Czech University of Life Sciences Prague
Department of Applied Ecology
Nature Conservation

Removal of pesticides and heavy metals from agricultural drainage in a constructed wetland

Master thesis of:
Rina Petric

Supervisor:
prof. Ing. Jan Vymazal, Ph.D.

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CZECH UNIVERSITY OF LIFE SCIENCES PRAGUE

Faculty of Environmental Sciences

DIPLOMA THESIS ASSIGNMENT

Rina Petric

Nature Conservation

Thesis title

Removal of pesticides and heavy metals from agricultural drainage in a constructed wetland

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Objectives of thesis

1. To review the technology of constructed wetlands for wastewater treatmnt.
2. To review the use of constructed wetlands for treatment of agricultural drainage.
3. To evaluate removal of pesticides and heavy metals in particular constructed wetlands treating agricultural drainage.

Methodology

In the first part, the technology of constructed wetlands will be reviewed based on literature. Special focus will be put on constructed wetlands treating agricultural drainage. The experimental work will deal with the evaluation of treatment performance of constructed wetlands at Velký Rybník which were designed to treat agricultural draiange.

The proposed extent of the thesis

60 pages including apendices

Keywords

constructed wetland, agricultural drainage, pesticides, heavy metals, treatment efficiency

Recommended information sources

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prof. Ing. Jan Vymazal, CSc.

Supervising department

Department of Applied Ecology

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prof. Ing. Jan Vymazal, CSc.

Head of department

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prof. RNDr. Vladimír Bejček, CSc.

Dean

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I hereby declare that I have independently elaborated the diploma/final thesis with the topic of: "Removal of pesticides and heavy metals from agricultural drainage in a constructed wetland" and that I have cited all the information sources that I used in the thesis and that are also listed at the end of the thesis in the list of used information sources. I am aware that my diploma thesis is subject to Act No. 121/2000 Coll., on copyright, on rights related to copyright and on amendment of some acts, as amended by later regulations, particularly the provisions of Section 35(3) of the act on the use of the thesis. I am aware that by submitting the diploma/final thesis I agree with its publication under Act No. 111/1998 Coll., on universities and on the change and amendments of some acts, as amended, regardless of the result of its defence. With my own signature, I also declare that the electronic version is identical to the printed version and the data stated in the thesis has been processed in relation to the GDPR.

Prague, 30.03.2022.

Rina Petric

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Abstract

The advantages of global pesticide use are outweighed by the fact that they have an extensive occurrence in the environment. Pesticides are effectively removed from the environment through a variety of abiotic and biotic transformations, however these transformation products may be hazardous for the environment and subsequently human health. Despite the considerable amount of pesticide degradation data obtained from regulatory testing and decades of pesticide research, predicting the extent and pathways of pesticide degradation in specific natural settings remains difficult. The aim of this thesis was to examine the growing potential of constructed wetlands for pesticide and heavy metal degradation processes in the controlled field setting in three constructed wetlands near Veliký Rybník, about 130 kilometers southeast of Prague (Czech Republic).

Keywords: constructed wetlands, agricultural drainage, pesticides, heavy metals, treatment efficiency

Abstract

Výhody globálního používání pesticidů jsou vyváženy skutečností, že mají v životním prostředí rozsáhlý výskyt. Pesticidy jsou účinně odstraňovány z prostředí prostřednictvím různých abiotických a biotických proměn. Tyto transformační produkty však mohou být nebezpečné pro životní prostředí a důležité lidské zdraví. Navzdory značnému množství údajů o degradaci pesticidů získaných z regulačního testování a desetiletí výzkumu pesticidů je předpovídání rozsahu a cest degradace pesticidů v konkrétních přírodních podmínkách stále obtížné. Cílem této práce bylo prozkoumat rostoucí potenciál vybudovaných mokřadů pro procesy snižující pesticidy a těžké kovy v prostředí řízeného pole ve třech vybudovaných mokřadech u Velikého Rybníka (Česká republika).

Klíčová slova: vybudované mokřady, zemědělské odvodnění, pesticidy, těžké kovy, účinnost čištění

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CHAPTER 1

Introduction

Pesticides have become critical water quality components in agricultural runoff as a result of their extensive use in contemporary agriculture to maximize crop production. Acetochlor and s- metolachlor are substitutes of alachlor and r-metolachlor, and are among the ten most commonly used herbicides in Europe and United States. Metolachlor is classified as a possible human carcinogen, while acetochlor is classified as suggestive evidence of carcinogenic potential. As a result, improving the quality of agricultural runoff water is necessary (EPA, 2011). Because of its widespread usage by organisms and great potential for direct exposure, contamination of fresh water sources is often the most dangerous of the environmental compartments into which pesticides might partition. Heavy metal contamination of drinking water has increased worldwide as well due to increasing industrialisation and urbanization during the past decades. When consumed in drinking water or through the intake of contaminated foods trace elements can be harmful to human health (Ezemonye et al., 2019). To avoid toxicities to non-target organisms, pesticide agrochemicals and trace elements must be carefully selected and managed. The use of constructed wetlands is considered as a promising management practice for treating pesticide-contaminated runoff water at the source. Due to low operation and maintenance (OM) costs (energy and supplies), ability to tolerate fluctuations in flow and load, easy maintenance, commercial and habitat value, the economic advantages of constructed wetlands to other wastewater system are continuously recognised (Dakua et al., 2016).

CHAPTER 2

Objectives

Objectives of the Diploma Thesis:

1. Reviewing the technology of constructed wetlands for wastewater treatment
2. Reviewing the use of constructed wetlands for treatment of agricultural drainage
3. Evaluating the removal of pesticides and heavy metals in particular constructed wetlands treating agricultural drainage

CHAPTER 3

Literature review

3.1 Water Pollution and Water Treatment

Almost all of the clean water on the earth is in the form of ice or is saline in ocean bodies. The majority of the remaining 3% of fresh water is locked in glaciers, leaving only 0.01 percent available for human and animal consumption. Unfortunately, this limited resource is also contaminated, resulting in water-borne diseases in humans and livestock. Aside from such negative causes, unpredicted climate change floods particular areas while leaving the rest of the planet dry (Nzihou, 2019). Anthropogenic activities are the primary sources of contamination, which migrate to both the surface and groundwater. Contaminants are gradually being transferred into drinking water supplies.

According to Romero (2008), contaminants are loaded into surface waters, groundwater, sediments, and drinking water from two main sources: the first is discrete sources, whose inputs into aquatic systems can generally be specified spatially. Industrial effluents (pulp and paper mills, steel facilities, food processing facilities), municipal sewage treatment plants and combined sewage-storm-water overflows, resource extraction (mining), and land disposal sites are all examples of this sort of pollution. The second kind of contamination is from diffuse, poorly defined sources that occur over large geographic scale. Agricultural runoff (pesticides, pathogens, and fertilizers), stormwater and urban runoff, and atmospheric deposition (wet and dry deposition of persistent organic pollutants, such as polychlorinated biphenyls (PCBs) and mercury) are all examples of this . Different microbiological organisms can all be found in source waters such as bacteria and viruses - which can come from sewage treatment plants, septic systems, agricultural livestock operations, and wildlife -, as well as inorganic substances such as salts and metals - which can be naturally occurring or outcome from urban storm water runoff, industrial or domestic wastewater discharges, oil and gas production, mining, farming, or domestic plumbing. According to the authors, additional substances that can be observed in source waters are synthetic and volatile organic substances, by-products of industrial processes and petroleum production – that can come from gas stations, urban storm water runoff, old landfill sites, and septic systems ; pesticides and herbicides – which can come from different sources including agriculture, storm water runoff, and residential use; and radioactive materials – that can occur naturally or result from nuclear power plants.

Water contamination by chemicals is a rising concern around the world. Chemicals are discharged into the world's aquatic environment as fluids, dust, fumes, or gases. These discharges can be intended (e.g., industrial smokestack emissions, vehicle exhaust that accumulates in rivers and lakes, discharge of domestic and industrial wastewater into rivers and streams, etc.) or unintended. Chemicals can also infiltrate the water system during transport (for example, from the place of production to the location of use), during intended use (for example, pesticide application), or through disposal in landfills and streams (Sinha, 2010). According to the authors, the impact of a chemical contaminant in water is determined by the pollutant's type as well as other parameters such as pH, temperature, water hardness, the amount of organic compounds such as algae and weeds, and the oxygen concentration of the water. Heavy metals and other pollutants in water at very low amounts can have a massive effect. As the pH of the water lowers, the toxic effects of certain heavy metals generally increases.

According to Howe (2012), the understanding of water quality and public health might be that water that has no measurable contaminants is safe to drink, and that the purpose of water treatment is to eliminate all measurable contaminants. However, over the last 30 to 40 years, advances in analytical equipment have made it possible to detect components in water at extremely low concentrations. As a result, anthropogenic contaminants can be found in almost all water sources. Because of atmospheric deposition, polychlorinated biphenyls (PCBs) and other anthropogenic pollutants have been detected in isolated high mountain lakes in the Pyrenees and Alps.

(Sinha, 2010), state that the chemical toxicity in water is determined by two main factors: 'bioaccumulation' and 'biomagnification.' The accumulation of a chemical by an organism to a degree that surpasses that of the immediate environment is known as bioaccumulation. Pesticides like aldrin, DDT, as well as mercury (Hg) in water are all good examples. Chemical compounds in the environment can become highly concentrated in the animal tissues higher up the food chain, reaching humans due to biomagnification. However, according to

Howe (2012), the presence of contaminents, does not mean that they are highly hazardous or harmful to one's health. People have varied chemical sensitivities; when exposed to the same concentration of a chemical, one person may be impacted while another is unaffected. Consequently, the human response to anthropogenic and natural chemicals is highly complex, making determining the "right" dose for human health protection difficult. For example, selenium, copper, and chromium are toxic at high doses, but they are essential minerals at low concentrations (they are present in multivitamins). At some point, reaching increasingly lower concentrations in water by treatment processes may have significant expenses with minimal benefit to public health. Modern analytical instruments can identify the presence of some substances at concentrations far below that at which they have a detectable effect on human health. It will be interesting and necessary to research the challenge of future water treatment practices balancing the extent of treatment with actual health benefits.

Drinking, cooking, bathing, cleaning clothing, flushing toilets, watering lawns, industrial applications, and other uses all depend on water from water treatment plants. Although only 3 to 4 percent of total of the water delivered to a home is intended for human consumption, all water is treated to the same high standard (Howe, 2012). Future water management strategies will need to find a balance between the water quality reached and the actual usage of the water, possibly delivering drinking water separately from water for other applications.

Pesticides are chemicals extensively used for the purpose of controlling diseases, pests, and weeds in plants. Different groups of pesticides are widely used in agriculture in the form of insecticides, herbicides, fungicides, rodenticides, nematicides, and chemical-based fertilizers. The intensification of agricultural activities including usage of pesticide and inorganic fertilizers application has increased with the growing demands of food, fiber, biofuel, and other bio-based materials needed for the world population in the past years. For many widely consumed crops like sunflower, sugar beet and maize, chloroacetanilide herbicides are often used to control annual grasses and broad-leaved weeds. Acetochlor and s- metolachlor are substitutes of alachlor and r-metolachlor, and are among the ten most commonly used herbicides in Europe and United States (EPA, 2011). Numerous agricultural pesticides have been discovered in surface water as a result of agricultural field run-off. Aldrin and dieldrin, DDT (all isomers), chlordane (all isomers), heptachlor and hexachloro-epoxy, methoxychlor, dichlorophenoxyacetic acid, simazin, and attrazine are some of the pesticides found in raw water. They have a high carcinogenic and mutagenic effects (Sinha, 2010). As a consequence, chloroacetanilide herbicides are often detected compounds in surface and ground water, in addition to their metabolites such as ethane sulfonic acids (ESA) and oxanilic acids (OA) (Baran and Gourcy, 2013; Hladik et al., 2005). According to (Silver et al., 2015), metolachlor is classified as possible human carcinogen and acetochlor is classified as suggestive evidence of carcinogenic potential.

According to FAO (2009), the human population has beyond doubled reaching seven billion people from 1960 to the present. It is predicted that the human population will increase by 30% in 2050 to about 9.2 billion. As a consequence of the increasing global population and changing dietary habits towards meat and milk products, it is projected that demand for food will increase by 70%.

