

**An Evaluative Model for Assessing Fate and Effects of Contaminants
in Engineered Wetlands**

by

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ABSTRACT

To investigate the potential of engineered wetlands to remove contaminants from wastewaters, a steady-state and temporal multimedia model was developed for a free water surface design. The model estimates contaminant fate throughout wetland media, assesses the potential for bioaccumulation, and evaluates ecological risk using relevant toxicological endpoints (i.e. EC₅). Illustrative examples for pyrene, arsenic, a naphthenic acid, and a chemical universe defined by a range of log K_{OW} (-0.5 – 7.5) and log K_{OA} (-4.5 – 11.5) were used to demonstrate the models applications. In these illustrative applications, the steady-state removal efficiencies of pyrene, arsenic, and the naphthenic acid from the wetland were 41%, 83%, and 31%, respectively. The most efficiently removed chemicals had a log K_{OW} ≈ 6 and log K_{OA} ≤ 2.5. Removal efficiency was lowest for substances showing reduced evapotranspiration flux. This study concluded that wetland treatment could be a feasible method of remediation for certain contaminants in wastewater.

Key words: contaminant fate model; engineered wetlands; wetland modelling; evapotranspiration; wastewater treatment; contaminant removal

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GLOSSARY

| | |
|------------------|--|
| adoc | DOC-octanol proportionality constant |
| BAF | Bioaccumulation factor |
| BCF | Bioconcentration factor |
| BOD ₅ | Biochemical oxygen demand, at 5 days |
| COD | Chemical oxygen demand |
| DO | Dissolved oxygen |
| DOC | Dissolved organic carbon |
| <i>E</i> | Removal Efficiency (%) |
| ET | Evapotranspiration |
| FWS | Free water surface |
| <i>H</i> | Henry's law constant |
| HSSF | Horizontal subsurface flow |
| K _{AW} | Air-water partition coefficient |
| K _{OA} | Octanol-air partition coefficient |
| K _{OC} | Organic carbon-water partition coefficient |
| K _{OW} | Octanol-water partition coefficient |
| OC | Organic carbon |
| SOCOW | Sediment organic carbon-octanol water equivalency factor |
| SSF | Subsurface flow |
| SVOC | Semi-volatile organic compound |
| TN | Total nitrogen |
| TOC | Total organic carbon |
| TP | Total phosphorus |
| TRI | Toxic Release Inventory |
| TSS | Total suspended solids |
| VOC | Volatile organic compound |
| VOCOW | Vegetation organic carbon-octanol water equivalency factor |
| VSSF | Vertical subsurface flow |

1. Introduction

In response to the rapid industrialization of our modern economies, ecological questions have shifted from being scientific intellectual curiosities to falling within the purview of the applied sciences – the birth of environmental toxicology. From the growing global demand for freshwater resources, there has been an emerging interest in the beneficial re-use of industrial wastewaters particularly for non-potable related uses (e.g. water parks, lawns, golf courses, fire fighting, washing cars, streets, fountains). Traditional methods of remediating processed industrial wastewater involve conventional wastewater treatment plants; however, this option is not always economically feasible.

One sustainable alternative for water treatment is the use of engineered wetlands, which are also referred to as constructed wetlands, treatment wetlands, or wet parks. These artificial ecosystems may be newly created or existing systems designed for wastewater treatment. The potential benefits of wetlands as wastewater remediation and reclamation alternative is outlined in U.S. EPA (2012a). The details of this report incorporate risk management strategies and approaches towards the sustainable use and operation of constructed wetlands. Wetlands act as a biofilters, removing sediments and chemical pollutants such as organics and heavy metals from the wastewater. Engineered wetlands have the potential to turn “brownfield liabilities” into “green-space assets” which mimic the natural environment (Davis, 2009). For example, a large hydrocarbon groundwater plume in a former Wyoming refinery site was remediated using an engineered wetland, which now plays a central role in a Robert Trent Jones-designed golf course, whitewater rafting park, commercial office, and light industrial park space (Davis, 2009). In addition to removing conventional and toxic pollutants, these natural treatment systems have the potential to capture storm water, create habitat for aquatic, semi-aquatic, and terrestrial wildlife, sustain local stream flows, recharge groundwater supplies, provide flood control, and serve as attractive, natural security buffers adjacent to industrial operations.

1.1 Engineered Wetlands - Designs

Engineered wetlands are categorized by their intended hydrologic flow regime. These categories include: free water surface (FWS; Figure 1-1), horizontal subsurface flow (HSSF; Figure 1-2), and vertical subsurface flow (VSSF; Figure 1-3). FWS wetlands are typically open areas of surface water with submerged, emergent, and floating vegetation.

As a result, this wetland configuration may attract and host many different wildlife assemblages including a variety of insects, mollusks, fish, amphibians, reptiles, birds, and mammals (Kadlec and Knight, 1996; Kadlec and Wallace, 2009). As a treatment system, the potential exposure of wildlife to pollutants in the wetland may have hazardous toxicological implications. Methods to control wildlife habitation may be required, otherwise HSSF or VSSF designs may be more appropriate to remove this pathway of environmental exposure.

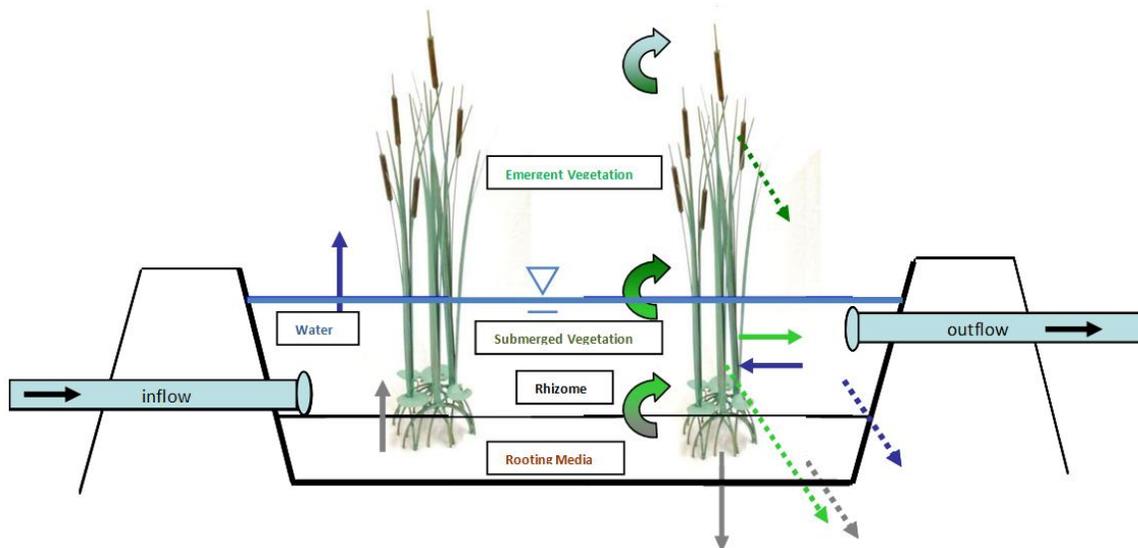


Figure 1-1: Conceptual diagram of the free water surface (FWS) engineered wetland model. Solid arrows represent transport processes between wetland media. Dashed arrows represent transformation processes (chemical, physical, biological) within the wetland media. Vegetation growth dilution is not shown.

A generic FWS flow wetland design is illustrated in Figure 1-1. FWS designs consist of an impermeable liner supporting the wetland's biogeological components, and directing the hydrology of the influent wastewater from the inlet zone to the outlet weir which regulates the water level. FWS designs are often used for their ancillary benefits since the wetland may be transformed into sustainable habitats for wildlife and recreational areas for humans (Davis, 2009; Kadlec and Wallace, 2009). These FWS wetlands can be adapted to be suitable for all climates, including colder northern areas where winter ice formation and low temperatures affect wetland hydrology, vegetation, and ultimately contaminant fate. Contaminant transport will be affected since the rate constants controlling contaminant fate are influenced by temperature, and may become negligible during times of senescence for vegetation which can reduce biological activity (Kadlec and Wallace, 2009).

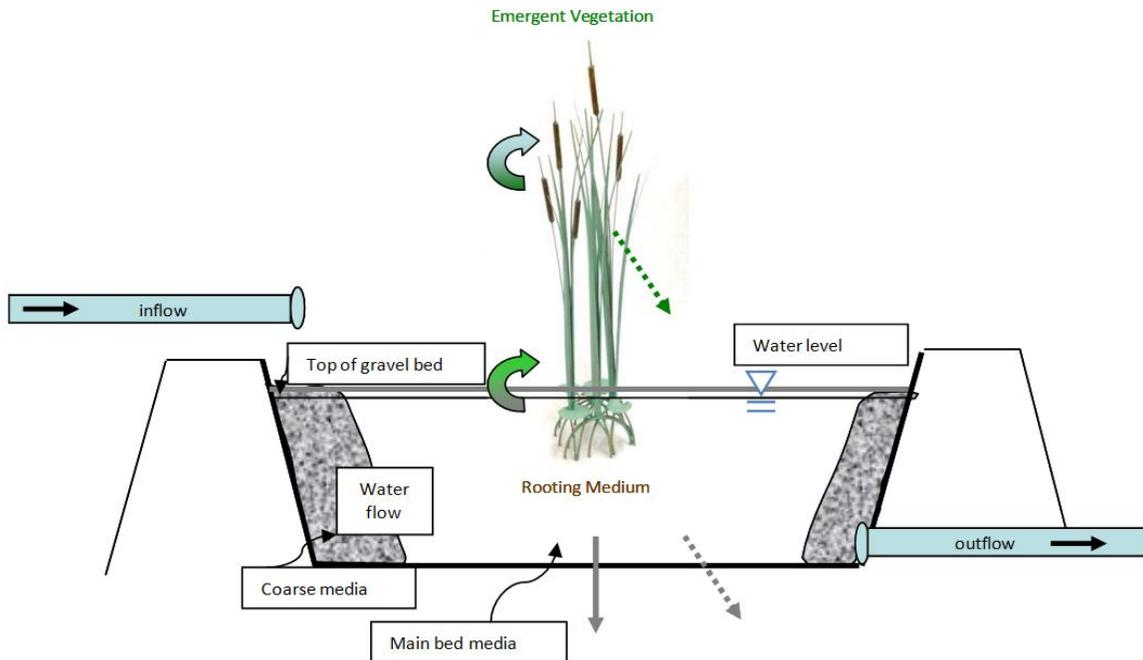


Figure 1-2: Conceptual diagram of the horizontal subsurface flow (HSSF) wetland model. Solid arrows represent transport processes between wetland media. Dashed arrows represent transformation processes. Vegetation growth dilution is not shown.

Figure 1-2 illustrates a conceptual design of the HSSF wetland. HSSF are constructed to contain high porosity rooting media such as coarse sand and gravel that support emergent wetland vegetation within an impermeable (clay or synthetic) liner (Kadlec and Wallace, 2009). This design introduces the wastewater from inlet piping into the coarse gravel, and guides the influent through the porous rooting medium containing microbial communities, roots, and rhizomes of the emergent vegetation. Since the water is not directly exposed or available to wildlife, this design removes much of the wetlands potential to act as a vector for environmental exposure and toxicity. Generally, these wetland designs are relatively expensive compared to FWS designs due to maintenance and operation costs, however costs still remain low compared to conventional wastewater treatment alternatives (Kadlec and Wallace, 2009).

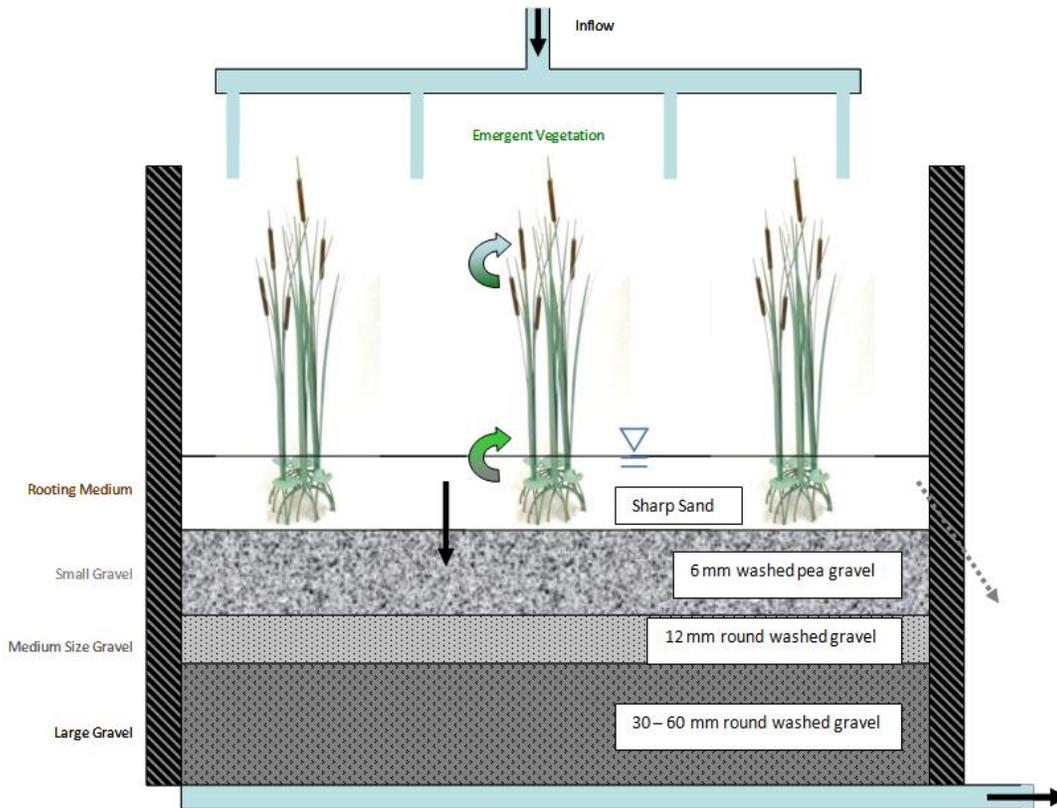


Figure 1-3: Conceptual diagram of the vertical subsurface flow (VSSF) wetland model. Solid arrows represent transport processes between wetland media. Dashed arrows represent transformation processes. Vegetation growth dilution is not shown. Stratification of rooting medium adapted from Kadlec and Wallace (2009).

Figure 1-3 illustrates the conceptual model of the VSSF wetland. Also referred to as 'infiltration wetlands', its design often uses pulse-loading regimes of the entire surface area of the wetland bed using perforated piping along the surface of the rooting media, or using buried inlet pipes within the upper rooting media (Kadlec and Wallace, 2009; Sundaravadivel and Vigneswaran, 2001). VSSF wetlands were developed to provide higher levels of oxygen transfer than HSSF designs, thus producing a more nitrified effluent (Kadlec and Wallace, 2009). The oscillating surface flooding induces more oxygen infiltration into the rooting media which improves ammonia oxidation. Therefore, this design has become a successful treatment option for wastewater with elevated ammonia levels or pollutants which require efficient oxidation. Similar to HSSF, the water stream through the rooting medium eliminates some of the concern for wildlife exposure to the wastewater influent.

1.2 Objective

The objectives of this study are to i) develop an evaluative contaminant fate model that include mechanisms of transformation and intermedia transport between rooting medium, water, and wetland biota, and ii) apply the model to assess the capabilities of an engineered wetland to remediate contaminated wastewaters. The methods that determine contaminant fate in the model have been derived using principles of conservation of mass for a free water surface (FWS) flow wetland. The model includes both steady state and time-dependent simulations. Models of the vertical subsurface flow (VSSF) and horizontal subsurface flow (HSSF) wetland designs have been developed with the same theoretical framework, but require a more dynamic approach that has not been fully refined in this research. The time-dependent simulations creates a profile for the removal efficiency of the wetland as it responds to contaminant loading and approaches steady state.

The framework of this multimedia modeling has been previously developed for application in such models as the QWASI model by Mackay (1989), Fugacity level III model by Mackay (1991), the Lake Ontario model by Gobas (1993), EcoFate Model by Gobas et al. (1998), and other partition-coefficient driven level III (assumes steady state has been reached but equilibrium does not exist) and level IV (time-dependent) environmental models. These models include fugacity and equivalence-based approaches to describe the environmental fate of both ionized and unionized organic substances and metals. This research integrates these established modeling techniques with accepted models for aquatic biota accumulation. The model includes a bioaccumulation sub-model based on Arnot and Gobas (2004), and an ecological risk assessment sub-model that compares the estimated concentrations in each compartment to applicable toxicity endpoint values. With the help of this ecological risk assessment of the inhabited biota, limits can be set to ensure the vegetation and microbes maintain a healthy level of productivity in the wetland.

The intention of this modeling scheme is to produce a parameterized model without requiring calibration using field or laboratory studies. This version of the model may therefore be viewed as an evaluative or screening-type model. For example, it may be used to estimate which contaminants would be expected to be effectively removed from influent wastewater by engineered wetlands, and which are not. With site-specific calibration and field testing, the model may evolve to make evaluative estimates of

contaminant fate, and support accurate quantitative exposure and risk assessments. In terms of risk management, this can be used on a site-specific basis to predict whether a FWS design could effectively treat specific wastewater. Conversely, the model may design a wetland that exhibits a removal efficiency that is required to meet certain water quality guidelines.

1.3 Wetland Models

There are no available models that integrate all of the components of a wetland system, but several models have been developed to describe the behaviour of contaminants in wetland vegetation. For example, Reid and Jaffe (2012) provide a model describing gas phase and transpiration driven mechanisms for volatilization of common volatile organic compounds (VOCs) through wetland macrophytes *Typha* spp. and *Scirpus* spp. The model focuses on the transport of VOCs in plants and uses flux chamber experiments to calibrate parameters that determine vegetation transpiration flux. Similar models include methane transport in *Phragmites* spp. (Becket et al. 2001). In addition, there are several models describing the uptake of non-ionic organic substances in various plants (Burken and Schnoor, 1998; Collins et al., 2006; Dettenmaier et al., 2009; Ryan et al., 1988). These empirical models use ratios of chemical concentrations in the plant compartment of interest (e.g. shoots, roots, xylem sap) to concentration in the exposure medium, (e.g. soil, soil pore water, hydroponic solution). These concentration ratios are generally referred to as BCFs (bioconcentration factors) but have also been named for the specific plant tissue sampled such as root concentration factors (Briggs et al. 1982, 1983, Topp et al, 1985) and stem concentration factors (Garbarini and Lion, 1986; Mackay and Gschwend, 2000; Trapp, 2002, 2004; Ma and Burken, 2003). Plant-soil BCF values have also been used to estimate plant tissue concentrations from analytical exposure data, and such models have been incorporated in exposure assessments used for managing and creating policies for chemicals (EUSES v.2.1.2, 2012). Correlations between BCFs and $\log K_{OW}$ (octanol-water partition coefficient) have been developed and used to predict plant-water bioconcentration factors in aquatic and terrestrial macrophytes (Travis and Arms, 1988, Gobas et al., 1991). Regression models have also been developed to relate air-shoot BCFs to an octanol-air partition coefficient (K_{OA}) (Tolls and McLachlan, 1994) or to a combination of Henry's Law constants (H) and octanol-water partition coefficients (K_{OW}) (Bacci et al., 1990). Mechanistic mass balance models for predicting plant tissue concentrations from chemical exposures to air and

soils have been developed by Chiou et al. (2001), Hung and Mackay (1997), McKone and Maddalena (2007), Ouyang et al. (2002, 2005), Paterson et al. (1991, 1994), Ryan et al. (1988), Topp et al. (1986), Trapp (2000, 2002, 2007), Trapp and Legind (2009), Trapp and Matthies (1995), Trapp et al. (2004). These models include one or more environmental compartments with defined rates of input, output, and accumulation through vegetation defined with flow rates, transformation rates, and diffusion rates.

Each of these approaches to modeling plant uptake contains inherent limitations for accurately describing the complex biogeochemical fate of all contaminants in wetland species. In semi-aquatic systems such as wetlands, it is important to integrate the dynamics of plant uptake with concurrent mechanisms of chemical fate such as sorption to wetland solids, bioaccumulation, and biotransformation. It is the purpose of this study to develop a complete wetland model that can illustrate the fate of nonionic and ionizing organic chemicals and heavy metals in wetlands. The purpose of the model is to provide a method for evaluating the effectiveness of various wetland configurations to treat wastewaters to meet water quality standards required for potential beneficial re-use.

1.4 Relevance

Industrial effluents have, since the origin of industrial practices, created a problem in resource management. Furthermore, industrial growth and demand for these resources continuously complicates these issues. In Canada especially, development in the oil sands mining and extraction stream contribute significantly towards economic growth, but as the complexity of the issues surrounding wastewater grow, sustainable solutions must be shown as feasible alternatives to conventional treatment methods. Model can provide tools to test the feasibility of an engineered wetland in response to specific wastewater challenges in the petroleum industry.

The bitumen from the northeastern Albertan oil sands is one of the largest reserves of available hydrocarbons in the world, and is currently being extracted at approximately 1.8 million barrels per day (Alberta Energy, 2013; Holowenko et al., 2002; Jasechko et al., 2012). According to the Government of Alberta (Alberta Energy: Facts and Statistics, 2013), crude bitumen production is expected to more than double to 3.7 million barrels per day by 2021. Modern methods of bitumen extraction from oil sands involves washing the sorbed bitumen off the subsurface sand with a mixture of clean freshwater and recycled effluent wastewater (Alberta Energy, 2013). For every 1 m³ of oil sand mined, approximately 3 m³ of water is required, and therefore roughly 4 m³ of

fluid tailings is produced, of which disposal and containment is an economical and environmental challenge (Alberta Energy, 2013; Jasechko et al., 2012). These tailings are stored in tailings ponds and contain a potentially dangerous array of organic and inorganic chemicals which can seep into groundwater and adjacent ecosystems. There is concern over the acute and sublethal toxicity to aquatic species and migratory birds exposed to the tailings toxicants. The most toxic of the mixtures, above the heavy metals and suite of organic compounds, are the naturally occurring naphthenic acids which consist of over 100 carboxylated cyclic and non-cyclic alkanes (Holowenko et al., 2002; Jasechko et al., 2012; Lai et al., 1996). According to the results of bioassays completed by Colavecchia et al (2004) on early life stages of fathead minnows, exposure to natural bitumen and wastewater pond sediments caused significant hatching alterations, mortality, malformations, and reduced size. Larval deformities included edemas, hemorrhaging, and spinal malformations. Siwik et al. (2000) found a significant increase in the length of fathead minnows exposed to oil sands wastewater from Syncrude Canada Ltd. at only day 7 of a 56-day bioassay.

Unreclaimed wastewater cannot be discharged directly into the environment, yet a feasible alternative to tailings ponds has not been developed. However, the expansion of oil sands operations, and continuous flow of tailings has made conventional wastewater treatments economically unfeasible (Jasechko et al., 2012; Lai et al., 1996). Moving forward, engineered wetlands may be the sustainable solution necessary to meet the needs of wastewater remediation.

1.5 Wetland Engineering

Engineered wetlands are often equipped with components of an engineered design that optimize pertinent removal mechanisms. However, this increases the complexity in the design, operation, and maintenance of the system. The spectrum of engineered wetland designs is defined as either having little to no energy demands to being highly engineered with demanding operation and maintenance requirements. Kadlec and Wallace (2009) refer to these two different systems as Type A and Type B, respectively. Type A designs include constructed FWS and low-tech SSF wetlands, and are typically lower in operational and construction cost despite having a larger footprint requirement. In areas where land is available and inexpensive, treatment potential is sufficient, and there is a small risk of human or wildlife exposure, Type A designs are preferable. Type B designs are considered when these criteria cannot be met, and include more

technologically advanced processes. Some specific examples of engineering principles include chemical, biological, and physical modifications that may optimize the power of wetland wastewater treatment (Table 1-1).

The emergence of engineering principles for wetland optimization stems from the investigations into the complex biogeochemistry of these systems. When appropriate, these modifications can improve transformation pathways, and intermedia transfer between environmental compartments to suit the wetland design criteria and physicochemical properties of the influent. This can be done with the help of thermodynamic principles. This type of modeling allows for a more tailored design of wetlands so that they may be applied to, for example, oil sands processed wastewater. Kadlec and Wallace (2009) indicated that the primary chemical loss pathways to consider in the functioning of wetlands are: microbial mediated processes, chemical networks, volatilization, sedimentation, sorption, photodegradation, plant uptake, transpiration flux, accretion – creation of new soils, and vertical diffusion in soils and sediment.

