Wastewater Treatment in Constructed Wetlands with Horizontal Sub-Surface Flow

ENVIRONMENTAL POLLUTION

VOLUME 14

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Wastewater Treatment in Constructed Wetlands with Horizontal Sub-Surface Flow

Springer

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ISBN 978-1-4020-8579-6 e-ISBN 978-1-4020-8580-2

Library of Congress Control Number: 2008931478

Printed on acid-free paper

9 8 7 6 5 4 3 2 1

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PREFACE

Wetlands have been used for uncontrolled wastewater disposal for centuries. However, the change in attitude towards wetlands during the 1950s and 1960s caused the minimization of the use of natural wetlands for wastewater treatment (at least in developed countries). Constructed wetlands have been used for wastewater treatment for about forty years. Constructed wetland treatment systems are engineered systems that have been designed and constructed to utilize the natural processes for removal of pollutants. 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.

The aim of this book is to summarize the knowledge on horizontal subsurface flow constructed wetlands (HF CWs) and objectively evaluate their treatment efficiency under various conditions. The information on this type of wastewater treatment technology is scattered in many publications but a comprehensive summary based on world-wide experience has been lacking. The book provides an extensive overview of this treatment technology around the world, including examples from more than 50 countries and examples of various types of wastewater treated in HF CWs.

As such, the book's intention is to provide a broad base of knowledge, including 1) basic information about processes occurring in wetland soils and overlying water, 2) general information about various types of constructed wetlands for wastewater treatment, 3) detailed information about functioning, performance, operation and maintenance, and costs of subsurface horizontal flow constructed wetland, 4) information on the use of HF CWs for various types of wastewater around the world, and 5) literature sources dealing with constructed wetlands, especially with HF CWs. The book is not intended as design manual and therefore it does not contain detailed guidelines for construction of these systems. Also, it is not the intention of the authors to provide a detailed theoretical analysis and does not deal with modeling. For this kind of focused practical theory, readers may wish to refer to other books – see *Suggested Reading* at the end of this volume.

Chapter 1 provides a general overview on wetland functions and values, and a brief history about the use of natural and constructed wetlands for wastewater treatment. The second chapter deals with oxidation-reduction conditions and transformations of carbon, nitrogen, phosphorus, sulfur, iron, manganese and trace elements in wetlands. Chapter 3 describes various types of wetland vegetation and provides a brief description of plant adaptations to waterlogged conditions and growth parameters of macrophytes. The fourth chapter provides information about various types of constructed wetlands used for wastewater treatment. For each type, brief descriptions of major design parameters, together with application examples, are presented. The fifth chapter focuses on horizontal sub-surface flow constructed wetlands. Major design parameters such as pretreatment, water distribution and collection, filtration materials, vegetation, sizing and costs are described. Special attention is paid to the evaluation of treatment performance of HF CWs with respect to major pollutants in various types of wastewater. Chapter 6 provides information on the use of HF CWs for various types of wastewater.

The final chapter reviews the use HF CWs around the world. Information from 56 countries is included. The volume of scientific literature on constructed wetlands has grown immensely in recent years and our survey revealed that more than 100 international journals have published papers on constructed wetlands. Obviously, while it is not possible to gather all the information into one book, and the book cannot bring the complete information about the use of constructed wetlands in every country, the representative sampling will provide a thorough picture of the science around the world. Also, there is considerably more information on HF CWs in some countries. However, we tried to balance the length of the material on individual countries. For more detailed information readers can use sources listed in the *Suggested Reading* section at the end of the volume.

We would like to thank many colleagues who kindly provided their photos, which definitely enrich the content of the book. We also appreciate the help of our colleagues who either kindly provided unpublished materials or were helpful in gathering materials from their own countries, namely Marco Belmont, Suresh Billore, Jacques Brisson, Hans Brix, Tjaša Bulc, David Cooper, Paul Cooper, Verissimo Dias, Nathalie Fonder, Magdalena Gajewska, Joan Garcia, Roberta Gorra, Raimund Haberl, Tom Headley, Peter Horvát, Petr Hrnčíř, Frank Kansiime, Kunihiko Kato, Els Lesage, Ülo Mander, Fabio Masi, Jaime Nivala, John Pries, Gabrielle Mitterer-Reichmann, Silvana Perdomo, Diederik Rousseau, Chris Tanner, Karin Tonderski, Frank van Dien, Gladys Vidal, Scott Wallace and Róbert Zvara. We would also like to sincerely thank Paul Cooper, who carefully reviewed the manuscript and also corrected the language of the book, and Betty van Herk from Springer, for her excellent editorial cooperation.

The data collection for this book was supported by grants No. 206/06/0058 “Monitoring of Heavy Metals and Selected Risk Elements during Wastewater Treatment in Constructed Wetlands” from the Czech Science Foundation and No. 2B06023 “Development of Mass and Energy Flows Evaluation in Selected Ecosystems” from the Ministry of Education, Youth and Sport of the Czech Republic.

November 2007

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Chapter 1

INTRODUCTION

1. 1 Wetland values and functions

Wetlands have played a crucial role in human history. Major stages of the evolution of the life itself probably took place in nutrient-rich coastal waters. Some of the first prehistoric cultures, such as those of the early mesolithic settlements around the post-glacial lake margins and coasts of Europe and those of the coastal Indian communities in North America, depended on wetlands for food and materials for building, shelter and clothing (Maltby, 1991). Boulé (1994) in his excellent overview on an early history of wetland ecology pointed out that the early Sumerians knew the names of plants and animals that occupied the marshes of the Tigris and Euphrates Rivers, as evidenced by clay tablets on which those names were inscribed (Kramer, 1981). The Babylonians, who followed the Sumerians in Mezopotamia, not only had names for wetland plant species, but also established municipal reed beds and reeds harvested from these beds were used to make rugs, coarse mats to strengthen walls of clay brick, and very fine mats to serve as a foundation for dikes made from material dredged from the rivers (the original filter fabric).