It is estimated that globally approximately 2 million tonnes of pesticides are used, from which 47.5% are herbicides, 29.5% are insecticides, 17.5% are fungicides and 5.5% make up other pesticides (De et al., 2014). The countries that utilize pesticides the most are China, the USA, Argentina, Thailand, Brasil, Italy, France, Canada, Japan, and India (Worldatlas, 2018). Sharma et al. (2019), stated that in the years 2010 and 2014 a few European countries including Denmark, France, Austria and the Netherlands reduced the usage of pesticides, while other countries like Germany, Greece, Ireland, Czech Republic, Spain and Portugal increased the use of pesticides.

Many studies point out that altogether elimination of pesticides from agricultural usage may have drastic consequences in terms of food production. Abhilash and Singh (2009); Oerke (2006); Oerke et al. (1994), state that globally, approximately 45 - 50% of the annual potential crop yield is lost due to pre-harvest pest infestation hence, the usage of pesticides is necessary to increase crop production and control diseases and pests. Nonetheless, agricultural extension and application of agriculture-based chemicals often cause devastating effects on the environment. Water, soil, and air serve as a predominant medium for transportation of pesticides from one site to another. Unwise usage of pesticides in extensive agriculture has devastating long-term consequences due to their bio-accumulation properties and high toxicity (UNEP, 2007). In research conducted by Vos et al. (2000), on Baltic gray and ringed seals, among other organisms, both reproduction and immune functions have been impaired by PBCs in the food chain. These chemicals were banned more than 30 years ago, nevertheless, our land, water, air are still contaminated. Even though most observed negative effects are documented in heavily polluted areas, according to the authors' endocrine disruption is a potential global problem.

Pesticides have the potential to enter water bodies through diffuse and point sources. Major pathways of diffuse pollution include surface runoff and erosion, leaching, and drainage. Most widespread methods of reducing the severity of pollution and preventing pesticide transportation through waterways include edge-of-field and riparian buffer strips, vegetated ditches, and constructed wetlands.

On Earth, green plants operate as a 'natural pollutant sink,' accumulating dust and pollutants from the air and water. Plants absorb CO2 as well as many other gases such as sulfur and nitrogen oxides (SO2 and NOx), ozone (O), and airborne ammonia (NH3) through their stomata during photosynthesis. Plants also help to clean the air by capturing and retaining suspended particulate matter (SPM) and aerosols on the leaf surface. Trees take up more contaminants along with the particulate pollutants (PM10), than shorter vegetation (Sinha, 2010). 'Radionuclides,' as well as 'organic' and 'inorganic' pollutants,' are major environmental pollutants of aquatic environment. Multiple inorganic pollutants serve as 'micro and macro nutrients' for aquatic organisms in trace amounts. Nitrate (N), phosphate (P), perchlorate (PC), cyanide (CN), boron (B), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), zinc (Zn), arsenic (As), cobalt (Co), chromium (Cr), nickel (Ni), selenium (Se), vandalium (V), fluoride (F), strontium (S) among others are inorganic contaminants. Inorganic elements including boron, copper, iron, manganese, molybdenum, and zinc are necessary as plant nutrition in small amounts, but they become pollutants when present in large amounts. Arsenic, cobalt, iron, manganese, zinc, chromium, nickel, selenium, vandalium, fluoride, and strontium are inorganic elements that are important as nutrients to aquatic organisms in small amounts but become contaminants if present in large amounts. Lead (Pb), cadmium (Cd), and mercury (Hg) are some of the most hazardous trace elements that are not needed by any organism (Sinha, 2010).

Because of their environmental persistence and tendency for bio-accumulation and bio-amplification, trace metals are predominantly discharged by industrial and agricultural activities, poorly treated sewage, and mining activities, and must be regularly monitored in bodies of water. Trace elements can be harmful to human health when consumed in drinking water or through the intake of contaminated foods (Ezemonye et al., 2019).

According to Romero (2008), some metals like copper, zinc, nickel, and lead, for example, may leach into drinking water from the distribution system and domestic plumbing. Fluoride is a chemical that can be added to municipal water as part of the treatment process to help improve tooth strength. Fluoride can also be found in source water as a result of natural deposit erosion or fertilizer and aluminum factory discharge. Nitrate is found in source water as a result of fertilizer runoff, septic tank leaching, sewage, and natural deposit erosion. As a result of erosion of natural deposits, lead can end up in source water. Corrosion of household plumbing is the most common source of lead. Water from the first flush at the user's tap may contain higher concentrations of lead than water flushed over several minutes. Selenium is found in low amounts in water due to geochemical processes such as rock weathering and soil erosion. Because of the complex interrelationships between selenium and dietary ingredients including protein, vitamin E, and other trace elements, determining toxic levels of selenium is challenging. Selenium is an important trace element in human nutrition. Heavy metal contamination of drinking water has increased worldwide as a result of increasing industrialisation and urbanization during the past decades.

Some plants are 'sensitive,' meaning they are damaged and show observable morphological and physiological changes as a result. These plants serve as a "bio-indicator" of pollutants in the air and a early warning system for informing people concerning levels of air pollution. Others are more 'resistant' of contaminants in the air, and they can accumulate contaminants in their cells and tissues (Sinha, 2010). According to the authors, different aquatic plants have been reported to absorb and detoxify chemical pollutants from water bodies, including heavy metals and organic pollutants. In the biodegradation of complex organics, plant enzymes and symbiotic microorganisms on their roots play a significant role. Both essential and non-essential metals can alter cell membranes, alter enzyme specificity, distort cellular function, or even destroy DNA structure if present in excess concentrations. Heavy metals can be removed by 20-100 percent using the floating hydrophyte water hyacinth (*Eichhornia cressipes*). The plant can remove more than 75% of lead (Pb) from polluted water in just 24 hours. Cadmium (Ca), nickel (Ni), chromium (Cr), zinc (Zn), copper (Cu), iron (Fe), pesticides, and other harmful compounds are also absorbed. *Ceratophyllum demersum*, another freshwater species, can bio-accumulate arsenic (As) from water at a 20,000-fold concentration factor. Certain plants (including terrestrial and aquatic) have also been shown to remove radionuclides from polluted water, such as uranium (U), strontium (Sr 90), and cesium (Cs 137). Sunflower plants cultivated hydroponically in the pond were able to absorb 90% of the cesium-137 (Cs 137) (from 80 Bq/L of Cs 137) in just 12 day. Within 48 hours, it decreased strontium – 90 (Sr 90) concentrations from 200 g/L to 35 g/L, that was then decreased to 1 g/L (Sinha, 2010).

For over 200 years, engineers have been engaged in the design, planning, and construction of wastewater treatment systems. However, due of advances in scientific understanding and increased human effect on the water resource supplies, the interrelationship among water quality and public health has changed significantly in the last 30 or 40 years. For many years, water quality management has centered on disrupting the fecal-to-oral route; reducing contamination of water supplies (through wastewater treatment) and preserving watersheds were key considerations. *Giardia lamblia* and *Cryptosporidium parvum* were shown in the 1970s and 1980s to not only follow the fecal-to-oral route, but also to be present in the natural environment. Simply blocking the fecal-to-oral pathway is not enough;

therefore, current water quality management strategies must protect against and treat a wider range of potential microbial contamination sources (Howe, 2012). As a result, the modern water treatment engineers are confronted with a growing number of obstacles, competing issues, and compromises that must be balanced in order to design an effective water treatment system. In order to tackle these complications, engineers must have a firm grasp on the scientific and fundamental concepts behind water treatment procedures, and on the improvement of previous successful techniques.

For agricultural and food production, human consumption, and sanitary uses, smart utilization of current water resources paired with waste water treatment measures may be promising. This rising demand for clean water emphasizes the importance of ensuring that clean water is available at all times. As a result, governments divert huge amounts of money to waste water treatment-related research and development. Strengthening the agricultural and food sector, conserving the environment, and decreasing, recycling, and reusing water can all increase energy efficiency in water treatment operations, minimize pollution, and save fuel resources. Because of the diverse composition of effluents, no single treatment technique is appropriate for all types of wastewater; thus, an integrated/combined treatment method is required to treat wastewater in order to meet pollution control board standards for discharge reuse (Nzihou, 2019). The development of innovative technologies/techniques to treat wastewater from various sources is a priority of research in the area of wastewater treatment methods/techniques.

Howe (2012), states that the water is purified to precise standards in central water treatment facilities before being distributed to the public via underground pipelines, some of which are old, clogged with deposits, corroded, or leaking. Furthermore, as water comes into touch with surrounding materials in storage tanks and household plumbing fixtures, the quality of the water lowers naturally. As a result, it is possible to attain far higher water quality at a water treatment plant's outflow than what actually reaches the kitchen faucet. Water treatment methods must consider the impact of water distribution on water quality and find a balance between plant effluent and point-of-use objectives. The intended use of the water and the legal criteria regulating that usage are the key factors influencing the choice of finished-water quality goals, such as focus on municipal drinking water.

Drinking water guidelines or regulations are defined at the national or state level around the world. The effective policies that identify, document, and manage watershed risks are necessary to accomplish and maintain clean drinking water sources. Romero (2008), states that these risks are classified according to their possible influence on human health. Governments and agencies, such as the US Environmental Protection Agency (EPA) and the World Health Organization (WHO), have set guidelines for chemical/physical parameters, radiological amounts, and many microbiological components that specify acceptable concentrations and limits (e.g., MCL: maximum contaminant levels; MAC: maximum acceptable concentrations). The future availability of clean drinking water sources can only be secured with these kind of targeted strategies.

According to Howe (2012), the selection of a treatment process begins with at least three critical pieces of information: (1) the quality of the source water, (2) the targeted finished-water quality, and (3) the quantity of water required (the capacity of the facility). The data on the quality of source water can be extracted from a variety of places. Firstly, there's a chance that historic data is available or it can be obtained from the operating facility located at the same or nearby location where another facility is being constructed. Water quality data can also be found from other utilities that withdraw water upstream or downstream. Finally, state and federal agencies may have collected water quality data from the proposed source water through long-term sample programs.

According to Woodard (2005), chemical methods, physical methods, and biological methods are the three categories of technologies used to treat industrial wastewaters. Chemical methods include chemical precipitation, chemical oxidation or reduction, formation of an insoluble gas followed by stripping, and other chemical reactions that involve exchanging or sharing electrons between atoms. Sedimentation, flotation, filtering, stripping, ion exchange, adsorption, and other processes that remove dissolved and nondissolved compounds without affecting their chemical structures are examples of physical treatment methods. Biological methods are those that involve living organisms using organic or inorganic components as a source of food. The chemical and physical properties of the organic and/or inorganic substance are altered as a result. According to the author, most pollutants present in industrial wastewaters can be classified according to whether chemical, physical, or biological treatment is the best option. Dairy wastewater, for example, should be treated biologically because the majority of the pollution load from a typical dairy is organic material from whole milk, which biodegrades quickly. When a relatively complete treatment is required and it can be made to work effectively, biological treatment is generally more cost-effective than any other type of treatment. Preliminary selections of suitable treatment technologies can usually be made based on fundamental properties of the pollutants and prior experience. For example, none of the biological treatment technologies would be appropriate for treating wastewaters from a metal plating facility since metal ions are not biodegradable. Based on the fundamental properties of the compounds to be treated (dissolved inorganic cations and anions), both chemical precipitation (a chemical treatment technology) and ion exchange (a physical treatment technology) should perform effectively . The subject is therefore reduced to a comparison of the benefits and drawbacks of these two technologies, and experience offers most of the relevant information for this judgement.