Table 1-1: Modifications that may improve engineered wetland systems.

| <i>Modification</i> | <i>Intended Improvement</i> | <i>Reference</i> |
|--|---|--|
| ECOLOGICAL OR ENVIRONMENTAL MODIFICATIONS | | |
| Microbial Enhancement | Optimize microbial environment to enhance transformation rates, i.e. bioaugmentation, and optimal temperature, salinity, pH, etc. Introduce specific microbes efficient at transforming pollutants of concern in influent. | Bhatia and Goyal, 2014; Runes et al., 2001. |
| Willow Wetlands with Zero Discharge | Configured with willows to enhance evapotranspiration (ET) through a 'windrow' design. Typically small-scale, capable of meeting regulatory requirements because no discharge to environment. | Brix and Arias, 2005; Brix and Gregersen, 2002; Gregersen and Brix, 2001. |
| Plant harvesting | Harvesting vegetation helps keep plants young and healthy to maintain high evapotranspiration rates. | Brix and Arias, 2005. |
| Engineered plants | Genetic engineering for enhanced phytoremediation. Includes controlling expression of genes linked to rate-limiting enzymes, and transgenic vegetation. Some plants are more capable of accumulation of certain pollutants. | Bhatia and Goyal, 2014; Berken et al., 2002; Heaton et al., 1998; Nandakumar et al., 2005. |
| Artificial enclosures | For example, greenhouses are often used to maximize available sunlight and manage risk. | U.S. EPA, 1997. |

| CHEMICAL ADDITIONS | | |
|---|--|---|
| Reactants via media | Selection of media designed to support certain chemical reactions, i.e. sorbents, reactive media to generate chelation, sources of organic carbon. | U.S. EPA, 1993a,b. |
| Reactants via supplementary streams | Chemical additions to regenerate factors such as DO, carbon source, precipitates, etc. | Gersberg et al., 1983; Reddy and D'Angelo, 1994; U.S. EPA, 1993a,b. |
| Aeration of FWS wetlands | Open surface water exposed to air may still be subject to constraints on oxygen mass transfer. Forced aeration may be required to improve DO for vegetation, BOD reduction, nitrification, and oxidation of specific pollutants. Aeration shown to improve removal of petroleum hydrocarbons through aerobic degradation and volatilization. | U.S. EPA, 2000a |
| Carbon additions to wetlands | Sometimes required in waters where nitrate concentrations are high and inadequate carbon source for removal is rate limiting. Potato wastewater was used as a carbon source in Lamb-Weston, Connell, WA to reduce COD | Burgoon et al., 1999; Kadlec et al., 1997; Reddy and DeLaune, 2008. |
| Aluminum and Iron additions to FWS wetlands | May be required for their phosphorus-binding capabilities. | Bachand et al., 1999; Reddy and DeLaune, 2008. |
| Aeration of SSF wetlands | Treatment wetland technology developed in literature and proprietary sector. Information on patented SSF aeration technology is too scarce for qualitative interpretation. Aeration shown to improve removal of petroleum hydrocarbons through aerobic degradation and volatilization. Oxygen transfer efficiency is a function of contact time and surface area of bubble and water column. Consider true velocity in SSF where porosity of gravel/soil bed influences bubble pathway through water column. | Dufay, 2000; Moore et al., 2000; Wallace, 1998; Wallace, 2002; Wallace and Lambrecht, 2003. |
| OPERATIONAL STRATEGIES | | |
| Step feed | Step feeding into wetlands reduces the impact of localized loading zones by introducing influent at multiple locations along flow path of wetland. | Crites and Tchobanoglous, 1998. |

| | | |
|-----------------------------------|---|--|
| Recycle | May bring product from wetland reactions back to the inlet, and can dilute reactants entering the system. This reduces contaminant loading on system and vegetation. | Brix et al., 2002; Sikora et al., 1994. |
| Timed operational sequences | Hydraulic loading: Steady flow, pulse loading, fill-and-drain, non-steady (non-continuous) flow, or batch-reactor mode. May help to reduce effective wetland area | Helsel, 1992; Kadlec and Wallace, 2009. |
| INTEGRATED NATURAL SYSTEMS | | |
| Sedimentation basin | Provides easy removal of accumulated sediment preceding the treatment system. | Schueler, 1992; Strecker et al., 1992. |
| Pond and wetland combinations | Common method for water treatment involves primary and secondary treatment via ponds or lagoons, following by constructed FWS wetland. Known for effective BOD and TSS removal (ponds) followed by pollutant removal (wetland). | Kadlec, 2003. |
| FWS and infiltration | Final effluent may be directed to infiltration systems if surface water discharge is not feasible, and effluent meets groundwater quality guidelines. The reverse can also be utilized; pond-infiltration-wetland. | Crites et al., 2006; Water Environment Federation, 2001. |
| Overland flow to FWS | Very shallow flow over a sloped grass and litter matrix. Eliminates oxygen transfer complications, and one method of pre-treatment before entering FWS wetlands. | Crites et al., 2006; Water Environment Federation, 2001. |
| Vertical flow to FWS | Vertical flow through a sand filter often effective at nitrification and removing BOD. Susceptible to clogging from suspended sediments. | Lamb-Weston potato-processing facility in Connell, Washington (Burgoon et al., 1999) |
| VSSF and HSSF combinations | Hybrid designs: Combination of FWS and SSF designs to meet specific process goals | Brix, 1998; Cooper, 1999; EC/EWPCA Emergent Hydrophyte Treatment Systems Expert Contact Group and Water Research Centre, 1990. |

1.6 Wetland Applications

Utilizing the natural characteristics of natural wetlands to treat domestic wastewater has been around for as long as sewage has been collected (Kadlec and Wallace, 2009). The earliest evidence of these applications suggests many of these sites are over 100

years old. Europeans began scientific investigations into wetland engineering during the 1950's, well before their introduction into North America (Reddy and DeLaune, 2008).

For treating commercial or industrial wastewater, constructed wetlands have a much shorter history, beginning in West Germany in 1952, and in the western hemisphere during the 1970's (Kadlec and Wallace, 2009). The first FWS constructed wetland in North America designed to receive wastewater discharge was completed in 1973 by the Mt. View Sanitary District in Martinez, California. Development of the first HSSF systems were completed in 1972 near Seymour, Wisconsin, and the conclusions of research there 3 years later suggested that this wetland design has a wide range of applications in wastewater treatment. VSSF designs were seldom used in North America and remain an infrequent application of engineered wetlands, however some adaptations of this technology are used in treatment plants in the form of gravel filters (Burgoon et al., 1999; Kadlec and Wallace, 2009).

Engineered wetlands have been proven as a useful remedial technique for a variety of treatment operations including municipal and domestic wastewater, animal wastewater, mine water, industrial wastewater (including petroleum refineries), urban storm water, field runoff, and leachate (Davis, 2009; Kadlec and Wallace, 2009; Mbuligwe et al., 2011; Reddy and DeLaune, 2008; Smoley, 1993). In the US, a former Wyoming refinery developed a hybrid design wetland (using forced aeration) to treat approximately 1.6 million gallons per day of hydrocarbon-contaminated groundwater (Davis, 2009). In Tanzania, a subsurface flow engineered wetland for treatment of domestic wastewater is in operation. Performance profiles documented in Mbuligwe et al. (2011) indicate that the HSSF wetland that treats domestic wastewater in Tanzania causes a decrease greater than 50% in levels of COD, BOD₅, ammonia, nitrate, phosphorus, sulphate, faecal and total coliform in domestic septic wastewaters. In the primary scientific literature, there are a limited number of references to wetland projects for treating petroleum industry process streams (Kadlec and Wallace, 2009). However, according to Knight et al. (1999), petroleum industry wastewaters contain many of the same contaminants as municipal wastewaters plus the addition of oil and grease, various hydrocarbons, phenolics, sulfides, and metals.

The basic design and implementation of engineered wetlands is outlined by Kadlec and Wallace (2009) and wetland biogeochemistry is comprehensively described in Reddy and DeLaune (2008). While the fundamentals of engineered wetlands are well

described, there are few tools available to predict the fate of pollutants in engineered wetlands. To anticipate the ability of a wetland to treat contaminated wastewater, it is important to be able to quantitatively assess the environmental behaviour of contaminants in these artificial ecosystems. In addition, it is important to be able to forecast whether contaminated wastewater can result in concentrations in wetland media that translate to adverse effects in organisms inhabiting the wetlands, or foraging on wetland biota. Wetlands must be designed and operated to be safe from a public health and environmental conservation perspective.

1.7 Engineered Wetland Examples

Keefe et al. (2004) report the effects of a constructed FWS wastewater treatment wetland in the remediation of volatile organic compounds (VOCs). This constructed wetland system is located near Phoenix, AZ where volatilization is favoured by dry and hot atmospheric conditions. Moreover, this wetland configuration includes four FWS wetlands each between 0.90-1.34 ha ($9000 - 1.34 \cdot 10^6 \text{ m}^2$) which more closely matches the wetland in series dimensions. Removal efficiencies ranged from 63% to 87% for select contaminants. Volatiles were estimated to be efficiently removed from the FWS design at ~98% since the environmental conditions were appropriate to induce evapotranspiration.

Tu et al. (2014) have studied the multi-function Kaoping River Rail Bridge Constructed Wetland (KRRBW) which consists of five wetland basins covering a total area of approximately 15 ha ($150,000 \text{ m}^2$) that accepts untreated domestic, agricultural, and industrial wastewater. Based on the removal efficiency of biochemical oxygen demand (BOD, a surrogate measurement for organics) of 91%, this system is believed to be able to effectively remove organics from the wastewater stream.

Knight et al. (1999) reviewed wetland treatment systems for petroleum industry effluents, specifically. Based on the seven engineered wetland sites (FWS and SSF) used as pilot projects for evaluating the removal of organics from petroleum effluent, the removal efficiency for BOD_5 was 60% to 98%, chemical oxygen demand (COD) was 38% to 72%, oil and grease was 60% to 94% and phenols were 10% to 94%. In all cases, the FWS designs showed the greatest removal efficiency, but SSF designs were all within a similar range of efficiency except for oil and grease.

2. Background

2.1 Engineering Wetlands Design

2.1.1 Wetland Rooting Media

The stratified soils in engineered wetlands play a defining role in the overall function and treatment of wastewater. This media hosts an active and diverse microbial community and the rhizosphere of the aquatic vegetation. Typically, FWS wetland soils are constructed with soil containing up to 20% organic and mineral matter (Reddy and DeLaune, 2008). Wetland organic soils, such as those contained in FWS wetlands are often completely saturated with water, the extent of which is a result of the soil particle distribution and porosity. The saturation of this sediment restricts the supply of oxygen into the rooting media pores, but provides other important physical effects such as:

- i) soil material is softened allowing easier root penetration, and reduced cohesive forces of soil resulting in the disintegration of soil structure;
- ii) the colour of soil may change which alters the absorption of heat; and
- iii) soil bulk density decreases due in part to high absorption capacity of organic matter (Reddy and DeLaune, 2008).

SSF wetland designs require components of soil that regulate the movement of water within the rooting media, while also hosting a variety of emergent wetland vegetation. VSSF designs stratify soil of different grain size and porosity to control the infiltration of influent and influence retention time in the system.

2.1.2 Wetland Hydrology

The hydrology in an engineered wetland is a critical component for wastewater treatment as well. The hydrology of a wetland refers to the flow of water from inlet to outlet, and artificial stream (FWS) or aquifer-like (SSF) flow directs the contaminant throughout the wetland. Therefore, it is important to optimize hydraulic retention time to ensure that sufficient biogeochemical processes can act on the free flowing chemical.

The success of wastewater treatment is contingent on the ability to maintain effective hydrologic flow, appropriate water depths, and a laminar regime to avoid sediment resuspension. Water budgeting is an important method that identifies all sources of water into the wetland (inflow, groundwater, precipitation) and water-loss processes out of the wetland (outflow, groundwater recharge, and evapotranspiration) despite their

inherent variability. A general water balance equation is provided in Equation 1 (Kadlec and Wallace, 2009):

$$\frac{dV}{dt} = Q_i - Q_o + Q_c - Q_b - Q_{gw} + Q_{sm} + (P \times A) - (ET \times A) \quad (1)$$

where A is the top surface area of the wetland (m^2), ET is the evapotranspiration rate that combines evaporation (water-to-air) and transpiration (plant-to-air) processes ($m \cdot d^{-1}$), P is the precipitation rate ($m \cdot d^{-1}$), Q_i is the input wastewater flow rate ($m^3 \cdot d^{-1}$), Q_o is the output wastewater flow rate ($m^3 \cdot d^{-1}$), Q_c is the catchment inflowing runoff rate ($m^3 \cdot d^{-1}$), Q_b is the bank loss rate due to seepage into adjacent aquifers ($m^3 \cdot d^{-1}$), Q_{gw} is the rate of infiltration of into groundwater ($m^3 \cdot d^{-1}$), Q_{sm} is the snowmelt rate ($m^3 \cdot d^{-1}$), t is time (d), and V is the water storage volume in the wetland (m^3). Therefore, dV/dt represents the accumulation or loss of water from the system over time. These parameters can be approximated from available geological and historical climate data, estimated from hydrogeological models, or empirically derived from the site-specific field measurements.

2.2 Wetland Biogeochemistry

Wetlands are fundamentally autotrophic systems designed to absorb and process energy from the environment through a series of highly complex and integrative biogeochemical processes. The contributions from each of these processes regulate the growth and ecological efficiency of the wetland and its ability to mediate transportation and transformation pathways. Wetlands can efficiently process wastewater while extracting useful energy in a variety of environmental conditions (Chazaranc et al., 2010). Discussed below are some key biogeochemical considerations that influence wetland treatment efficiency.

2.2.1 Biochemical Oxygen Demand

First modeled by Streeter and Phelps (1925), biochemical oxygen demand (BOD) is a non-specific indicator of surface water quality. It describes the amount of oxygen required by microorganisms to oxidize the available biodegradable fraction of the aqueous organic waste under aerobic conditions (Ramaswami et al., 2005). Both COD and BOD are surrogate measurements for the amount of organic pollutants in the water. Therefore, a reduction in these parameters is often a sign that water quality is improving, and organic chemicals are being removed. Microbial degradation processes play a

significant role in the treatment of wastewater, but can create an oxygen deficit within the system. Re-aeration occurs primarily through air-to-water diffusion and gas transport via aerenchymal tubules of wetland vegetation (see 2.2.6 – *Wetland Vegetation*) unless engineering mechanisms are applied to force dissolved oxygen (DO) into the water column. The amount of DO consumed by the microbial community is partly dependent on temperature and total incubation time when performing a BOD analysis. The experimental method involves the inoculation of diluted wastewater with microorganisms, and is measured as the difference in oxygen content before and after incubation (Kunz, 2009). A 5-day incubation time at 20°C has become the standard for BOD testing, and is denoted as BOD₅ (Kunz, 2009). BOD₅ is typically determined experimentally using standard bioassay methods, but downstream oxygen deficits can be estimated using the Streeter-Phelps Model (Streeter and Phelps, 1925).

Engineered wetlands have long been observed to be a useful treatment option for water with elevated BOD₅ values, if influent levels are above background levels in the receiving system (Kadlec and Wallace, 2009). Wetlands actively induce carbon conversion processes that both consume and produce BOD₅, and therefore both rates must be considered. Generally, BOD₅ within a wetland can be modeled along the flow direction using standard first-order rate constant and mass balance approach (Kadlec and Wallace, 2009). Most FWS wetlands are highly capable of BOD reduction, and often the discharged water has approached background values (Kadlec and Wallace, 2009). Similarly, VSSF wetlands with pulse loading allows oxygen to re-saturate the coarse rooting media as water drains through and is replaced by air. For this reason, VSSF designs are often an ideal design to reduce elevated BOD values. Conversely, HSSF designs are relatively weak BOD regulators since continuous flow through the rooting media creates an oxygen-limited environment, and conditions become anaerobic removing any consumption of oxygen for organic waste biodegradation (Kadlec and Wallace, 2009).

Chemical Oxygen Demand (COD) is a measurement of the organic compounds in the wastewater that are subject to microbial biodegradation (Kunz, 2009). The COD test is intended to include the BOD and the nitrification component for oxygen demand. It is an indirect measurement of the total amount of organic compounds in the sample. It is typically expressed in mg·L⁻¹ which represents the amount of oxygen consumed per unit volume of the sample.

The COD test is performed using methods that measure the susceptibility of organic compounds in the sample to be oxidized to carbon dioxide (CO₂) and water (H₂O) by a strong oxidizing agent. Potassium dichromate (K₂Cr₂O₇) is the most commonly used oxidizing agent, and the chemical reaction is performed at boiling temperature (~100°C) for 2 hours (Kunz, 2009; Knight et al., 1999).

2.2.2 Total Suspended Solids

The density and particle size of the solids suspended in the influent wastewater is determined on a site-specific basis. Typically, these particulates settle through the water column and become trapped in the sediment when flow is laminar and there is sufficient shelter from wind and weathering (Knight et al., 1999). Particulate sequestration is an important process for improving water quality because suspended solids often contain elevated levels of BOD, COD, hydrocarbons and other sorbed organic pollutants, trace metals, nitrogen and phosphorus (Knight et al., 1999). The sorbed fraction may be subject to accretion as sediments are deposited, buried and effectively removed from the system. Kadlec and Wallace (2009) report accretion rates that can vary from a few millimeters per year to a few centimeters per year (from a study of 17 natural, treatment, or constructed wetlands). This process is largely controlled by the hydrologic flow regime, particulate size and density of the influent, and vegetation which act as biofilters (Bhatia and Goyal, 2014; Knight et al., 1999).

2.2.3 Electrochemical Properties

Many biogeochemical reactions in natural wetlands involve nutrient and trace metal cycling which are regulated by redox potential (Eh), pH, and the ionic strength of the soil pore water (Reddy and DeLaune, 2008). Wetland sediments that become completely saturated, respond with a significant reduction in DO in the freestanding and pore water. As a result, wetlands typically develop very low Eh, which represents the electron activity or potential in the media. In principle, the loss of electrons (oxidation) is matched by another molecules gain in electrons (reduction). This notion is illustrated in FWS wetlands where low oxygen concentrations limit the potential for both of these processes to continue. This shifts the biogeochemical equilibrium towards more reduced forms of chemical substrates (Reddy and DeLaune, 2008). This is important to inorganic substances since their toxicity is often highly dependent on its speciation which is controlled by the redox potential and pH of their environment. In strongly oxidizing

environments Eh is more positive, whereas in strongly reducing environments, Eh is more negative. Table 2-1 explains that for organic matter (denoted by CH₂O) when oxygen is available, it is used as the terminal electron acceptor for true aerobic microorganisms. This is because the Eh of this reaction is most positive, and therefore thermodynamically favourable. As oxygen is depleted, reduced substrates accumulate which create an abundance of electrons. Eventually, as the electron partial pressure grows, the available oxidant (usually NO₃⁻) that has the next most Eh-favourable reaction proceeds. Following the depletion of NO₃⁻, a thermodynamically organized succession of electron acceptors is used: oxidized manganese, ferric iron compounds, sulfate, and carbon dioxide (Table 2-1; Kadlec and Wallace, 2009; Lewis et al., 1999; Ramaswami et al., 2005; Reddy and DeLaune, 2008; Spray and McGlothlin, 2004). Facultative microbes include both anaerobic and aerobic organisms, whereas obligate aerobic species are those which cannot live in an aerobic environment. The active microbes differentiate themselves by metabolically performing at different ranges of Eh.

Table 2-1: A typical redox scheme in FWS wetlands from thermodynamic energy yield.

| Chemical Reaction | Redox Potential (E_h – Range, mV) | Microbial Group |
|---|--|------------------------|
| CH ₂ O + O ₂ → CO ₂ + H ₂ O | > +300 | Obligate aerobes |
| 5CH ₂ O + 4NO ₃ ⁻ → 2N ₂ + 4HCO ₃ ⁻ + CO ₂ + 3H ₂ O | +250 to +100 | Facultative aerobes |
| CH ₂ O + 3CO ₂ + H ₂ O + 2MnO ₂ → 2Mn ²⁺ + 4HCO ₃ ⁻ | +225 to -100 [†] | Facultative aerobes |
| CH ₂ O + 7CO ₂ + 4Fe(OH) ₃ → 4Fe ²⁺ + 8HCO ₃ ⁻ + 3H ₂ O | +100 to -100 | Facultative aerobes |
| CH ₂ O + SO ₄ ²⁻ → H ₂ S + 2HCO ₃ ⁻ | -100 to -200 | Obligate anaerobes |
| 4H ₂ + CO ₂ → CH ₄ + H ₂ O | < -200 | Obligate anaerobes |

[†]Mn⁴⁺ reduction begins at approximately +200 mV, Mn³⁺ reductions begins at approximately +100 mV

Within the rooting media of the wetland, gradients of redox potential form, creating anisotropic environments within the wetland (Kadlec and Wallace, 2009). This occurs both vertically through the sediment depth, as well as radially outwards from the rhizomes and roots in the soil (Kadlec and Wallace, 2009). Section 2.2.5 *Wetland Vegetation* discusses the roles of wetland plants in controlling redox potential in the rooting media and water column of the wetland (Szogi et al., 2004).

2.2.4 Nutrient cycles – Carbon, Nitrogen, Phosphorus

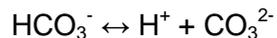
Carbon

The distribution of essential components in an ecological system requires complex elemental recycling to benefit the entire web of micro- and macro-biota (Knight et al., 1999). Many sources of essential nutrients are available to contribute to overall health of the system. Deposits of carbon species within the wetland include: carbon dioxide sequestration by the wetland vegetation from the atmosphere for photosynthesis, inorganics of the particulate matter and organic compounds from influent, and growth followed by decomposition of vegetation. These biotic and abiotic components of the wetland compartments generate the mechanisms for the carbon cycle which reflects the treatment capacity for certain wastewater. Table 2-2 lists the forms of carbon available in the carbon cycle.

Table 2-2: Wetland carbon species.

| | |
|------|--|
| TC | Total carbon (dissolved + suspended) |
| PC | Particulate carbon (organic + inorganic) |
| DC | Dissolved carbon (organic + inorganic) |
| IC | Inorganic carbon (dissolved + suspended) |
| DIC | Dissolved inorganic carbon (CO ₂ , HCO ₃ ⁻ , H ₂ CO ₃) |
| TOC | Total organic carbon (dissolved + suspended) |
| DOC | Dissolved organic carbon |
| NDOC | Non-dissolved organic carbon |
| VOC | Volatile organic (carbon) compounds |

DIC contribute a small fraction of total carbon within wetlands and consists primarily of carbon dioxide, carbonate, and bicarbonate. The relative proportions of these inorganic carbon species is controlled by temperature and pH-dependent dissolution and dissociation reactions described below (Kadlec and Wallace, 2009; Reddy and DeLaune, 2008):



The pH of the water may fluctuate diurnally depending on the extent of photosynthesis by algae and submerged macrophytes (Reddy and DeLaune, 2008). During light-dependent photosynthetic reactions, water is split into its components of oxygen (O) and hydrogen (2H⁺) to create a H⁺ gradient that forms NADPH and ATP molecules. These hydrogen ions result in a decrease in pH in the aquatic system during the day when photosynthesis is occurring. Conversely, light-independent photosynthetic reactions

involve CO₂ sequestration to form 5-carbon sugar molecules in the Calvin-Benson Cycle. By utilizing CO₂ in this way, photosynthesis forces these inorganic chemical reactions to shift towards a new equilibrium. In doing so, the hydrogen ion concentration depreciates causing an increase in pH at night.

This process feeds further into the carbon cycle by way of producing organic carbon molecules via Calvin-Benson cycle (primary production) from sequestered inorganic atmospheric carbon (i.e. CO₂). The productivity of wetlands to capture carbon is at such a remarkable efficiency, that it can be considered on the same order of magnitude as tropical rainforest (1,300 gC·m⁻²·year⁻¹; Reddy and DeLaune, 2008). Although this efficiency is highly variable, wetland production plays a significant role in land-based carbon sinks (Schlesinger, 1997). The extent of this organic carbon transfer is best observed by the annual growth and decomposition patterns of vegetation. According to Kadlec and Wallace (2009), a eutrophic treatment marsh in a northern climate can produce up to 3 kg·m⁻² (dry weight) of above-ground biomass each year. With an approximate carbon content for *Typha latifolia* (cattails) of 43%, the annual average carbon requirement is estimated to be approximately 35 kg·ha⁻¹·d⁻¹. Submerged, emergent, and rhizospheric vegetation seizes this carbon from the water column (DC – organic and inorganic), atmosphere (CO_{2,gas} and CH_{4,gas}) and pore spaces in rooting material (CO_{2,gas} and CH_{4,gas}). This carbon pool is recycled back into the wetlands during plant senescence, where the biomass fractions fertilize the sediment as detritus, and undergo microbial decomposition at the rooting media-water interface. This decomposition converts complex carbohydrates (i.e. cellulose) into its monomers (i.e. glucose), eventually producing CO₂ and CH₄.

Nitrogen and Phosphorus

Nitrogen and phosphorus availability in aquatic systems can be the most significant limiting factors towards the activity of wetland transformation and transport processes (Reddy and DeLaune, 2008; Kadlec and Wallace, 2009). These nutrients are involved in processed within and between water, plants, microbiota, litter (detritus), and sediment (rooting zone + deep sediment). The distribution and utilization of these nutrients, in their various forms, are dependent on wetland design and abiotic components, plant and microbotic species, and influent properties. The implications of unfavourable concentrations of either of these nutrients include eutrophication or oligotrophication, and potential biological toxicity to wildlife (Kadlec and Wallace, 2009). In excess, these

nutrients will cause extensive algal blooms and promote microbial activity that can quickly deplete the oxygen content in the water, changing the redox state of the system and ultimately impacting the ability of a wetland to remove contaminants (Reddy and DeLaune, 2008).

Nitrogen, in both inorganic and organic forms, is constantly interchanging, mostly catalyzed by enzymes in the living organisms they benefit, or microbes that fix nitrogen in the water and rhizosphere. Inorganic nitrogen exists in the following forms: ammonia/ammonium (NH_3 , NH_4^+), nitric oxide (NO), nitrite (NO_2^-), nitrate (NO_3^-), nitrous oxide (N_2O), and dinitrogen ($\text{N}_{2(\text{aq})}$). Ammonium and nitrate are the two most bioavailable inorganic nitrogen forms because they are readily soluble in water, and the latter is highly mobile in soils. Commonly used as a nutrient, these forms are also common electron acceptors for microorganism cellular respiration (Reddy and DeLaune, 2008). Organic nitrogen exists as proteins (polymers of amino acids), nucleic acids (polymers of mononucleotides), amino sugars (structural component of certain saccharides and chitin), and urea (a waste product from animals). Transformation between inorganic and organic species is mediated by five processes: ammonification (mineralization), nitrification, denitrification, assimilation, and decomposition. Wastewater containing elevated nitrogen levels often come from fertilizer and pesticide runoff from polymer manufacturing (amines), potato farming operations (imides), and aluminum and gold mining (leachate, e.g. cyanide: CN^- ; Kadlec and Wallace, 2009).

Elevated phosphorus levels are most often reported in domestic and municipal wastewater effluents, however typical phosphorus concentrations are approximately 10-fold less than those for nitrogen (Kadlec and Wallace, 2009; Reddy and DeLaune, 2008). Like nitrogen and carbon, phosphorus exists in many organic (nucleic acids, phospholipids, sugar phosphates in microorganisms and vegetation) and inorganic (orthophosphates, $\text{PO}_4\text{-P}$) forms as both dissolved and particulate species. The fate of inorganic phosphorus, in addition to chemical transformation to organophosphorus, is through soil adsorption and ionic precipitation. The primary mechanisms responsible for the mineralization of phosphorus include leaching, fragmentation, and photolysis (Reddy and DeLaune, 2008). Wetland soils usually have a large concentration of organic phosphorus from humic and fulvic acids which are commonly derived from plant litter and organic matter deposition (Reddy and DeLaune, 2008).

The overall productivity of a wetland is dependent on the balance and cycling of these required elements. A common index of measurement for nutrient balance is the carbon, nitrogen and phosphorus elemental ratio (C:N:P) in the environment, and known as the Redfield ratio to be 106:16:1, respectively (Redfield, 1934). This ratio has been found to provide the most favourable nutrient conditions to promote healthy ecological efficiency (Jackson and Williams, 1985).

Trace Metals

In addition to the aforementioned necessary primary nutrients needed are the trace elements iron, manganese, and sulfur. They are essential to living organisms, play an important role in the redox reactions in soils, and provide an overall contribution to general wetland performance. Iron and manganese in particular are vital components for plant photosynthesis. However, if sulfur becomes excessive, wetlands may be subject to sulfur-induced eutrophication, toxicity, and oxidation which promote the formation of hydrogen sulfide (H₂S). Halogens are considered conservative elements in that they have very little effect on the dynamics of a wetland. For this reason, chloride, fluoride and bromide, if background or influent concentrations are low enough, are often used as tracers to estimate water budget and study hydrology. Alkali metals such as sodium, potassium, calcium and magnesium are rarely concerns for toxicity, but the divalent species contribute to water hardness and may pose operational concerns in engineered wetlands.

2.2.5 Wetland Vegetation

With respect to engineered wetland design and implementation, efficiency depends on the inauguration of aquatic vegetation to the conditions of the wetland environment. These plants regulate a number of significant chemical and biological removal mechanisms. Emergent plants are important to contaminant fate mechanisms in a wetland since they are in direct contact with all abiotic and many biotic compartments. Emergent vegetation exists within the bioavailable fraction of the sediment and its pore water, throughout the entire freestanding water column, and emerging out into the atmosphere. Just as they mediate nutrient and water movement via phloem and xylem tubules, they act as an artery for chemical transport.

