	(Matamoros et al., 2007)
Atrazine	CW cells	Typha latifolia	(Runes et al., 2003)
	CW mesocosms	Primarily Juncus spp.	(Moore et al., 2000)
	VSSF	Schoenoplectus lacustris, Typha latifolia, Iris pseudacorus and Phragmites australis	(McKinlay and Kasperek, 1999)
Azinphos-methyl	CW	Typha capensis, Juncus kraussii, and Cyperus dives	(Schulz et al., 2003)
Endosulfan	Flow-trough	Typha capensis, Juncus kraussii	(Schulz and Peall, 2001)

	wetlands	and Cyperus dives	
Mecoprop	CW	Sparganium erectum, Phragmites australis, Phalaris arundinacea, Myostis scorpioides, Urtica dioica	(Braskerud and Haarstad, 2003)
	SSF	Phragmites australis	(Matamoros et al., 2007)
Methyl parathion	CW mesocosms	Juncus effusus and Leersia oryzoides	(Moore et al., 2006)
Simazine	CW cells	Scirpus validus	(Stearman et al., 2003)
Others			
Acid orange 7 (AO7) dye	VSSF	Phragmites australis	(Davies et al., 2005)
Benzoic acid	SSF	Scirpus validus	(Zachritz et al., 1996)
PCBs	FWS	Typha latifolia	(Haberl et al., 2003)
Several organic solvents	SSF	Juncus effusus, Carex lurida, Iris pseudocarus, Pondeteric cordata	(Grove and Stein, 2005)
Surfactants	Hybrid system	Phragmites australis	(Bulc and Ojstrsek, 2008)
	SSF	Zantedeschia aethiopica	(Belmont and Metcalfe, 2003)

The case studies for treatment of waters contaminated with special organic compounds display a variety of applications for constructed wetlands. The reported removal efficiencies of organic xenobiotics show in many cases surprisingly good results, with values above 70% being frequently achieved in these studies. However, very little is commonly known about the exact pathways of the xenobiotics removal. Given the diversity of chemical characteristics of these compounds, which despite being classified under a common designation of xenobiotics are in fact formed by widely unrelated families of chemical substances, it is of no surprise that several very different mechanisms are responsible for removal of different xenobiotic. A comprehensive description of xenobiotic removal in CWS is therefore not an easy task to accomplish and these systems are still largely operated as a “black box”.

Although much of the design of CWS in the past has been done with little knowledge of the roles played by each component and how its function could be optimized, treating the system primarily as a black box, nowadays the study base that has been accumulating is beginning to be applied. We now can see a much greater variety of plant species, matrix materials and wetlands designs being introduced. The goals of the target contaminants to remove in CWS are also becoming progressively more ambitious.

5. New trends in constructed wetlands systems applications

In the past, CWS have been used mainly as wastewater treatment alternatives or complementary to the conventional treatment for domestic wastewaters of small communities. Thus, CWS have been mostly applied in the reduction of TSS, organic matter, excess of nutrients and faecal microorganisms. This is somewhat overlapping with the design goals of WWTPs, but with the benefits of low cost and low maintenance which are characteristic of CWS.

More recently, CWS applications to deal with more specific types of pollution (such as that caused by xenobiotics, as described in the previous section) have been meeting a larger interest and have been the subject of an increasing number of studies. CWS have been proving to be efficient and cost-effective solutions for the removal of some pollutants, where the use of conventional wastewater treatment processes does not satisfactorily solve the problem and a resort to more advanced treatments are too costly to become viable alternatives on a larger scale.

Among the several types of organic xenobiotics, pharmaceuticals have been recently attracting much attention of the international scientific community and emerging as a new important class of environmental contaminants. Compounds used in human and veterinary medicine are being continuously introduced in the environment, mainly due to improper disposal of unused or expired drugs, and through metabolic excretion. Some of these pharmaceutical residues are discharged directly in the environment without going through appropriate treatment, but even those receiving appropriate disposal in WWTPs in many cases are not effectively removed by the conventional wastewater treatment processes (Halling-Sørensen et al., 1998; Daughton and Ternes, 1999; Heberer, 2002; Fent et al., 2006).