Etienne and Yu (2012), state that municipal wastewater or sewage contains (1) organic compounds such as carbohydrates, proteins, and fats; (2) nitrogen, primarily in the form of ammonia; and (3) phosphorus, primarily in the form of phosphate derived from human waste and detergents. Pathogens, plastics, sand, grit, live organisms, metals, anions, and cations are among the many additional types of particulate and dissolved substances found in municipal wastewater. At wastewater treatment plants, all of these components must be dealt with. Carbonaceous, nitrogenous, and phosphorus components are usually the most important factors to consider since they affect biological activity and eutrophication in the receiving water. According to the authors, when municipal wastewater is released into a water body, the organic components drive heterotrophic organism growth, lowering dissolved oxygen levels. When oxygen is present, ammonia, which is toxic to many higher life forms such as fish and insects, is converted to nitrate by nitrifying microorganisms, resulting in an increase in oxygen demand. The water body can become anoxic depending on the volume of wastewater released and the amount of oxygen available. If the water body becomes anoxic, the autotrophic bacteria will cease nitrification ammonia to nitrate. However, some heterotrophic bacteria will continue their metabolic reactions by using nitrate instead of oxygen as a terminal electron acceptor. The nitrate may become depleted depending on the relative amounts of organics and nitrate. The water will become anaerobic and begin to ferment in these conditions. The water body will begin to recover, clear, and become aerobic once the organic compounds in the wastewater have been depleted. However, the majority of the nutrients, nitrogen (N) and phosphorus (P), remain in the water and boost the growth of aquatic plants like algae. The water body can only become eutrophically stable again if the nutrients N and P have been depleted and the organic compounds have been reduced sufficiently.

The most essential unit operations in wastewater treatment are biological treatment procedures (Etienne and Yu, 2012). Purification methods used in biological treatment units are comparable to the self-purification process occurring in rivers and streams, and many of the same microorganisms are involved. Heterotrophic microorganisms, primarily bacteria but also fungus, are responsible for the decomposition of organic matter. Microorganisms breakdown organic matter through two distinct processes: biological oxidation and biosynthesis, both of which remove organic matter from wastewater.

3.2 Constructed Wetlands Technology for Water Treatment

Natural wetlands are most commonly described as areas of land, where water is the primary factor controlling the environment and accompanying plant and animal life. They occur where the water table is near or at the surface of the land, or where shallow water covers the land. Wetlands are often located between dry terrestrial systems and permanently flooded deepwater aquatic systems such as rivers, lakes, estuaries, or oceans and are influenced by both systems.

Natural wetlands can also occur as isolated basins with little outflow and no adjacent deepwater system. Wetlands often have unique soil conditions that differ from neighboring terrestrial areas. They support vegetation adapted to the wet conditions (hydrophytes) and are characterized by a lack of flooding-intolerant biota. The early classification of natural wetlands began in the early 1990s, firstly with the peatland classification of Europe and North America. Penfound (1952) classified waterbodies as freshwater and coastal along with vegetation as herbaceous and woody. The U.S. Fish and Wildlife Service carried out an inventory of wetlands of the United States in 1954. to assess the amount and types of valuable waterfowl habitats. The results of the inventory were published as U.S. Fish and Wildlife Service Circular 39 containing the illustrated description of the 20 wetland types based on flooding depth classified in four groups: I. Inland fresh areas; II. Inland saline areas; III. Coastal freshwater wetlands; IV: Coastal saline areas (Shaw and Fredine, 1956).

Later classification according to U.S. Fish and Wildlife Service shows five major systems (marine, estuarine, riverine, lacustrine/lake, palustrine/marsh); eight subsystems (subtidal, intertidal, tidal, lower perennial, upper perennial, intermittent, limnetic, littoral) and numerous classes. Natural wetlands are considered as lands transitional between terrestrial and aquatic systems where the water table is usually at or near the surface or the land is covered by shallow water. For the purposes of this classification, wetlands must have one or more of the following three attributes: (1) at least periodically, the land supports predominantly hydrophytes; (2) the substrate is predominantly undrained hydric soil; and (3) the substrate is non-soil and is saturated with water or covered by shallow water at some time during the growing season of the year (Cowardin and Golet, 1995).

Based on the Ramsar Convention natural 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 meters at low tide. There are even underground wetlands (Ramsar, 1998). According to Kandasamy and V (2008) , different types of natural wetlands include swamps, sloughs, marshes, bogs, or ecotones depending on plants growing in these areas and the geographic locations. Swamps are wetlands that are dominated by water-tolerant woody plants; marshes are those with soft-stemmed plant species, and bogs are those with mosses. Marshes and swamps can be saltwater as well as freshwater type.

Macrophytes, hydrophytes, helophytes, and aquatic plants are all terminology for vascular (angiosperms and pteridophytes) and avascular (mosses) plants that occur in aquatic or boggy environments. Macrophytes are classified as immersed, emergent, floating, submerged free, submerged rooted, submerged with floating leaves, or amphiphytes based on their biotypes, reflecting their interactions with the aquatic environment (Brix, 1997). While pteridophytes (like *Salvinia sp.* and *Azolla sp.*) and algae (like *Cladophora sp.*) are beneficial, angiosperms dominate constructed wetland systems, according to the authors.

Machado et al. (2017), highlighted the most commonly used macrophytes in wetland constructions, indicating that species of the Poaceae family are the most common, with *Cynodon* genus species dominating, followed by species *Typha domingensis* and *T. latifolia* (family Typhaceae). However, Zurita et al. (2009), suggest using commercially valuable terrestrial plants such as *Agapanthus africanus* (African Lily), *Anturium andreanum* (Painter's Palette), *Zantedeschia aethiopica* (Arum-lily), and *Strelitzia reginae* (Bird of Paradise flower), which can add commercial value to wetlands while also efficiently remove waterborne contaminants.

As stated by Brix (1994), one of the three critical aspects of constructed mitigation wetlands is the presence of vegetation. Benefits of plants include physical filtration, providing a large surface area for microbial attachment, stabilization of bed sediments controlling erosion, heat proofing during winter, prevention of vertical flow systems from clogging, which will be further explained in the next chapters. Phytoremediation is the natural ability of certain plants to bioaccumulate, degrade, or render harmless contaminants in soils, water, or air. Furthermore, macrophytes have additional site-specific functions including a suitable habitat for wildlife and an aesthetic appearance. Plant uptake of nitrogen, oxygen release, and other metabolisms of the macrophytes affects the treatment process in different ways depending on the design. Brix (1997), states that the macrophytes' vegetative organs play an important role in wetland systems, preventing particle resuspension, absorbing nutrients and removing contaminants, producing oxygen, and minimizing the effects of solar radiation and are also aesthetically pleasing. Even if they are not present in all wetland systems, plants can play a vital role in eliminating contaminants, providing oxygen, increasing substrate porosity and infiltration rates, and creating an environment favorable to microorganism fixation (Kumar and Dutta, 2019).

Machado et al. (2017), argued that the requirements for plants in those systems are influenced by wetland designs and operations, making it difficult to reach a single conclusion about their use. Furthermore, because most research have focused on analyzing a variety of plants (and hence did not involve replicates), there is a lack of solid data on which to draw definite conclusions. In such studies, environmental variations can also have an impact on plant efficiency. During the summer, (Wang et al., 2016), found no significant differences between planted and non-planted wetlands in terms of oxygen demands or ammonia removal; however, planted wetlands were more efficient in relation to those measures during the winter. These differences were related to the actions of microbiological communities, which are more sensitive to environmental temperatures when they are not associated with plants.

Constructed wetlands, unlike natural wetlands, have predefined sizes, locations, substrate types, hydraulic conditions, and controlled retention times. Constructed wetlands have several advantages over other water treatment facilities, including low maintenance costs, the use of renewable energy resources (solar and kinetic) and natural elements (microorganisms and plants) that do not require high technology, and the ability to process large volumes of water containing various types of contaminants. Those systems can also be used as public visiting locations, as well as for environmental education and research purposes (Hua, 2003).

Wetland systems combine physical, chemical, and biotic processes to manage waste and contaminated water in a combination with adapted plants, microorganisms, macro-organisms (vertebrates and invertebrates), and substrates. Macrophytes (rooted emergent plants) increase physical filtering, prevent vertical flow system clogging, mediate oxygen transmission to the rhizosphere, and help microbial colonization. There is an oxygen gradient in subsurface systems, with high partial pressures near the plant roots, which is gradually replaced by anaerobic and anoxic environments (Sinha, 2010). Ecologists and environmental biotechnologists are working to promote the development of constructed wetlands and using them to treat municipal and industrial wastewater, urban stormwater runoff, agricultural wastewater runoff, acid mine drainage, and leachates from metal mines and waste landfills understanding of the chemical breakdown and nutrient removal properties of aquatic organisms (plants, animals, and microbes) in natural wetland systems. The potential of wetlands for the removal of pesticides and other organic chemicals is referred to in different studies in the last four decades. The initial experiments on usage of wetland macrophytes for pesticide removal were performed in the 1970s and the constructed wetlands (CWs) for pesticide mitigation from agricultural runoff became widespread in the last decade (Kadlec and Hey, 1994; Lewis et al., 1999; Wolverton and Harrison, 1975).

In a survey by Vymazal and Březinová (2015), where 47 studies were summarized with 87 pesticides monitored it was concluded that constructed wetlands with free water surface are the most commonly used type. According to the authors, the lowest removals were observed for pesticides of the triazinone, aryloxyalkanoic acid, and urea groups, whereas the highest pesticide removal was achieved for pesticides of the organochlorine, strobilurin/strobin, organosphosphate, and pyrethroid groups. It was observed that the removal of pesticides generally increases with the increasing value of Koc but the relationship is not strong.

Kadlec and Wallace (2008), defined constructed wetlands as man-made systems created for improved treatment capacity based on emphasizing specific characteristics of natural wetland ecosystems. CWs have primarily been used for municipal treatment purposes, but also to treat agricultural and industrial wastewater, as well as mine drainage, landfill leachates, and storm-water runoff. Municipal wastewater treatment wetlands are most commonly used for secondary treatment (receiving effluent of primary treatment systems to degrade biological content) or as add-ons to existing secondary treatment plants for tertiary treatment (further and final polishing of the wastewater beyond regulatory discharge requirements) (Kadlec and Wallace, 2008). The authors state three commonly used types of wetlands. In figure 3.1 three common types of CW are shown: Free water surface (FWS) wetlands contain open water areas that are much the same in appearance as natural marshes. Horizontal subsurface flow (HSSF) wetlands generally contain a gravel bed that is planted with wetland vegetation. The water flows horizontally from the inlet to the outlet, below the surface of the bed. In vertical flow (VF) wetlands the water is treated as it filters through the plant root zone. Water is distributed across the surface of a sand or gravel bed which is planted with wetland vegetation.

According to Vymazal and Březinová (2015), primarily used CWs are those with free water surfaces, but both vertical and horizontal subsurface flow CWs have recently been used as well. However, there are no side-by-side experiments that would study different types of CWs at one location. In the last three decades, constructed wetlands are recognized as one of the best management practices whose ecological value and multiple functions can be wisely used for their many advantages (low maintenance costs, multi-functional, water treatment, habitats with great diversity and heterogeneity, temperature lowering, flood control, visual attraction, biogas production after harvesting), especially for management practices for mitigating agricultural runoff before going into receiving aquatic ecosystems.

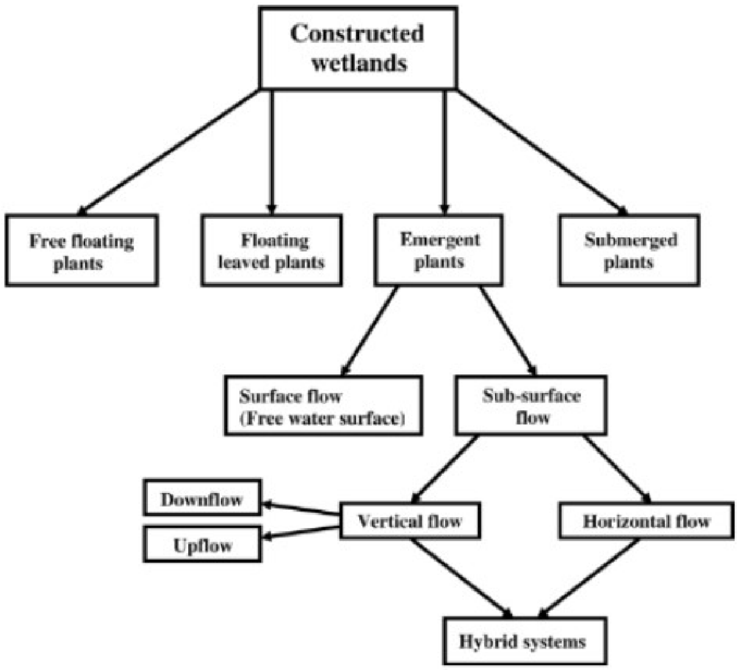

FIGURE 3.1: Classification of constructed wetlands for wastewater treatment (Vymazal, 2001)

Tanaka et al. (2011), state that constructed wetlands are engineered systems, that are along with other functions, intended to provide secondary treatment of municipal wastewaters, and polishing of secondary effluent and urban runoff based on macrophytes and other plants and co-existing microbial populations. Constructed wetlands may be suitable and incorporated as part of the landscaping in urban applications, not just limited to rural areas, consequently enhancing its applications in urban areas. According to Tanaka et al. (2011), wetland functions may be greatly affected by differences between tropical and temperate environments and this will sequentially have an impact on the use of wetlands for wastewater treatment. As wetlands can be found in all climate zonesthe possible applications of these systems modeled based on naturally occurring processes can have a great cumulative effect which can be used for the preservation of water as one of our most jeopardized resources.