Hydrophytic plants have the ability to survive in an anoxic rhizosphere because they form intercellular air spaces, develop both water and adventitious roots, and can supply their root systems with the oxygen they require from the atmosphere (Reddy and

DeLaune, 2008; Stottmeister et al., 2003). These intercellular air spaces, called aerenchyma, are permeable gas chambers (impermeable to liquid), and take up as much as 60% of the total tissue volume of the plant. This gas transport mechanism is most notable in the common wetland vegetation, *Typha latifolia* (cattail) and *Phragmites australis* (reed), which are capable of creating strong pressure differentials between the oxygen-containing plant leaves and regions of oxygen consumption (Allen, 1997; Stottmeister et al., 2003). Allen (1997) reported that this phenomena is mainly due to thermoosmosis – a process whereby fluid moves with a temperature gradient, in this case caused by solar radiation. The pressure build-up in the leaves drives oxygen transport through the aerenchyma of the plant, down to its roots. This oxygen release supplies the rhizosphere with enough O₂ to maintain an aerobic environment, and forms an oxidative protective film on the root surface to protect against an environment of high biological and chemical oxygen demand (Allen, 1997; Reddy and DeLaune, 2008; Stottmeister et al., 2003).

Many wetlands, depending on their design, are capable of incorporating a combination of submerged, floating, and emergent vegetation species to promote a more diverse microbial community (U.S. EPA, 1999). The saturated soil conditions in a wetland system create an environment supportive of all hydrophytic vegetation (i.e. vegetation that live completely or partly in water, whether rooted in saturated sediment, or living freely such as floating vegetation like hyacinth; Reddy and DeLaune, 2008). These aquatic types of vegetation have evolved physiological, anatomical, and morphological features which allow them to thrive in conditions of saturation and sometimes oxygen deficiency.

Bhatia and Goyal (2014) described remediation with wetland vegetation as five overlapping processes: phytoextraction, phytodegradation, rhizofiltration, phytostabilization, phytovolatilization. Bioremediation refers to these mechanisms of phytoremediation that are in symbiosis with associated rhizospheric microbes. Together, the mechanisms of plant uptake, accumulation, and transformation regulate removal processes through the rooting media of a wetland. Bhatia and Goyal (2014) reported the frequency of used for different types of vegetation in engineered wetlands. It was found that the remediation of wastewater in constructed wetlands is most common with *Phragmites* (41%), followed by *Typha* (23%), *Spartina* (15%), *Scirpus* (8%), *Juncus* (5%), and *Cyperus*, *Acorns*, *Lemna*, *Paspalam* (~8% total). Generally, a combination of

submerged, emergent, and floating vegetation improves the biological diversity and activity in the wetland, and provides the most effective removal of xenobiotics, TSS, BOD, and COD (Bhatia and Goyal, 2014; Farid et al., 2014).

2.2.6 *Wetland Microorganisms*

The biogeochemistry of nutrient cycling, wastewater filtration, and purification is largely controlled by the microbial communities, but many other factors play supportive roles for these processes. The extent of microbial activity is directly influenced by the presence of appropriate electron donors and acceptors under acceptable environmental conditions (i.e. redox and temperature; Reddy and DeLaune, 2008; Truu et al., 2009). Chemotrophic microorganisms are most responsible for contaminant removal, whereas heterotrophic microorganisms regulate nutrient cycling in wetlands. There is a sophisticated symbiosis within wetland systems that determines treatment capacity. No single microorganism is universally used because conditions in the environment are unique to every site, and these conditions determine the viability of different microbiota. The measurement of total microbial biomass, activity, and the C:N:P ratio subsidizes specific data for individual microbe species since this data is difficult to gather, and constantly changing. Each of these measurements has merits and limitations to defining the state of the microbe population. Truu et al. (2009) review these characteristics in different wetland designs, and observe that HSSF designs have a higher C:N ratio than VSSF, which suggest a different community composition. But SSF designs, in general, have higher heterotrophic organism growth relative to FWS designs, although total microbial activity is not statistically different. Chazaranc et al. (2010) states the most influential component on microbial activity and treatment performance was the season and age of the wetlands. Warmer summers and the older wetland systems contained the most favourable wetland microbe diversity and activity. Tao et al. (2007) performed an analysis on surface flow wetlands in response to different influent strengths of wood-waste leachate. According to the study, the majority of microbes were found in the sediment, however only 3-4% were actively transforming the contaminants. The greatest activity was found in the water column, but overall heterotrophic activity and their distribution among water, epiphytic biofilm, and sediment was proportional to the availability of substrates. The nanoflagellates were believed to impart a grazing pressure for respiring planktonic bacteria which served as a disadvantage to the wetland that had an over-abundance of nanoflagellates.

3. Modeling Theory

Three sub-models describing environmental fate have been integrated to provide a complete model of treatment in engineered wetlands. These sub-models include:

- (i) abiotic compartments (sediment, water, air) with a biotic compartment (vegetation) to estimate contaminant fate from intermedia transport and transformation;
- (ii) food web bioaccumulation describing mechanisms of intake, removal, and transformation in aquatic species (phytoplankton, zooplankton, benthos, and fish species); and
- (iii) ecological risk assessment of the organisms in the food web using relevant toxicological endpoint values (i.e. EC₅ or LC₅).

These sub-models have been integrated to describe the pathways for contaminant transport, and transformation using the principles of conservation of mass. The complete model estimates the steady state and time-dependent contaminant concentration in each compartment, which occurs when wastewater enters the wetland. The food web bioaccumulation sub-model investigates the potential for bioaccumulation using a modified Arnot and Gobas (2004) model. The final concentrations estimated in each compartment are used to assess the risk to the aquatic species based on available toxicity endpoint values for both steady state and temporal responses.

Defining a unit world for environmental modeling to profile the dynamics of chemical partitioning involves a series of differential equations derived for each environmental compartment (Equation 2, general equation) (Mackay, 2001; Snell, 1967).

$$\frac{dM_i}{dt} = I_i + \sum (k_{j \rightarrow i} M_j) - \sum (k_{i \rightarrow j} M_i) - k_{T_i} M_i \quad (2)$$

Where subscripts i and j refer to different environmental compartments. $M_{i,j}$ is the mass (g) of chemical in compartment i or j , t is time (day), I_i is the chemical input rate into the compartment ($\text{g} \cdot \text{day}^{-1}$), $k_{j \rightarrow i}$ is the transport rate constant (day^{-1}) from compartment j to i , and k_{T_i} is the total (sum) transformation rate constant (day^{-1}) from compartment i to j .

The models were compartmentalized into bulk phases of: water, rooting media, submerged and emergent vegetation fractions. The food web consists of phytoplankton, zooplankton, benthic-dwelling organisms, and three fish species of successive trophic

level and size (small, medium, large). Table 3-1 lists the transport and transformation processes included in the wetland models. For each medium, the mass balance equations are solved through (i) an Euler-type numerical integration to derive the time course of the chemical mass, and (ii) through a solution to derive the balanced concentrations in the steady state wetland system.

Table 3-1: Rate constants (day⁻¹) for contaminant fate in the FWS model.

| Symbol | Pathway |
|---------------|---|
| k_o | Outflow |
| k_v | Volatilization |
| k_{ws} | Overall water-to-sediment transport |
| k_{sw} | Overall sediment-to-water transport |
| k_B | Burial |
| k_{rvsv} | Rhizome vegetation to submerged vegetation |
| k_{wsv} | Water-to-submerged vegetation diffusion |
| k_{svw} | Submerged vegetation to water diffusion |
| k_{svev} | Submerged vegetation to emergent vegetation transport |
| k_{rvev} | Rhizome vegetation fraction to emergent vegetation |
| k_{evair} | Emergent vegetation to air transport |
| k_{wr} | Transformation in water |
| k_{sr} | Transformation in vegetated rooting medium |
| k_{svr} | Transformation in submerged vegetation |
| k_{evr} | Transformation in emergent vegetation |
| k_{gsv} | Growth factor in submerged vegetation |
| k_{gev} | Growth factor in emergent vegetation |
| k_M | Metabolism in aquatic biota |

When the sum of all mass flux processes entering and leaving a compartment is equivalent, the whole system is considered to be at steady state (i.e. $dM_i/dt = 0$, where ' M ' is mass, ' t ' is time, and ' i ' represents one environmental compartment). This assumption creates a series of four equations (water, rooting medium, submerged vegetation, emergent vegetation) containing four unknowns (M_W , M_{RM} , M_{SV} , M_{EV}) which is capable of being solved algebraically.

The temporal simulation requires a Euler-type finite difference numerical method approximation that iteratively estimates the accumulation of mass in each compartment for an unrestricted, but user-defined, simulation length (t) and time-step ($dt \rightarrow \Delta t$). This involves creating step-wise iterations that use each increment of accumulated mass (i.e. M_1 at t_1) in the next time-step calculation (M_2 at $t_2=t_1+\Delta t$; Equation 3).

$$M_{i, t+\Delta t} = \left[\left(I_{i,t} + \sum (k_{j \rightarrow i,t} M_{j,t}) - \sum (k_{i \rightarrow j,t} M_{i,t}) - k_{T_{i,t}} M_{i,t} \right) \times \Delta t \right] + M_{i,t} \quad (3)$$

We can use the results of steady state and temporal simulation to observe the response of the concentration of contaminant in wetland media throughout the lifetime of the wetland.

3.1 Contaminant Fate Wetland Sub-Model

Figures 1-1, 1-2, and 1-3 conceptualize FWS, HSSF, and VSSF wetland configurations. These are the three basic engineered wetland designs described by Bhatia and Goyal (2014), Brix (1998), Kadlec and Wallace (2009), Knight et al. (1999), and U.S. EPA (2000b). A similar approach to environmental contaminant modeling has been previously used in the Fugacity level III by Mackay (1991), EcoFate Model by Gobas et al. (1998), QWASI model by Mackay (1989), and the Lake Ontario model by Gobas (1993). These methods have been the foundation for the techniques used in the development of this model.

The purpose of this contaminant fate sub-model is to estimate chemical transformation losses and partitioning within the compartments of the engineered wetland designs. The model calculates chemical removal efficiency (E) from the ratio of the chemical removed from the wetland processes (influent flux – effluent flux), to the amount of contaminant that entered in the influent wastewater (influent flux; Equation 4).

$$E = 1 - (\text{Effluent Flux} / \text{Influent Flux}) \quad (4)$$

For the FWS wetland model, the bulk-phase mass balance equations are developed for the water (W), the vegetated rooting medium (RM), the submerged vegetation (SV) and the emergent vegetation (EV):

$$dM_W/dt = L + k_{RM-W} \cdot M_{RM} + k_{SV-W} \cdot M_{SV} - (k_{W-RM} + k_{W-SV} + k_V + k_O + k_{WT}) \cdot M_W \quad (5)$$

$$dM_{RM}/dt = k_{W-RM} \cdot M_W - (k_{RM-W} + k_B + k_{RM-SV} + k_{RMT}) \cdot M_{RM} \quad (6)$$

$$dM_{SV}/dt = k_{RM-SV} \cdot M_{RM} + k_{W-SV} \cdot M_W - (k_{SV-W} + k_{SV-EV} + k_{SVT} + k_{SVG}) \cdot M_{SV} \quad (7)$$

$$dM_{EV}/dt = k_{SV-EV} \cdot M_{SV} - (k_E + k_{EVT} + k_{EVG}) \cdot M_{EV} \quad (8)$$

where M represents the contaminant mass (g) in its respective compartment, t is time (d) and k represents the first-order rate constant (day^{-1}) for various transport, combined abiotic and biotic transformation processes, and biomass growth dilution as described in Table 3-1. The algorithms used to calculate the rate constants of this model are

available in Appendix A. The contaminant enters the wetland in the bulk wastewater phase represented by loading rate, L ($\text{g}\cdot\text{day}^{-1}$). Chemical effluent flux from the wetland occurs via volatilization from the water, transpiration from emergent vegetation (collectively referred to as evapotranspiration (ET)), transformation in each of the environmental compartments (Stannard et al., 2013; Zhou and Zhou, 2009). Also included is a mechanism for dilution through submerged and emergent vegetation biomass increase, which is considered a pseudo-loss mechanism. The model can also account for chemical loss through rooting medium accretion, a process whereby newer deposits bury older sediment and therefore the chemical is no longer bioavailable or accessible to biota or resuspension. This process is defined by the user with a sediment burial rate ($\text{m}\cdot\text{day}^{-1}$), but may be more relevant in natural wetlands since engineered designs may intend to minimize this process to maintain consistent operation and maintenance. The model is encoded with first-order rate constants to describe all of the processes involved in the engineered wetland (contaminant loading, outflow, transformations, intermedia diffusion transport, evapotranspiration, accretion, growth dilution). The processes of transformation in the model are inclusive of all possible mechanisms including biotic and abiotic reactions.

The temporal response of the contaminant concentration in the wetland system can be described by the half-life time (t_{50} ; Equation 9) and the time to achieve 95% of steady state (t_{95} ; Equation 10):

$$t_{50} = 0.693/\sum k_{out,i} \quad (9)$$

$$t_{95} = 3/\sum k_{out,i} \quad (10)$$

where $\sum k_{out,i}$ refers to the sum of the rate constants describing contaminant removal from all wetland environmental compartments (Table 3-1; k_v , k_B , k_{evair} , k_{wr} , k_{sr} , k_{svr} , k_{evr} , k_{gsv} , k_{gev}).

3.2 Plant Uptake

The FWS model considers plant uptake through the diffusion from water, and the xylem transport from the rooting medium. The rooting media is a bulk phase of sediment, pore water, and rhizomes in order to remove the necessity to distinguish all three as separate compartments, and to simplify the model.

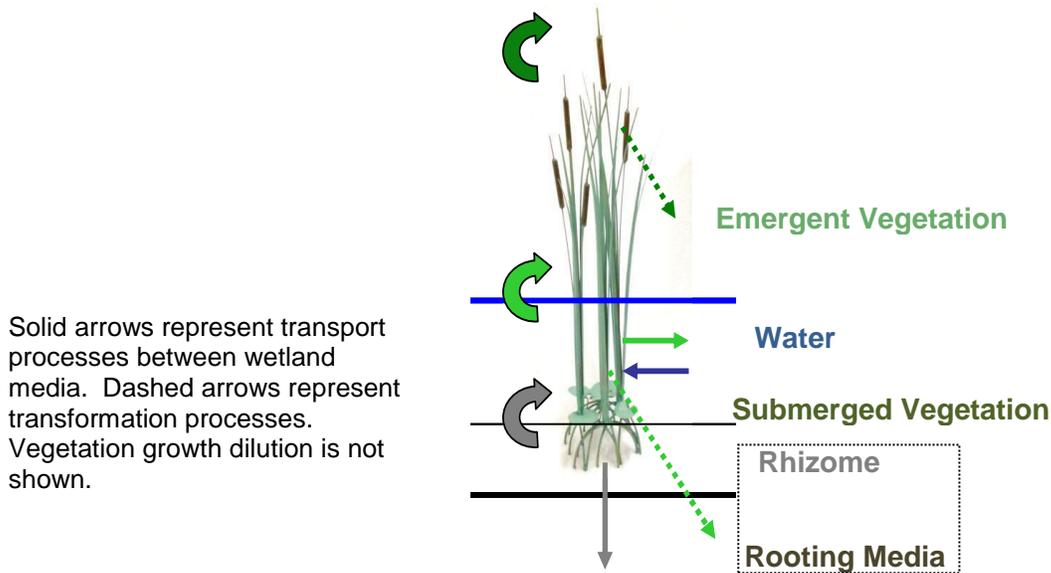


Figure 3-1: Conceptual diagram of an illustrative wetland plant system.

Contaminant transport from rooting media through vegetation is estimated partially with Equation 11. It describes uptake from rooting medium as the fraction of freely dissolved contaminant in the pore water (f_{DS}) relative to the total volume of rooting medium (V_{RM}), and multiplied by the volumetric flux (Q_w , L·day⁻¹) of water flowing through the xylem tubules of an aquatic species (parameterized) and the total number of plants (N_{plants}) present in the wetland. This provides an overall estimate for the fraction of contaminant uptake into the submerged fraction of the plant (k_{RV-SV} ; Equation 11).

$$k_{RM-SV}[\text{day}^{-1}] = \frac{f_{DS} \cdot Q_w \cdot N_{plants}}{V_{RM}} \quad (11)$$

The movement of chemical from the submerged to the emergent parts of the plant is regulated by Equation 12. The rate constant k_{SV-EV} represents this movement of contaminant based on the fraction of water in the vegetation (f_{Wveg}), xylem flow (Q_w), weight of the submerged vegetation (W_{SV}), and plant tissue density (ρ_{veg}).

$$k_{SV-EV}[\text{day}^{-1}] = \frac{f_{Wveg} \cdot Q_w}{W_{SV} \cdot \rho_{veg}} \quad (12)$$

The submerged part of the plant, which is only considered in FWS designs, is also susceptible to intermedia diffusion with water ($k_{water-sub.}$ and $k_{sub-water}$; Equations 13 and 14).

$$k_{water-to-sub.}[day^{-1}] = \frac{SA_{SV} \cdot f_{DW} \cdot v_{water-veg}}{V_{water}} \quad (13)$$

$$k_{sub.-to-water}[day^{-1}] = \frac{k_{water-sub.} \cdot V_{water}}{K_{veg-water} \cdot V_{SV}} \quad (14)$$

where SA_{SV} is the surface area of the submerged vegetation (m^2), f_{DW} is the fraction of freely dissolved contaminant in the surface water (unitless), $v_{water-veg}$ is the mass transfer diffusion coefficient from water to the submerged vegetation ($m \cdot day^{-1}$), V_{water} is the volume of water (m^3), $K_{veg-water}$ is the partitioning coefficient between vegetation and water ($OC_V \cdot VOCOW \cdot K_{OW}$; unitless), OC_V is the organic carbon content of the vegetation, and V_{SV} is the total volume of the submerged vegetation (m^3).

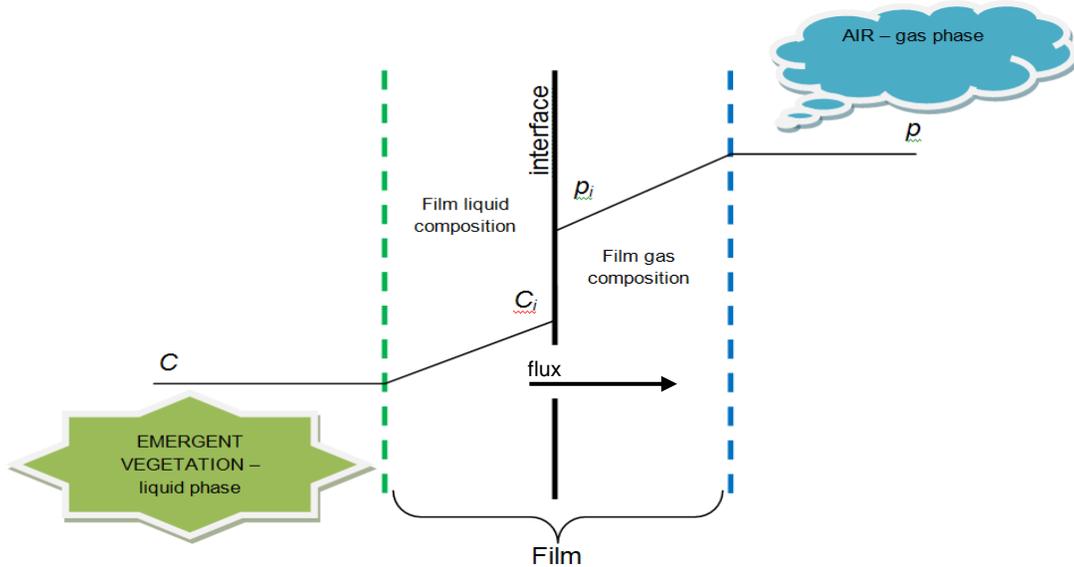


Figure 3-2: Conceptual diagram of the two-film theory approach for transpiration mass transfer of contaminant.

Figure 3-2 illustrates the two-film theory implemented in the model for both evaporation, and transpiration mass transfer. C represents the aqueous concentration of the contaminant, and p represents partial pressure of the contaminant in the atmosphere. The overall flux is controlled by the partition coefficient between plant and air ($K_{VEG-AIR}$), and mass transfer coefficients representing the concentration gradient from C to C_i (k_{plant-}

side), and from p_i to p ($k_{air-side}$). The model assumes steady state between the contaminant composition in the liquid phase (emergent vegetation, i.e. leaves), and the gaseous phase (air). This assumption helps to derive the overall mass transfer coefficient as a function of the plant-side and air-side mass transfer coefficients. Transpiration in the emergent parts of the plant is described by an overall diffusive mass transfer coefficient (v_T) based on this two-film diffusion model (Equation 15). A similar model for evaporation creates mass transfer as a function of water-side and air-side mass transfer coefficients.

$$v_T = \frac{1}{\left(\frac{1}{K_{veg-air} \cdot k_{air-side}}\right) + \left(\frac{1}{k_{plant-side}}\right)} \quad (15)$$

where $K_{veg-air}$ is the partitioning coefficient between vegetation and air ($OC_V \cdot VOCOW \cdot K_{OA}$; $L \cdot kg^{-1}$), and $k_{air-side}$ and $k_{plant-side}$ are the air-side and plant-side mass transfer coefficients, respectively ($m \cdot day^{-1}$). Therefore, the fraction of contaminant removal from emergent vegetation to air is represented by rate constant k_{EV-air} in Equation 16. This process is estimated from the total surface area exposed to the atmosphere (i.e. emergent fraction), organic carbon fraction in the emergent vegetation (f_{OCveg}), and the transpiration mass transfer coefficient (v_T) relative to the volume of emergent vegetation (V_{EV} ; Equation 15).

$$k_{EV-air} [day^{-1}] = \frac{SA_{EV} \cdot f_{OCveg} \cdot v_T}{V_{EV}} \quad (16)$$

Many of the components involved in these mechanisms that involve the submerged and emergent parts of the plant are parameterized by the user. The atmosphere in the model, acts as a final sink for chemical evaporation and transpiration processes (i.e. no re-deposition or absorption is permitted).

ET rates are poorly known but some measured diffusion rate constants for water evapotranspiration have been reported (Lafleur, 1990; Stannard et al., 2013). Other studies suggest chemical specific mass transfer coefficients in an environment other than wetlands (Mukherji et al., 1997; Tasdemir and Esen, 2008). The diffusion constants typically decrease proportional to molecular size and weight, and inversely with ambient temperature. However, most environmental applications will suffice with an order-of-

magnitude estimate (Ramaswami et al., 2005). While substantial testing of an ET model is needed to reliably estimate these rates as a function of site-specific and physicochemical properties, the model will illustrate the relative importance of ET among a range of contaminants with different properties.

3.3 Food-Web Bioaccumulation Sub-Model

This sub-model evaluates each chemical for the intake, excretion, transformation, and accumulation in each organism of the structured food web illustrated in Figure 3-3. Biotransformation of the contaminant in fish (k_M) is defined from empirical datasets evaluated by Arnot et al. (2008), and available in EPISuite v4.11 (U.S. EPA, 2013a). Additional removal mechanisms are calculated within the sub-model based on equations developed by Arnot and Gobas (2004).

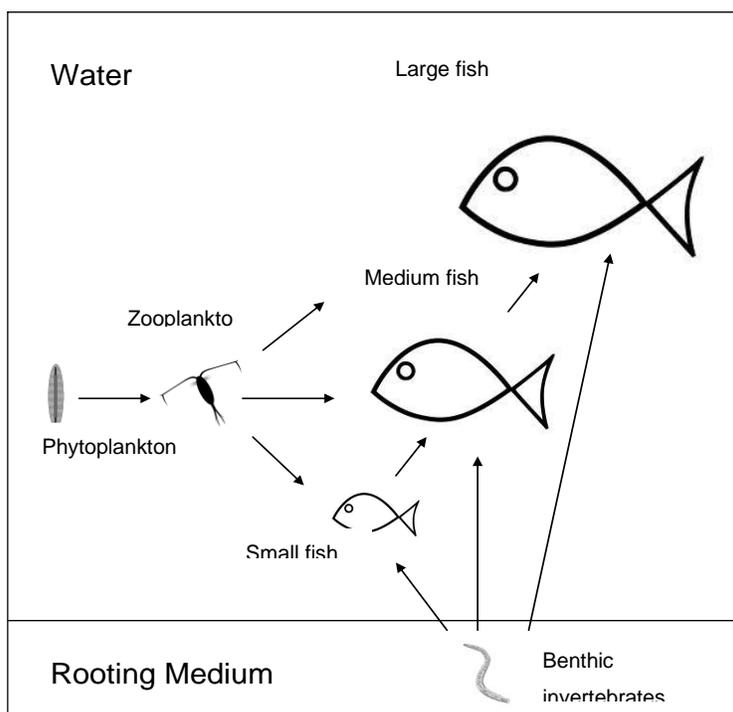


Figure 3-3: Conceptual diagram of an illustrative wetland food web.

The steady state bioaccumulation sub-model developed by Arnot and Gobas (2004), derives bioaccumulation factors (BAFs) for organisms in a parameterized food web. These estimates may help to suggest whether long-term treatment is likely to produce biologically harmful concentrations and whether bioaccumulation of the influent chemical is a concern. These BAFs are applied to the predicted freely dissolved aqueous contaminant at steady state, to estimate concentrations in wetland biota. The chemical concentration in the organism (C_B ; $g \cdot kg^{-1}_{ww}$) is estimated with Equation 17.

$$C_B = \frac{\{k_1 \cdot (m_o \cdot \phi \cdot C_{WT,O} + m_p \cdot C_{WD,S}) + k_D \cdot \sum P_i \cdot C_{D,i}\}}{k_2 + k_E + k_G + k_M} \quad (17)$$

where k_1 is the clearance rate constants ($L \cdot kg^{-1} \cdot day^{-1}$), m_o is the fraction of the respiratory ventilation that involves overlying water, ϕ is the fraction of the total chemical concentration in the overlying water that is freely dissolved and can be absorbed via membrane diffusion, $C_{WT,O}$ is the total chemical concentration in the water column above the rooting media ($g \cdot L^{-1}$), m_p is the fraction of the respiratory ventilation that involves sediment-associated pore water, $C_{WD,S}$ is the freely dissolved chemical concentration in the sediment associated pore (or interstitial) water ($g \cdot L^{-1}$), k_D is the dietary uptake rate constant via ingestion of food and water ($kg \cdot kg^{-1} \cdot day^{-1}$), P_i is the fraction of the diet consisting of prey item i , $C_{D,i}$ is the concentration of the chemical in prey item i ($g \cdot kg^{-1}$). The removal rate constants, k_2 , k_E , k_G , and k_M (day^{-1}) are the gill elimination, fecal egestion, growth dilution, and metabolic transformation rate constants, respectively. Equation 18 represents the corresponding BAF for each organism relative to the concentration in the water phase from the sub-model calculations.

$$BAF = \frac{C_B}{C_{WT,O}} \quad (18)$$

Inorganic (Type II) substances such as arsenic cannot be calculated with this bioaccumulation sub-model, but the user-defined distribution coefficients ($D_{i \rightarrow water}$) can describe the accumulation and partitioning of the chemical in the environment relative to water (e.g. $D_{benthos-to-water}$, $D_{fish-to-water}$, etc.). If all compartments are parameterized in this way, the partitioning and removal of arsenic can be deduced in each compartment using these values.