Understanding regional hydrology was crucial to the success of both Mesopotamian, and later Egyptian, cultures. Not only did this knowledge make extensive agricultural enterprises possible, it also allowed for the creation of water gardens in the homes of the wealthy and powerful (Boulé, 1994). Early agricultural and horticultural experiments that led to the cultivation of wetland plant species are a major part of the origins of wetland science. Rice cultivation in China originated about 5000 B.C., while the oldest paddies have been dated at about 800 B.C. (Needham et al., 1986). By 1300 B.C. the municipal reeds were established in Babylon. Some evidence also exists for the ancient introduction of papyrus to Italy, although once cultivation ceased, it was gradually extirpated (Pickering, 1879).

The value of a wetland is a measure of its importance to society. Wetland functions are valued to various degrees by society, but there is no precise, general relationship between wetland functions and the value of wetlands to society, and values can be difficult to determine objectively. A wetland's value can be weighed directly or relative to other uses that could be made of the site; thus, the location of a wetland affects its value to society (Lewis 1995).

Wetlands are transitional environments. In a spatial context, they lie between dry land and open water – at the coast, around inland lakes and rivers, or as mires draped across the landscape. In an ecological context, wetlands are intermediate between terrestrial and aquatic ecosystems. In a temporal context, most wetlands are destined either to evolve into dry land as a result of lowered water tables, sedimentation and plant succession, or to be submerged by rising water tables associated with relative sea-level rise or climatic change. Wetlands often form part of a large continuum of community type, and therefore it is difficult to set boundaries. Consequently, few definitions adequately describe wetlands with the problem of definition usually arising on the edges of wetland, toward either wetter or drier conditions (Vymazal, 1995a).

As wetlands were considered as neither "true" terrestrial ecosystem nor "true" aquatic ecosystems, not many researchers were interested in wetland ecosystems. However, there has been an explosive growth of knowledge about, and a radical change of attitude toward wetlands since the 1950s (Williams, 1990). Wetlands have been recognized as providing many benefits including water supply and control (recharge of groundwater aquifers, drinking water, irrigation, flood control, water quality and wastewater treatment), mining (peat, sand, gravel), use of plants (staple food plants, grazing land, timber, paper production, roofing, agriculture, horticulture, fertilizers, fodder), wildlife (e.g. breeding grounds for waterfowl, preservation of flora and fauna), fish and invertebrates (shrimps, crabs, oysters, clams, mussels), integrated systems and aquaculture (e.g. fish cultivation combined with rice production), erosion control, gene pools and diversity, energy (hydroelectric, solar energy, heat pumps, gas, solid and liquid fuel), education and training, recreation and reclamation (Maltby, 1986; Löffler, 1990; Sather et al., 1990; Larson, 1990; Whigham and Brinson, 1990; Tinner, 1999; Mitsch and Gosselink, 2000).

Wetlands are not easily defined because they have a considerable range of hydrologic conditions, because they are found along a gradient at the

margins of well-defined uplands and deepwater systems, and because of their great variation in size, location, and human influences. Wetland definitions, then, often include three major components (Mitsch and Gosselink, 2000):
1.Wetlands are distinguished by the presence of water, either at the surface or within the root zone.
2. Wetlands often have unique soil conditions (hydric soils) that differ from adjacent uplands.
3. Wetlands support vegetation adapted to the wet conditions (hydrophytes) and, conversely, are characterized by an absence of flooding-intolerant vegetation.

However, Mitsch and Gosselink (2000) pointed out that although the concepts of shallow water or saturated conditions, unique wetland soils, and vegetation adapted to wet conditions are fairly straightforward, combining these three factors to obtain a precise definition is difficult because of number of characteristics that distinguish wetlands from other ecosystems yet make them less easy to define.

1.2 Natural and constructed wetlands for wastewater treatment

Natural wetlands are characterized by extreme variability in functional components, making it virtually impossible to predict responses to wastewater application and to translate results from one geographical area to another. Although significant improvement in the quality of the wastewater is generally observed as a result of flow through natural wetlands, the extent of their treatment capability is largely unknown (Brix, 1993a). While most of natural wetland systems were not designed for wastewater treatment, 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 (Pries, 1994). It has only been during the past few decades that the planned use of wetlands for meeting wastewater treatment and water quality objectives has been seriously studied and implemented in a controlled manner. The functional role of wetlands in improving water quality has been a compelling argument for the preservation of natural wetlands and the construction of wetland systems for wastewater treatment (Bastian, 1993). Constructed wetlands can be built with a much greater degree of control, thus allowing the establishment of experimental treatment facilities with a well-defined composition of substrate, type of vegetation, and flow pattern. In addition, constructed wetlands offer several additional advantages compared to natural wetlands, include site selection, flexibility in sizing, and most importantly, control over the hydraulic pathways and retention time. The pollutants in such systems are removed through a combination of physical, chemical, and biological processes including sedimentation, precipitation, adsorption to soil particles, assimilation by the plant tissue, and microbial transformations (Brix, 1993a).

Natural wetlands have been used for wastewater treatment for centuries. In many cases, however, the reasoning behind this use was disposal, rather than treatment and the wetland simply served as a convenient recipient that was closer than the nearest river or other waterway (Wentz, 1987). Uncontrolled discharge of wastewater led in many cases to an irreversible degradation of many wetland areas. Wetlands have been considered for a long time as "wastelands", were scientifically neglected and, therefore, the impact of wastewaters on different wetlands was not properly assessed. Cooper and Boon (1987), for example, pointed out that the use of natural wetlands for treatment of wastewater has been practiced in the United Kingdom for more than a century. In 1877, it was reported (Stanbridge, 1976) that a 6 m^3 of sewage was being applied daily per m^2 of land resulting in the production of an offensive-smelling swamp which produced a highly-polluted effluent. By providing suitable under-drainage, at a depth of about 1.8 m, it was possible to treat effectively about 50 liters of sewage daily per m^2 of land without the soil becoming clogged (Stanbridge, 1976).

Natural wetlands are still used for wastewater treatment uder controlled conditions (e.g. Kadlec and Tilton, 1979; Chan et al., 1982; Ewel et al., 1982; Olson, 1993, Mander and Jenssen, 2002) but the use of constructed wetlands has become more popular and effective around the world since the 1980s (e.g. Reddy and Smith, 1987; Hammer, 1989a; Cooper and Findlater, 1990; Moshiri, 1993; Kadlec and Knight, 1996; Vymazal et al., 1998; Kadlec et al., 2000; Mander and Jenssen, 2003).