Regarding the treatment processes of constructed wetlands, the removal of different pollutants is carried out in several ways: by the direct uptake of pollutants by the plants, degradation of pollutants by micro-organisms that grow rapidly on the large surface area provided by plants and substrate media, by filtering of large particles which happens through reed masses and root, by sedimentation of solids due to the declining velocity of flow through constructed wetlands, by the adsorption of nutrients by soil and substrate media, by UV radiation and throwing off of waste materials or waste substances (antibiotics) from the cells and tissues of plants to destroy pathogens and through natural die-off of pathogens over the period of the wetland detention time (Kandasamy and V, 2008)

The economic advantages of CWs to other wastewater system, especially due to low operation and maintenance (OM) costs (energy and supplies), ability to tolerate fluctuations in flow and load, easy maintenance, commercial and habitat value was pointed out by many authors (Ávila and García, 2015; Dakua et al., 2016; Gkika et al., 2014; Sudarsan et al., 2015; Vymazal, 2010). For this reason, CWs are often considered to enhance existing wastewater treatment systems in relatively poor communities (Ghrabi et al., 2011; Kivaisi, 2001; Li et al., 2014; Møller et al., 2012). In view of the fact that CWs store great volumes of water, they can also facilitate water reuse practices in regions that experience long periods of drought and water shortages and/or are likely to suffer from such in the future (Ávila and García, 2015; Barbagallo et al., 2014; Ghermandi et al., 2007; Greenway, 2005).

Along with the improvement of the chemical water quality, wetlands may considerably improve the ecological situation by reducing concentrations and loads of pesticides. There are many papers on the retention capability of constructed wetlands as a possible way to mitigate pesticide loss from arable land (Braskerud and Haarstad, 2003; Haarstad and Braskerud, 2005). Gopal and Goel (1993), discovered that acids like tannic acid and gallic acid are released from the roots of many aquatic plants, disinfecting the water.

Metazachlor is a herbicide inhibiting ergosterol. Passeport et al. (2013), observed 66% removal of metazachlor in an off-stream CW receiving runoff from an agricultural watershed in France. In an off-stream CW, Tournebize et al. (2013), observed metazachlor load reduction of 70% during the four-year period. Diflufenican is a selective contact herbicide inhibiting carotenoid biosynthesis. Passeport et al. (2013) observed 58% removal of diflufenican in an off-stream CW receiving runoff from the agricultural watershed in France. In the off-stream CW, Tournebize et al. (2013), observed diflufenican load reduction of 75% during the four-year period.

Atrazine is a systemic, selective broadleaf herbicide inhibiting photosynthesis (photosystem II) and is a widely used pesticide in corn fields. Atrazine was banned in the EU in 2004. Alvord and Kadlec (1996), modelled atrazine fate in Des Plaines CWs in Illinois, USA. Depending on the residence time, the removal of atrazine varied between 26 and 64%. Runes et al. (2003), reported atrazine removal from the nursery irrigation runoff in Portland, Oregon, USA, in the range of 16-24% in a FWS CW. Lin et al. (2008), observed atrazine half-life of 17.5 days with initial atrazine concentration of 0.1 mg/l being reduced to 0.054 in 15 days. Also, the authors pointed out that salinity substantially inhibited atrazine degradation. In their study from Tunica County, Mississippi, USA, (Lizotte Jr et al., 2009) found atrazine retention of 63% from a drainage ditch in a modified backwater wetland.

Aclonifen is a systemic and selective herbicide inhibiting carotenoid biosynthesis. Absorbed by the weed's leaves, the systemic herbicide starts to circulate inside the plant and reaches its roots. Tournebize et al. (2013), observed complete removal of aclonifen in the in-stream CW and 84% removal in off-stream CW receiving runoff from the agricultural watershed in France. In the off-stream CW, Passeport et al. (2013), observed aclonifen load reduction of 80% during the four-year period.

Azinphos-methyl is a non-systemic insecticide inhibiting acetylcholinesterase. Schulz and Peall (2001), reported the average removal of azinphos-methyl of 91% from the orchard runoff in South Africa. In terms of load, the removal amounted to 54%. Schulz and Peall (2001) and Schulz et al. (2003), reported azinphos-methyl retention between 77 and 93% and 90%, respectively, in the same constructed wetland. The authors also pointed out that during a period of five months, an increased concentration of azinphos-methyl (43 $\mu g/kg$) was observed in the wetland inlet zone suspended particles, while no pesticide was measurable in the suspended particles of the outflow zone (Schulz and Peall, 2001).

Chlorotoluron is a selective, non-systemic herbicide absorbed by roots and foliage. It acts by the inhibition of photosynthetic electron transport. Tournebize et al. (2013), observed release of chlorotoluron from the in-stream CW, but 86% removal in off-stream CW receiving runoff from the agricultural watershed in France were observed. In the off-stream CW, Passeport et al. (2013), observed chlorotoluron load reduction of 84% during the four-year period.

Chlorothalonil is a non-systemic, broad spectrum herbicide preventing spore germination and zoospore motility. In the off-stream CW, Passeport et al. (2013), observed 79% chlorothalonil load reduction during the four-year period. In a laboratory experiment (Sherrard et al., 2004), aqueous chlorothalonil concentration of 296 $\mu g/l-1$ was decreased by 98% in 12.5 hours after which the concentrations dropped below 0.1 $\mu g/l-1$.

Lambda-Cyhalothrin is a fourth generation non-systemic insecticide which modulates the sodium channel. Budd et al. (2009), observed concentration reduction of lambda-cyhalothrin in two CWs in the Central Valley, California of 71% and 90%. In terms of load, the estimated removal amounted to 98% and 99% in two wetlands. Moore et al. (2009), found that overall, water, plant and sediment compartments were responsible for 3%, 34% and 63%, respectively, of the measured lambda-cyhalothrin concentrations.

Cypermethrin is a non-systemic contact and stomach action insecticide modulating the sodium channel. Budd et al. (2009), observed concentration reduction of cypermethrinin two CWs in the Central Valley, California of 52% and 64%. In terms of load, the estimated removal amounted to 97% and 95%.

Epoxiconazole is a fungicide which is used for preventative and curative action. Tournebize et al. (2013), observed 83% removal of epoxiconazole in the in-stream CW and 72% removal in off-stream CW receiving runoff from the agricultural watershed in France. In the off-stream CW, (Passeport et al., 2013), observed epoxiconazole load reduction of 71% during the four-year period.

Esfenvalerate is a contact insecticide and sodium channel modulator. Budd et al. (2009), observed concentration reduction of esfenvaleratein two CWs in the Central Valley, California of 87% and 77%.

Fluometuron is a selective herbicide inhibiting photosynthesis. Rose et al. (2006), reported fluometuron removal between 0 and 34% in a pilot-scale CW treating irrigation tail water from a cotton field in New South Wales, Australia. Locke et al. (2011), reported removal of fluometuron in an experimental CW in Misissippi, USA, of 81% and 58% in shallow and deeper cells, respectively.

Isoproturon is as elective, systemic herbicide absorbed by roots and leaves inhibiting photosynthesis (photosystem II). Tournebize et al. (2013), observed 50% removal of isoproturon in the in-stream CW and 53% removal in off-stream CW receiving runoff from an agricultural watershed in France. In an off-stream CW, (Passeport et al., 2013), observed isoproturon load reduction of 45% during the four-year period.

S-Metolachlor is a selective, extensively used herbicide that controls broad-leaf weeds and grasses absorbed through roots and shoots. Lizotte Jr et al. (2009), reported 51% removal of S-metolachlor in a modified backwater wetland in the catchment of the Coldwater River in Mississippi, USA. Tournebize et al. (2013), observed only 16% removal of S-metolachlor in an in-stream CW but 87% removal in an off-stream CW receiving runoff from an agricultural runoff in France. In the off-stream CW, (Passeport et al., 2013), observed S-metolachlor load reduction of 80% during the four-year period.

Napropamide is a selective, systemic, herbicide absorbed through roots and translocated aboveground. It acts by preventing root cell elongation which disrupts growth. Tournebize et al. (2013), observed a 56% removal of napropamide in an off-stream CW receiving runoff from an agricultural watershed in France. In the same system, Passeport et al. (2013), observed napropamide load reduction of 73% during the four-year period.

Permethrin is a broad spectrum insecticide with contact and stomach action, and it acts as a sodium channel modulator. Budd et al. (2009), observed concentration reduction of permethrin in two CWs in the Central Valley, California, USA, of 90% and 94%. In terms of load, the estimated removal amounted to

100% and 99%. Moore et al. (2013), also observed high removal in permethrin in experimental mesocosms planted with Leersia oryzoides, Sparganium americanum and Typha latifolia. The removal of cis-permethrin varied between 85% and 87% among plants while unplanted mesocosm exhibited removal of 72%. For trans-permethrin, planted mesocosms exhibited removal between 78% and 88%, while unvegetated mesocosm removed 68% of the pesticide.

Prosulfocarb is a selective herbicide absorbed by leaves and roots. It inhibits chain extension of fatty acids. Tournebize et al. (2013), observed a 65% removal of prosulfocarb in off-stream CW receiving runoff from an agricultural watershed in France. In the same system, Passeport et al. (2013), observed prosulfocarb load reduction of 93% during the four-year period.

Tebuconazole is a systemic fungicide that disrupts membrane function. Tournebize et al. (2013), observed complete removal of tebuconazole in the in-stream constructed wetland and 61% removal in off-stream CW receiving runoff from an agricultural watershed in France. In the same CW, Passeport et al. (2013), observed tebuconazole load reduction of 86% during the four-year period.

Kivaisi (2001), classified constructed wetlands based on the life forms of the macrophytes or the dominating large aquatic plants in the system, further classification is mostly derived from the water flow regime (Vymazal, 2007), shown in Figure 3.2.

Free water surface (FWS) wetlands

Reed et al. (1988), state that constructed wetlands with surface flow or free water constructed wetlands (FWS CWs) consist of a basin or channel, water at a relatively shallow depth flowing through the unit, and a suitable medium, usually soil to support the rooted vegetation. The shallow water depth, the presence of plant stems and litter, and low flow velocity regulate water flow, especially in long, narrow channels.

According to Jorgensen (2009), the water surface is above the sediment, litter, and soil, but live and dead plant parts are above the water level. In FWS CWs the near-surface layer is aerobic, whereas deeper water and substrate are usually anoxic or anaerobic. Water depths usually range from a few centimeters to a meter. Dense vegetation covers a large portion of the surface, typically more than 50%. Natural assemblages of volunteer regrowth from native seed banks are frequently used in addition to planted macrophytes. Contracting wastewater with reactive biological surfaces is one of their key design objectives.

Kadlec and Wallace (2008), describe FWS wetlands as areas that consist of open water, floating vegetation, and emergent plants. Dependent upon the locality and soil conditions, liners, berms, and dikes are used to control infiltration and water flow. The wastewater moving through the FWS wetland is treated by different processes, such as sedimentation, filtration, oxidation, reduction, adsorption, and precipitation. Authors state that as the FWS constructed wetlands have the appearance of natural wetlands, they attract many different forms of wildlife such as insects, mollusks, fish, amphibians, reptiles, birds, and mammals.

Common applications of FWS wetlands are for advanced treatment of effluent from secondary to tertiary treatment processes like activated sludge systems and trickling filters. As FWS wetlands can deal with pulse flows and changing water levels, they are commonly used in treating urban, agricultural, and industrial stormwater. They are often used for the treatment of mine waters, and for groundwater remediation and leachate treatment (Kadlec and Wallace, 2008).