3.4 Eco-toxicity Sub-Model

To assess the potential for adverse effects in biota, the chemical concentration in the freely dissolved fraction of the water and rooting medium solids are compared to toxicological endpoints. The model derives a ratio of this comparison using chosen effects concentrations (EC_5). A ratio greater than one suggests the organism will experience the endpoint effect. A ratio less than one suggest the organism is below the threshold that illicit biological effects. This sub-model may helps to illustrate the most

appropriate wetland configuration (FWS or SSF) that balances environmental risk with effective wastewater treatment. A species sensitivity curve is recommended to identify species that are more tolerant to a specific influent than alternative species may be.

3.5 Type I and Type II Chemicals

Following the techniques developed for the models available from the Center for Environmental Modeling and Chemistry (CEMC), this model provides chemical fate modeling calculations for both type I and II chemicals. Type I chemicals are organic substances for which partitioning properties such as a K_{OW} and a Henry Law Constant (H) exist for calculating transport processes. Traditionally, type I chemicals include non-ionic substances, however if K_{OW} and H can be derived, then this method can be applied to both non-ionic and ionic organic substances. Computational software such as *ChemSilico* (ChemSilico, 2013) and *SPARC* (ARCHem, 2010) estimates the log K_{OW} of ionic substances (i.e. Log D, a frequently used substitute for K_{OW} for many ionizing substances) as a function of pH, temperature, and ionic strength. With log D and H available, and the environmental conditions are consistent with those used to derive these parameters; the model may carry out its calculations for ionizing substances such as naphthenic acids.

Type II chemicals are those for which there are currently no available methods to reliably estimating environmental media partitioning. However, if empirical data is available for the concentrations in wetland media, the distribution coefficients can be estimated and entered in the model. For these substances, the distribution coefficients replace log K_{OW} and H , and explicitly detail the behaviour of these substances in a wetland. Type II chemicals include heavy metals such which are subject to speciation due to environmental conditions.

3.6 Model Assumptions

The performance of the model is built upon some inherent assumptions. This section expresses transparency in the derivation of the multimedia estimations. First, the model assumes that each chemical that is introduced to the wetland is homogeneously distributed within each of the wetland media, and that the wetland media can be described as single bulk compartments in exchange with an adjacent environment. For example, model identifies the rhizospheric zone to include the rhizomes and associated microorganisms, and combines them with sediment to describe the bulk phase

vegetated rooting medium. Therefore, the solids, water, and rhizomes making up the rhizospheric zone are assumed to be in constant equilibrium with one another. This assumption may be reasonable for many organic contaminants and non-essential metals, but not for essential nutrients such as nitrogen and phosphorus. Transport of contaminants from the rhizomes is assumed to occur predominantly through xylem flow, while the biological functions of phloem and aerenchymal transport are not considered in the fate of many contaminants within the plants. As a result, the model does not apply to gases such as methane and oxygen.

The model considers pseudo-loss through biomass increase of the vegetation, which effectively dilutes the chemical concentration in plant compartments. No net loss of chemical mass from the wetland will occur unless plants are physically removed from the wetlands. The model also accounts for chemical transformation by microbial populations in the rooting medium and by biotransformation in the submerged and emergent parts of the vegetation. The microbial transformation rate is estimated from reported ready biodegradation tests. The reported biodegradation rates are assumed to represent inherent biodegradation rates of the freely dissolved contaminant in the aqueous phase of the water and the rooting medium. Particle bound contaminant in the water is assumed not to be subject to biodegradation (Kickham et al. 2010).

Transpiration driven transport in the plant is characterized by a transpiration flow rate through xylem tubules, Q_w in $L \cdot day^{-1}$. This transpiration flow moves the aqueous dissolved fraction of the chemical in the vegetation from the rhizomes to the submerged and to the emergent parts of the plants. In the free surface flow wetland model, diffusion controlled transport between the water and the submerged part of the vegetation occurs. In the horizontal and vertical subsurface flow models, contaminants are only absorbed through the rhizomes and transpire to the emergent parts of the plants.

In addition to the assumptions regarding inherent performance of the model, the parameterization is defined by available information. Many of the default values in the illustrations are assumed appropriate values, but until model calibration can be complete, there is no accuracy in the results. For all parameters where scientific literature was not available, best scientific judgement was used.

4. Methodology

The illustrations of the multimedia wetland contaminant partitioning, bioaccumulation, and eco-toxicity sub-models were done in an evaluative fashion. This required extensive parameterization to create the simulations that were considered relevant and justified. The objective was to formulate the variables in the model to be able to draw conclusions upon practical applications. The parameters were divided into three major groups: chemical specific parameters, wetland design parameters, and simulation parameters. The values were obtained from a variety of available sources, but those parameters where data was unavailable the best scientific judgement was used. The following sections describe the development and application of these parameters within each sub-model.

4.1 Model Development

The wetland model was developed using Microsoft Excel (2007) spreadsheet calculations for the steady state model, and Microsoft Excel (2007) Visual Basics for Applications (VBA) developer code to build macros that simulate temporal responses of contaminant fate. Each model contains cells that hold the numeric input parameters and the engraved calculations that function with those parameters, throughout the spreadsheet. All cells within the spreadsheets are named according to their parameter name to make the calculations more transparent and accessible throughout the model. Steady state estimates automatically re-calculate and update when numerical input values are changed. To enable the temporal simulation macro in VBA, the '*Run Simulation*' button is engaged on the '*Model*' ('I' or 'II') spreadsheet. A separate spreadsheet tabulates and graphically illustrates the simulated response of mass flux estimates and compartmental concentrations if a valid simulation length and an acceptable time step is entered. This temporal simulation is computed by the '*Run Simulation*' macro developed for this model that calculates the response to contaminant loading in each compartment using the values assigned to the input cells. The temporal results were compiled in a separate spreadsheet ('*Simulation Output*'). Regardless of the length of simulation, the output shown in this spreadsheet lists only ~100 values evenly spread throughout the results in order to minimize space without losing information. The full list of simulated data points are written to a text file automatically labelled '*simulationoutput*' ('I' or 'II' depending on whether it is creating Model I or II output), and created in the default documents directory of the active computer.

The food web bioaccumulation sub-model runs for steady state conditions, but is not capable of modeling non-organic substances. As the user parameterizes the chemical, they will include a Boolean term to describe the chemical as organic or inorganic. By stating 'Y' (organic) or 'N' (inorganic) in the appropriate cell, the model will modify the mode of the food web calculations. If the contaminant is organic, the default bioaccumulation sub-model will engage and perform the necessary calculations described in section 3.3 *Food web bioaccumulation sub-model*. If parameterized as inorganic, the accumulation and partitioning into biota is controlled by the parameterized distribution coefficients (4.2.3 *Food web*). All input cells provide comments that assist the user in defining appropriate values; however, these are suggested estimates and must be re-considered when conducting simulations on a site-specific basis.

The model contains a second wetland in series, parameterized identically to the first in-series wetland, with the chemical outflow flux from 'Model I' fed into the influent flux of the 'Model II'. This provides an opportunity to examine wetland designs in series, or perhaps evaluate an analysis of hybrid designs that incorporate both FWS and SSF wetland designs. There may be a positive effect from integrating these designs.

4.2 Model parameterization

Input parameters are divided into categories of physicochemical and toxicological properties of the contaminant, wetland design criteria including the characteristic properties of each compartment, and simulation parameters. Recommended values that were used are provided in Appendix B.1, C.1, and D.1 for FWS, HSSF, and VSSF models respectively.

4.2.1 Contaminants

To illustrate the application of the model, three contaminants with different chemical properties were chosen:

- (i) **pyrene** (CAS Number: 129-00-0), an example of a non-ionic organic substance, which is a combustion by-product and a constituent in crude oil and petroleum substances;
- (ii) **arsenic** (CAS Number: 1327-53-3), an example of a metalloid present as a soil-constituent in mining practices;

- (iii) **a naphthenic acid** (SMILES: CCC1CCC(C1)CCC(=O)O), an example of an ionizable organic substance, also found in certain oils and oil sands processed wastewaters.

These contaminants were chosen for this illustrative purpose because each can be attributed to common industrial effluents. Intentionally, these chemicals represent those which are commonly found at appreciable concentrations in oil sands processed wastewater. The application of this model to petroleum industry effluent is the ultimate goal.

Table 4-1: Physicochemical and toxicological properties of pyrene, arsenic, and a naphthenic acid for the FWS wetland model.

| <i>Properties</i> | <i>Pyrene</i> | <i>Arsenic</i> | <i>Naphthenic Acid</i> | <i>References</i> |
|---|---|---|-------------------------------|--|
| Molecule |  | As | CCC1CC C(C1)CC C(=O)O)) | U.S. EPA, 2013a, EPISuite v4.11. |
| molecular weight (g·mol ⁻¹) | 202.26 | 74.92 | 170.25 | U.S. EPA, 2013a, EPISuite v4.11. |
| contaminant is an organic substance (Y or N) | Y | N | Y | U.S. EPA, 2013a, EPISuite v4.11. |
| contaminant half life in water (day) | 60 | 15 | 15 | U.S. EPA, 2013a, EPISuite v4.11. |
| ♦contaminant half-life in submerged parts of vegetation (day) | 600 | 150 | 150 | --Estimated-- |
| ♦contaminant half-life in non- submerged parts of vegetation (day) | 600 | 150 | 150 | --Estimated-- |
| ∅LC ₅ or EC ₅ (sediment) in microorganisms (g·kg ⁻¹ _{dw} sediment) | 7.26·10 ⁻³ _a | 3.73·10 ⁻³ _b | na | ^a Romero-Freire et al, 2014. (<i>Vibrio fischeri</i>) ^b Fulladosa et al., 2005 (<i>Vibrio fischeri</i>) |
| ∅LC ₅ or EC ₅ (water) in vegetation (g·L ⁻¹ water) | na | na | na | --Not available -- |
| ∅LC ₅ or EC ₅ (water) in fish (g·L ⁻¹ water) | 2.00·10 ⁻⁴ _c | [†] 9.90·10 ⁻⁴ _d | na | ^c Kennedy, 1990. (<i>Oncorhynchus mykiss</i>) ^d Dyer et al., 1993. (<i>Pimephales promelas</i>) |
| ∅LC ₅ or EC ₅ (sediment) in benthic invertebrates (g·kg ⁻¹ _{dw} sediment) | 0.127 _e | 0.532 _f | na | ^e Landrum et al., 1994. (<i>Diporeia</i> spp.) ^f Liber et al., 2011. (<i>Hyalella azteca</i>) |

| | | | | |
|---|------------------------------------|--------------------------|------------------------------------|---|
| water solubility of contaminant (g·L ⁻¹) | 1.35·10 ⁻¹ | ‡ [†] Insoluble | 9.44·10 ⁻² | U.S. EPA, 2013a, EPISuite v4.11 |
| density of pure contaminant (kg·L ⁻¹) | 1.27·10 ⁻³ _g | 5.78 _h | 9.15·10 ⁻¹ _i | ^g Thomas Jefferson NAC, 2013. ^h ChemicalBook, 2008. ⁱ Sigma-Aldrich, 2013. |
| -- For Organic Substances (neutral or ionic) -- | | | | |
| Henry's Law Constant (Pa·m ³ /mol) | 1.21 | ----- | 0.572 | U.S. EPA, 2013a, EPISuite v4.11 |
| log K _{OW} (for neutral organic) or log D (for organic acid or base) of the contaminant (unitless) | 4.88 _j | ----- | 0.83 _k | ^j U.S. EPA, 2013a, EPISuite v4.11. ^k Hilal et al., 2003, SPARC |
| Solids organic carbon to octanol equivalency factor (L·kg ⁻¹) | 0.955 _l | ----- | 0.35 _m | ^l U.S. EPA, 2013a, EPISuite v4.11. ^m Seth et al., 1999. |
| DOC-octanol proportionality constant (unitless) | 0.08 | ----- | 0.08 | Burkhard, 2000. |
| Vegetation organic carbon to octanol equivalency factor (L·kg ⁻¹) | 0.35 | ----- | 0.35 | Seth et al., 1999. |

na – not available

----- Not applicable

dw – dry weight basis

† - LC5 value reported by Dyer et al. (1993) is for fathead minnow exposure to sodium arsenite (NaAsO₂).

‡ - refers to elemental arsenic. Solubility depends on the arsenic compound (e.g. As<As₂O₃) (ATSDR, 2007).

◆ - contaminant half-life values for submerged and emergent vegetation have been estimated from reported t_{1/2} in water.

◇ - Toxicological endpoint values have been estimated from LC₅₀ values reported in respective reference (see 4.2.4 Toxicity).

The physicochemical properties for pyrene and the naphthenic acid that were used in the model are presented in Table 4-1, and were largely supplied by the Estimation Program Interface Suite (EPISuite) v4.11 calculations by U.S. EPA (2013a). Chemical properties at 25°C were extracted from experimental databases and include molecular weight (MW), octanol-water partition coefficient (K_{OW}), water-solubility (S), and Henry's Law constant (H). However, the naphthenic acid, using only the SMILES to obtain chemical properties, did not contain the same abundance of experimental data as pyrene, but was only able to estimate values for H, S, K_{OC} using HENRYWIN v3.20, WSKOW v1.42, and KOCWIN v2.00 (from K_{OW} method), respectively. The ionic species substitute for K_{OW} is log D, which was estimated using SPARC online software for a pH of 7 at 25°C, and ionic strength of zero (ARCHem, 2010; Hilal et al., 2003). Seth et al. (1999) and Burkhard (2000) have suggested a SOCOW of 0.35 (95% CI of a factor of 2.5), and DOC-to-octanol proportionality constant (adoc) for non-ionic organic

compounds of 0.08 (95% CI of a factor of 20). These were implemented as default values in place of chemical data that could not be found or accurately determined.

Contaminant half-life (t_{50}) in water was estimated in EPISuite v4.11 from the Level III Fugacity model (LEV3EPI). In order to parameterize each model for each contaminant, the half-life transformation rate constants in submerged and emergent vegetation were estimated by applying a factor of 10 to t_{50} in water (i.e. $t_{50,sub./emergent} = 10 \cdot t_{50,water}$). Using the selection of EPISuite v4.11 results, the solids organic carbon to octanol equivalency factor (SOCOW) for organic substances was estimated for pyrene and from the ratio of K_{OC} (organic carbon-to-water partition coefficient) to K_{OW} .

Table 4-2: Arsenic distribution coefficients among abiotic compartments.

| <i>-- For Non-Organic Substances (neutral or ionic) --</i> Distribution Coefficient | Value | Reference |
|---|--------------|--|
| Air-Water Distribution Coefficient (L/L) | na | No partitioning between air and water. |
| Rooting Solids-Water Distribution Coefficient (L/kg dw) | 6190 | Zhang et al., 2009. |
| Suspended Solids Water Distribution Coefficient (L/kg dw) | 2511 | Allison and Allison, 2005. |

For inorganic substances such as arsenic, partition coefficients cannot be accurately estimated due to the complex nature of their chemical speciation. Therefore, measured concentrations in environmental media have been used to derive distribution coefficients for the wetland media (Table 4-2). The distribution coefficients for rooting media – water, and suspended sediment – water were found to be 6190 L·kg⁻¹ and 2511 L·kg⁻¹ based on studies from Zhang et al. (2009) and Allison and Allison (2005), respectively. The air – water distribution coefficient is parameterized as negligible since volatilization and transpiration of arsenic is not observed. Transformation of arsenic is a function of chemical speciation which is dependent on several environmental factors (Sharma and Sohn, 2009). Yin et al. (2011) discuss arsenic biotransformation with three cyanobacterial species (*Microcystis* sp. PCC7806, 36 *Nostoc* sp. PCC7120 and *Synechocystis* sp. PCC6803). The study concludes that the microbial activity from these cyanobacterium play a significant role in the biogeochemistry of arsenic within an aquatic environment. Eary and Schramke (1990) measured rates of inorganic arsenic oxidation in aerated groundwater and discuss the difficult-to-predict nature of Type II chemicals. Half-life values were measured from seconds to years depending on solution conditions. For arsenic, a neutral value for its half-life of 15 days in water was used based on calculations found in EPISuite v4.11 (U.S. EPA, 2013a)

4.2.2 Wetland Design Criteria

The FWS and SSF wetland configurations were parameterized as shown in Appendix A.1, B.1, and C.1 tables. The FWS wetland illustration is a relatively large 10,000 m² wetland, receiving a wastewater flow of 2·10⁶ L·day⁻¹. The HSSF and VSSF models were parameterized for a relatively smaller wetland at 100 m² that receives a proportionately lower inflow of 2·10⁴ L·day⁻¹. Inflow consisted partially of freely dissolved and partially sorbed chemical at a total bulk concentration of 1 mg·L⁻¹. The rooting medium contains a natural organic carbon rich (5%) environment that is suitable for the aquatic plant species, and is a result of dynamic carbon cycling (Reddy and DeLaune, 2008). The variables within the model that are dependent on temperature are fixed at a mean temperature of 25°C. If different environmental temperatures are warranted, the user is required to adjust the dependent variables accordingly. The recommended values for illustrative purposes are provided in Appendix A.

FWS wetlands are capable of hosting a variety of emergent, submerged, and floating vegetation. The aquatic vascular plants flourish in the saturated sediments due to their unique ability to regulate the redox state in the rhizosphere, and from their efficient xylem and phloem transport mechanisms. For the purpose of the illustrative application in this work, a vegetative monoculture of *Typha latifolia* was used. This is an emergent aquatic plant species common in many engineered wetland applications. Mature *T. latifolia* grows to approximately 1.5 to 3 metres in height with broad 2 to 4 cm leaves. A function of the growth of the wetland vegetation is to act as a dilution factor for the accumulated contaminant. As the volume of a plant increases through the growing season, a dilution factor influences the concentrations in the vegetation compartments. The model parameterizes this growth dilution factor for submerged (k_{gsv}) and emergent (k_{gev}) vegetation and applies it to the contaminant fate calculations as a pseudo-loss mechanism ($k_{gsv}, k_{gev} = 10^{-3} \text{ days}^{-1}$). Based on a U.S. EPA (1999) report, *Typha* spp. and *Scirpus* spp. are often in healthy populations at densities of approximately 40 - 50 stems·m⁻² and 100 - 300 stems·m⁻², respectively. Ibekwe et al. (2006) indicate that microbial diversity and activity is highest in wetland cells constructed with an overall plant coverage of 50% compared with 100% plant coverage, and therefore the parameterized vegetation density was rationalized as 25 plants·m⁻² for *T. latifolia*.

Water in the FWS flow model was limited to a recommended depth of 1 m for the most common wetland plants (bulrush, cattails, and reeds) (Bhatia and Goyal, 2013; U.S.

EPA, 1999). This promotes a healthy rhizosphere by regulating dissolved oxygen through aerenchymal tubules, and improving pressure differential to initiate vascular transport through plant xylem (U.S. EPA, 1999; Sculthorpe, 1985). Moreover, an appropriate water depth maintains a healthy fraction of emergent and submerged vegetation to facilitate transpiration and diffusive flux associated with plant uptake (Trapp and McFarlane, 1995).

The weights of the illustrative vegetation sub-compartments were estimated using the dimensions of a descriptive plant-soil-air system by Trapp and McFarlane (1999). Weights were allocated to rhizome, submerged and emergent fractions of the plant. In the FWS wetland it was assumed that 50% of a plant is submerged and 50% is emergent. In the SSF wetland models, a negligible fraction of the plant is submerged since no water column develops. Using an approximate stem diameter of 0.05 cm for illustrative vegetation, an estimate of the surface-area-to-volume ratio was determined (Appendix A; illustrative plant dimensions are available in Table A-3 and A-4). The transpiration flow rate through the plant xylem was adapted from Crank et al. (1981) as $2 \cdot 10^{-4} \text{ m}^3 \cdot \text{hour}^{-1}$ per square centimeter of foliage area. With the total foliage of 0.05 m^2 , the resulting xylem flow rate for this illustrative system is $10^{-5} \text{ m}^3 \cdot \text{h}^{-1}$. Since aquatic vegetation has evolved a more efficient water transport through xylem tubules, this transpiration rate was increased 10-fold ($2.4 \text{ L} \cdot \text{day}^{-1}$) for illustrative practice (Lafleur, 1990; Sculthorpe, 1967).

This model provides an opportunity to evaluate the overall evapotranspiration rates for chemicals with different physicochemical properties (i.e. H , K_{OW} , and K_{OA}). A mass transfer coefficient for evapotranspiration was estimated from data produced by Stannard et al. (2013) and Lafleur (1990) for North American wetland areas. Lafleur (1990) estimated the summertime mean daily evapotranspiration rate of water for aquatic macrophytic vegetation at $3.1 \text{ mm} \cdot \text{day}^{-1}$ for a study area with surface moisture near complete saturation. In a long-term field study designed by the U.S. Geological Survey in Oregon, Stannard et al. (2013) measured ET rates for a wetland dominated by hard stem bulrush (*Scirpus acutus*) and cattails (*Typha latifolia*) between May 2008 and September 2010. The measurements estimated an average evapotranspiration rate for water of $0.938 \text{ m} \cdot \text{yr}^{-1}$, translating to an annual daily average of approximately $2.6 \text{ mm} \cdot \text{day}^{-1}$. Although Burba et al. (1999) showed that evapotranspiration rates are negligible following periods of senescence, and ET responds strongly to seasonal and

diurnal climatic patterns, this estimation from Stannard et al. (2013) is a reasonable approximation for this evaluative purpose. The mass transfer coefficients of the model partly reflected these ranges of overall ET. Further studies are required if the model is to be developed for predictive purposes.

4.2.3 Food-Web

The bioaccumulation sub-model was designed for a food web similar to that used by the U.S. EPA's KABAM Model (U.S. EPA, 2009). This food web consists of phytoplankton, zooplankton, a benthic invertebrate species, and a small, medium, and large fish species (VanderZanden and Rasmussen, 1996). In the FWS wetland model, the available compartments are capable of hosting all biota of this food web. The SSF designs only include phytoplankton, zooplankton, and the benthic invertebrate species because of the lack of a freestanding water habitat for fish. The estimates of accumulated concentration can be useful to assess the risk in predator species such as mammals and birds. The concentrations can be multiplied by the feeding rate of the animals on wetland prey to derive a dose in units of $\text{mg}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$ that can be compared to thresholds of toxicological effects. The full parameterization of the food web sub-model for bioaccumulation is provided in Table 4-3.

Table 4-3: Parameterization of the food web sub-model for pyrene and the naphthenic acid.

| | <i>Phyto-</i> | <i>Zoo-</i> | <i>Bentho</i> <i>s</i> | <i>Sm.</i> <i>fish†</i> | <i>Med.</i> <i>fish†</i> | <i>Lg. fish†</i> |
|---|---------------|-------------|---------------------------|----------------------------|-----------------------------|------------------|
| Weight of biota (kg) | ----- | 1.0E-07 | 1.0E-04 | 0.01 | 0.1 | 1 |
| Lipid fraction in biota (kg/kg) | 0.5% | 3% | 3% | 4% | 10% | 12% |
| Non-lipid organic matter fraction in biota (kg/kg) | 20% | 20% | 20% | 22% | 22% | 20% |
| Water fraction in biota (kg/kg) | 79.5% | 77% | 77% | 74% | 72% | 76% |
| Non-lipid organic matter-octanol proportionality constant (unitless) | 0.35 | 0.035 | 0.035 | 0.035 | 0.035 | 0.035 |
| Dietary absorption efficiency of lipid (%) | 75% | 72% | 75% | 92% | 92% | 92% |
| Dietary absorption efficiency of non-lipid organic matter (%) | 75% | 72% | 75% | 55% | 55% | 55% |
| Dietary absorption efficiency of water (%) | 25% | 25% | 25% | 25% | 25% | 25% |
| Fraction of the respiratory ventilation that involves overlying water (%) | 95% | 95% | 95% | 100% | 100% | 100% |
| Fraction of the respiratory ventilation that involves | 5% | 5% | 5% | 0% | 0% | 0% |

| | | | | | | |
|---|-----------------------|---------|---------|--|---|--|
| sediment-associated pore water (%) | | | | | | |
| Particle scavenging efficiency (%) | 100% | 100% | 100% | ----- | ----- | ----- |
| Resistance to contaminant uptake through the aqueous (unitless) | 0.00006 | ----- | ----- | ----- | ----- | ----- |
| Resistance to contaminant uptake through the organic phase (unitless) | 5.5 | ----- | ----- | ----- | ----- | ----- |
| Invertebrate growth rate coefficient (T <17.5 deg C) (unitless) | ----- | 5.0E-04 | 5.0E-04 | 5.0E-4 | 5.0E-04 | 5.0E-04 |
| Invertebrate growth rate coefficient (T >17.5 deg C) (unitless) | ----- | 2.5E-3 | 2.5E-3 | 2.5E-3 | 2.5E-3 | 2.5E-3 |
| Constant A (ew) (unitless) | 1.85 | 1.85 | 1.85 | 1.85 | 1.85 | 1.85 |
| Constant B (ew) (unitless) | 155 | 155 | 155 | 155 | 155 | 155 |
| Constant A (ed) (unitless) | ----- | 3.0E-07 | 3.0E-07 | 3.0E-07 | 3.0E-07 | 3.0E-07 |
| Constant B (ed) (unitless) | ----- | 2 | 2 | 2 | 2 | 2 |
| Metabolic transformation rate constant (day ⁻¹) | 0 | 0 | 0 | 1.246 _{Pyr} 0.4447 _{NA} | 0.7007 _{Pyr} 0.2501 _{NA} | 0.394 _{Pyr} 0.1406 _{NA} |
| Diet | -- Food web -- | | | | | |
| Sediment | ----- | ----- | 100% | ----- | ----- | ----- |
| Phytoplankton | 0% | 100% | 0% | ----- | ----- | ----- |
| Zooplankton | ----- | 0% | 0% | 50% | 50% | 0% |
| Benthos | ----- | ----- | 0% | 50% | 50% | 0% |
| Small fish | ----- | ----- | ----- | 0% | 0% | 50% |
| Medium fish | ----- | ----- | ----- | ----- | 0% | 50% |
| Large fish | ----- | ----- | ----- | ----- | ----- | 0% |

† - Not used in SSF designs

----- Not applicable

Pyr – pyrene; NA – naphthenic acid; As – arsenic (not applicable)

ew – efficiency of contaminant transfer via gills

ed – efficiency of contaminant transfer via intestinal tract

For more information on parameters, see Arnot and Gobas (2004)

Outlined in Arnot and Gobas (2004), this food-web bioaccumulation model requires estimates of the metabolic transformation rate constants (k_M) in units of reciprocal days (day⁻¹). These biotransformation rate constants have been calculated for organic compounds (pyrene and a naphthenic acid) using EPISuite v4.11 (BAFBCF Model) for small (0.01 kg), medium (0.1 kg), and large (1 kg) fish. There are no biotransformation rate constants available for inorganic chemicals such as arsenic.