Humans depend upon a symbiotic relationship between green plants and microorganisms for existence on earth. Photosynthetizing plants produce oxygen and regulate its atmospheric concentration while transforming radiant energy into useful chemical energy. In the process, carbon dioxide and other gaseous chemicals produced by humans, animals, and microorganisms during their metabolic processes are used and their atmospheric concentrations mediated. Plants in conjunction with microorganisms therefore produce food for humans and also recycle their wastes. These fundamental facts have been known for a long time and taken for granted. What has not been known for a long time is the potential of plants in conjunction with microorganisms for correcting environmental imbalances caused by industrial development and environmental abuse (Wolverton, 1987).

Constructed wetland treatment systems are 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. They are designed to take an advantage of many of the same processes that occur in natural wetlands, but do so within a more controlled environment. Constructed wetlands consist of former terrestrial environment that have been modified to create poorly drained soils and wetlands flora and fauna for the primary purpose of contaminant or pollution removal from wastewater. Constructed wetlands are essentially wastewater treatment systems and are designed and operated as such, though many systems do support other functional values. Synonymous terms to constructed include man-made, engineered, and artificial wetlands (Hammer and Bastian, 1989a).

Wolverton (1987) pointed out that the scientific basis for wastewater treatment in a vascular aquatic plant system is the cooperative growth of both the plants and the microorganisms associated with the plants. A major part of the treatment process for degradation of organics is attributed to the microorganisms living on and around the plant root systems. Once microorganisms are established on aquatic plant roots, they form a symbiotic relationship in most cases with the higher plants. This relationship normally produces a synergistic effect resulting in increased degradation rates and removal of organic compounds from the wastewater surrounding the plant root systems. Also, microorganisms can use some or all metabolites released through plant roots as a food source. By each using the others waste products, this allows a reaction to be sustained in favor of rapid removal of organics from wastewater.

The first experiments aimed at the possibility of wastewater treatment by wetland plants were undertaken by Käthe Seidel in Germany in 1952 at the Max Planck Institute in Plön (Seidel, 1955). From 1955, Seidel carried out numerous experiments on the use of wetland plants, and especially Bulrush (*Schoenoplectus* = *Scirpus lacustris*), for treatment of various types of wastewater (Seidel 1961, 1965a, 1966, 1976). Although Seidel's experiments were heavily criticized (e.g. Nümann, 1970), many researchers continued in her ideas. The major reason for the criticism was the fact that investigations and calculations were mostly aimed only at the use of plants for nutrient removal by plant uptake. This would have required a regular harvest regime (which is not easy in many cases) and large areas needed for aquatic plants growth.

Wissing (1995) mentioned that with the application of the sewage treatment by activated sludge during the 1950s and 1960s on a large scale in German cities, Seidel recognized the arising problem of mounting contaminated sewage sludges from centralized treatment plants. She intensified her trial to grow helophytes and hydrophytes in wastewater and sludge of different origin and she tried to improve the performance of rural and decentralized wastewater treatment facilities which were either septic tanks or pond systems with poor cleaning effect. She planted macrophytes into the shallow embankment of tray-like ditches and created artificial trays and ditches grown with macropyhtes. Seidel names this early system the "hydrobotanical method".

However, at that time, views on wastewater treatment among experts were limited to physical, chemical and biological (bacterial) methods and the controlled use of macrophytes for water purification was not taken into consideration. In addition, it was believed that most macrophytes cannot grow well in polluted water and the ability of macrophytes to eliminate toxic substances in water was not recognized as well (Seidel, 1976). Seidel's concept to apply macrophytes to sewage treatment was difficult to understand for sewage engineers who had eradicated any visible plants on a treatment site for more than 50 years (Börner et al., 1998) and therefore, it was no surprise that the first full-scale constructed wetlands were built outside Germany.

In spite of many prejudices among civil engineers about odour nuisance, attraction of flies, poor performance in cold periods the IJssel Lake Polder Authority in Flevoland in The Netherlands constructed its first free water surface constructed wetland (FWS CW) in 1967 (de Jong, 1976; Greiner and de Jong, 1984; Veenstra, 1998). In 1968, FWS CW was created in Hungary near Keszthely in order to preserve the water quality of Lake Balaton and to treat wastewater of the town (Lakatos, 1998). However, FWS CWs did not spread significantly throughout the Europe as much as in North America (see section 4.1.4). Instead, constructed wetlands with sub-surface flow drew more attention in Europe; during the 1980s CW with horizontal flow (for details see Chapters 5, 6 and 7) and in 1990s also with vertical flow (see section 4.2.2) and their combinations (Cooper et al., 1996; Vymazal et al., 1998; Vymazal, 1999b, 2001a, 2003a, 2005c; see also section 4.3).

In North America, the free water surface wetland technology started with the ecological engineering of natural wetlands for wastewater treatment. Between 1967 and 1972, Howard T. Odum of the University of North Carolina, Chapel Hill, began a study using coastal lagoons for recycling and reuse of municipal wastewaters (Odum, 1985). In 1972, Odum, who had relocated to the University of Florida in Gainesville, began with Katherine Ewel to study the effectiveness of natural cypress wetlands for municipal wastewater recycling (Odum et al., 1977, Ewel and Odum, 1984). About at the same time, researchers at the University of Michigan in Ann Arbor began the Houghton Lake project, the first in-depth study using engineered wetlands for wastewater treatment in a cold climate region (Kadlec et al., 1975, Kadlec and Tilton, 1979). Since then constructed wetlands with free water surface have been used in North America for various types of wastewater including municipal sewage and industrial and agricultural effluents (e.g., Kadlec and Knight, 1996; Kadlec, 2003).

The sub-surface technology was started in North America during the early 1970s. (Spangler et al., 1976; Fetter et al., 1976; Small and Wurm, 1977, see section 7.2.3). In recent years the use of these systems has drawn more attention and it is estimated that there are about 8 000 subsurface constructed wetlands at present (Kadlec, 2003). However, the information on these systems is quite sparse as compared to free water CWs.