Removal of atrazine of 60% was reported by Page et al. (2010), in a CW for storm-water runoff in Adelaide, Australia. Locke et al. (2011), reported removal of atrazine in an experimental CW in Mississippi, USA, of 89% and 70% in shallow and deeper cells, respectively. Moore et al. (2013), observed removal of atrazine load of 45%, 35% and 31% in mesocosms planted with *Leersia Oryzoides, Typha latifolia* and *Sparganium americanum*, respectively. The removal in planted mesocosms was substantially higher than in unplanted mesocosm (13% removal). Weaver et al. (2004), studying the sediment from a CW receiving pesticides, found atrazine dissipated rapidly in saturated and flooded soils, but only 10% of atrazine was mineralized to CO2. In a FWS CW in France, (Passeport et al., 2013), observed atrazine load reduction of 64% during the four-year period. In a combination of saturated and unsaturated wetlands (rain gardens), atrazine was eliminated by 90% in a simulated stormwater runoff (Yang et al., 2013).

Diazinon is a non-systemic organophosphate insecticide with respiratory and contact action that inhibits acetylcholinesterase. It is part of a class of compounds originally designed to replace the more persistent organochlorine insecticides (Moore et al., 2013). Experiments carried out by (Moore et al., 2007), revealed that 43%, 23% and 34% of the study´s measured diazinon mass was associated with plants, sediments and water, respectively, of the FWS CW in Mississippi. Moore et al. (2013), reported removal of diazinon load of 61%, 50% and 25% in mesocosms planted with *Leersia Oryzoides, Sparganium Americanum* and *Typha Latifolia*, respectively. The removal in mesocosms planted with *Leersia oryzoides* and *Sparganium americanum* was substantially higher than in unplanted mesocosm (28% removal).

Fenpropimorp is a systemic fungicide that disrupts membrane function. It is used for protective and curative purposes. Removal of fenpropimorph amounted to 36% and 10% during two consecutive years in a FWS CW in Norway (Braskerud and Haarstad, 2003). In another study from Norway, Blankenberg et al. (2007), observed an average fenpropimorph removal of 39%.

Metalaxyl is a systemic fungicide which suppress sporangial formation and mycelial growth. Braskerud and Haarstad (2003), found 41% retention of metalaxyl in a FWS CW in Norway. However, during the following year, the same CW became a source of this pesticide (-11%). In another study from Norway, (Blankenberg et al., 2007), observed an average metalaxyl removal of only 19%, suggesting that retention of this pesticide in CWs may not be effective.

Metamitron is a selective, systemic herbicide which is absorbed mainly by roots and is translocated aboveground. It inhibits photosynthesis (photosystem II). Removal of metamitron amounted to 58% and 7% during two consecutive years in a FWS CW in Norway (Braskerud and Haarstad, 2003). In another study from Norway, Blankenberg et al. (2007), observed average metamitron removal of 35%.

Metribuzin is a selective, systemic herbicide with contact and residual activity which inhibits photosynthesis (photosystem II).Removal of metribuzin amounted to 40% and 19% during two consecutive years in a FWS CW in Norway (Braskerud and Haarstad, 2003). In another study from Norway, Blankenberg et al. (2007), observed average metribuzin removal of only 15%.

Propachlor is a selective, systemic herbicide that effects cell formation and protein synthesis. Removal of propachlor amounted to 67% and 14% during two consecutive years in a FWS CW in Norway (Braskerud and Haarstad, 2003). In another study from Norway, Blankenberg et al. (2007), observed average propachlor removal of 35%.

Linuron is a selective, systemic herbicide with contact and residual action inhibiting photosynthesis (photosystem II). Braskerud and Haarstad (2003), observed removal of linuron of 30% and 3% during two consecutive years in a FWS CW in Norway. In another study from Norway, Blankenberg et al. (2007), observed average linuron removal of 26% and 56% in 2003 and 2004, respectively.

FWS systems provide the necessary support and benefits in form of human uses like lowering the temperature and for wildlife habitat among others. Kadlec and Wallace (2008), state that the operating costs are mostly low and cost-competitive with alternative technologies.

Horizontal subsurface flow wetlands

Constructed wetlands with the subsurface flow are classified in accordance with the direction of flow to horizontal flow (HSSF CW) and vertical flow (VF CW). Kadlec and Wallace (2008), state that HSSF wetlands generally consist of inlet piping, filter media, clay or synthetic liner, emergent vegetation, berms, and outlet piping with water level control. The wastewater stays underneath the surface of filter media and flows around and in the rhizomes and roots of the plant. They are mostly treating primary effluent ahead of surface water discharge or soil dispersion. As the wastewater during the process is underneath the surface, the exposure to pathogenic organisms for humans and wildlife is minimized. According to the authors, the operational downside or consideration is the tendency for clogging the media. HSSF wetland construction is commonly more expensive than FWS wetlands, but the maintenance costs are still low compared to alternatives. Horizontal subsurface flow constructed wetlands have suitable conditions for nitrate reduction as they have anoxic/anaerobic conditions in the filtration bed. The necessary organics are provided through release from decomposing plant biomass and the release of organics from rhizomes and roots in order to ensure the anaerobic conditions (Z et al., 2013). There is a limited amount of available information published about the use of horizontal subsurface flow constructed wetlands (Bruun et al., 2016; Carstensen et al., 2019; Vymazal et al., 2020).

Alachlor, a selective lipid synthesis inhibitor absorbed by germinating shoots was detected in a pilot plant HF CW in Spain. Matamoros et al. (2007), observed 80% removal of alachlor from a municipal wastewater spiked with a mixture of pesticides. Elsayed et al. (2014b), reported alachlor removal of 51% in a laboratory VFS wetland. Using the CSIA (Compound-Specific Isotope Analysis), the authors concluded that biodegradation was responsible for alachlor removal.

Metolachlor is a selective herbicide that reduces seed germination and inhibits mitosis and cell division. Moore et al. (2001), observed an average 73% metolachlor removal in the experimental wetlands in Mississippi, USA. The authors observed that up to 25% of measured metalochlor mass was found in the first 30-36 m of the wetland immediately after application and about 10% of metolachlor mass was sequestered in the plant biomass. In a HF CW, George et al. (2003), reported removal of metolachlor from a container nursery runoff in Tennessee, USA, in the range of 62-96% for areal mass loadings of 1037 and 260 mg m-2, respectively. The wetlands planted with *Scirpus Validus* removed more pesticide (62%) as compared to identical filters without plants (34%). In the same system, metolachlor removal of 82.4% and 63.2% in mesocosms planted with *Scirpus Validus* and unplanted units, respectively,were obsereved. Elsayed et al. (2014a), observed only 23% removal of metolachlor in an experimental up-flow VF CW.

Simazine is a selective, systemic herbicide absorbed through roots and foliage and translocated aboveground. It inhibits photosynthesis (photosystem II). George et al. (2003), reported removal of simazine from a container nursery runoff in HF CW in Tennessee, USA, in the range of 60-96% in the mass balance. The authors also pointed out that removal of simazine was significantly higher in planted wetlands than in unplanted filters which were otherwise identical. In the same system, removal of simazine was observed at 77.1% and 64.3% in vegetated and unvegetated mesocosms. In a pilot plant HF CW in Spain, Matamoros et al. (2007), observed 25% removal of simazine with about 2% of the injected pesticide being found in the gravel bed associated with the biofilms. Removal of 57% simazine was reported by (Page et al., 2010), in a CW for stormwater runoff in Adelaide, Australia. Maillard et al., reported removal of simazine of 36%, 60% and 39% during the spring, summer and wine growing season, respectively in FWS-HF CW treating runoff from a vineyard in France.

Chlorpyrifos is a non-systemic organophosphate insecticide inhibiting acetylcholinesterase applied both in agriculture and urban areas. Schulz and Peall (2001), reported that inflow chlorpyrifos concentration of 0.02 $\mu g/l$ was reduced to undetectable values at the outflow from a CW treating orchard runoff in South Africa. In a series of laboratory experiments, Sherrard et al. (2004), observed removal of chlorpyrifos of at least 98%. In a pilot plant HF CW in Spain, Matamoros et al. (2007), observed 83% removal of chlorpyrifos in Spain. Budd et al. (2009), observed chlorpyrifos concentration reduction of 61% and 52% in two CWs in the Central Valley, California. In terms of load, the estimated removal amounted to 98% and 93%. In a mesocosm study in Colombia, Agudelo et al., observed overall removal of chlorpyrifos of 96.2% in CWs filled with igneous rock and planted with *Phragmites Australis*.

Diuron is a systemic herbicide absorbed via roots andstrongly inhibits photosynthesis. Rose et al. (2006), reported diuron removal between 27 and 55% in a pilot-scale CW treating irrigation tailwater from a cotton field in New South Wales, Australia. In a pilot plant HF CW in Spain, Matamoros et al. (2007), observed zero removal of diuron from a municipal wastewater spiked with a mixture of pesticides. Removal of diuron of 51% was reported by Page et al. (2010), in a CW for stormwater runoff in Adelaide, Australia. Maillard et al., reported removal of diuron of 72%, 57% and 67% during the spring, summer and wine growing season, respectively in FWS-HF CW treating runoff from a vineyard in France.

Endosulfan is a non-systemic contact insecticide. Rose et al. (2006), reported an endosulfan half-life of only 7.5 days with enhanced removal in the presence of vegetation in the wetland. In HF constructed wetland at Les Franqueses del Valles in Spain, Matamoros et al. (2007), observed >99% removal of endosulfan from a wastewater spiked with a mixture of pesticides.

Glyphosate is a broad spectrum, systemic, post-emergence herbicide which inhibits lycopene cyclase. It is used worldwide to control weeds in agricultural, silvicultural, and urban areas (Imfeld et al., 2013). The major degradation product of glyphosate is aminomethylphosphonic acid (AMPA). Maillard et al., reported removal of glyphosate of 90%, 77% and 79% during the spring, summer and wine growing season, respectively in a HF CW treating runoff from a vineyard in France. However, the retention of the degradation product AMPA was much lower and amounted to only 10%, 59% and 52%, respectively. In the same system, Imfeld et al. (2013), observed glyphosate load removal between 92 and 100% while AMPA load removal varied between 30 and 95%. The authors pointed out that biodegradation of AMPA is generally slower as compared to glyphosate, probably due to AMPA´s ability to adsorb through the phosponate group that results in lower desorption and consequent bioavailability (Borggaard and Gimsing, 2008). In a combination of saturated and unsaturated wetlands (rain gardens), glyphosate was eliminated by 99% in a simulated stormwater runoff (Yang et al., 2013).

Azoxystrobin is a systemic fungicide inhibiting respiration. Maillard et al., reported 93% removal of azoxystrobin during both summer and wine growing seasons in a FWS-HF CW treating runoff from a vineyard in France. Tournebize et al. (2013), observed complete removal of azoxystrobin in the in-stream CW receiving runoff from the agricultural watershed in France.

Vertical subsurface flow wetlands

Kadlec and Wallace (2008), state that VF constructed wetlands in Europe contain a flat bed of soil that contains particles of a wide range of sizes with a good representation of all sizes with sand that is planted with *Phragmites*. The surface of the beds is pulse-loaded with a large volume of water to temporarily flood the surface. The wastewater drains vertically through the bed with an unsaturated flow (some of the soil pores become air-filled and the conductivity decreases). The air is drawn into the beds as the bed drains which leads to reaerating the microbial biofilms. Good oxygen transfer is provided by the pulse loading which enables VF wetlands to nitrify. Contradictory, the removal of total nitrogen in VF systems is limited as these systems usually provide hardly any denitrification. According to the authors, VF constructed wetlands are generally used more in colder climates for the reason that freezing during winter helps in dewatering. VF constructed wetlands were initially utilized as filtration beds in the first stage of the wastewater treatment process. In comparison to the HF systems which take up about 5-10 m^2/PE, VF constructed wetlands require less land (1-3 m^2/PE). According to the authors, VF technology is adapted in most european countries, especially for small sources of pollution in Austria, Denmark, France, Germany, and the United Kingdom.

MCPA is a selective, systemic herbicide which is translocated in the plant. Cheng et al. (2002), observed a 36% removal of MCPA in a small VF CW. Similar removals of 27% were observed by Braskerud and Haarstad (2003), in a FWS CW in Norway. Dordio and Carvalho (2013), described removal of MCPA under various contact times and influent concentrations. In wetland beds planted with *Phragmites australis*, the removal was much higher (89.3%) than in unplanted beds (52.4%) with a contact time of 3 hours. When the contact time was extended to 6 hours, removal in the planted unit (99.1%) was only slightly higher than in unplanted units (96.7%).