The Arnot and Gobas (2004) bioaccumulation sub-model cannot compute biological fate of inorganic substances. The behaviour of these substances must be described in the model from empirical measurements in similar environmental scenarios (wetland or aquatic system). Available material from Williams et al. (2006), Zhang et al. (2009), and

Zhang et al. (2013) provides measurements of arsenic concentration in the biological media. Using this data, distribution coefficients for the arsenic illustrations can be derived (Table 4-4). Zhang et al. (2009) included arsenic concentrations in sediment, water, and macrophytic vegetation for a wetland studied in Northern China. Williams et al. (2006) and Zhang et al. (2013) provided suggestions for some of the remaining arsenic biota-water partitioning, reported as bioaccumulation factors (BAFs) suitable for the models bioaccumulation estimates. The values used for the BAFs of fish in the modeled food web were from reported risk assessment guidelines presented by the U.S. EPA in 1980 as a consumption-weighted average based on two data points for oysters and fish (Williams et al., 2006). Given the lack of experimental measurements of arsenic food web bioaccumulation in aquatic freshwaters systems, the distribution coefficients for small, medium, and large fish are assumed equivalent.

Table 4-4: Arsenic distribution coefficients among biotic compartments.

| <i>-- For Non-Organic Substances (neutral or ionic) -- Distribution Coefficient</i> | Value | Reference |
|---|--------------|------------------------|
| Vegetation-Water Distribution Coefficient (L/kg ww) | 2096 | Zhang et al., 2009. |
| Phytoplankton-Water Distribution Coefficient (L/kg ww) | 0.286 | Zhang et al., 2013. |
| Zooplankton-Water Distribution Coefficient (L/kg ww) | 0.286 | Zhang et al., 2013. |
| Benthos-Water Distribution Coefficient (L/kg ww) | 1.7 | Williams et al., 2006. |
| Fish One-Water Distribution Coefficient (L/kg ww) | 44 | Williams et al., 2006. |
| Fish Two-Water Distribution Coefficient (L/kg ww) | 44 | Williams et al., 2006. |
| Fish Three-Water Distribution Coefficient (L/kg ww) | 44 | Williams et al., 2006. |

4.2.4 Toxicity

Toxicological bioassays regularly report median lethality concentrations (LC₅₀), where the exposure concentration in water results in mortality of 50% of the test species. This model uses the LC₅ or EC₅ to indicate the lower-limit for toxicological effects from the contaminants in organisms of the wetland. An estimated LC₅ and EC₅ are used in the model because they are believed to better represent limits that protect the biological activity within the wetland. Biotransformation plays a significant role in contaminant removal, and micro- and macro-organisms are vital in maintaining healthy biogeochemical cycling within the wetland. Therefore, these toxicological endpoints provide a more valuable limit on the contaminant inflow to protect wetland productivity.

Toxicity endpoint values were gathered from empirically derived LC₅₀ concentrations available from the U.S. EPA EcoTox Database (US EPA, 2013b). In cases where sub-lethal endpoint values were not reported, apparent LC₅ or EC₅ values were estimated by

reducing the available LC_{50} endpoint values by a factor of 10. These estimated values are likely an overestimation of the true LC_5 or EC_5 values because the dose-response relationship is assumed linear in this estimation as oppose to sigmoidal. If there is no toxicological data available, this often suggests that toxicity profiling of the contaminant is scientifically premature. To alert the model, the user may input 'na' (referring to 'not available') in the appropriate cells, which indicates to the model that toxicity thresholds for a chemical or species is unknown. In this case, the toxicity profiling will not occur for this test species.

4.3 Model Application

The model uses the physicochemical properties of a contaminant to model their fate within an engineered wetland system. These parameters are the foundations for the calculations in the model because together, they define the inherent chemical behaviour among all media of interest (e.g. partitioning between air, water, biota can be determined from only the octanol-water and octanol-air partition coefficients). To illustrate this concept within our model, a chemical universe described by $\log K_{OW}$ and $\log K_{OA}$ values was created. A comprehensive array of appropriate ranges of $\log K_{OW}$ and $\log K_{OA}$ can describe a spectrum of chemical behaviours (Figure 4-1). At any point in Figure 4-1 a K_{OW} and K_{OA} value can be extracted, and supplied to the model. Therefore, for all combinations of K_{OW} and K_{OA} , the removal efficiency can be estimated. Using the FWS model to assess the distribution of removal efficiency throughout this chemical universe can provide more criteria to evaluate engineered wetland application.

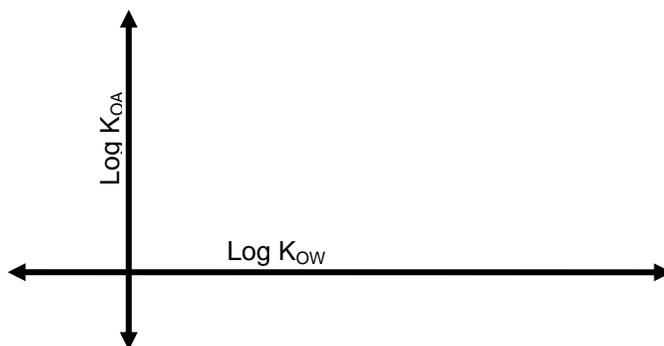


Figure 4-1: Conceptual illustration of a chemical universe defined by $\log K_{OW}$ and $\log K_{OA}$.

Physicochemical properties including K_{AW} (air-water partition coefficient), H (Henry's Law constant), K_{OC} (organic carbon-water partition coefficient) and $SOCOW$ (sediment organic carbon-water partition coefficient relative to octanol-water partition coefficient)

can be estimated from these $\log K_{OW}$ and $\log K_{OA}$ values (Equations provided in Appendix A). The values for chemical parameters are entered into the wetland model, and the calculated steady state removal efficiency, rate constants, and mass fluxes are recorded.

The model simulations are designed to show variations in removal efficiencies among chemicals with various physicochemical properties (namely K_{OW} and K_{OA}). This data is then compiled into a table of input parameters (K_{OW} , K_{OA}), and output parameters (removal efficiency, rate constants, and mass fluxes), and builds a three-dimensional contour plot of the results (K_{OW} , K_{OA} , and an output parameter). The outcome of the model is highly dependent on the parameterization of the model with respect to evapotranspiration and transformation. The remaining mechanisms are not influenced by the physicochemical properties within the model. Transformation was effectively removed from the model to better illustrate the role of the physicochemical properties of the chemical on wetland remediation efficiency. Growth dilution was not modified in this simulation since this mechanism is dependent on the accumulation of contaminant in the vegetation. Uptake and accumulation is directly influenced by K_{OW} and K_{OA} values and hence growth dilution may play a significant role in this evaluative illustration. Also, since the maximum uptake of contaminants is not limited and seasonal senescence is not integrated into the model, a conservative approach was taken in regards to growth dilution factors. The water budget was adjusted to increase hydraulic retention time in the wetland, to make the chemicals more susceptible to the chemical property-dependent removal mechanisms. Inflow (F) was reduced to $2 \cdot 10^5 \text{ L} \cdot \text{day}^{-1}$ and outflow (F_{out}) to $5 \cdot 10^4 \text{ L} \cdot \text{day}^{-1}$ balanced with the natural losses of water as described in Equation 1. This water budget was parameterized in the model to help better illustrate the roles of K_{OW} and K_{OA} on transpiration flux, volatilization flux, and removal efficiency.

Model parameterization was completed for a list of chemicals with supplemental data on chemical properties (U.S. EPA, 2012b). Using a separate Microsoft VBA macro to perform calculations in the model, each chemical was introduced individually to calculate the steady state removal efficiency. The objective was to complement the chemical universe illustration with chemicals from *Appendix B: Toxic Release Inventory (TRI)* tabulated in U.S. EPA (2012b) in order to show practical examples of treatment capacities. This is a valuable example of some industrial effluents containing toxic chemicals requiring treatment before discharge into the environment or wastewater

treatment facility. In this list were the chemical properties $\log K_{OW}$, K_{OC} , S , and H . Like the chemical universe simulation, all other required physicochemical properties were estimated from these parameters, or fixed at a recommended value.

5. Results and Discussion

5.1 Selected Chemicals - Pyrene, Arsenic, and a Naphthenic Acid

Table 5-1: FWS wetland model summary of steady state results for pyrene, arsenic, and a naphthenic acid.

| <i>Measurement</i> | <i>Units</i> | <i>Pyrene</i> | <i>Arsenic</i> | <i>Naphthenic Acid</i> |
|---|---------------------------------------|---------------|-----------------------|------------------------|
| Removal Efficiency (Wetland I only; WI) | [†] % Removed | 41.9 | 83.2 | 31.3 |
| Removal Efficiency (Wetlands in series; WI + WII) | [†] % Removed | 73.8 | 98.3 | 61.4 |
| Loss to Atmosphere | [‡] % of removed contaminant | 16.8 | 0.00 | 4.7 |
| Transformation | [‡] % of removed contaminant | 19.8 | 70.6 | 26.6 |
| Pseudo loss – vegetation biomass increase | [‡] % of removed contaminant | 5.3 | 12.6 | <0.01 |
| Vegetated Rooting Medium | g·kg ⁻¹ | 1.15 | 0.366 | 1.7·10 ⁻⁴ |
| Water | mg·L ⁻¹ | 0.843 | 0.241 | 0.982 |
| Submerged Vegetation | g·kg ⁻¹ | 1.90 | 4.17·10 ⁻³ | 2.1·10 ⁻⁴ |
| Emergent Vegetation | g·kg ⁻¹ | 0.054 | 2.79 | 1.4·10 ⁻⁵ |
| Vegetated Rooting Medium | * (%) | 99.0 | 99.5 | 15.0 |
| Water | * (%) | 0.07 | 0.06 | 84.9 |
| Submerged Vegetation | * (%) | 0.88 | <0.01 | 0.1 |
| Emergent Vegetation | * (%) | 0.04 | 6.41 | 0.01 |
| Total Capacity of the Wetland | kg | 11,500 | 3,930 | 11.6 |
| t _{1/2} | days | 0.71 | 0.10 | 0.002 |
| t ₉₅ | days | 3.1 | 0.42 | 0.01 |

[†]Represents the percentage of the contaminant removed through the wetland, i.e. (influx – outflux)/influx.

[‡]Represents the relative contribution of each process to the overall removal of the contaminant through the wetland, e.g. (evapotranspiration flux)/(influx – outflux).

* Represents the distribution of total mass of the contaminant present in the wetland at steady state, in each compartment.

t_{1/2} – estimated overall half-life of contaminant in evaluative engineered wetland (Equation 9).

t₉₅ – estimated overall time estimated to reach 95% of steady state in evaluative engineered wetland (Equation 10).

The results of the chemical illustrations in the FWS model are summarized in Table 5-1. The contribution of each mechanism of contaminant removal and distribution of mass throughout the FWS wetland media are discussed in the following section. Results of the HSSF and VSSF models for pyrene, arsenic, and a naphthenic acid are provided in Appendix C.2 and D.2, respectively. For all three illustrative contaminants, removal efficiency is greatest in the FWS design. This is due to the larger footprint of the design, and therefore a greater volume of each compartment, but also because more compartments are involved in the FWS design, i.e. water compartment. Therefore, some mass-fraction of the contaminant can exist in that phase where it may be

susceptible to the transformation and removal processes active in that compartment. Specifically, evaporation is only modeled for the interface between water and air which is not present in the SSF designs. In the SSF designs, there is no separate water compartment because influent is introduced directly into the rooting medium. These models identify the vegetative rooting medium as the bulk phase consisting of sediment, pore water (influent), and rhizome.

Pyrene

Figure 5-1 illustrates the application of the model to pyrene. Pyrene enters a free water surface flow wetland at a concentration of $1 \text{ mg}\cdot\text{L}^{-1}$ and a contaminant loading of $2000 \text{ g}\cdot\text{day}^{-1}$. The majority (i.e. 58.1%) of the pyrene entering the wetland also leaves the wetland in the wetland's effluent at a rate of $116 \text{ g}\cdot\text{day}^{-1}$. The steady state removal efficiency is therefore 41.9% for pyrene. The chemical loss from the emergent vegetation to air ($290 \text{ g}\cdot\text{day}^{-1}$) and volatilization ($45.4 \text{ g}\cdot\text{day}^{-1}$) contribute a combined 16.8% removal. The total transformation flux ($634 \text{ g}\cdot\text{day}^{-1}$) from all compartments represents 19.8% removal efficiency of pyrene from the wetland. Pseudo loss due to vegetation biomass increase in submerged ($181 \text{ g}\cdot\text{day}^{-1}$) and emergent ($89.6 \text{ g}\cdot\text{day}^{-1}$) vegetation represents 5.3% removal efficiency. The removal efficiency and removal fluxes of pyrene for each removal mechanism within the wetland are summarized in Figure 5-2 and Figure 5-3, respectively. If two FWS wetlands are joined in series, then the combined removal efficiency of pyrene nearly doubles from 41.9% in wetland I (WI only) to 73.8% in the combined wetlands (WI + WII). While approximately one-third of the pyrene from the wastewater stream in each wetland is removed, the concentration of pyrene in water is reduced by only 17% in wetland I and by 35% in the two wetlands combined. The difference between the reduction of mass and concentration is due to losses of water from the wetland through processes described in Equation 1. This water budget (represented in the model by parameters F and F_{OUT}) concentrates the chemical in the surface water resulting in an elevated concentration. This competes with the decrease of contaminant concentration due to evapotranspiration, biotransformation, and vegetation biomass increase.

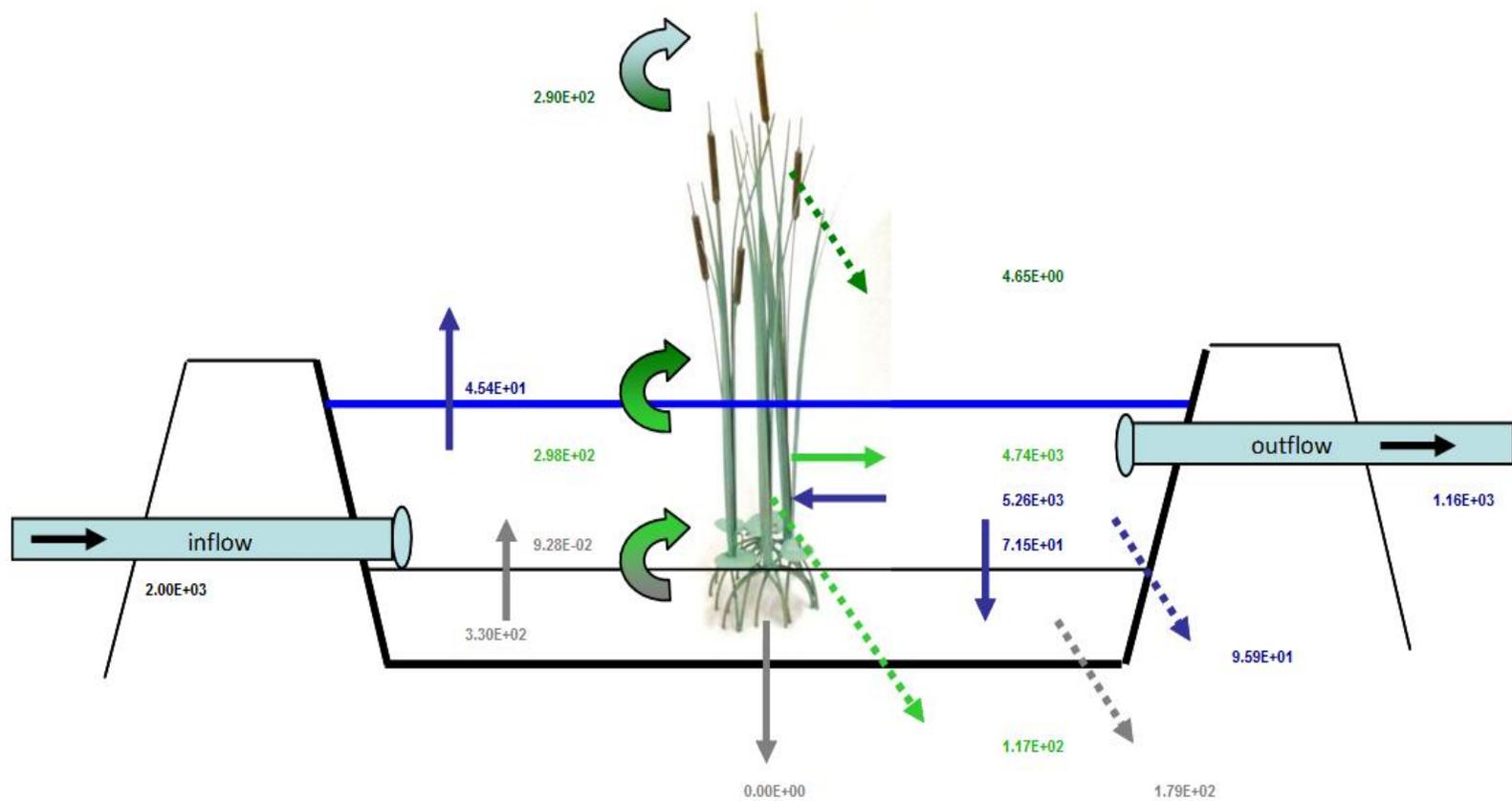


Figure 5-1: Mass flux diagram for pyrene in the FWS flow wetland receiving a chemical influx of $2 \cdot 10^3 \text{ g} \cdot \text{day}^{-1}$. Solid arrows represent transport processes between wetland media. Dashed arrows represent transformation processes. Vegetation growth dilution is not shown. All values in $\text{g} \cdot \text{day}^{-1}$.

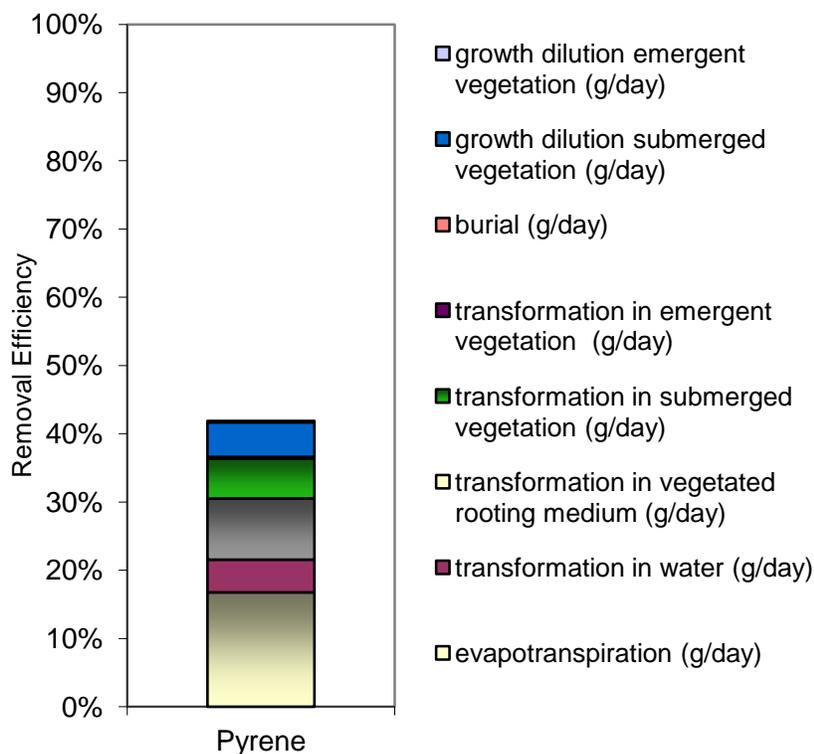


Figure 5-2: Steady state removal efficiency breakdown by removal mechanism for pyrene.

The temporal simulations provided in Appendix B.2 show that while the steady state removal efficiency of the wetland for pyrene is 41.9%, the initial removal efficiency is essentially 100%. This is because the environmental compartments are initially at their greatest capacity to absorb the contaminant. The removal efficiency begins to decrease and stabilize after contaminant loading has begun. As the wetland media reaches their total capacity to contain the contaminant, the system approaches steady state. Each compartment has a different capacity to absorb a chemical based on the physicochemical properties of the substance. Each of the compartments of the wetland responds with unique mechanisms of removal and intermedia transport that determines the temporal profile of the concentration of pyrene in the compartment. The majority of the pyrene mass in the wetland, i.e. 99% of pyrene mass at steady state, will be in the vegetated rooting medium. The remainder of the pyrene mass will be in the submerged and emergent vegetation (0.88% and 0.04% at steady state, respectively) and in the water (0.07%) of the wetland. The total capacity of the wetland to absorb pyrene is approximately 11.5 metric tonnes at the selected initial concentration of $1 \text{ mg}\cdot\text{L}^{-1}$. With the significant majority of the pyrene mass in the vegetated rooting medium relative to the other compartments, the temporal response is predominantly influenced by the

mechanisms associated with this compartment: intermedia transport (solids resuspension, sediment-to-water diffusion, rhizome vegetation to submerged vegetation), and transformation (microbial degradation).

The chemical removal mass fluxes are summarized in Figure 5-3. To show that the model is mass balanced, the inflow flux must equal the sum of the removal fluxes (i.e. total outflux). The greatest flux is shown to be the outflow flux, which represents the contaminant transport through the wetland system that has not been subject to any removal mechanisms. This outflow flux of $1.16 \text{ kg}\cdot\text{day}^{-1}$ is a function of the hydraulic retention time of the wetland, and the inflow concentration. Evapotranspiration flux includes volatilization and transpiration removal flux, and together make up a total removal flux of $335 \text{ g}\cdot\text{day}^{-1}$ for pyrene. Transformation of pyrene is greatest in the vegetated rooting medium and nearly negligible in the emergent vegetation compartment. Therefore, the model indicates that rooting media is the most important compartment to maintain for the removal of pyrene from wastewater. The total transformation flux, in all compartments combined was $397 \text{ g}\cdot\text{day}^{-1}$. Growth dilution was also nearly negligible for the emergent vegetation compartment (0.20% of total flux), but the submerged vegetation contributed more significantly to overall growth dilution flux (5.07% of total flux). The total growth dilution flux is $105 \text{ kg}\cdot\text{day}^{-1}$ for both vegetation compartments combined.

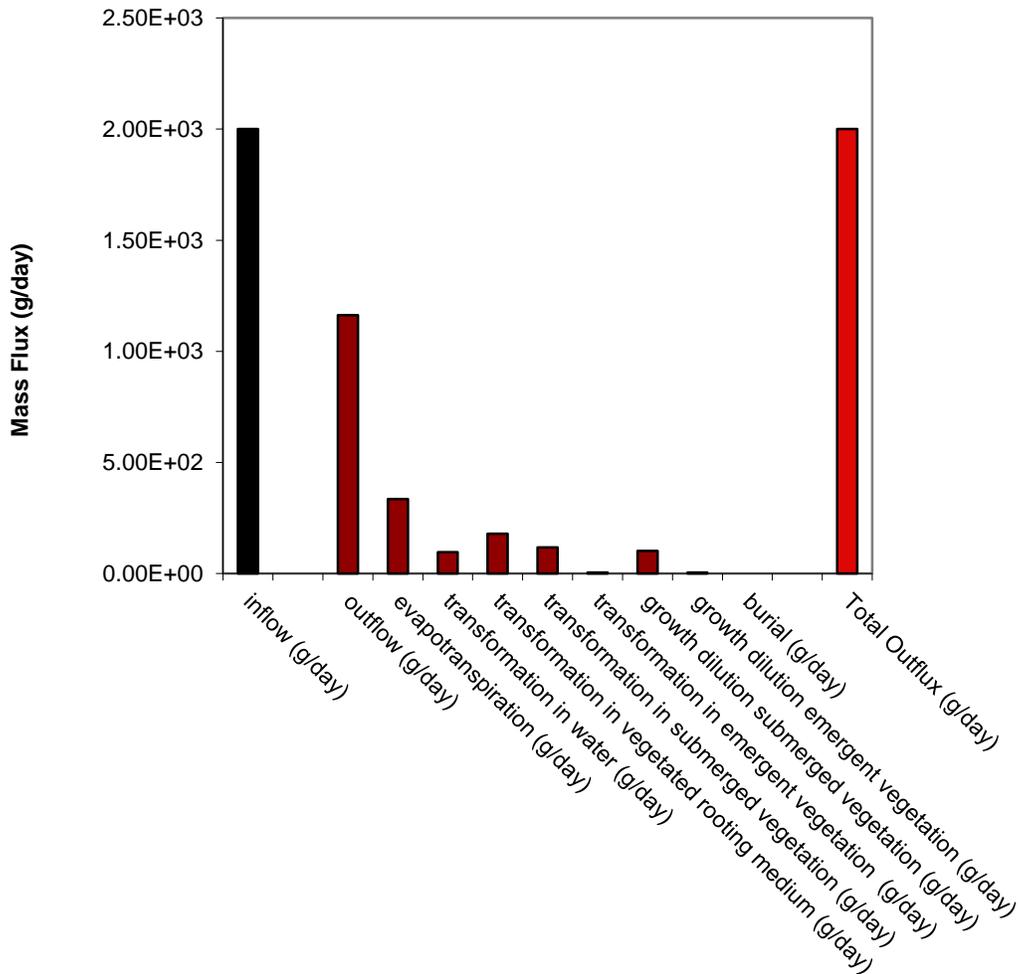


Figure 5-3: Steady state mass flux distribution among removal mechanisms of pyrene.

Throughout the operation of the wetland, the concentrations of pyrene in bulk wetland media will climb to levels of $0.83 \text{ mg}\cdot\text{L}^{-1}$ in water, $1.13 \text{ g}\cdot\text{kg}^{-1}_{\text{dw}}$ in the vegetated rooting medium and concentrations of 0.05 and $1.9 \text{ g}\cdot\text{kg}^{-1}$ in emergent and submerged vegetation, respectively. The aqueous solubility of pyrene is $0.23 \text{ mg}\cdot\text{L}^{-1}$ at 25°C (U.S. EPA, 2013b). The predicted concentration in the water exceeds the solubility of pyrene in water. This suggests that at the given inflow rate, pure contaminant phase may form in the wetland. With the proposed model, the formation of the pure contaminant phase is not accounted for, but since the specific gravity of pyrene is approximately 1.271 (Van Mouwerik et al., 1997), the pure contaminant phase will sink to the bottom of the water compartment. The creation of a new compartment of pure pyrene may affect many functions of the FWS wetland. If present between the water and rooting medium compartments, it may eliminate the water-rooting medium interface and affects

intermedia transport. Furthermore, there may be significant concerns for environmental toxicity to wetland biota, particularly microbial organisms in the rooting medium, which may affect each process of removal in the wetland system.

According to these results, there is a relatively large difference between the concentration in emergent and submerged fractions of the wetland vegetation. This may be a product of limiting the rate of xylem flow (Q_w , L·day⁻¹) through the vegetation. The submerged parts of the plant exhibit uptake through plant rhizome and diffusive influx at the water-plant interface. These transport processes each contribute to the accumulation of pyrene in this compartment. Emergent vegetation receives contaminant mass from the submerged vegetation, but because xylem flow is limited to a value of 2.4 L·day⁻¹, there is little pyrene moving into the emergent vegetation. Also, since the emergent vegetation is subject to loss of contaminant via transpiration the accumulation of pyrene cannot reach the levels observed in the submerged vegetation. In other words, pyrene as a semi-volatile transpires faster from emergent vegetation than xylem transport can introduce pyrene from submerged vegetation, and therefore accumulation is not expected to occur based on this parameterization.