In spite of being contaminants of many water bodies for already quite a long time (Garrison et al., 1976; Hignite and Azarnoff, 1977), environmental issues related with pharmaceuticals contamination are only recently becoming subject of more intensive study (Daughton and Ternes, 1999; Petrovic et al., 2003; Fent et al., 2006; Kemper, 2008). The low concentrations of these compounds in the environment, which are typically at trace levels (ng/L to low μg/L), associated to the unavailability, until recently, of suitably sensitive methods of analysis for these low concentration ranges has been the main reason for the late interest on the environmental problems raised by these compounds. Over the latest years, in numerous monitoring studies, residues of lipid regulating drugs, analgesics and anti-inflammatory drugs, antibiotics, hormones, chemotherapy agents, antidiabetics, neuroactive compounds and beta-blocking heart drugs have all been detected in wastewaters, surfacewaters and even groundwaters worldwide (Daughton and Ternes, 1999; Fent et al., 2006; Hernando et al., 2006).

Despite the trace level concentrations of pharmaceutical residues, such low amounts can sometimes be large enough to induce toxic effects on organisms (Halling-Sørensen et al., 1998; Ferrari et al., 2003; Fent et al., 2006; Crane et al., 2006; Hernando et al., 2006). A major problem is caused by the very nature of some pharmaceuticals since these compounds are designed to have very specific modes of action and biological effects, and many are persistent in the body. Because of their physicochemical and biological properties, when released into environment, it may be possible for them to cause serious impacts on non-target species, e.g., aquatic and terrestrial organisms. Concern has been mostly focused on antibiotics that may cause resistance among bacteria or steroids that can induce estrogenic effects on aquatic species (Halling-Sørensen et al., 1998; Fent et al., 2006). It was a surprise when in 2004, diclofenac, an analgesic and anti-inflammatory drug frequently detected in WWTPs effluents and water courses was found to be the culprit of the nearly extinction of some species of Asian vultures (Oaks et al., 2004). The metabolites and degradation by-products of pharmaceuticals are also of concern, because many of them have a toxicity which in many cases is similar to or even higher than the parent compounds (Fent et al., 2006).

Besides toxicity, the element of persistence is of particular importance when considering the environmental significance of pharmaceuticals. Unlike persistent organic pollutants like pesticides, many pharmaceuticals are not lipophilic, so they do not bioaccumulate in the environment. However, some of those are “pseudo persistent pollutants” due to their continuous introduction in the environment. While not persistent in terms of a long half-life, these chemicals are constantly entering the environment, resulting in long-term exposure for the aquatic ecosystem. Potential synergetic and chronic effects have been mostly overlooked in the past, but recent ecotoxicological studies indicate that pharmaceutical residues pose a major threat especially for the aquatic species due to the continuous life-long exposure to which they are subjected (Fent et al., 2006) . The possible development of antibiotic-resistant bacteria, the genotoxic effects of some drugs, and endocrine disruption by therapeutically administered synthetic and natural hormones have all been discussed (Halling-Sørensen et al., 1998; Daughton and Ternes, 1999; Fent et al., 2006), but very little is known about possible long-term subtle effects on non-target organisms.

The foreseeable environmental consequences of high environmental loads of pharmaceuticals points out to the urgent need of finding ways to retain and remove these pollutants before they reach the waterbodies. Optimization of the WWTP processes has been tried by increasing sludge residence times, and some advanced technologies have been evaluated to decrease their discharge into water bodies, e.g. oxidative processes, activated carbon and membrane filtration (Andreozzi et al., 2002; Fent et al., 2006; Esplugas et al., 2007; Kim et al., 2007; Snyder et al., 2007). However, despite the sometimes high removal efficiencies attained, these processes are generally not cost-effective on a large scale (Fent et al., 2006) .

Due to the recent emergence of this environmental problem, CWS have not yet been fully evaluated for the removal of pharmaceutical residues. While they are being used efficiently (as shown in the previous section) for removing several other types of organic xenobiotics (Williams, 2002; Hannink et al., 2002; Braskerud and Haarstad, 2003; Haberl et al., 2003), fewer studies exist on their use for pharmaceuticals depuration (Gross et al., 2004; Matamoros et al., 2005; Matamoros and Bayona, 2006; Matamoros et al., 2007; Dordio et al., 2008a; Matamoros et al., 2008b).

Pharmaceutical substances span a wide range of chemical behaviors: a diversity of acid-base properties provide for both easily ionizable as well as neutral compounds; while some compounds are very water soluble and hydrophilic, others are significantly hydrophobic/lipophilic; some compounds are very stable to a wide range of redox conditions whereas others are readily oxidizable or reduced. Conversely, the effective mechanisms of pharmaceutical removal in a CWS are also varied.