Dicamba is a selective, systemic herbicide absorbed through leaves. In a small VF CW, Cheng et al. (2002), observed zero removal of dicamba. Also Braskerud and Haarstad (2003), measured very low removal of only 3% in a FWS CW in an agricultural watershed in Norway. Elsaesser et al. (2011), reported 80% removal of dicamba in vegetated cells of an experimental FWS CWs in Norway. Identical cells without plants exhibited only 47% removal. In a combination of saturated and unsaturated wetlands (rain gardens), dicamba was eliminated by 92% in a simulated stormwater runoff (Yang et al., 2013).

Higher removal efficiency can be accomplished by joining together different types of constructed wetlands. The combination of various types of CWs in a staged manner is called a hybrid CW. According to (Kadlec and Wallace, 2008) and Jorgensen (2009), most hybrid systems are combined of horizontal and vertical flow wetland cells. The common configuration is the vertical flow stage followed by the horizontal SSF wetland cells. The benefits of HF and VF are coupled in hybrid systems to enhance each other. It is possible to produce a low-BOD (biochemical oxygen demand) effluent that is completely nitrified and partially denitrified, with substantially lower total-N concentrations. Hybrid CWs can include any sort of CW, however the majority of research is focused on those with subsurface flow. Many of the VF-HF systems are based on Seidel's original system at the Max Planck Institute in Krefels, Germany. The Seidel system, the Krefeld system, or the Max Planck Institute Process (MPIP) are all names for the same process. Two stages of several parallel VF beds are followed by two or three HF beds in sequence in the Seidel design. The VF stages are commonly planted with P. australis, whilst the HF stages are planted with *Iris, Schoenoplectus, Sparganium, Carex, Typha*, or *Acorus*, among other emergent macrophytes. The main idea behind this design is to achieve some organics and suspended solids removal as well as ammonia nitrification in the first VF stage, while further organics and suspended solids removal as well as denitrification occurs in the second HF stage (Jorgensen, 2009).

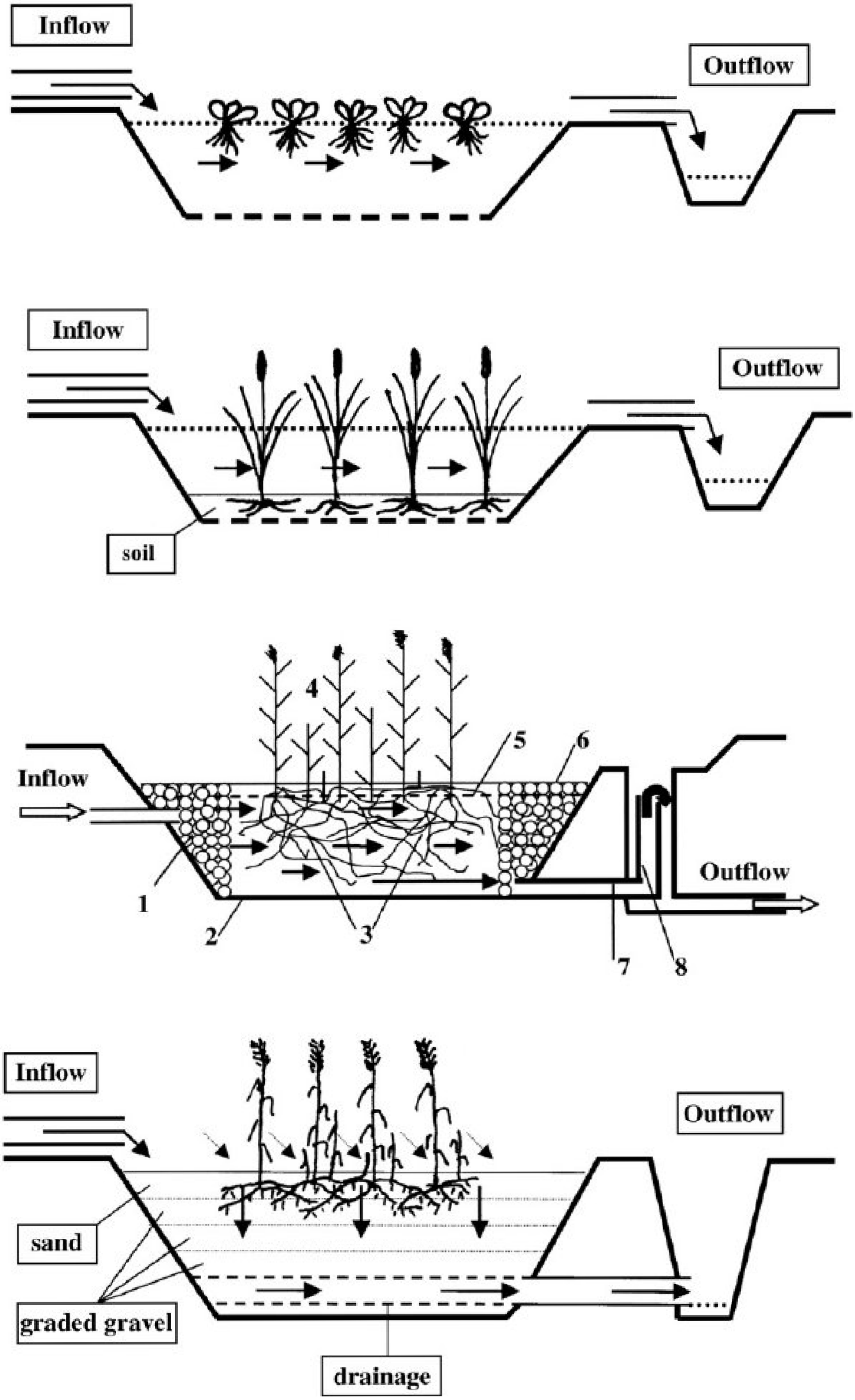

FIGURE 3.2: CW with free-floating plants (FFP), CW with free water surface and emergent macrophytes (FWS), CW with horizontal sub-surface flow (HSSF, HF), CW with vertical sub-surface flow (VSSF, VF) (Vymazal, 2001)

CHAPTER 4

Characteristics of study area

In 2018, three experimental constructed wetlands with horizontal subsurface flow were established at the discharge of a tile drainage from 15.73 ha watershed near Veliký Rybník, about 130 kilometers southeast of Prague (Czech Republic). The average altitude of the watershed is 510 m a.s.l. and the area of drained fields within the watershed is 9.85 ha. The wetlands have surface areas of 79 m^2 (M1), 90 m^2 (M2) and 98 m^2 (M3) and are planted with a combination of *Phalaris arundinacea* (Reed canarygrass) and *Glyceria maxima* (Sweet mannagrass) planted in parallel bands. The substrate in the first two CWs is crushed rock (4–8 mm) mixed with air-dried (one month) birch woodchips with the volume ratio of 10:1.

The water level in the first wetland (M1) is kept 10 cm above the surface, whereas the water level in the second wetland (M2) is kept 5 cm below the surface. The third wetland (M3) has a 20-centimeter layer of birch woodchips on top of gravel (4–8 mm), and the water level is kept about 10 centimeters above the surface to keep the woodchips flooded. Schematic layout is shown in Figure 4.4. All of the wetlands are 1.0 meters deep and also have a 1 mm plastic liner.

The period evaluated in this study started on August, 2018 and finished on August, 2021. During this period, the water samples were taken at four locations, at the inflow to the wetlands and outflows from M1, M2 and M3 (Vymazal et al., 2020).

The inflow is equipped with a continuous measurement of flow and dissolved oxygen with 10-min reading. All outflows are equipped with continuous measurements of flow, dissolved oxygen and water temperature.

FIGURE 4.1: Experimental constructed wetland M1 with horizontal subsurface flow near Veliký Rybník (Vymazal, September 2021).

FIGURE 4.2: Experimental constructed wetland M2 with horizontal subsurface flow near Veliký Rybník (Vymazal, September 2021).

FIGURE 4.3: Experimental constructed wetland M3 with horizontal subsurface flow near Veliký Rybník (Vymazal, September 2021).

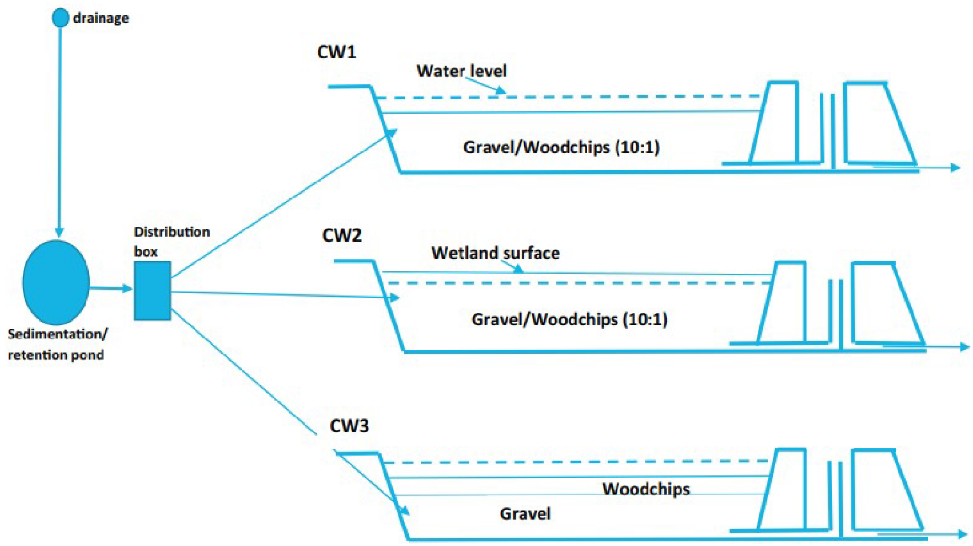

FIGURE 4.4: Schematic layout of constructed wetlands M1, M2 and M3 (Vymazal et al., 2020).

CHAPTER 5

Methodology

The observations and samples from Veliky Rybnik were collected during 4 years. The data from field was analyzed and used to understand the potential of the M1,M2 and M3 constructed wetlands for mitigation of ESA and OA metabolites of Acetochlor, Alachlor, Dimetachlor, Metazachlor and Metolachlor, as well as DEET by analyzing the annual flow for the pesticides and their metabolites for 2018, 2019,2020, and 2021. The analysis for pesticides and their metabolites were done by means of the state owned Vltava River Board, equipped with highly sophisticated devices.

Several chloroacetanilide herbicides and their metabolites ethane sulfonic acids (ESA) and oxanilic acids (OA) were monitored. Outflow from individual wetlands M1, M2 and M3 is considered on an annual base, the inflow equals outflow. Flow at outflows was measured every 10 minutes, providing the daily means for the day when samples were taken. The period evaluated in this study started on August 22, 2018 and finished on August 11, 2021. During this period, the water samples were taken at four locations - inflow of the wetlands and outflows from M1, M2 and M3. Mostly metabolites (OA and ESA) of several chloroacetanilides (alachlor, acetochlor, metolachlor, metazachlor and dimethachlor) were detected. Total pesticide concentrations over 1 year and over the whole monitoring were calculated by summing individual sample loads during the corresponding period.

Using the R software, the analysis for the annual flow for the pesticides for 2018., 2019.,2020., and 2021. was done to detect differences between artificial wetlands M1, M2 and M3 during this period.

The analysis of heavy metals was done in the department of Environmental Geo-sciences using ICP-OES (Agilent Technologies, Santa Clara, California).

The heavy metals were not analysed in the beginning of the project so the results present are for the period of 2020-2021.

CHAPTER 6

Results

As shown the ESA and OA metabolites of the analysed Acetochlor, Alachlor, Dimetachlor, Metazachlor and Metolachlor pesticides were detected. Despite the fact that Alachlor and Acetochlor were banned in EU in 2007 and 2013, respectively, the ESA and OA metabolites of both pesticides were still detected.

Removal of Alachlor ESA (Figure 6.1) in 2018 was highest in M1 CW and lowest in M2 CW. During 2019, removal of Alachlor ESA was lowest in M1, slightly higher in M2 and highest in M3. In 2020 removal was similar in M1, M2 and M3, slightly higher efficiency in M2. 2021 was the only year where removal in M1 was not detected, with small removal in M2 and M3 CW.