The concentration of pyrene in water can be compared to the EC₅ or LC₅ to assess whether concentrations can be expected to be of concern for the ecological efficiency of wetland biota. An LC₅ for pyrene in fish of 0.2 mg·L⁻¹ was estimated from a 24-hr acute LC₅₀ for rainbow trout (*Oncorhynchus mykiss*) of 2 mg·L⁻¹ reported by Kennedy (1990). The predicted concentration from the model of 0.83 mg·L⁻¹ in water exceeds this estimated LC₅ value, and therefore the wetland biota is considered potentially at risk of toxicity. Based on a study of the toxicity of sediment-associated pyrene in the amphipod *Diporeia* spp. by Landrum et al. (1994), the LC₅ for pyrene in sediments was estimated to be 127 mg·kg⁻¹_{dw}. The model predicts that pyrene concentration in the rooting medium will exceed the estimated LC₅ before the wetland will reach steady state conditions. At an estimated EC₅ of 7.26 mg·kg⁻¹_{dw} sediment for luminescence inhibition on *Vibrio fischeri*, possible adverse effects may result from pyrene exposure on the microorganisms in the wetland sediment. *Vibrio fischeri* is a bacterium predominantly found in symbiosis with marine animals (Urbanczyk et al., 2007). The predicted concentration in the rooting media is 1,130 mg·kg⁻¹_{dw} sediment, which is also significantly higher than the EC₅₀ from Romero-Freire et al. (2014) of 72.6 mg·kg⁻¹_{dw} sediment. The food web sub-model simulation output indicates that pyrene does not biomagnify in the

aquatic species of the food web (Appendix B.2). The BAFs determined with this sub-model indicate that the upper trophic organisms will accumulate a lower concentration of pyrene than lower trophic organisms. This is a product of the parameterization of the food web. The largest BAF is observed in the benthic invertebrates at $2.86 \cdot 10^3$ (concentration in biota/total concentration in water).

Arsenic

Figure 5-4 illustrates the application of the model to arsenic. At an inflow concentration of $1 \text{ mg} \cdot \text{L}^{-1}$, the model predicts arsenic will be removed at an efficiency of 83.2%. A total of $337 \text{ g} \cdot \text{day}^{-1}$ (16.8%) of arsenic exits the wetland system through the out-flowing water. Evapotranspiration mechanisms do not contribute to the overall removal flux of arsenic from the wastewater since volatilization and transpiration flux is negligible for arsenic. Transformation losses from water, rooting medium, submerged, and emergent vegetation combined, remove 70.6% of the arsenic from the wetland at steady state ($141 \text{ g} \cdot \text{day}^{-1}$). Pseudo loss due to increase in vegetation biomass for submerged ($0.23 \text{ g} \cdot \text{day}^{-1}$) and emergent ($252 \text{ g} \cdot \text{day}^{-1}$) vegetation represents 12.6% removal efficiency (Table 5-1). Removal efficiency and mass flux are broken down for each removal mechanism in Figure 5-5 and Figure 5-6, respectively. In a combined wetlands scenario with two FWS wetlands in series, the removal efficiency for arsenic increases to 98.3%.

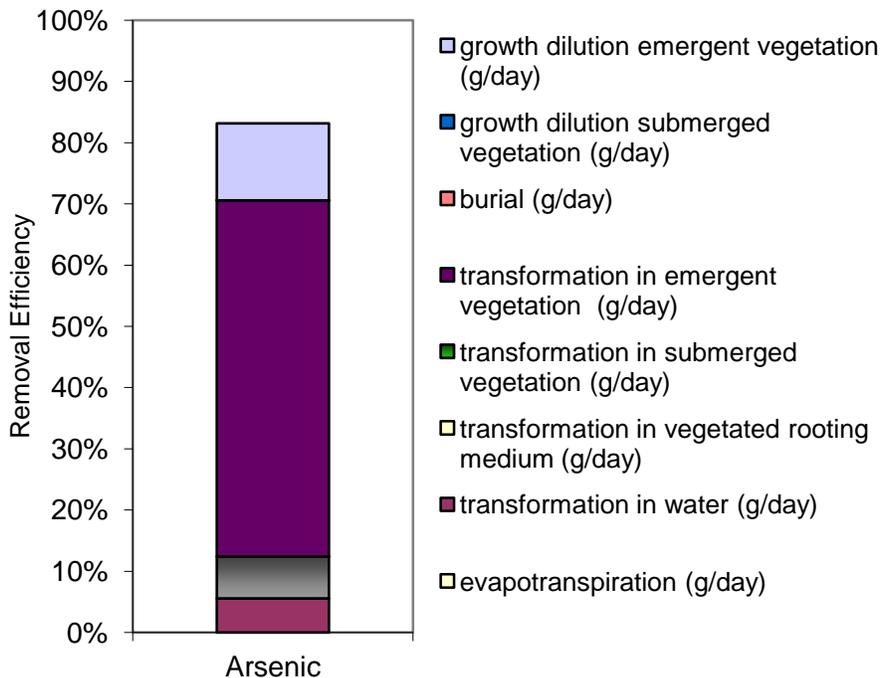


Figure 5-4: Steady state removal efficiency breakdown by removal mechanism for arsenic.

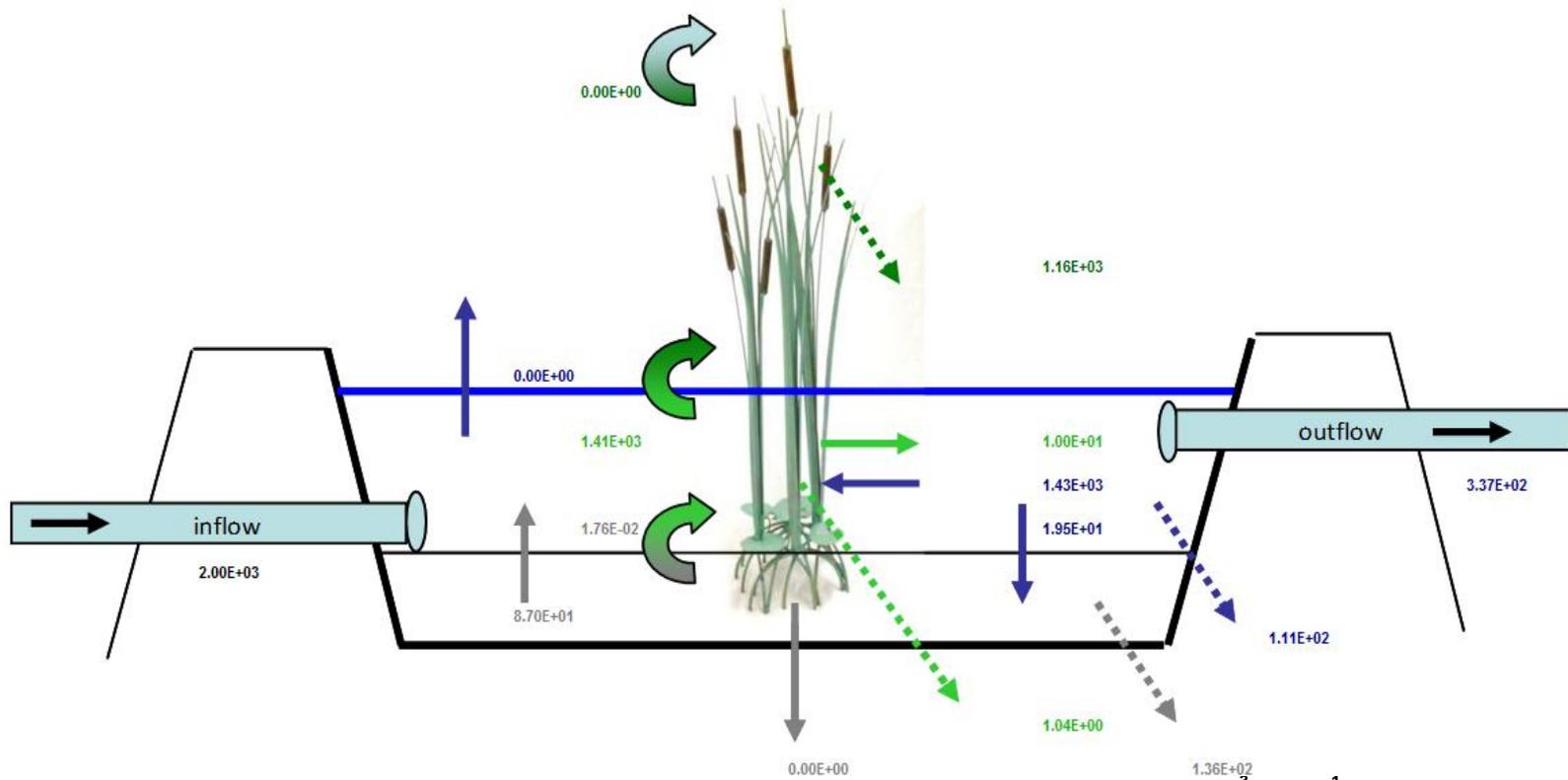


Figure 5-5: Mass flux diagram for arsenic in the FWS flow wetland receiving a chemical influx of $2 \cdot 10^3 \text{ g} \cdot \text{day}^{-1}$. Solid arrows represent transport processes between wetland media. Dashed arrows represent transformation processes. Vegetation growth dilution is not shown. All values in $\text{g} \cdot \text{day}^{-1}$.

Arsenic concentration in the water stream effluent was $0.24 \text{ mg}\cdot\text{L}^{-1}$ from wetland I, and $0.044 \text{ mg}\cdot\text{L}^{-1}$ from the two wetlands combined. The removal efficiency for arsenic changes very little during the lifetime of the wetland. Removal of arsenic from the wetland is limited to fewer removal processes than that for pyrene and a naphthenic acid because evapotranspiration does not occur. The result is a dominant removal by transformation processes that causes steady state to be reached quickly with the wetland system.

The majority of the arsenic mass is in the vegetated rooting medium (93.5%), with the remainder being in the emergent vegetation (6.4%), and negligible amounts in water and submerged vegetation (<0.1%). The total capacity of the wetland to absorb arsenic is approximately 3.93 metric tonnes at an inflow concentration of $1 \text{ mg}\cdot\text{L}^{-1}$. Relatively little arsenic persists in the wetland compartments because of the efficient biological and chemical transformation to organo-metallic species in the water, vegetated rooting medium, submerged vegetation, and emergent vegetation (i.e. $t_{50, \text{water}} = 15$ days).

The steady state mass fluxes of arsenic in the wetland are described in Figure 5-6. For arsenic, the greatest flux is shown to be from the transformation processes in emergent vegetation with a value of $1,160 \text{ g}\cdot\text{day}^{-1}$. The outflow flux of $337 \text{ g}\cdot\text{day}^{-1}$ is relatively small compared to this flux value, which can be observed by the ability of the wetland system to remove arsenic from influent wastewater based on this simulation. Evapotranspiration is negligible, but the transformation and growth dilution flux sum up a total removal flux of $1,410 \text{ g}\cdot\text{day}^{-1}$ and $252 \text{ g}\cdot\text{day}^{-1}$, respectively.

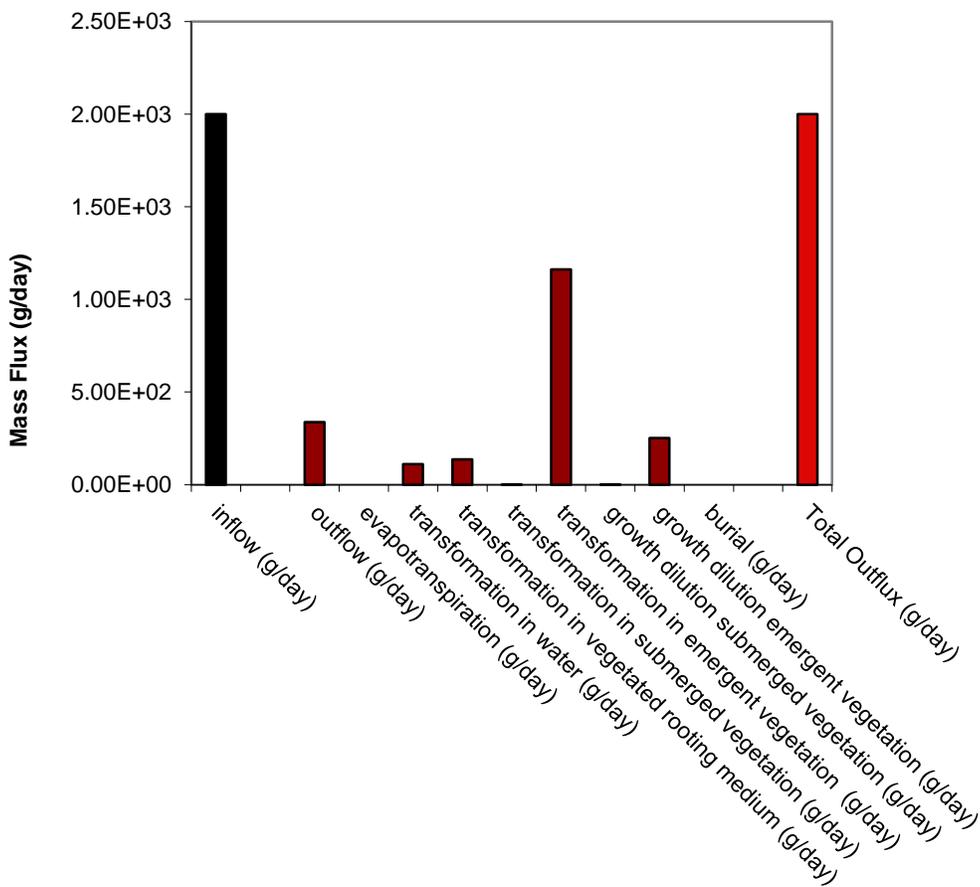


Figure 5-6: Steady state mass flux distribution among removal mechanism of arsenic.

Concentrations of arsenic at steady state are $0.24 \text{ mg}\cdot\text{L}^{-1}$ in water, $366 \text{ mg}\cdot\text{kg}^{-1}$ in vegetated rooting medium and concentrations of $2,790 \text{ mg}\cdot\text{kg}^{-1}$ and $4.17 \text{ mg}\cdot\text{kg}^{-1}$ in emergent and submerged vegetation, respectively. The emergent fraction contains a significant portion of the mass of arsenic and a high concentration delivered by xylem flow. Since there is no transpiration of arsenic from plant to air, or reverse flow back into the submerged vegetation, arsenic accumulates. These estimates agree with the results from studies involving phytoremediation of heavy metals (Berken et al., 2002; Bhatia and Goyal, 2014; Farid et al., 2014). Heavy metals, including arsenic, often accumulate in the vegetation. They can be effectively removed from the environment by harvesting the plant population, and replacing with virgin plants.

Given a 10-d LC_{50} whole-sediment measurement for arsenic of $532 \text{ mg}\cdot\text{kg}^{-1}_{\text{dw}}$ sediment for *Hyalella azteca*, extensive mortality of this invertebrate population is not likely to be observed at an inflow concentration of $1 \text{ mg}\cdot\text{L}^{-1}$ (Liber et al., 2011). The estimated LC_5 ($53.2 \text{ mg}\cdot\text{kg}^{-1}_{\text{dw}}$ sediment) for *Hyalella azteca* is below the estimated sediment concentration, and therefore productivity is expected to be impacted. Dyer et al. (1993)

performed aquatic toxicity testing on fathead minnows using sodium arsenite (NaAsO₂), a more soluble vehicle for arsenic in an aquatic environment. The estimated LC₅ from this study was 0.99 mg·L⁻¹ which suggests effects may not be significant to exposed fish via the water. Benthos and fish species will accumulate arsenic from the surrounding sediment and surface water, respectively. The greatest concentration is expected in benthic invertebrates at 5.6 g·kg⁻¹_{ww} since they were exposed to the rooting medium which contains a relatively high concentration arsenic.

Naphthenic Acid

Figure 5-7 illustrates the application of the FWS model to a naphthenic acid (SMILES: CCC1CCC(C1)CCC(=O)O). At an inflow concentration of 1 mg·L⁻¹, the steady state removal efficiency of the wetland is 31.3%. The majority of the naphthenic acid (68.7%) entering the wetland passes through untreated within the water column at a flux of 1,370 g·day⁻¹. Loss to the atmosphere via volatilization flux (28.4 g·day⁻¹) and transpiration flux (65.3 g·day⁻¹) represent 4.7% removal of the naphthenic acid. The total transformation flux from all compartments (532 g·day⁻¹) represents 26.6% steady state removal from the wetland. Transformation is only observed in the water and rooting medium because of the high aqueous solubility of the naphthenic acid. Pseudo loss through biomass increase of the vegetation compartments represents less than 0.01% naphthenic acid removal (Table 5-1).

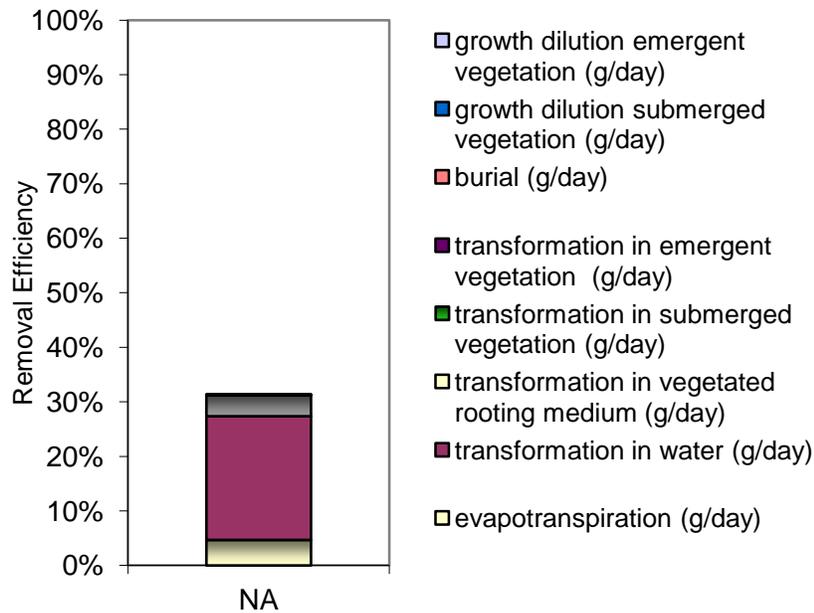


Figure 5-7: Steady state removal efficiency breakdown by removal mechanism of a naphthenic acid.

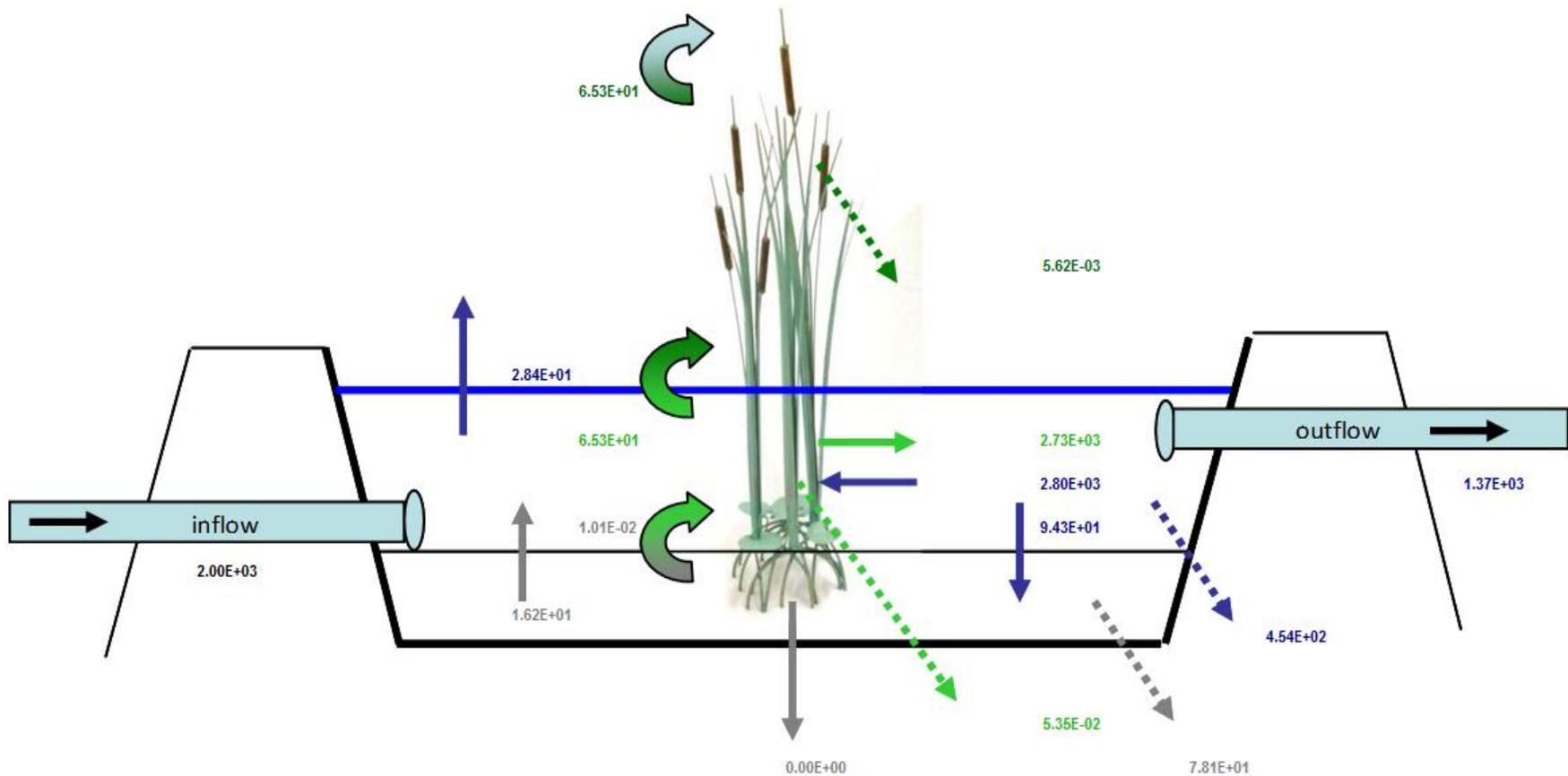


Figure 5-8: Mass flux diagram for a naphthenic acid in the FWS flow wetland receiving a chemical influx of $2 \cdot 10^3 \text{ g-day}^{-1}$. Solid arrows represent transport processes between wetland media. Dashed arrows represent transformation processes. Vegetation growth dilution is not shown. All values in g-day^{-1} .

Removal efficiency and mass flux of the naphthenic acid are broken down for each removal mechanism in Figure 5-8 and Figure 5-9, respectively. In a wetland series design of two FWS configurations, the removal efficiency of the combined wetlands increases to 61.4%. During the initial phase of operation of the wetland, removal efficiency is effectively 100% in wetland I, but rapidly decreases as the capacity of the wetland is reached. This capacity is significantly reduced because of the high aqueous solubility of the naphthenic acids ($S = 94 \text{ mg}\cdot\text{L}^{-1}$ according to EPISuite v.4.11: WSKOWWIN; U.S. EPA, 2013a).

The concentration of the naphthenic acid is reduced by only 2%, to $0.98 \text{ mg}\cdot\text{L}^{-1}$, and in the combined wetlands is reduced by only 3.6%, to $0.964 \text{ mg}\cdot\text{L}^{-1}$. Based on these results, remediating naphthenic acids from wastewater may be a challenge if evaporation rates are high for water. The removal of water via evaporation causes the naphthenic acid to concentrate in the wetland surface water, and effectively increases the concentration of the naphthenic acid. For an ionic organic such as a naphthenic acid, having high water solubility permits the chemical to favourably remain in aqueous form. The majority of the naphthenic acid mass is in the water column (84.9%) and the volatilization of the naphthenic acid is insufficient in competing with the predicted water evaporation. The remaining mass of the naphthenic acid is found in the rooting medium (15.0%, $C_{\text{RM}} = 0.17 \text{ mg}\cdot\text{kg}^{-1}$), submerged vegetation (0.1%, $C_{\text{SV}} = 0.21 \text{ mg}\cdot\text{kg}^{-1}$), and emergent vegetation (0.01%, $C_{\text{EV}} = 0.014 \text{ mg}\cdot\text{kg}^{-1}$).

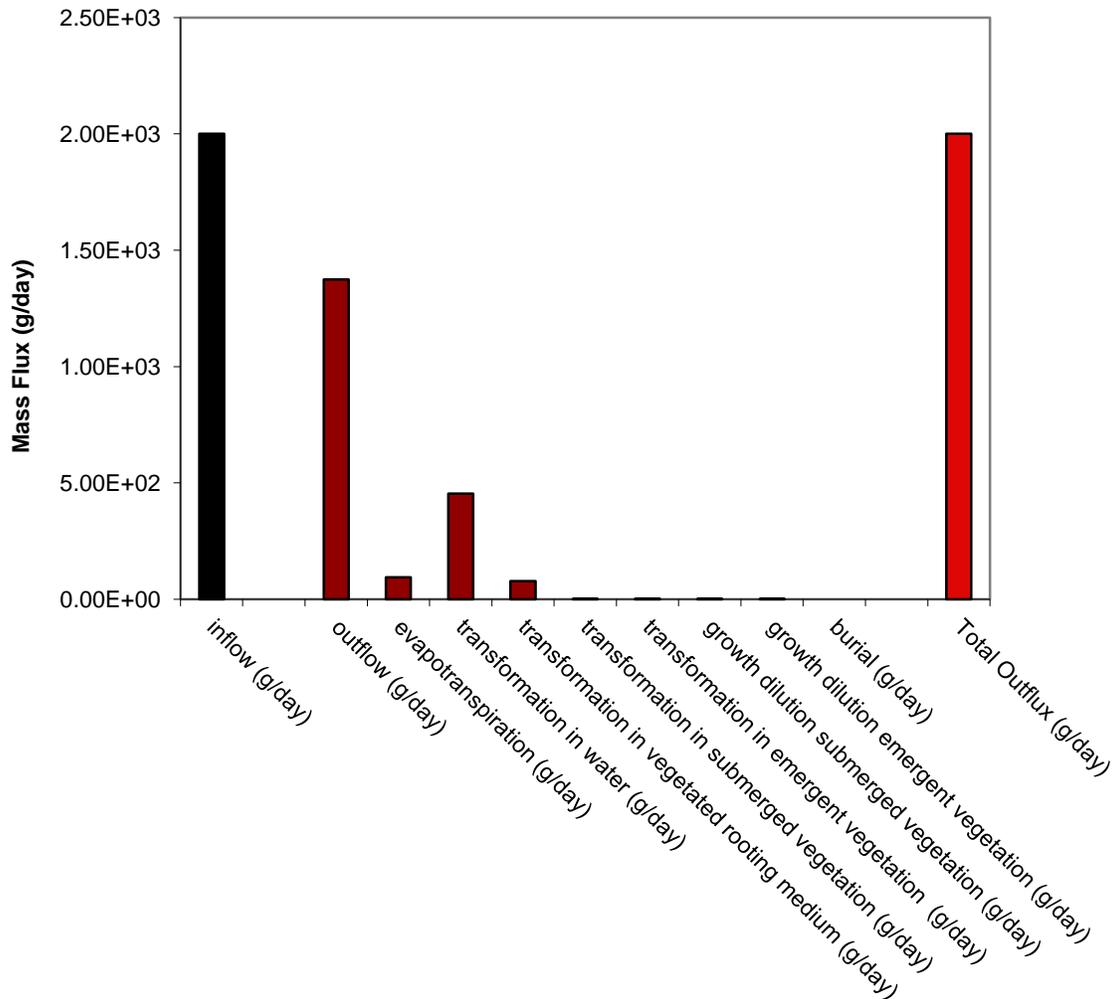


Figure 5-9: Steady state mass flux distribution among removal mechanism of a naphthenic acid.