During the late 1970s and early 1980s, there was an explosion of research studies on the use of Water hyacinth (*Eichhornia crassipes*) for wastewater treatment (e.g., Bastian and Reed, 1979; Reed and Bastian, 1980; Reddy and Smith, 1987; Reed et al., 1988). However, after this period the interest disappeared because these systems proved to be difficult to manage and very costly in operation.

The potential use of aquatic and wetland macrophytes for wastewater treatment was evaluated in Australia by Mitchell during the mid 1970s (Mitchell, 1976). In 1980, the assimilative capacity of wetlands for sewage effluent was evaluated (Bavor et al., 1981) and Finlayson and co-workers performed pilot-scale experiments on the use of sub-surface constructed wetlands for the treatment of piggery wastes and abattoir wastewater (Finlayson and Chick, 1983; Finlayson et al., 1987). Extensive pilot-scale experiments were also carried out at University of Western Sydney (Bavor et al., 1987). At present, constructed wetlands in Australia are predominantly used for stormwater runoff treatment (free water surface CWs) but other applications could also been found including sub-surface systems.

Tanner et al. (2000) reported that constructed wetlands had been adopted enthusiastically by many New Zealand communities as a cost-effective means of secondary and tertiary wastewater treatment. The survey revealed that there were mere than 80 constructed wetlands for wastewater treatment excluding those treating stormwaters and farm dairy wastes. Surface flow CWs were most common (45%) followed by subsurface flow and hybrid systems (35% and 14%, respectively). At present, constructed wetlands in New Zealand are also very often used to treat agricultural runoff waters.

Since the mid 1980s, the concept of using constructed wetlands has gained increasing support in Southern Africa. By 1990, there were approximately 30 systems either in operation or under construction. These have been designed to serve a number of functions from treating raw sewage and secondary domestic effluents, upgrading septic tank and oxidation pond effluents, storm waters, agricultural and aquaculture wastes and a variety of industrial and mining wastewaters. Several of the systems have been constructed on the “root-zone” principles, other systems incorporated surface or vertical flow (Wood, 1990; Wood and Hensman, 1989). However, after the mid 1990s, the information from the South Africa diminished so it is not possible to find out if constructed wetlands became more widely spread there. On the other hand, at the end of the 20th century constructed wetland became more popular in tropical parts of Africa and there are now many fine examples of all types of constructed wetlands treating municipal sewage as well as industrial wastewaters and mine drainage waters in (Proceedings, 1998, 2000, 2002, 2004).

The traditional expertise of Asian farmers in recycling human and animal wastes through aquaculture and the practices intuitively developed by them for recovering nutrients from wastes by aquatic macrophytes propagated over waste-fed ponds gave a good basis for more engineered systems (Abassi, 1987). As early as in 1969, Sinha and Sinha reported on the use water hyacinth to treat digested sugar factory wastes. During the 1970s and 1980s numerous experiments with Water hyacinth were conducted across Asia to treat various types of wastewater, e.g. from dairies, palm oil production, distillery, natural rubber production, tannery, textile, electroplating, pulp and paper production, pesticide production and heavy metals (Abassi, 1987). However, the first information about the use of constructed wetlands with emergent vegetation appeared only in the early 1990s (Juwarkar et al., 1992). During the IWA conference in China in 1994, many papers on both horizontal and vertical flow CWs from Asia, and especially China, were presented and, therefore, it is probably a lack of literature information which made the Asian systems "unrecognized". At present, CWs are in operation, among others, in India, China, Korea, Taiwan, Japan, Nepal, Malaysia or Thailand (Proceedings, 1998, 2000, 2002, 2004) for various types of wastewater.

Since 1980, research has been conducted in Brazil on the possibility of the use of water hyacinth ponds in combination with constructed wetlands planted with rice, here called "filtering soil" (Salati, 1987). Under current classification, these systems would be called vertical upflow CWs. However, other types of constructed wetlands with emergent macrophytes have been adopted recently (Proceedings, 2000). The information on the use of constructed wetlands with emergent vegetation in South America is limited but these systems are apparently in operation Brazil, Colombia, Ecuador, Uruguay, Argentina (e.g. Proceedings, 1998; Hadad et al., 2006; Perdomo, pers. comm.) and also in Central America (e.g., Platzer et al., 2002).

The very early attempts to use wetland macrophytes for water treatment were aimed at removal of various chemical compounds (Table 1-1). However, over the years constructed wetlands have primarily been used to treat municipal or domestic wastewaters. At present, constructed wetlands are used to treat all kinds of wastewaters including those from industrial and agricultural operations, stormwater runoff or landfill leachates (Table 1-1).

The first European national guideline was published in Germany by ATV (Abwassertechnische Vereinigung) in 1989 (ATV H 262, 1989) followed by European Guidelines (Cooper, 1990). At present, there are some kind of

Table 1-1. Examples of the first use of macrophytes and/or constructed wetlands for the treatment of different types of pollution (EXP = experimental, OP = operational). Updated from Vymazal et al. (1998a), with permission from Backhuys Publishers.