Regarding the Acetochlor removal of the ESA derivatives of the studied compounds, the M2 and M3 constructed wetlands showed significantly lower removal of the ESA derivatives than the M1 constructed wetland in 2018. However, during 2019, concentrations of Acetochlor ESA in M1 were higher than at the Inflow, while in M2 and M3 were lower than at the Inflow. During 2020, and 2021. M1, M2 and M3 removal of Acetochlor ESA was successful as shown in Figure 6.2.

DEET or diethyltoluamide, the most common active ingredient in insect repellents was slightly removed in M2 during 2018, while a higher efficiency was observed in M3 and highest in M1. During 2019, DEET was detected in M1 and M3. In 2020 M1, M2 and M3 were successful in eliminating DEET, with the highest removal efficiency in M3. In 2021. the M2 CW was not efficient in removal, M1 CW had slight removal efficiency, while the M3 CW showed the highest removal efficiency, as shown in Figure 6.3

Dimetachlor ESA derivatives were removed during 2018 in M1, M2 and M3, however there was no removal during 2019. In 2020, there was a small removal in M1 and M2 and slightly higher removal in M3. In 2021. all CW had a slight removal efficiency of Dimetachlor ESA derivatives as shown in Figure 6.4.

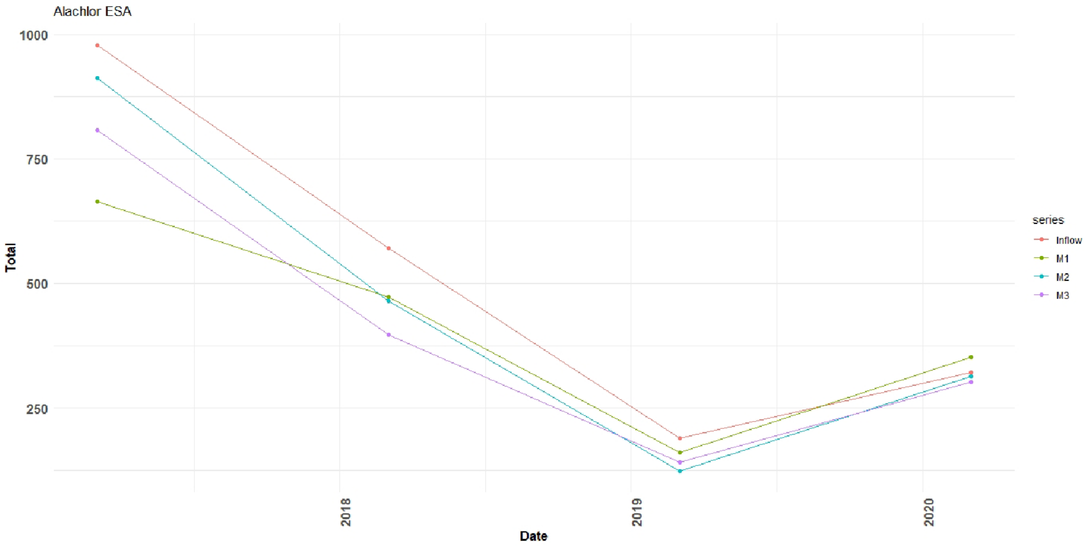

FIGURE 6.1: Alachlor ESA

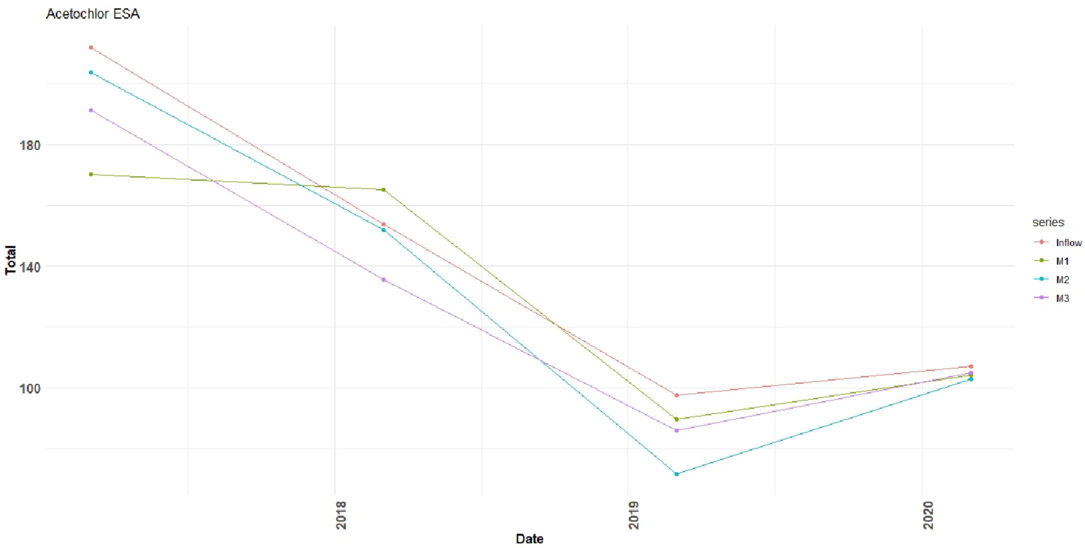

FIGURE 6.2: Acetochlor ESA

Metazachlor ESA derivatives were removed to a slight extent during 2018.in M1 and M3. In 2019., Metazachlor ESA derivatives were moderately removed in M1 and M3 with a lesser efficiency in M2. A corresponding removal was detected for M1, M2 and M3 CW during 2020. and during 2021. there was no considerable removal efficiency for any of monitored CW, as shown in Figure 6.5.

Regarding the Metazachlor OA derivatives removal, Figure 6.6, there was no observed removal in M2 during 2018 and no considerable removal in M1 and M3. During 2019, the highest removal was observed in M1 and moderately lower removal was detected in M2 and M3 CW. The same removal effectiveness was observed in the next year 2020. In 2021 there was no considerable removal efficiency for any of monitored CW M1, M2 or M3.

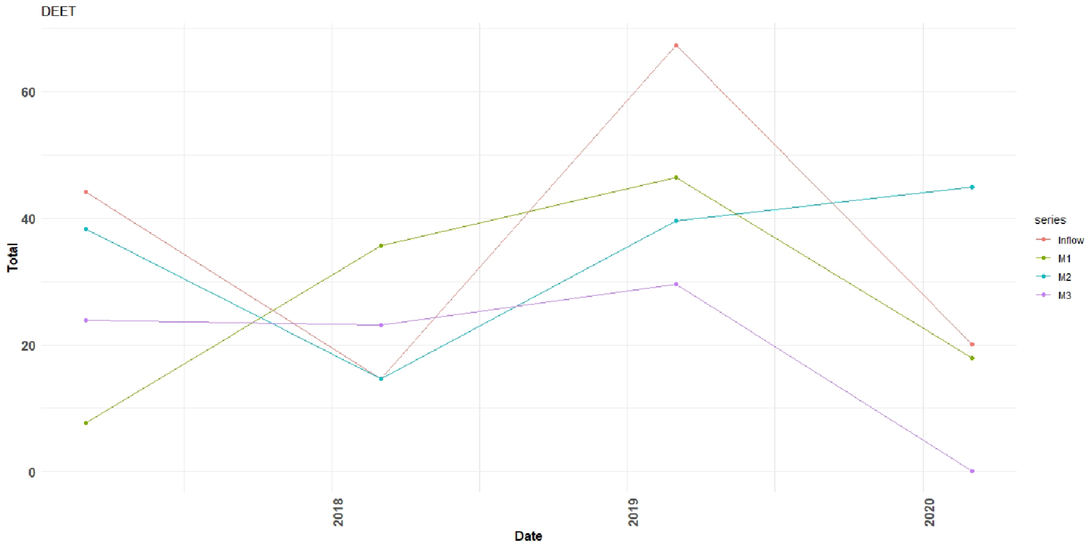

FIGURE 6.3: DEET

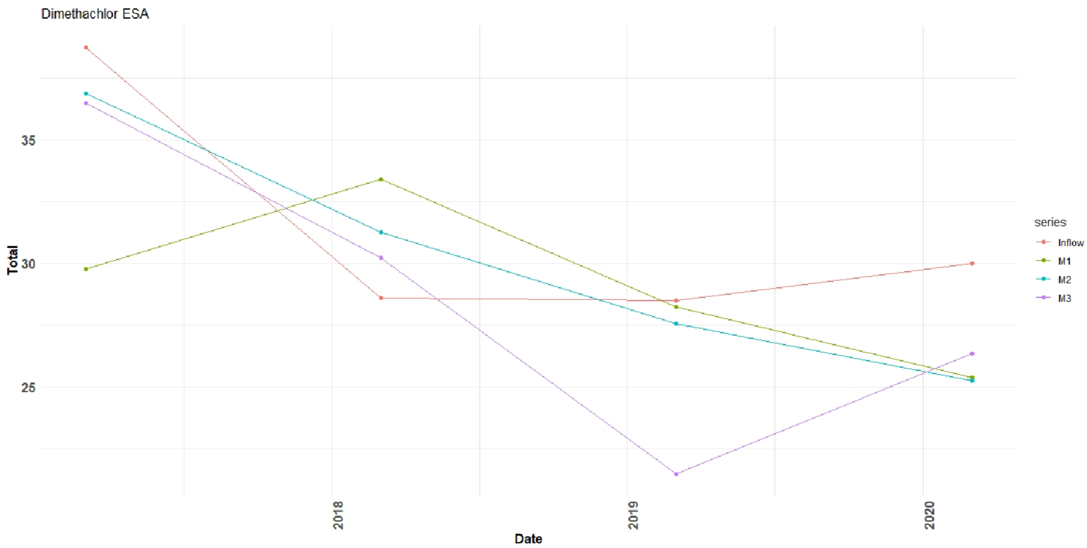

FIGURE 6.4: Dimetachlor ESA

Metolachlor ESA derivatives were moderately removed in M1 and M3 during 2018. and there was no significant removal observed in M2 in this year. During 2019., removal of Metolachlor ESA derivatives was observed in M3, with no removal efficiency for M1 and M2 during this year. During 2020, however, all 3 observed CW M1, M2 and M3 showed removal efficiency, with the highest removal in M2 CW. In year 2021, there was no noteworthy removal in any of the observed CW M1, M2 or M3, as shown in Figure 6.7.

Metolachlor OA derivatives were not significantly removed during 2018., even though there was a slight removal detected in observed M1 CW. In 2019., the highest removal efficiency was detected in M3 CW. Lower removal was observed in M1 CW and there was no removal efficiency in M2 CW during this year. In