In this model illustration with naphthenic acid, the minor reduction in actual concentration suggests this engineered wetland design may not be a feasible solution for remediating naphthenic acids. Similar findings have been reported by Quagraine et al. (2005) describing the high solubility of many naphthenic acids in the high pH wastewater influent associated with oil sands processed wastewater. The result is a large fraction of these contaminants dissolving in the free water compartment that do not partition into adjacent media. Without this movement through different media, these contaminants experience a limited pathway of removal, and remediation via wetland mechanisms is difficult. Since this natural attenuation in the wetland system does not produce satisfying treatment efficiency, engineering applications may need to be implemented in practice. To improve the bioremediation of these compounds, applying mechanisms of bio-

stimulation or bio-augmentation may improve the wetland capacity to remediate naphthenic acids (Quagraine et al., 2005).

A toxicity evaluation for the naphthenic acid illustration was not performed since available toxicity endpoint data is inadequate. Bauer (2013) estimated an LC₅₀ for *Daphnia magna* of 61-78 mg·L⁻¹ using an array of naphthenic acids from oil sands processed wastewater. Since the inflow concentration used in this simulation is only 1 mg·L⁻¹, even the steady state concentration in water will not create a potential for toxicity in these aquatic invertebrates. The naphthenic acid used as the illustrative compound in the model is described as a generic naphthenic acid defined by a SMILES configuration. In order to identify an appropriate toxicity threshold for this chemical, a more specific carboxylated alkane would be necessary. However, according to Lai et al. (1996), Siwik et al. (2000) and Colavecchia et al. (2004), naphthenic acids are a significant cause of the toxicity related to oil sands processed wastewater but choosing just one naphthenic acid is not representative of toxicity. The food-web bioaccumulation sub-model estimates BAF of approximately one, for all species of the food web. This indicates the naphthenic acid does not bioaccumulate.

5.2 “Chemical Universe” – Log K_{OW} vs. Log K_{OA}

Table 5-2 illustrates the predicted removal efficiency within the chemical universe simulation for the FWS flow wetland model. As indicated from these results, the model is sensitive to changes in K_{OW} (octanol-water partition coefficient) and K_{OA} (octanol-air partition coefficient). Some substances are more susceptible to the mechanisms of evapotranspiration and growth dilution in the wetlands than others are. The results illustrated in Table 5-2 represent the overall percent removal (E) by these mechanisms (i.e. $\frac{\text{influx} - \text{outflux}}{\text{influx}}$).

The results of the chemical universe simulation suggest that chemicals with moderate to moderately high log K_{OW} (~2 – 7) and low to moderate log K_{OA} (~-4.5 – 2) are most effectively removed from wastewater (dark red region in Table 5-2; E ≈ 97%), based on the parameterization of the model. These ranges of K_{OW} and K_{OA} promote movement of the chemical from the water and vegetation to the air phase based on the correlation with high K_{AW} (air-water partition coefficient) and moderately low K_{veg-air} (vegetation-air partition coefficient). The lowest removal efficiency is found for chemicals with the lowest K_{OW} and highest K_{OA} region (dark green region in Table 5-2; E ≈ 7%).

Table 5-2: Removal efficiencies (E) for different log K_{OW} and log K_{OA} in the FWS model.

| | | Log K_{OW} | | | | | | | | |
|--------------|-------|--------------|--------|--------|--------|--------|--------|--------|--------|--------|
| | | -0.5 | 0.5 | 1.5 | 2.5 | 3.5 | 4.5 | 5.5 | 6.5 | 7.5 |
| Log K_{OA} | -4.5 | 96.01% | 96.11% | 96.52% | 96.86% | 96.92% | 96.93% | 97.08% | 96.55% | 80.89% |
| | -3.5 | 96.01% | 96.11% | 96.52% | 96.86% | 96.92% | 96.93% | 97.08% | 96.55% | 80.89% |
| | -2.5 | 95.98% | 96.10% | 96.52% | 96.86% | 96.92% | 96.93% | 97.08% | 96.55% | 80.89% |
| | -1.5 | 95.65% | 96.07% | 96.52% | 96.86% | 96.92% | 96.93% | 97.08% | 96.55% | 80.89% |
| | -0.5 | 92.51% | 95.76% | 96.50% | 96.86% | 96.92% | 96.93% | 97.08% | 96.55% | 80.89% |
| | 0.5 | 70.13% | 92.84% | 96.25% | 96.84% | 96.92% | 96.93% | 97.08% | 96.55% | 80.89% |
| | 1.5 | 24.43% | 74.74% | 94.13% | 96.64% | 96.90% | 96.93% | 97.08% | 96.55% | 80.89% |
| | 2.5 | 9.08% | 48.31% | 85.81% | 95.03% | 96.71% | 96.91% | 97.08% | 96.55% | 80.89% |
| | 3.5 | 7.17% | 41.57% | 80.09% | 90.14% | 95.19% | 96.73% | 97.06% | 96.55% | 80.89% |
| | 4.5 | 6.98% | 40.78% | 79.17% | 87.69% | 90.77% | 95.30% | 96.94% | 96.55% | 80.89% |
| | 5.5 | 6.96% | 40.71% | 79.07% | 87.34% | 88.66% | 91.46% | 96.14% | 96.50% | 80.87% |
| | 6.5 | 6.96% | 40.70% | 79.06% | 87.30% | 88.37% | 89.76% | 94.67% | 96.24% | 80.69% |
| | 7.5 | 6.96% | 40.70% | 79.06% | 87.30% | 88.34% | 89.53% | 94.23% | 95.94% | 79.72% |
| 8.5 | 6.96% | 40.70% | 79.06% | 87.30% | 88.34% | 89.50% | 94.18% | 95.87% | 78.61% | |
| 9.5 | 6.96% | 40.70% | 79.06% | 87.30% | 88.34% | 89.50% | 94.17% | 95.86% | 78.37% | |
| 10.5 | 6.96% | 40.70% | 79.06% | 87.30% | 88.34% | 89.50% | 94.17% | 95.86% | 78.34% | |
| 11.5 | 6.96% | 40.70% | 79.06% | 87.30% | 88.34% | 89.50% | 94.17% | 95.86% | 78.34% | |

The values of these physicochemical properties inhibit the escaping tendency of the chemical from the influent wastewater via evapotranspiration. At this low K_{OW} range, the model is more sensitive to changes in K_{OA} than to changes in K_{OW} . There is a rapid improvement in removal efficiency through each incremental increase in log K_{OW} from -0.5 to 1.5. The larger the K_{OW} of the chemical, the less sensitive the removal efficiency is to changes in K_{OA} . For instance, at a fixed log K_{OW} of -0.5, the removal efficiency changes by ~90% within the full range of K_{OA} . At a fixed log K_{OW} of 7.5, the removal efficiency fluctuates by ~2% within the full range of K_{OA} . The further the deviation from log K_{OW} ~ 6.5, the more significant K_{OA} is on removal efficiency. This relationship between K_{OW} , K_{OA} , and removal efficiency appears to illustrate the roles of each physicochemical property on the general behaviour of the chemical in the wetland. K_{OW} is used in calculating the intermedia transport of the chemical between water, rooting medium, and vegetation, whereas K_{OA} is used in calculating the removal mechanisms into air. For instance, K_{OC} (organic carbon-water partition coefficient), K_{PW} (suspended solids-water partition coefficient), K_{PS} (rooting medium solids-water partition coefficient), K_{DOM} (dissolved organic matter-water partition coefficient), $K_{VEG-WATER}$ (vegetation-water partition coefficient), and K_{OCVEG} (vegetation organic carbon-water partition coefficient) are each proportional to K_{OW} (see Appendix A for parameter explanations). As K_{OW} decreases, the chemical develops a preference for the water phase. This limits the degree to which evapotranspiration processes may act on the chemical. Volatilization is

minimized since the chemical does not significantly partition out of the water column. Similarly, only a relatively small fraction of the chemical partitions into the submerged vegetation (i.e. $K_{\text{VEG-WATER}}$) for transport into emergent vegetation, and therefore very little will undergo transpiration. The results of the removal efficiency distribution provided in Table 5-2 and Appendix B.3 show the preferred balance between K_{OW} and K_{OA} .

In a wetland system where the microbial transformation is insignificant, volatilization and transpiration (collectively referred to as evapotranspiration) are the only mechanism responsible for the removal of mass from the system. Pseudo loss through growth dilution of the vegetation also contributes to overall removal efficiency, but does not remove the contaminant. This process is responsible for diluting the mass and reducing the overall concentration in the submerged and emergent vegetation. Hence, chemicals preferring the water-phase to air, plant, or rooting medium will be subject to a limited number of removal mechanisms.

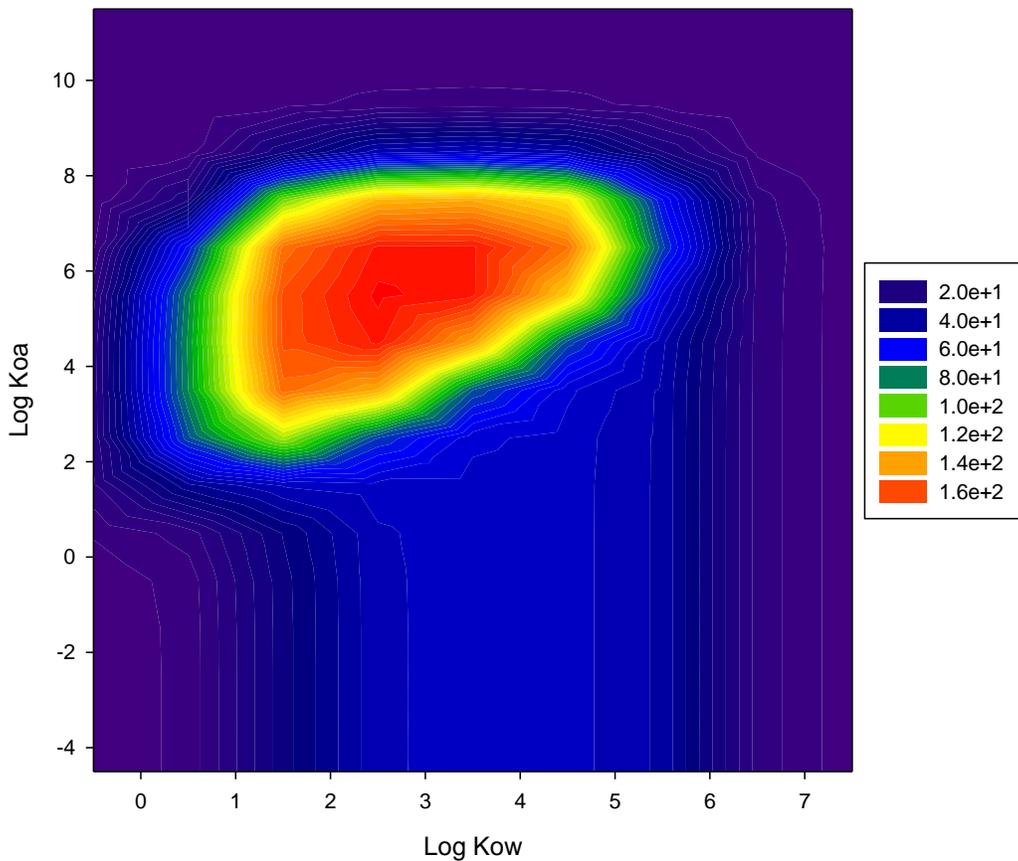


Figure 5-10: Removal flux ($\text{g}\cdot\text{day}^{-1}$) via transpiration (EV – Air) in a FWS wetland receiving a chemical influx of $2\cdot 10^2 \text{ g}\cdot\text{day}^{-1}$.

The chemical removal in the chemical universe illustration is mostly controlled by the removal mechanisms: (i) volatilization from water to atmosphere, and (ii) transpiration from emergent vegetation to atmosphere. Figures 5-10 and 5-11 demonstrate the distribution of these fluxes for chemicals of various $\log K_{OW}$ and $\log K_{OA}$, but illustrate somewhat competing preferences on chemical removal. Emergent vegetation to air flux is optimal for chemicals with a $\log K_{OW}$ from ~ 2 to 3 and a $\log K_{OA}$ from ~ 4.5 to 6.5, providing a total mass flux $\leq 170 \text{ g}\cdot\text{day}^{-1}$ (Figure 5-10). The vegetation-air partitioning coefficient ($K_{\text{veg-air}}$) is estimated for organics using K_{OA} (octanol-air partition coefficient). Similar to K_{AW} (air-water partition coefficient), lowering K_{OA} reduces the $K_{\text{veg-air}}$ which translates to a greater transfer of the contaminant to the air phase. This relationship between $K_{\text{veg-air}}$, K_{OA} and mass flux is limited by the rate of xylem transport through the plant ($Q_W = 2.4 \text{ L}\cdot\text{day}^{-1}$). When Q_W is increased, the transpiration mass flux will increase because a greater mass of the contaminant is transported into the emergent parts of the plant. This increase in Q_W in the model can allow significant transpiration, even if the contaminant has a low K_{AW} (i.e. relatively low air-solubility). Where optimal transpiration is observed (dark orange in Figure 5-10), the model shows a balance between the fraction that is sorbed into the plant and transported within xylem (controlled by K_{OW} of the chemical universe), and the amount that reaches the emergent vegetation – air interface for transpiration (controlled by K_{OA} of the chemical universe). In the model, the VOCOW (Vegetation Organic Carbon to Octanol-Water equivalency factor) remains constant, and is used to convert K_{OW} into $K_{OC\text{veg}}$ (organic carbon to water partitioning coefficient). Therefore, $K_{OC\text{veg}}$ is directly proportional to K_{OW} so that the contaminant with relatively high K_{OW} corresponds to a relatively high $K_{OC\text{veg}}$. At the relatively high values of $K_{OC\text{veg}}$ and K_{OW} , the contaminant binds strongly to the organic carbon content in the vegetation and is not efficiently mobile within the vegetation, and hence relatively little transpiration will occur. When K_{OW} (and $K_{OC\text{veg}}$) is too low, the contaminant remains largely dissolved into the water-phase and the $K_{\text{veg-water}}$ partitioning coefficient is proportionally small. This results in low diffusion into the submerged vegetation and uptake from rooting medium.

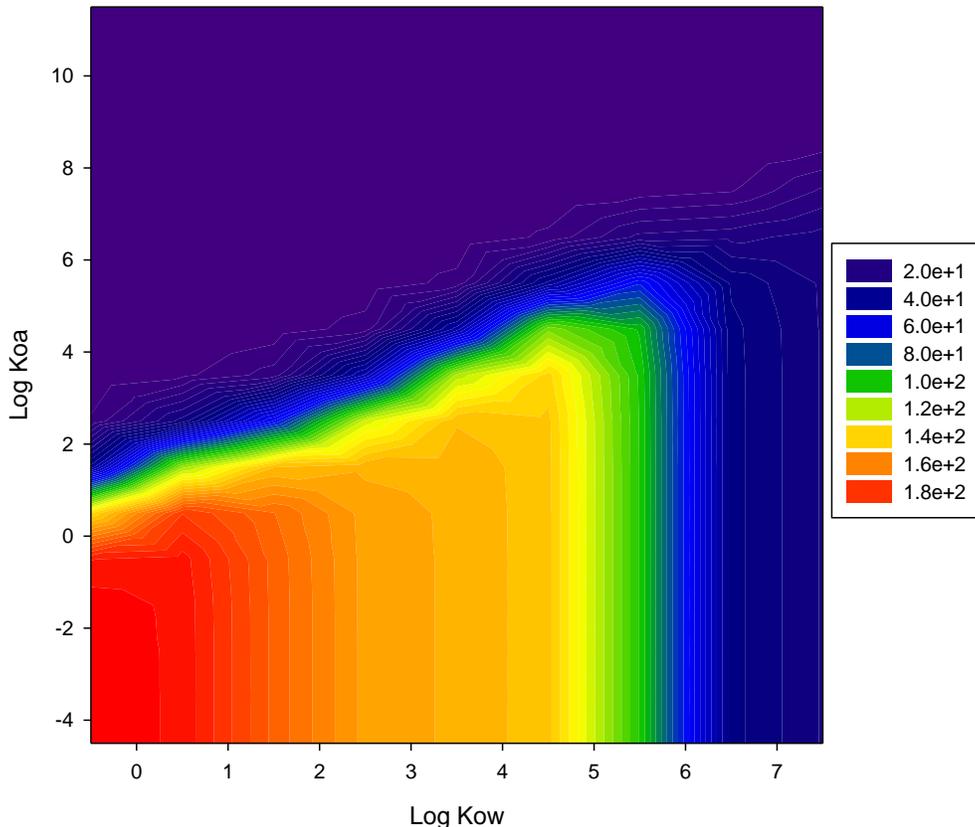


Figure 5-11: Removal flux ($\text{g}\cdot\text{day}^{-1}$) via volatilization in a FWS wetland receiving a chemical influx of $2\cdot 10^2 \text{ g}\cdot\text{day}^{-1}$.

Volatilization is a product of the fraction of freely dissolved chemical in water, and the overall volatilization mass transfer coefficient (mass transfer estimated from K_{AW} and the evaporation two-film theory mass transfer coefficients). Therefore, the optimal volatilization occurs at the lowest K_{OA} values. This is shown in Figure 5-11 (dark orange) by the maximum volatilization flux of $191 \text{ g}\cdot\text{day}^{-1}$ occurring at $\log K_{OA}$ between -4.5 and 1.5, and $\log K_{OW}$ of -0.5. Like transpiration, K_{OW} is a variable that also predicts intermedia transport by influencing partitioning coefficients between rooting medium, vegetation, and water. Increasing K_{OW} results in a greater movement of contaminant out of the water phase and into rooting medium and vegetation. Therefore, there is a smaller amount of freely dissolved chemical in the water, and volatilization is reduced.

The overall removal efficiency represents the ratio of chemical influx (as prescribed by the user) to the sum of mass removal fluxes (as calculated by the model). Although the maximum values for transpiration and volatilization are each observed at minimally overlapping regions within the chemical universe, the greatest removal efficiency is found where the sum of all removal mechanisms is greatest. Evidently, it is no indication

of the overall treatment to look exclusively at one process (volatilization or transpiration). At optimal K_{OW} and K_{OA} for both volatilization and transpiration, the mass removal fluxes are quantitatively similar at steady state. The processes that determine these fluxes are aligned with K_{OW} and K_{OA} both directly and indirectly in the calculations for removal fluxes and intermedia transport.

When mapping the change in flux for the active processes, it was found that growth dilution in both submerged and emergent parts of the plant vary within the chemical universe. The values associated to these growth dilution fluxes do not represent actual loss of mass, but may be significant factors to consider for various contaminants such as heavy metals, since these mechanisms directly affect the accumulated mass within the vegetation. Submerged vegetation, which contains mechanisms of diffusion between vegetation and water, are very sensitive to K_{OW} (octanol-water partition coefficient) because this is the underlying partitioning coefficient defining this process. The controlling parameter is the vegetation-water partition coefficient (i.e. $K_{veg-water}$) which translates to a greater affinity for the organic carbon in the vegetation over the water-phase. As K_{OW} increases, the pseudo-loss via growth dilution increases. Emergent vegetation is dependent on K_{OA} to determine the $K_{veg-air}$ partitioning coefficient which defines the chemical behaviour between plant tissue and air. High K_{OA} values indicate a chemical favours the organic carbon content in the plant tissue over the air phase resulting in a reduced transpiration removal flux. However, as the chemical accumulates in the vegetation, growth will play a more significant role in dilution. For those contaminants such as arsenic where evapotranspiration processes do not occur, but affinity for organic carbon is relatively high, harvesting the vegetation once steady state is reached and introducing virgin vegetation may help to continue the process of chemical removal.

The transformation processes in the model are driven by half-life constants defined by the user which calculate a rate constant. Transformation flux is estimated as the product of the accumulated chemical mass in each compartment and this fixed rate constant. Therefore, the magnitudes of these transformation fluxes are dependent on the total mass accumulated in each compartment. As K_{OW} (and therefore K_{OCveg}) decreases and K_{OA} (and therefore $K_{veg-air}$) increases there is a greater mass of contaminant available for transformation. Growth dilution in the submerged and emergent vegetation reacts to

variations in K_{OW} and K_{OA} in the same manner as transformation because both of these mechanisms are dependent on the accumulated mass available.

5.3 EPA Toxic Release Inventory Chemicals

The list of chemicals provided by U.S. EPA (2012b) is a summary of contaminants from the Toxic Release Inventory (TRI). This illustration is similar to the chemical universe calculations but uses actual chemicals reported by industry, to the U.S. EPA in 2012. Removal efficiencies were reported for the 544 substances with respective $\log K_{OW}$ (octanol-water partition coefficient), K_{OC} (organic carbon-water partition coefficient), S (solubility in water), and H (Henry's Law constant) values (Appendix B.4). The removal efficiency of each chemical from the FWS flow wetland model was estimated for all chemicals listed, but only select chemicals are discussed here. The full simulation results are included in Appendix B.4.

The TRI simulation data from the FWS model suggests that the engineered wetland may effectively remove a wide-range of chemicals from wastewater. The chemicals which are the least removed are those with the lowest K_{OW} and H , which are highly soluble in water, and that do not partition out of the water phase into adjacent compartments. The high solubility in water limits intermedia transfer from water and thereby reduces the number of different removal mechanisms that may act on the chemical available in the wetland system. Even when K_{OW} values are low, having relatively higher H values indicates the chemical is more likely to be removed through the mechanisms which H dictates (i.e. volatilization and transpiration from emergent vegetation). Such chemicals from the TRI include chlorine dioxide ($\log K_{OW} = -3.22$, $H = 2.5 \text{ kPa}\cdot\text{m}^3\cdot\text{mole}^{-1}$), and carbonyl sulfide ($\log K_{OW} = -1.33$, $H = 61.8 \text{ kPa}\cdot\text{m}^3\cdot\text{mole}^{-1}$) experience removal efficiencies >92%.

The efficient treatment of those chemicals with only moderate K_{OW} and H values may be due to a favourable K_{OC} . In this chemical list, K_{OC} is not estimated from K_{OW} , but is empirically derived for the chemical and included in the data within the TRI list. SOCOW (sediment organic carbon to octanol-water equivalency factor) and VOCOW (vegetation organic carbon to octanol-water equivalency factor) is the ratio of K_{OC} to K_{OW} , and is supplied to the input parameters of the model. For this illustration, SOCOW and VOCOW were assumed equivalent, since no data is available to relate the affinity for vegetation organic carbon compared to sediment organic carbon. Therefore, SOCOW and VOCOW increase with K_{OC} , which correlates to greater $K_{veg-air}$ (vegetation-air

partition coefficient), $K_{\text{veg-water}}$ (vegetation-water partition coefficient), K_{OCveg} (vegetation organic carbon-water partition coefficient), and K_{PS} (rooting medium to water). The result is an increased movement of contaminant into the vegetation or rooting medium phase from the water phase. This facilitates processes of transformation, growth dilution, and some moderate evapotranspiration depending on the value of H . For example, 1,1,2-trichloroethane ($\log K_{\text{OW}} = 1.89$, $H = 48.5 \text{ Pa}\cdot\text{m}^3\cdot\text{mole}^{-1}$ ($\log K_{\text{AW}} = -1.71$, $K_{\text{OC}} = 83.5 \text{ L}\cdot\text{kg}^{-1}$), and potassium dimethyldithiocarbamate ($\log K_{\text{OW}} = 1.67$, $H = 69.3 \text{ Pa}\cdot\text{m}^3\cdot\text{mole}^{-1}$, $K_{\text{OC}} = 57 \text{ L}\cdot\text{kg}^{-1}$) have a removal efficiency greater than 83% due the contributions from these physicochemical properties.

K_{OC} and K_{OW} are significant parameters in defining the partitioning coefficients between the organic carbon content in rooting medium and vegetation. H relates to K_{AW} and is the dominant parameter in defining the evapotranspiration mechanisms in the model. Together these parameters contribute to mechanisms of contaminant fate and correlate to total removal efficiency. Therefore, the most efficiently removed chemicals are those that have at least one physicochemical property (K_{OW} , H , or K_{OC}) that will force the movement of the chemical out of the wastewater, as long as the other properties do not significantly inhibit this mobility. Therefore, an appropriate balance between these properties is favourable for efficient removal from wastewater in an engineered wetland, according to the model simulations.

By examining similar compounds simulated from the U.S. EPA (2012b) chemical TRI list such as BTEX, pentafluoropropane, or 2-chloro-1,1,1-trifluoroethane, we observe removal efficiencies above 90%. Semi-volatile compounds such as nitrobenzene or bis(2-chloroethyl)ether are expected to exhibit a removal efficiency of 83% and 74%, respectively. The range of values observed from the FWS model simulations agree with the measured values reported by Keefe et al. (2004), Tuu et al. (2014) and Knight et al. (1999). No SSF simulations were run for these chemicals and therefore the wetland designs, and likely the treatment capacity, are different. No direct comparison of the results from these studies to the output of the model is feasible since it would require a full parameterization of the model to represent the site-specific variables in each study.

Bhatia and Goyal (2014) review wetland plants in remediation applications for a variety of industrial wastewater streams. Many include a heavy metal composition that was observed to accumulate through *Phragmites* spp. uptake mechanisms ($\text{Al} > \text{Pb} > \text{Cd} > \text{Co} > \text{Ni} > \text{Cr}$). In a series of constructed SSF wetlands in Navan, Ireland, mine effluent

containing Zn and Pb experienced variable removal in wetland I, but effective removal (94% - 99% for Zn, and 25% - 60% for Pb) for the combined three-wetland series. Based on the results of these studies on inorganics for remediation in constructed wetland systems, it appears that the developed model may be under-predicting the respective removal efficiency of type II contaminants. However, the parameterization of this model will have to better reflect these test sites for a more appropriate comparison, particularly for metals and SSF designs which have not been exhaustively applied in this research.

5.4 Limitations

Foremost, the lack of calibration or testing with empirical data means that the accuracy of finite values is unclear. With the lack of data to conduct this model performance analysis, it is premature to treat the concentrations calculated by the model in the wetland media and the effluent as estimates of real world contaminant concentrations. Improving the estimates would require field-tested parameterization, and additional contributing mechanisms or correction factors that can account for their absence. In general, the models may only be as useful as an evaluative tool at this stage. However, with future efforts in model parameterization and performance analysis, the model may become more useful as a predictive tool for assessing the remediation capacity of contaminants using various engineered wetland designs.