1952 - phenol wastewaters - EXP (Seidel, 1955, 1965a, 1966)
1956 - dairy wastewater - EXP (Seidel, 1976)
1956 - livestock wastewater - EXP (Seidel, 1961)
1965 - sludge dewatering - EXP (Bittmann and Seidel, 1967)
1967 - sewage OP (De Jong, 1976)
1973 - textile wastewater - EXP (Widyanto, 1975)
1974 - sludge dewatering - OP (Neurohr, 1983)
1975 - oil refinery wastewaters - OP (Litchfield and Schatz, 1989)
1975 - photographic laboratory wastewaters - EXP (Wolverton and McDonald, 1976)
1978 - textile mill wastewaters - OP (Kickuth, 1982a)
1978 - acid mine drainage - EXP (Huntsman et al., 1978)
1979 - fish rearing pond discharge - OP (Hammer and Rogers, 1980)
1980 - electroplating wastewater - EXP (Shroff, 1982)
1980 - removal of cresol - EXP (Wolverton and McDonald, 1981)
1980 - piggery effluent - EXP (Finlayson et al., 1987)
1980 - abattoir wastewater - EXP (Finlayson and Chick, 1983)
1981 - heavy metals removal - EXP (Gersberg et al., 1984)
1981 - tannery wastewater - EXP (Prasad et al., 1983)
1982 - acid mine drainage - OP (Stone, 1984; Pesavento, 1984)
1982 - agricultural drainage effluents - EXP (Reddy et al., 1982)
1982 - urban stormwater runoff - OP (Silverman, 1989)
1982 - pesticides - EXP (Gudekar et al., 1984)
1982 - sugar refinery wastewater - EXP (Yeoh, 1983)
1982 - benzene and its derivatives - EXP (Wolverton et al., 1984a)
1982 - rubber industry effluent - EXP (John, 1984)
1983 - rubber industry effluent - OP (John, 1984)
1983 - pulp/paper mill wastewaters - EXP (Allender, 1984; Thut, 1989, 1990a)
1985 - dairy wastewaters - OP (Brix and Schierup, 1989a)
1985 - seafood processing wastewater - EXP (Guida and Kugelman, 1989)
1986 - potato starch industry wastewater - EXP (De Zeeuw et al., 1990)
1986 - seepage from piled pig muck - OP (Gray et al., 1990)
1986 - cyanides and chlorphenols - EXP (Wolverton and Bounds, 1988)
1986 - ash pond seepage - OP (Brodie et al., 1989)
1987 - thermally affected wastewater - OP (Ailstock, 1989)
1987 - meat processing effluent - EXP (van Oostrom and Cooper, 1990)
1988 - landfill leachate - EXP (Staubitz et al., 1989; Birkbeck et al., 1990)
1988 - livestock wastewaters - OP (Hammer, 1989b; Hammer, 1992)
1988 - pulp/paper mill wastewater - OP (Thut, 1990b, 1993)
1989 - landfill leachate - OP (Surface et al., 1993)
1989 - agricultural runoff - OP (Higgins et al., 1993)
1989 - reduction of lake eutrophication - OP (Szilagyi et al., 1990)
1989 - chicken manure - EXP (Vymazal, 1990)
1990 - water from a swimming area in the lake OP (Vincent, 1992)
1991 - fish aquaculture EXP (Zachritz and Jacquez, 1993)
1991 - phenanthrene EXP (Machate et al., 1997)
1991 - woodwaste leachate - OP (Hunter et al., 1993)
1992 - bakery wastewater - OP (Vymazal, 1994)
1992 - sugar beet processing wastewaters - OP (Anderson, 1993)
1992 - combined sewer overflow OP (Cooper et al., 1996)

1993 - pesticides contaminated agricultural runoff OP (Braskerud and Haarstad, 2003)
1993 - highway runoff - OP (Swift a Landsdown, 1994)
1994 - abattoir wastewaters - OP (Vymazal, 1998)
1994 - glycol contaminated airport runoff - OP (Worrall, 1995)
1994 - poultry wastewaters OP (Hill and Rogers, 1997)
1994 - hydrocarbons EXP (Salmon et al., 1998)
1994 - urban surface water outfalls - OP (Scholes et al., 1995)
1995 - lignite pyrolysis wastewater EXP (Wiessner et al., 1999)
1995 - greenhouse wastewaters OP (Prystay and Lo, 1996)
1995 - nitroaromatic organic compounds OP (Novais and Martins-Dias, 2003)
1996 - explosives OP (Best et al., 2000; Behrends et al., 2000)
1997 - hydrocarbons (TPH/BTEX) OP (Moore et al., 2000a)
1998 - trout farm effluent OP (Comeau et al., 2001)
1998 - coke plant effluent EXP (Jardinier et al., 2001)
1998 - golf course runoff OP (Kohler et al., 2004)
1998 - nylon intermediates and ethylene based polymers OP (Snyder and Mokry, 2000)
1999 - molasses based distillery effluent OP (Billore et al., 2001)
2000 - winery wastewater OP (Masi et al., 2002; Rochard et al., 2002)
2000 - linear alkylbenzensulfonates (LAS) EXP (Del Bubba et al., 2000)
2000 - steel processing industry wastewaters EXP (Yang et al., 2002)
2000 - subsurface drainage from grazed dairy pastures OP (Tanner et al., 2003)
2001 - brewery wastewater EXP (Kalibbala et al., 2002)
2002 - tool factory wastewaters - OP (Maine et al., 2006)
2003 - olive mill wastewater OP (Kapellakis et al., 2004)
2003 - azo dyes EXP (Davies et al., 2005)
2003 - Endocrine Disrupting Chemicals OP (Masi et al., 2004)*
2004 - chlorobenzene EXP (Braeckevelt et al., 2006)

*not especially built for this purpose

guidelines for design and operation of constructed wetlands in most European countries. In some countries, such as Denmark, the guidelines have been issued for various types of constructed wetlands (horizontal flow, vertical flow, willow systems) separately (Ministry of Environment and Energy, 1999, 2003a, 2003b; Brix and Johansen, 2004). In the United States, a design manual on constructed wetlands and aquatic plant systems for municipal wastewater treatment was issued by U.S. Environmental Protection Agency in 1988 (U.S. EPA, 1988). The manual was replaced with an updated manual in 2000 (U.S. EPA, 2000). In Australia, Guidelines for using FWS constructed wetlands for the municipal sewage treatment were issued in 2000 (QDNR, 2000).

Chapter 2

TRANSFORMATION MECHANISMS OF MAJOR NUTRIENTS AND METALS IN WETLANDS

The three most important physicochemical properties of the soil that are affected by flooding are pH value, ionic strength, and oxidation-reduction potential (Eh or redox potential) (Patrick et al., 1985).