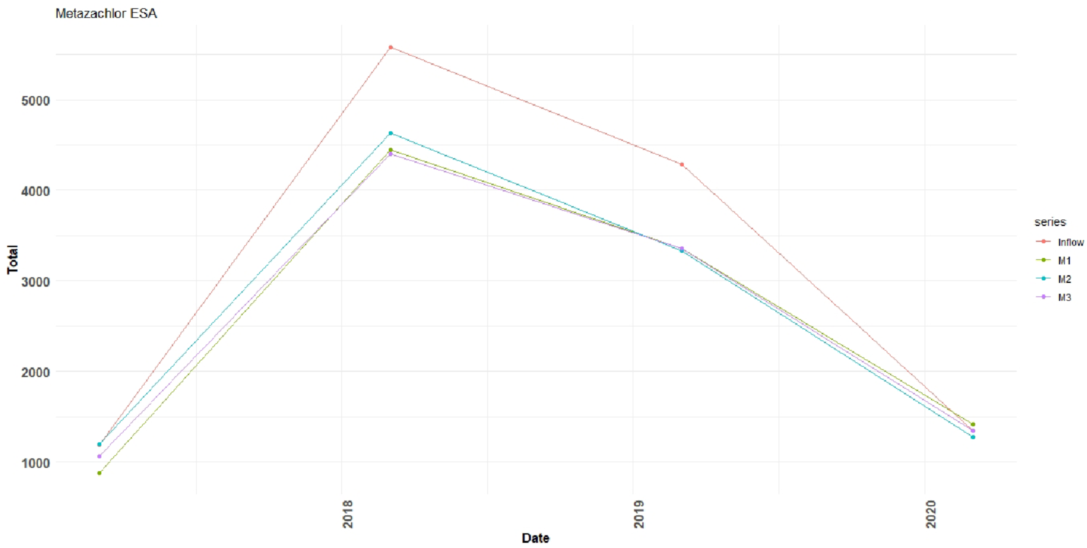

FIGURE 6.5: Metazachlor ESA

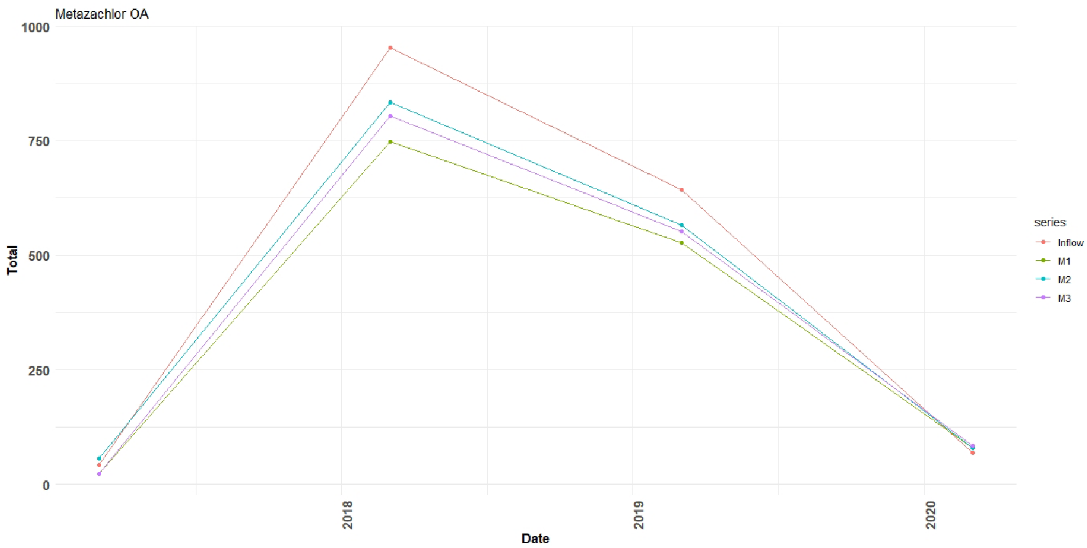

FIGURE 6.6: Metazachlor OA

2020, all 3 observed CWs M1, M2 and M3 showed some removal efficiency with the highest being in M3 CW and lowest in M1 CW. In the year 2021., there was no noteworthy removal in any of the observed CW M1, M2 or M3, as shown in Figure 6.8.

The results revealed that metal and metalloids removal was frequently low during two subsequent years, in all CWs M1, M2 and M3 shown in Table 6.1. This could be explained by metals precipitating in the anoxic/anaerobic filtration bed, rendering them inaccessible for plant uptake. No attempt has yet been made to explain the variability in metals and metalloids accumulation or to selecting the optimal conditions for metal uptake by plants in constructed wetlands. There were no elevated concentrations, hence they did not pose serious problem in the

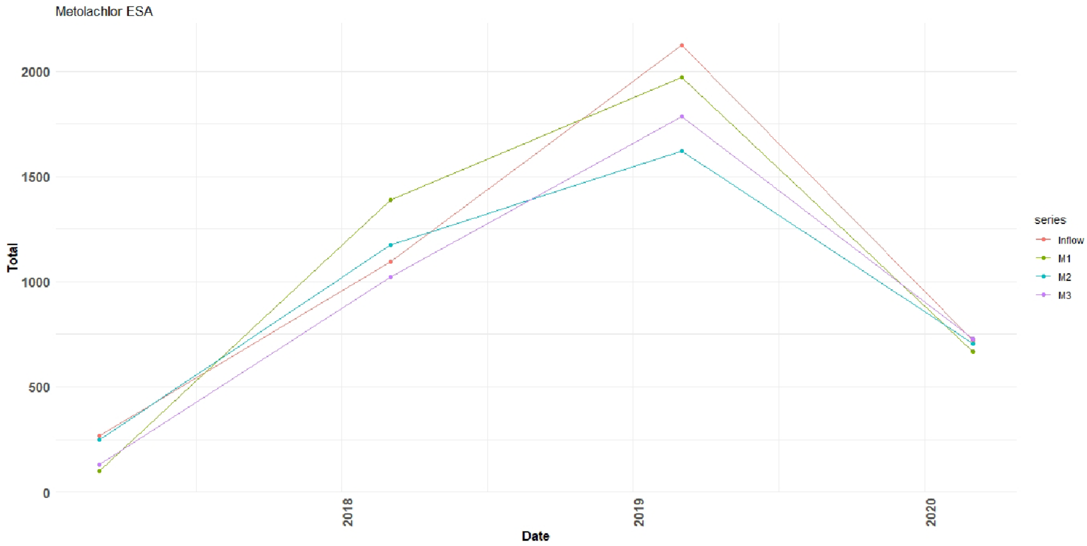

FIGURE 6.7: Metolachlor ESA

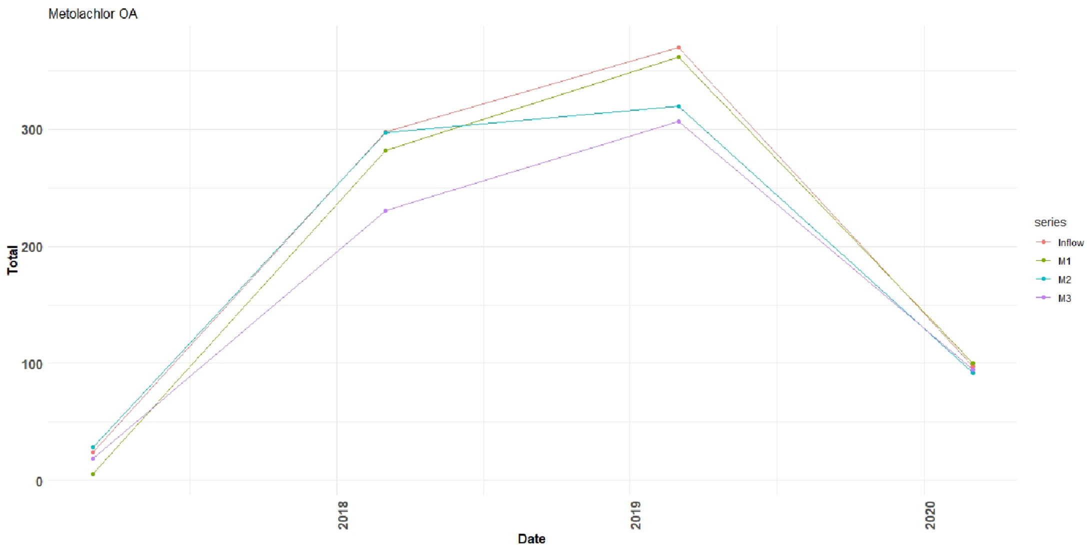

FIGURE 6.8: Metolachlor OA

drainage waters during 2020 and 2021. Ca, K, Na and Mg are usually not retained in constructed wetlands.

Table 6.1: Average values of metals and metalloids in M1,M2 and M3 CW in 2020 and 2021 (mg/l)

Year	Inflow l/s	Ca	Fe	K	Mg	Mn	Na	Pb
2020	0,23	34,6	0,0004	9,61	8,77	0,21	9,86	0,007
2021	0,28	38,9	0,0055	2,93	12,60	0,01	12,79	11,38

CHAPTER 7

Discussion

The removal of pesticides in constructed wetlands M1, M2 and M3 was generally not high, as these constructed wetlands were primarily built for removal of Nitrates and denitrification is an anaerobic process, while the pesticides are rather removed in aerobic conditions. Hence, the removal of pesticides and heavy metals was an additional effect.

Tentatively, the removal of the ESA derivatives appears to be correlated with the nitrate removal, because the CWs provided significantly higher elimination of nitrate in previous studies at the same monitored constructed wetlands (Vymazal et al., 2020). Thus, it is suggested that the conditions specific of denitrification can be conducive to the elimination of the ESA derivatives.

The evaluation of the disappearance of the parent compounds and the accumulation of their metabolites is frequently carried out in order to determine their dissipation in the environment (Fenner et al., 2013). In a study conducted by Elsayed et al. (2015), the difference in metolachlor enantiomer fractions between the oxic zone and the rhizosphere zone in CWs was used to estimate preferred biodegradation of s-metolachlor. Ethane sulfonic acids (ESA) and oxanilic acids (OA) are the most frequently detected chloroacetanilide metabolites. Although anaerobic degradation of metolachlor has been observed, its metabolites (ESA and OA) do not accumulate significantly under anaerobic conditions, which is in correspondence with obtained results of this thesis. The biodegradation of metolachlor, acetochlor, and alachlor in lab-scale wetlands was demonstrated by compound-specific isotope analyses by Elsayed et al. (2014b).

Pesticide concentrations at the watershed outlet varied over the years most likely due to farmer pesticide application masses and timings, as well as rain events, as observed in previous studies (Branger et al., 2009; Passeport et al., 2013). This could explain the considerably high removal of Metolachlor ESA derivatives in M2 measured in 2020 (Figure 6.7), Metazachlor ESA derivates in M1, M2 and M3 in 2019 and 2020 (Figure 6.5). Furthermore, interruptions in drainage flows allow for pesticide molecular diffusion toward less concentrated zones and accelerated leaching when flow resumes (Cote et al., 2000). This suggests that previously applied pesticides were likely re-mobilized during the observation period, as shown for Dimetachlor ESA in 2019 for M1, M2, and M3 CWs (Figure 6.4), as well as for DEET in 2019 for M1 and M3 and in 2021 for M2 (Figure 6.3).

Heavy metals, unlike organic pollutants, are not degraded through biological processes and must be removed for water purification. Phytoremediation is a viable approach of treating polluted soil and water by utilizing vegetation to remove, detoxify, or stabilize persistent pollutants. Constructed wetlands system is potentially good economical tool for protecting aquatic ecosystems from metal pollution as well as providing good quality drinking water from polluted water from wells and springs due to its low operating cost and high decontamination efficiency. Because the compact design of these treatment units makes it possible for greenhouse operation where industrial surplus energy (e.g. exothermal production processes, air conditioning) is available, these systems can be used for cost-effective decontamination of industrial runoff and metal polluted water all year, even in industrialized areas with a cold season (Shuiping et al., 2002).

The science of water treatment is continuously evolving. The public's expectations for water quality, on the other hand, have never been higher. As new challenges emerge and the core mission develops, it is critical to integrate existing strategies and innovative tactics. Water treatment techniques in the future must be considered holistically, taking into account all benefits and impacts on the community, environment, and society.

The major focus of treatment of drainage waters using constructed wetlands around the world is on nitrates, but there is a potential for the removal of pesticides and metals.

CHAPTER 8

Conclusion and contribution

The aim of this thesis was to examine the growing potential of usage of constructed wetlands for treatment of agriculture drainage from pesticides and heavy metals by degradation processes in the controlled field setting in three constructed wetlands near Veliký Rybník, about 130 kilometers southeast of Prague (Czech Republic). The experiments were done at three experimental constructed wetlands with horizontal subsurface flow planted with a combination of *Phalaris arundinacea* (Reed canarygrass) and *Glyceria maxima* (Sweet mannagrass) planted in parallel bands during 4 years.

The results indicate that the ESA and OA metabolites of the analysed Acetochlor, Alachlor, Dimetachlor, Metazachlor and Metolachlor, as well as DEET pesticides were detected. Despite the fact that Alachlor and Acetochlor were banned in EU in 2007 and 2013, respectively, the ESA and OA metabolites of both pesticides were still detected.

The amount of metals sequestered in plant tissue as a percentage of total metal removal in the constructed wetland differs in studies. Furthermore, there is still a significant knowledge gap in our understanding of heavy metal accumulation in aboveground tissues, specifically the conditions that enhance heavy metal uptake and subsequent translocation to aboveground biomass.

Metal and pesticide removal was generally low in constructed wetlands M1, M2, and M3, since these experimental wetlands were primarily designed to remove nitrates, and denitrification is an anaerobic process, whereas pesticides are removed under aerobic conditions. As a result, the removal of pesticides and metals seemed to have a secondary effect. The conditions characteristic to denitrification, on the other hand, may be favourable to the removal of ESA derivatives.

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