Easily bio-degradable pharmaceuticals are most effectively removed by the biotic components of a CWS. The action of the rhizostimulated microbial populations on one hand, and uptake by plant on the other, are both possible mechanisms (as described in the previous section, only now acting on much lower concentration levels of pollutants which is *per se* a relevant issue for the system's efficiency) that can be responsible for pharmaceuticals removal, depending on the compounds properties. An aspect to consider when designing a CWS for treatment of these types of substances and when selecting the type of biotic components is the assessment of the long-term tolerance to possible toxic effects which may be caused by pharmaceutical residues as well as other xenobiotics.

Removal of more recalcitrant pharmaceuticals has also been observed in CWS (Gross et al., 2004; Matamoros et al., 2005; Matamoros and Bayona, 2006; Matamoros et al., 2008a; Matamoros et al., 2008b). Sorption by the substrate plays a major role in such cases. However, the characteristics of the substrate are crucial for the effectiveness of this process, and some materials do provide for substantial removal efficiencies (Dordio et al., 2007; Dordio et al., 2008a) whereas other do not (Matamoros et al., 2005; Matamoros et al., 2008a; Matamoros et al., 2008b). Therefore, a careful selection of the type of substrate which displays great affinity for the type of compounds to be removed by the CWS is an essential step in the system's optimization and the achievement of acceptable efficiencies.

Ultimately, the optimization of a CWS for the removal of more specific targets requires a basic knowledge of the processes involved in the pollutants removal and the interactions between the CWS components. New trends in CWS research are moving towards the study of such processes and interactions and focus on the selection and optimization of the components for more specific applications.

6. Conclusion

Wetlands have long been known to have water depuration capabilities and, in fact, have been frequently used as wastewater discharge sites. However, in spite of these characteristics, such practice has led over the years to a substantial degradation of many of these ecosystems and in many countries the discharge of wastewaters in natural wetlands is no longer allowed. Furthermore, drainage of wetlands for agricultural purposes has also contributed to the decline in the quality of these regions. For the purpose of the restoration of some of these ecosystems or creation of habitats for wetlands wildlife, the construction of artificial wetlands has been carried out in many former natural wetlands areas. In addition, constructed wetlands have also been developed to imitate the functions provided by natural wetlands, in particular their wastewater treatment capabilities, which can also contribute to the preservation of natural wetlands and neighboring water bodies, and as well perform wastewater treatment in a more controlled and optimized environment to achieve better wastewater treatment efficiencies.

Constructed treatment wetlands systems are a biotechnology for wastewater treatment that is becoming increasingly popular as an alternative to conventional treatments or integrated in conventional systems as a secondary or tertiary treatment step. Low cost and low maintenance are some of its most attractive characteristics along with the aesthetic and landscape enhancement qualities, although they do have the disadvantages of requiring substantially more land area occupation and showing a less reproducible behavior than conventional technologies.

These systems are now becoming a mature technology for the removal of suspended solids, organic matter and nutrients. Focus is now moving into the removal of more specific and recalcitrant compounds for which the conventional treatment systems are not effective. CWS are nowadays being increasingly used for the cleanup of specific pollutant types such as organic xenobiotics and new challenges have been emerging such as the removal of pharmaceuticals and other micropollutants which present new problems to be solved.

Often CWS have been looked at as a “black box” where only influent and effluent pollutants concentrations where measured and where no more in-depth investigations were run. To use CWS as an efficient response to these new challenges this “black-box” approach to CWS operation has to be abandoned and a thorough understanding of the variety of processes involved in pollutants removal in CWS as well as the way the CWS components interact is direly needed. This has been in fact an effort which has been increasingly undertaken in the most recent years in the area of CWS research and development, not only in field studies but also in numerous lab studies as well.

Already a considerable base of knowledge exists about the CWS components and the removal processes for which they are responsible. Still, there is plenty of room for further research, as is the case of the most advanced genetic engineering technology applied both to the vegetation as to the microbial components, but also in the more traditional research subjects such as the advantages of polyculture vegetation or use of composite substrates. Additional areas to explore may be how the components may interact to provide synergetic enhancements for pollutants removal.

In conclusion, the results obtained in the research currently being conducted in this area are mostly very positive and show the potential of this promising technology even for the type of wastewater contamination that the conventional systems have not been able to cope with. Naturally constructed treatment wetlands systems have their own shortcomings and these will not be the one-size-fits-all solution to every wastewater contamination problem but it can certainly be in some cases an alternative, with advantages, to conventional wastewater treatment (e.g., for the case of single-family or small community municipal wastewaters) and in other cases complimentary to such conventional treatment.

Ultimately, the services provided by constructed wetlands may also contribute to a wider recognition of the value of natural wetlands and the role they play in the preservation of water quality in their surroundings.

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