Wetland soils and overlying waters occur in a wide range of pH values. Organic soils in wetlands are often acidic, particularly in peatlands in which there is little groundwater inflow. On the other hand, mineral soils often have more neutral or alkaline conditions (Mitsch and Gosselink, 2000). The pH of most soils tend to change toward the neutral point after flooding, with acidic soils increasing and alkaline soils decreasing in pH. Increases as great as 3 pH units have been measured in some acid soils. The equilibrium pH for waterlogged soils is usually between pH 6.5 and 7.5 (Patrick et al., 1985). The tendency of soils of low pH to decrease in acidity and for soils of high pH to increase in acidity when submerged indicates that the pH of a submerged soil is buffered around neutrality by substances produced as a result of reduction reactions. Among the more likely compounds involved in buffering the pH of waterlogged soils are Fe and Mn compounds in the form of hydroxides and carbonates, and carbonic acid (Patrick et al., 1985). For some organic soils high in iron content, submergence does not always increase pH (Ponnamperuma, 1972). Peat soils often remain acidic during submergence through the slow oxidation of sulfur compounds near the surface, producing sulfuric acid and the production of humic acids and selective cation exchange by *Sphagnum* moss (Mitsch and Gosselink. 2000).

Flooding the soil causes an increase in the concentration of ions in the soil solution, although the increase may not persist throughout the growing season. In slightly acid and acid soils, the reduction of insoluble Fe, and possible Mn compounds, to more soluble forms accounts for much of the increase in cations. In neutral to slightly alkaline soils, Ca^{2+}, and Mg^{2+} in the soil solution make significant contributions to the ionic strength. Ferrous and manganous ions produced through reduction reactions displace other cations from the exchange complex to the soil solution (Patrick et al., 1985).

2.1 Oxygen and redox potential

In well drained soils, most of the pore spaces surrounding individual soil particles and aggregates are gas-filled and interconnected with the atmosphere. This permits relatively rapid gaseous diffusion of oxygen throughout the plant rooting depth. Though there may be a reduction in gaseous oxygen content with depth in some soils (Russell, 1961), there is sufficient molecular oxygen transport across the gas-liquid interface of the soil solution to maintain some dissolved oxygen in this solution. As a result, the soil is maintained in an oxidized condition. The potential oxygen re-supply rate by this process is usually more than sufficient to meet soil and root oxygen demand (Gambrell and Patrick, 1978).

Excess water applied to a permeable soil by precipitation, irrigation, or temporary flooding will rapidly drain from the upper profile through the interconnected pore spaces. Much of this pore space is again filled with gas, which is continuous with the atmosphere, after draining for several hours. When soils are inundated the pore spaces are filled with water and the rate at which oxygen can diffuse through the soil is drastically reduced. Diffusion of oxygen in an aqueous solution has been estimated at 10 000 times slower than oxygen diffusion through a porous medium such as drained soils (Greenwood, 1961; Greenwood and Goodman, 1964). As a result of prolonged flooding and continued oxygen demand for root and microbial respiration, as well as chemical oxidation of reduced organic and inorganic components, the oxygen content of the soil solution begins an immediate decline and may be depleted within several hours to a few days (Fig. 2-1). The rate at which the oxygen is depleted depends on the ambient temperature, the availability of organic substrates for microbial respiration, and sometimes the chemical oxygen demands from reductants such as ferrous iron. The resulting lack of oxygen prevents plants from carrying out normal aerobic root respiration and strongly affects the availability of plant nutrients in the soil. As a result, plants that grow in anaerobic wetland soils generally have a number of specific adaptations to these conditions (Mitsch and Gosselink, 2000).

It is not always true that oxygen is totally depleted from the soil water of wetlands. There is usually a thin layer of oxidized soil, sometimes only a few

centimeters thick at the surface of the soil at the soil-water interface. The thickness of the oxidized layer is directly related to:
- the rate of oxygen transport across the atmosphere-surface water interface
- the small population of oxygen-consuming organisms present
- photosynthetic oxygen production by algae within the water column
- surface mixing by convection currents and wind action (Gambrell and Patrick, 1978).

The depth of the oxidized layer depends on a balance between the rate of oxygen diffusion into the surface horizon and its consumption (Mortimer, 1942). Oxygen consumption rates have been thought to be a function of microbial respiration. However, Howeler and Bouldin (1971) demonstrated that oxygen consumption rates in some flooded soils can best be described by models including oxygen consumption for both biological respiration and for chemical oxidation of both mobile and non-mobile constituents. Reduced

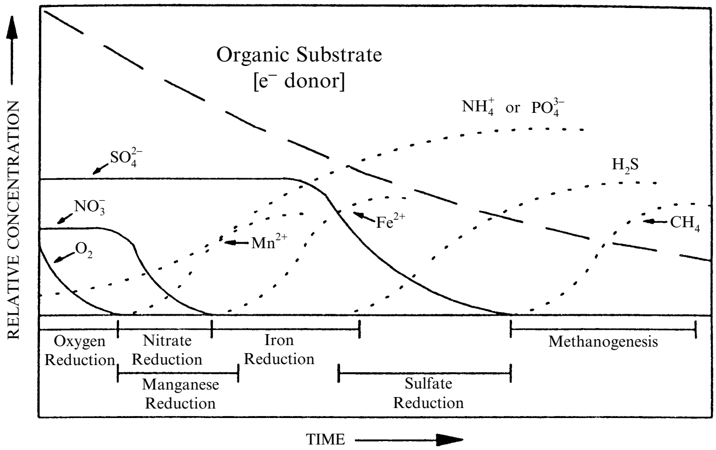

Figure 2-1. Sequence time of transformations in soil flooding, beginning with oxygen depletion and followed by nitrate and then sulfate reduction. Increases are seen in reduced manganese (manganous), reduced iron (ferrous), hydrogen sulfide, and methane. Note the gradual decrease in organic substrate (electron donor) and increase in available ammonium and phosphate ions. (After Reddy and D'Angelo, 1994, with permission from Elsevier).

iron and manganese ions were thought to represent the bulk of the mobile reductants while precipitated ferrous iron, manganous manganese and sulfide compounds, encountered as the oxidized zone increased in thickness, likely comprised much of the non-mobile constituents. Howeler (1972) pointed out that the ratio between biological and chemical oxygen consumption rates may vary widely depending on the organic matter content of the soil or sediment.

Oxygen diffusion is not the only route for oxygen transport in the flooded soil. It is well documented that aquatic and wetland macrophytes release oxygen from roots into the rhizosphere and that this release influences the biogeochemical cycles in the sediments through the effects on the redox status of the soils and sediments (e.g., Barko et al., 1991; Sorrell and Boon, 1992). Qualitatively, this is easily visualized by the reddish color associated with oxidized forms of iron on the surface of the roots. But the quantitative magnitude of the oxygen release under *in situ* conditions remains a matter of controversy (Bedford et al., 1991; Sorrell and Armstrong, 1994, Brix, 1998).

Oxygen release rates from roots depend on the internal oxygen concentration, the oxygen demand of the surrounding medium and the permeability of the root-walls (Sorrell and Armstrong, 1994). Wetland plants conserve internal oxygen because of suberized and lignified layers in the hypodermis and outer cortex (Armstrong and Armstrong, 1988). These stop radial leakage outward, allowing more oxygen to reach the apical meristem. Thus, wetland plants attempt to minimize their oxygen losses to the rhizosphere. Wetland plants do, however, leak oxygen from their roots (Brix, 1998). Rates of oxygen leakage are generally highest in the sub-apical region of roots and decrease with distance from the root-apex (Armstrong, 1979). The oxygen leakage at the root-tips serve to oxidize and and detoxify potentially harmful reducing substances in the rhizosphere. Species possessing an internal convective throughflow ventilation system have higher internal oxygen concentrations in the rhizomes and roots than species relying exclusively on diffusive transfer of oxygen (Armstrong and Armstrong, 1990), and the convective throughflow of gas significantly increases the root length by diffusion alone (Brix, 1994a). Wetland plants with a convective throughflow mechanism therefore have the potential to release more oxygen from their roots compared to species without convective throughflow.

Using different assumptions of root oxygen release rates, root dimensions, numbers, permeability, etc., Lawson (1985) calculated a possible oxygen flux from roots of *Phragmites australis* up to 4.3 g m^{-2} d^{-1}. Others, using different techniques, have estimated root oxygen release rates from *Phragmites* to be 0.02 g m^{-2} d^{-1} (Brix, 1990a; Brix and Schierup, 1990), 1-2 g m^{-2} d^{-1} (Gries et al., 1990) and 5-12 g m^{-2} d^{-1} (Armstrong et al., 1990). Root oxygen release rates from a number of submerged plants are reported to be in the range of 0.5 to 5.2 g m^{-2} d^{-1} (Sand-Jensen et al., 1982; Kemp and Murray, 1986; Caffrey and Kemp, 1991) and from free-floating plants 0.25 to 9.6 g m^{-2} d^{-1} (Moorhead and Reddy, 1988; Perdomo et al., 1996). Brix (1998) reported that gas exchange experiments in Denmark have shown that 4 g O_2 m^{-2} d^{-1} is transferred from the atmosphere to the soil. The reed vegetation transport 2 g O_2 m^{-2} d^{-1} to the root zone is mainly utilized by the roots and rhizomes themselves.

In the summer period, pressure may built up in the lacunar air spaces of the plants, which induces a mass flow of gasses internally in the plant and hence a better aeration of the buried root system (Brix et al., 1992). However, the roots and rhizomes also have a higher oxygen demand during summer because of the higher temperature. In natural *Phragmites* stands a net flux of up to 8 g O_2 m^{-2} d^{-1} through the reeds has been estimated (Brix et al., 1996). However, most of this oxygen is probably used to cover the respiratory demand of the root-rhizome system leaving only insignificant amounts of oxygen available for waste treatment processes (Brix, 1998).

Redox potential (Eh) is a measure of the electrochemical potential or electron availability in chemical and biological systems. Electrons are essential to all chemical reactions – chemical species that lose electrons become oxidized and conversely, reduction occurs as a chemical species gains electrons. Thus, a measure of redox potential (electron availability) indicates the intensity of oxidation or reduction of a chemical or biological system (Gambrell and Patrick, 1978). In an aqueous system, the intensity of oxidation is limited by the electrochemical potential at which water becomes unstable and releases molecular oxygen. Similarly, the potential at which molecular hydrogen is released from water represents the lower limit of reduction in aqueous systems (Baas Becking et al., 1960). Within the limits imposed by the stability of water, the oxidation states of hydrogen, carbon, nitrogen, oxygen, sulfur and several metals may be affected by the oxidation-reduction potential of a system, though the measured redox potential is dependent on the chemical activity of a few of the more abundant oxidized and reduced forms of these elements present (Bohn, 1971).

Non-photosynthetic biological activity in the soil derives energy from the oxidation or reduced substrates, which may be either organic (for heterotrophic metabolism) or inorganic (chemoautotrophic metabolism) in nature. Plants, of course, get this energy directly from sunlight (Killham, 1994). The metabolism of all living cells is an open system which is characterized by a continuous input and output of matter and energy. Each cell is endowed with a system that transforms the chemical and physical energy taken up into biological useful energy (ATP) and utilizes the latter to perform work (Thauer et al., 1977). It also should be noticed that energy utilization does not occur with 100% efficiency (Reddy et al., 1986). The oxidation of organic matter produced in photosynthesis yields energy; the amount of energy depends on the nature of oxidant, or electron acceptor. Energetically, the most favorable oxidant is oxygen; after oxygen is depleted there follows a succession of organisms capable of reducing NO_3^-, MnO_2, FeOOH, SO_4^{2-} and CO_2 with each oxidant yielding successively less energy for the organism mediating the reaction (Westall and Stumm, 1980).

Two important points pertaining to microbial activity in flooded soils vs. upland terrestrial soils that should be noted are that (Gambrell et al., 1991): 1) energy release from microbial utilization of soil organic matter is much more efficient under aerobic conditions than anaerobic conditions, and, 2) the organic and inorganic end products of microbial metabolic processes differ between aerobic and anaerobic respiration (Alexander, 1961; Reddy and Patrick, 1975; Tusneem and Patrick, 1971). Because of the lower energy efficiency, anaerobic organisms are less efficient in assimilating soil organic matter during decomposition, thus the rate of soil organic matter mineralization is less in soils with poor aeration (Acharya, 1935; DeLaune et al., 1981). This accounts for sediments, swamp soils and flooded field soils having greater organic matter content that upland soils in the same area (Gambrell et al., 1991).

Another important difference in microbial activity in anaerobic vs. aerobic soils is the end products of microbial metabolism. Anaerobic metabolism results in the formation of low molecular weight organic acids, complex residual humic materials, carbon dioxide, methane, hydrogen, ammonia, amines, mercaptanes, and hydrogen sulfide, though the formation of some of these depends on the intensity of reduction. Aerobic metabolism, on the other hand, results in mostly the formation of carbon dioxide, nitrate, sulfate, plus residual humic materials. It is believed the humic materials formed and transformed under anaerobic conditions may tend to have a larger molecular weight and be structurally more complex, factors that may affect the mobility of trace and toxic metals (Gambrell et al., 1980).

In addition to the difference in the end products of aerobic and anaerobic decomposition, there is a large disparity in the amount of energy released; this greater energy release allows a more efficient synthesis of cellular material per unit of organic nutrient. Under aerobic conditions, utilization of substrate C is relatively high, ranging from 20 to 40%, depending on the microbial population. Anaerobic bacteria typically realize a C assimilation rate of only 2 to 5%. Consequently, organic matter decomposition is retarded in flooded soils (Patrick et al., 1985).

Oxygen is the terminal electron acceptor in aerobic systems and is reduced while organic electron donors are being oxidized (Fig. 2-2A, Table 2-1). This reduction of O_2 to H_2O is carried out by true aerobic microorganisms and CO_2 is evolved as a waste product. Therefore, a supply of oxidizable organic compounds, as well as a supply of O_2 and some means of removing CO_2 produced are indispensable for aerobic respiration to occur (Reddy et al., 1986).

Aerobic soils have values of Eh between +300 and +800 mV and usually between +400 and +700 mV (Patrick and Mahapatra, 1968; Gambrell and Patrick, 1978; Reddy et al., 1986) and the CO_2 evolved during aerobic respiration diffuses relatively quickly when the air filled porosity is large. The relatively narrow range and poor reproducibility in oxidized systems

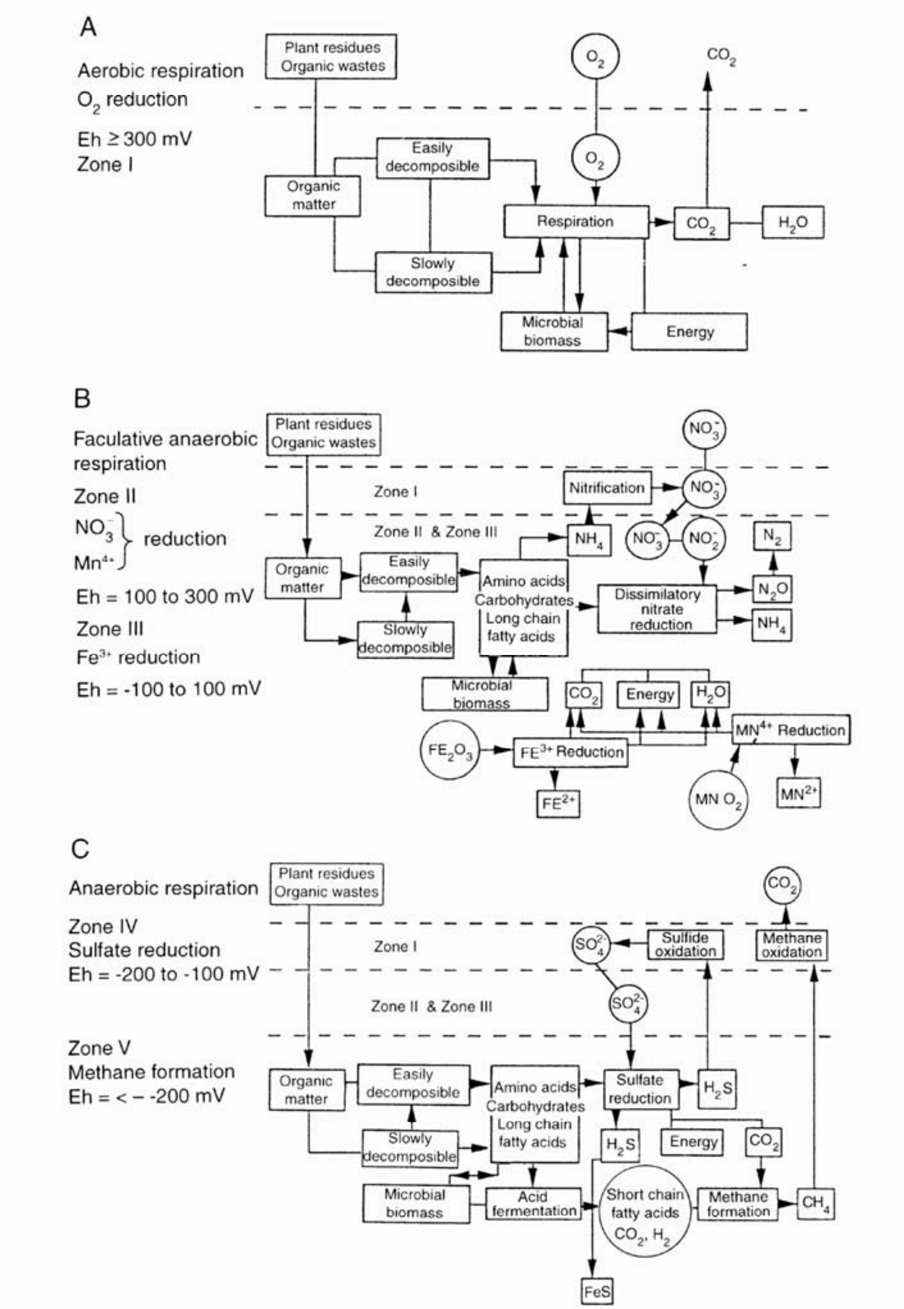

Figure 2.-2. Pathways of organic matter decomposition during aerobic respiration (A), facultative anaerobic respiration (B) and anaerobic respiration (C). From Reddy et al. (1986), with kind permission of Springer Science and Business Media.