The most limiting factor of this model design thus far has been with regards to the evapotranspiration parameterization (i.e. mass transfer coefficients of the two-film model). The illustrations have been kept consistent with evaporation MTCs of 1.2 and 12 $\text{m}\cdot\text{day}^{-1}$ for water- and air-side, respectively. These values align with the default MTCs for air-water partitioning found in the TaPL3 model developed by Beyer et al. (2000). However, relevant MTCs for transpiration from emergent vegetation to air could not be found. As an approximation, the same MTCs of evaporation were used for transpiration in order to roughly align the overall mass transfer through evapotranspiration with the values reported by Stannard et al. (2013). This resulted in elevated evapotranspiration rates which greatly affected the chemical universe and TRI list illustrations. These parameters have a strong influence on the predicted removal efficiency of chemicals from wetlands. These mechanisms must be calibrated in order to provide realistic model outcomes.

In its current state, the model calculations do not account for the effects of changing climatic conditions, and its effect on temperature dependent model variables. Instead, the conditions of our model require a fixed temperature and the respective parameters must be appropriately defined. Simply changing the temperature value of the model will not adjust the dependent parameters. Similarly, a full water budget including precipitation, runoff, snowmelt, and infiltration is not available for parameterization, and the influent wastewater is the only input of water. This would help differentiate site-specific simulations from these models and expand its territory of use. Currently, the model does not support the dependencies of vaporization and vegetative growth on seasonally or diurnally variable temperature, and observed average annual estimates have been applied as parameter approximations. Biotransformation rates in wetland vegetation are largely unavailable, and therefore estimating the respective submerged and emergent half-lives was simplified by applying an order of magnitude increase from reported water half-life time of each chemical. The model also does not contain the capacity to limit chemical concentrations to the solubility limit, above which would be considered to form pure chemical solute if not capable of intermedia transport.

Although the model encompasses a general approach to estimate the fate of all species of chemicals, not all factors can be explicitly defined. Section 1.6.5 – *Nutrient cycles*, describes the cycling of nutrients and the roles of vegetation in these complex biogeochemical processes. Since phloem tubule flow is not identified within the model, we have not included a method to describe nutrient flow within the wetland system. This mechanism of nutrient fate is not considered in our calculations, but it is understood to play a significant role in the biogeochemistry, and hence treatment capacity in wetlands. Likewise, due to the nature of speciation of inorganic compounds, the food web bioaccumulation sub-model cannot be used to evaluate bioaccumulation of these substances. Instead, the user is required to define distribution coefficients for the partitioning mechanisms at each media interface (water-air, plant-water, fish-water, etc.). Additionally, certain organic chemicals like many PAHs are subject to photodegradation according to Fasnacht et al. (2002). Both abiotic and biotic removal mechanism are not explicitly noted in the model parameterization, but are meant to be included into the transformation half-life value provided by the user.

6. Recommendations

Further work begins with the mass transfer coefficients of the two-film theory processes describing removal of the contaminant into the atmosphere (evaporation and transpiration). Since these values are generally unknown, they require further scientific investigation, especially with how they relate to physicochemical properties and plant species. This revision will tune the model to better represent the flux from rooting medium through emergent parts of the plant into the atmosphere. Particularly, the SSF designs are significantly limited by the rate of transport through xylem flow (controlled by parameter Q_w , L·day⁻¹).

Implementing some additional functions that consider more specific contaminant behaviour into the model may help to improve contaminant fate predictions. This may involve considering photodegradation of PAHs in the photic zone of the water column (Fasnacht et al., 2002), and environmental conditions (i.e. climate) as they relate to the growth, seasonal senescence, and sequestration rate from vegetation (Acreman et al., 1999; Apfelbaum, 1985; Asaeda and Karunaratne, 2000; Burba et al., 1999; Zhou and Zhou, 2009). Further development should implement a site-specific water budget if additional sources include precipitation and runoff into the wetland. Integrating and enhancing these processes in the model will improve the overall design and implementation of engineered wetlands.

The bulk of future work on the model involves testing each sub-model with empirical data followed by calibration of the entire model. The objective is to maintain its generality and be able to function accurately with a variety of contaminant and environmental properties. Using pilot studies, the limits of application for these models can be illustrated and it can begin to be used for an industrial tool for engineered wetland design and feasibility. The calibrated and tested version of this model may facilitate an investigation of the engineering components of the engineered wetlands. Applying and testing different engineering designs to improve removal efficiency for specific contaminants of concern would be a useful area of investigation. This complexity will involve an extended series of scientific inquiry from a community of invested scientists and institutions, but could become an extremely valuable endeavour. In general, the models could include the engineering aspects in the mechanisms of fate rather than just in the wetland hydrology. The intention for modeling engineered wetlands has been to influence their feasibility of remediation of oil sands processed wastewater.

7. Conclusions

This study has developed and applied a multimedia environmental fate model for a free water surface (FWS) engineered wetland design. The estimates of chemical fate within the engineered wetland is coupled with a food web bioaccumulation sub-model modified from the Arnot and Gobas (2004), and an ecological risk assessment sub-model to identify hazardous concentrations to biota.

The FWS model estimated environmental fate and transport of pyrene, arsenic, and a naphthenic acid in wastewater under parameterized conditions. A multi-dimensional chemical universe was also designed with $\log K_{OW}$ (octanol-water partition coefficient) and $\log K_{OA}$ (octanol-air partition coefficient), and a chemical array of industrial contaminants was evaluated in the FWS design. In the chemical illustration with pyrene, arsenic, and a naphthenic acid, the removal efficiencies were estimated at 41%, 83%, and 31%. Some of these estimates harmonize with available constructed wetland literature that reports removal efficiencies for specific compounds or criteria (i.e. BOD₅, COD) (Bhatia and Goyal, 2014; Keefe et al., 2004; Knight et al., 1999; Tu et al., 2014). The temporal simulations indicate that the rooting medium requires the greatest length of time to reach a steady state because it has the greatest capacity to absorb the illustrative contaminants. It can be observed that even though the concentrations are not always greatest in this compartment, there is a large total mass of contaminant available at steady state because pyrene and arsenic favour the organic carbon content present in the rooting medium. The naphthenic acid simulation shows how this group of contaminants are relatively difficult to remediate with this design and parameterization. This is because of the tendency of these chemicals to remain in aqueous form which limits its exposure to important removal mechanisms.

The chemical universe application suggests the most appropriate chemicals for the FWS design have physicochemical properties with a moderately high K_{OW} , and low K_{OA} . The removal efficiency is much more influenced by K_{OW} than K_{OA} , but together these parameters define the air-water partition coefficient (K_{AW}) which drives the evapotranspiration flux mechanisms. This high dependency on K_{OW} optimizes removal efficiency at a log-value of 6.5. At the extreme corners of the chemical universe, particularly when coupled by a low K_{OW} value, there is little movement of contaminant out of the water, and the outflow of contaminant is relatively unchanged unless biotic or abiotic transformation is enabled. Since these mechanisms are not dependent on the

physicochemical properties of a contaminant, they were reduced to negligible proportions. The only mechanisms acting on the transport and transformation of the inflowing contaminant were those which were directly or indirectly dependent on K_{OW} and K_{OA} . The illustration looking at a chemical list summarized from the Toxic Release Inventory provided in U.S. EPA (2012b) performs a similar simulation to the chemical universe evaluation, but with relevant industrial effluents. The results of each simulation are complementary as K_{OW} is responsible for influencing the removal efficiency much more than K_{OA} or H (Henry's Law constant). The predictions from the models are highly dependent on the balance of physicochemical properties introduced into the model for each chemical of the chemical illustrations (pyrene, arsenic, and a naphthenic acid), chemical universe (K_{OW} and K_{OA}), and U.S. EPA list (TRI).

8. References

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9. Appendices

Appendix A. Calculated Model Parameters

Appendix B. Free Water Surface Flow Wetland Model Output Data

Appendix B.1: Parameterization of the FWS flow wetland model

Appendix B.2: Output data from the FWS model contaminant illustrations

Appendix B.3: Output data from the FWS model chemical universe illustration

*Appendix B.4: Output data from the FWS model U.S. EPA TRI list evaluation
(refer to Appendix E)*

Appendix C. Horizontal Subsurface Flow Wetland Model Output Data

Appendix C.1: Parameterization of the HSSF wetland model

Appendix C.2: Output data from the HSSF model contaminant illustrations

Appendix D. Vertical Subsurface Flow Wetland Model Output Data

Appendix D.1: Parameterization of the VSSF wetland model

Appendix D.2: Output data from the VSSF model contaminant illustrations

Appendix E. Data File Index

Appendix A. Calculated Model Parameters

For a list of input parameter values, refer to parameterization sections in Appendix B-1 (FWS), C-1 (HSSF), and D-1 (VSSF).

Table A-1: Calculated fate and transport parameters.

| Symbol | Pathway | Mechanism |
|---------------|---|--|
| k_o | Outflow | The fraction of untreated contaminant discharged in the wetland effluent. |
| k_v | Volatilization | Removal from water to atmosphere via volatilization of contaminants. Calculated from physicochemical properties. |
| k_{ws} | Overall water-to-sediment transport | Contaminant transport from water to sediment. Represented by solids settling rate for contaminant fraction sorbed to suspended sediment and diffusion from water to rooting media. |
| k_{sw} | Overall sediment-to-water transport | Contaminant transport from sediment to water. Represented by resuspension and diffusion from sediment. |
| k_B | Burial | Mechanism of removal where contaminated sediment is buried and considered no longer bioavailable. Also referred to as soil accretion. |
| k_{rsv} | Rhizome vegetation to submerged vegetation | Transport through roots of vegetation from rhizosphere to stalk via xylem tubules. |
| k_{wsv} | Water-to-submerged vegetation diffusion | Diffusion into submerged stalk of vegetation from water column. |
| k_{svw} | Submerged vegetation to water diffusion | Diffusion into water column from submerged stalk of vegetation. |
| k_{svev} | Submerged vegetation to emergent vegetation transport | Transport in FWS designs from submerged fraction to emergent fraction of vegetation. |
| k_{rvev} | Rhizome vegetation fraction to emergent vegetation | Transport in SSF designs directly from rhizomes to emergent fraction of vegetation. |
| k_{evair} | Emergent vegetation to air transport | Transportation and removal of contaminant by transpiration mechanisms from vegetation to atmosphere. |
| k_{wr} | Transformation in water | Biotic and abiotic transformation in water |
| k_{sr} | Transformation in vegetated rooting medium | Biotic and abiotic transformation in rooting media |
| k_{svr} | Transformation in submerged vegetation | Biotic and abiotic transformation in submerged fraction of vegetation |
| k_{evr} | Transformation in emergent vegetation | Biotic and abiotic transformation in emergent fraction of vegetation |
| k_{gsv} | Growth factor in submerged vegetation | Rate of growth of submerged vegetation as a dilution factor for. |
| k_{gev} | Growth factor in emergent vegetation | Rate of growth of emergent vegetation as a dilution factor for contaminants. |
| k_M | Metabolism in aquatic biota | Rate of metabolism in aquatic food-web organisms. |

Table A-2: Engineered wetland model algorithms – parameters, symbols, and equations.

| Parameter | Symbol | Statement |
|---|---------------------|--|
| Calculated Parameters | | |
| Octanol-water partition coefficient (unitless) | K_{ow} | =IF(Organic="y", $10^{\log K_{ow}}$,"na") |
| organic carbon-water partition coefficient (L/Kg) | K_{oc} | =IF(Organic="y",SOCOW* K_{ow} ,"na") |
| Air-Water Distribution Coefficient (L/L) | K_{aw} | =IF(Organic="y", $H/(8.314*(273+T_w))$,DAirWater) |
| Suspended Solids Water Distribution Coefficient (L/kg dw) | K_{pw} | =IF(Organic="y", O_{cpw} *SOCOW* K_{ow} ,DSusSolidsWater) |
| Rooting medium Solids-water partition coefficient (L/kg dw) | K_{ps} | =IF(Organic="y", O_{css} *SOCOW* K_{ow} ,DRootingSolidsWater) |
| Dissolved Organic Matter Water Partition Coefficient | K_{dom} | =IF(Organic="y",adoc* K_{ow} ,"na") |
| vegetation to air partition coefficient(L/kg) | K_{vegair} | =IF(Organic="y",VOCOW* O_{cv} * $10^{\log K_{oa}}$, (IF(DAirWater="na","na", $K_{veqwater}/K_{aw}$))) |
| vegetation-water partition coefficient (L/kg) | $K_{vegwater}$ | =IF(Organic="y",(O_{cv} *VOCOW* K_{ow}), $D_{vegwater}$) |
| plant organic carbon-water partition coefficient | K_{ocveg} | =IF(Organic="y",VOCOW* K_{ow} ,"na") |
| Vegetation-Air Distribution Coefficient (L/kg ww) | D_{vegair} | = K_{vegair} |
| log transformed rooting medium organic carbon-water partition coefficient | $\log K_{oc}$ | =IF(Organic="y",LOG(K_{oc}),"na") |
| log Air-Water Distribution Coefficient (L/L) | $\log K_{aw}$ | =IF(K_{aw} ="na","na",LOG(K_{aw})) |
| log Suspended Solids Water Distribution Coefficient (L/kg dw) | $\log K_{pw}$ | =LOG(K_{pw}) |
| log Rooting medium Solids-water partition coefficient (L/kg dw) | $\log K_{ps}$ | =LOG(K_{ps}) |
| log Dissolved Organic Matter Water Partition Coefficient | $\log K_{dom}$ | =IF(K_{dom} ="na","na",LOG(K_{dom})) |
| log transformed vegetation to air partition coefficient | $\log K_{va}$ | =IF(K_{vegair} ="na","na",LOG(K_{vegair})) |
| log vegetation-water partition coefficient | $\log K_{vegwater}$ | =LOG($K_{vegwater}$) |
| log plant organic carbon-water partition coefficient | $\log K_{ocveg}$ | =IF(K_{ocveg} ="na","na",LOG(K_{ocveg})) |
| log Koa of the contaminant (unitless) | $\log K_{oa}$ | =IF(K_{ow} ="na","na", $\log K_{ow}$ -LOG(K_{aw})) |
| total external loading (g/day) | L | = $F * C_{in}$ |
| water out-flow (L/day) | F_{out} | = $F - (\text{NumberOfPlants} * S_{as} * Q_w)$ |
| solids settling rate (kg/day) | v_{ss} | = $C_{pw} * v_{solidsinwater} * S_{aw} * 1000$ |
| sediment burial rate (kg/day) | v_b | = $C_{ss} * v_{accretion} * S_{as} * 1000$ |
| solids resuspension rate (kg/day) | v_{rs} | = $v_{ss} - v_b$ |
| volatilization mass transfer coefficient (m/day) | v_e | =IF(K_{aw} ="na", $0, 1/((1/v_{ew})+1/(K_{aw} * v_{ea}))$) |
| temperature dependence of Henry law constant (H) | $\ln HT_w$ | =LN(H)+20.18-6013.6/(273+ T_w) |
| fraction of freely dissolved contaminant in water (unitless) | f_{DW} | =IF(Organic="y", $1/(1+(C_{pw} * K_{pw})+(C_{doc} * adoc * K_{ow}))$, $1/(1+(C_{pw} * K_{pw}))$) |

| | | |
|--|----------------|--|
| fraction of particle bound contaminant in water (unitless) | f_{PW} | $=IF(K_{dom}="na", (K_{ps} * C_{pw}) / (1 + (K_{ps} * C_{pw}) + (K_{ps} * C_{pw}) / (1 + (K_{ps} * C_{pw}) + (K_{dom} * C_{doc}))))$ |
| fraction of DOC bound contaminant in water (unitless) | f_{DOCW} | $=IF(K_{dom}="na", 0, (K_{dom} * C_{doc}) / (1 + (K_{ps} * C_{pw}) + (K_{dom} * C_{doc})))$ |
| fraction of (freely dissolved) contaminant in water of vegetated rooting medium (unitless) | f_{DS} | $=(V_{sw}/V_s) / ((V_{sw}/V_s) + (K_{ps} * d_{ss} * V_{sss} / V_s) + (K_{vegwater} * V_{rv} / V_s))$ |
| fraction in solids of vegetated rooting medium | f_{SS} | $=(K_{ps} * d_{ss} * (V_{sss}/V_s)) / ((V_{sw}/V_s) + (K_{ps} * d_{ss} * V_{sss}/V_s) + (K_{vegwater} * V_{rv}/V_s))$ |
| fraction in vegetation of vegetated rooting medium | f_{VS} | $=(K_{vegwater} * dv) * (V_{rv}/V_s) / ((V_{sw}/V_s) + (K_{ps} * d_{ss} * V_{sss}/V_s) + (K_{vegwater} * V_{rv}/V_s))$ |
| settling of suspended solids flux (kg/day) | SetFlux | $=v_{ss} * S_{aw}$ |
| burial flux of sediment solids (kg/day) | BurFlux | $=v_b * S_{as}$ |
| temperature dependence of Henry law constant (H) | HT_w | $=EXP(\ln HT_w)$ |
| sediment solids mass balance and resuspension flux (kg/day) | ResFlux | $=SetFlux - BurFlux$ |
| volume of water (m ³) | V_w | $=S_{aw} * D_w$ |
| volume of vegetated rooting medium (m ³) | V_s | $=(S_{as} * D_s) + V_{rv}$ |
| volume of rooting medium (m ³) | V_{rm} | $=(S_{as} * D_s)$ |
| volume of solids in vegetated rooting medium (m ³) | V_{sss} | $=(C_{ss}/d_{ss}) * V_{rm}$ |
| volume of water in vegetated rooting medium (m ³) | V_{sw} | $=V_{rm} - V_{sss}$ |
| Bioavailable solute fraction (unitless) | Φ | $=f_{DW}$ |
| Concentration of particulate organic carbon (kg/L) | X_{poc} | $=C_{pw} * OC_{pw}$ |
| evapotranspiration mass transfer coefficient (m/day) | vT | $=IF(K_{vegair}="na", "na", 1 / ((1/vT_{plantside}) + 1/(vT_{airside}/K_{vegair})))$ |
| water to submerged vegetation diffusion mass transfer coefficient (m/d) | $v_{WaterVeg}$ | $=IF(Organic="y", 1 / ((1/v_{vegwater}) + 1/(K_{ow} * v_{veglipid})), 1 / ((1/v_{vegwater}) + 1/(K_{vegwater} * v_{veglipid})))$ |
| contaminant fraction in water of vegetation | f_{WVeg} | $=IF(Organic="y", (1 - OC_v) / ((1 - OC_v) + K_{ocveg} * OC_v), (1 - OC_v))$ |
| contaminant fraction in organic carbon of vegetation | f_{OCVeg} | $=1 - f_{WVeg}$ |
| volume of emergent vegetation (m ³) | V_{ev} | $=WeightEmergent * NumberOfPlants * Sas / 1000 * dv$ |
| volume of submerged vegetation (m ³) | V_{sv} | $=WeightSubmerged * NumberOfPlants * Sas / 1000 * dv$ |
| volume of rhizomes (m ³) | V_{rv} | $=WeightRhizomes * NumberOfPlants * Sas / 1000 * dv$ |
| submerged vegetation surface area (m ²) | S_{sv} | $=NumberOfPlants * WeightSubmerged * Saw * AreaVol_{sv} / (dv * 1000)$ |
| emergent vegetation surface area (m ²) | S_{ev} | $=NumberOfPlants * WeightEmergent * Saw * AreaVol_{EV} / (dv * 1000)$ |
| Rate Constants | | |
| outflow (/day) | k_o | $=IF(F - F_{out} > 0, F_{out} / (1000 * V_w), 0)$ |
| volatilization (/day) | k_v | $=Saw * f_{DW} * v_e / V_w$ |

| | | |
|---|---------------|--|
| overall water-to-sediment transport (/day) | k_{ws} | $=k_{ws1}+k_{ws2}$ |
| overall sediment-to-water transport (/day) | k_{sw} | $=k_{sw1}+k_{sw2}$ |
| solids settling (/day) | k_{ws1} | $=v_{ss} * f_{DW} * K_{pw} / (d_{ss} * 1000 * V_w)$ |
| water-to-sediment diffusion (/day) | k_{ws2} | $=Sas * vd * f_{DW} / V_w$ |
| solids resuspension (/day) | k_{sw1} | $=v_{rs} * f_{SS} / (V_s * 1000 * d_{ss})$ |
| sediment-to-water diffusion (/day) | k_{sw2} | $=Sas * vd * f_{DS} / V_s$ |
| burial (/day) | k_B | $=v_b * Sas * f_{SS} / (d_{ss} * 1000 * V_s)$ |
| rhizome vegetation to submerged vegetation | k_{rvsv} | $=f_{DS} * Q_w * \text{NumberOfPlants} / (1000 * V_s)$ |
| water-to-submerged vegetation diffusion (/day) | k_{wsv} | $=S_{sv} * f_{DW} * v_{WaterVeg} / V_w$ |
| submerged vegetation to water diffusion (/day) | k_{svw} | $=k_{wsv} * V_w / (K_{vegwater} * V_{sv})$ |
| submerged vegetation to emergent vegetation transport (/day) | k_{svev} | $=f_{wVeg} * Q_w / (\text{WeightSubmerged} / d_v)$ |
| emergent vegetation to air transport (/day) | k_{evair} | $=IF(vT="na", 0, Sev * f_{OCveg} * vT / V_{ev})$ |
| transformation in water (/day) | k_{wr} | $=0.693/hlw$ |
| transformation in vegetated rooting medium (/day) | k_{sr} | $=f_{DS} * 0.693/hlw$ |
| transformation in submerged vegetation (/day) | k_{svr} | $=0.693/hlsubmerged$ |
| transformation in emergent vegetation (/day) | k_{evr} | $=0.693/hlmerged$ |
| Solving the Mass Balance | | |
| rooting medium depuration (1/day) | AAA | $=k_{sw}+k_B+k_{rvsv}+k_{sr}$ |
| water medium depuration (1/day) | BBB | $=k_{ws}+k_{wsv}+k_v+k_o+k_{wr}$ |
| submerged vegetation depuration (1/day) | CCC | $=k_{svw}+k_{svev}+k_{svr}+k_{gsv}$ |
| emergent plant depuration (1/day) | DDD | $=k_{evair}+k_{evr}+k_{gev}$ |
| Steady State Solution | | |
| total mass of contaminant in water (g) | M_w | $=L / (BBB - GGG - HHH)$ |
| total mass of contaminant in vegetated rooting medium (g) | M_s | $=k_{ws} * M_w / AAA$ |
| total mass of contaminant in submerged vegetation (g) | M_{sv} | $=FFF * M_w$ |
| total mass of contaminant in emergent vegetation (g) | M_{ev} | $=k_{svev} * M_{sv} / DDD$ |
| total mass of contaminant in rhizomes (g) | M_{rva} | $=M_s * f_{VS}$ |
| Concentrations | | |
| freely dissolved concentration of contaminant in water (g/L) | C_{wdo} | $=C_w * f_{DW}$ |
| concentration of contaminant in water (g/L) | C_w | $=M_w / (V_w * 1000)$ |
| concentration of contaminant in vegetated rooting medium (g/kg dry) | C_s | $=(M_s / V_s) / 1000$ |
| concentration of contaminant in solids of vegetated rooting medium (g/kg dry) | $C_{ssolids}$ | $=M_s * f_{SS} / (1000 * V_{sss} * d_{ss})$ |

| | | |
|---|--|---|
| concentration of contaminant in water of vegetated rooting medium (g/L) | C_{swater} | $=M_s * f_{DS} / (1000 * V_{sw})$ |
| concentration of contaminant in vegetation of vegetated rooting medium (g/kg dry) | C_{sveg} | $=M_s * f_{VS} / (1000 * V_{rv} * d_v)$ |
| concentration of contaminant in solids of rooting medium normalized to organic carbon (g/kg OC) | C_{soc} | $=C_{ssolids} / OC_{ss}$ |
| concentration of contaminant in vegetation of rooting medium normalized to organic carbon (g/kg OC) | C_{svegoc} | $=C_{sveg} / OC_v$ |
| concentration of contaminant in submerged vegetation (g/kg) | C_{sv} | $=M_{sv} / (1000 * V_{sv} * d_v)$ |
| concentration of contaminant in emergent vegetation (g/kg) | C_{ev} | $=M_{ev} / (1000 * V_{ev} * d_v)$ |
| Fluxes | | |
| inflow (g/day) | In Flow Flux | $=L$ |
| outflow (g/day) | Outflow Flux | $=k_o * M_w$ |
| volatilization (g/day) | Volatilization Flux | $=k_v * M_w$ |
| overall water-to-rooting medium transport (g/day) | Water To Rooting Medium Flux | $=k_{ws} * M_w$ |
| overall rooting medium-to-water transport (g/day) | Rooting Medium To Water Flux | $=k_{sw} * M_s$ |
| solids settling in water (g/day) | Solids Settling Flux | $=k_{ws1} * M_w$ |
| water-to-rooting medium diffusion (g/day) | Water To Rooting Medium Diffusion Flux | $=k_{ws2} * M_w$ |
| solids resuspension (g/day) | Solids Resuspension Flux | $=k_{sw1} * M_s$ |
| rooting medium-to-water diffusion (g/day) | Sediment To Water Diffusion Flux | $=k_{sw2} * M_s$ |
| burial (g/day) | Burial Flux | $=k_B * M_s$ |
| rhizome vegetation to submerged vegetation | Rhizome To Submerged Vegetation Flux | $=k_{rvsv} * M_s$ |
| water-to-submerged vegetation diffusion (g/day) | Water To Submerged Vegetation Diffusion Flux | $=k_{wsv} * M_w$ |
| submerged vegetation to water diffusion (g/day) | Submerged Vegetation To Water Diffusion Flux | $=k_{svw} * M_{sv}$ |
| submerged vegetation to emergent vegetation transport (g/day) | Submerged Vegetation To Emergent | $=k_{svev} * M_{sv}$ |

| | Vegetation Flux | |
|--|---|-----------------------|
| emergent vegetation to air transport (g/day) | Emergent Vegetation To Air Flux | $=k_{evair} * M_{ev}$ |
| transformation in water (g/day) | Transformation In Water Flux | $=k_{wr} * M_w$ |
| transformation in vegetated rooting medium (g/day) | Transformation In Vegetated Rooting Medium Flux | $=k_{sr} * M_s$ |
| transformation in submerged vegetation (g/day) | Transformation In Submerged Vegetation Flux | $=k_{svr} * M_{sv}$ |
| transformation in emergent vegetation (g/day) | Transformation In Emergent Vegetation Flux | $=k_{evr} * M_{ev}$ |
| growth dilution submerged vegetation (g/day) | Growth Dilution Submerged Vegetation Flux | $=k_{gsv} * M_{sv}$ |
| growth dilution emergent vegetation (g/day) | Growth Dilution Emergent Vegetation Flux | $=k_{gev} * M_{ev}$ |

Table A-3: Dimensions of an illustrative plant (adopted from Trapp and McFarlane, 1995)

| Vegetation Compartment | Volume (m³) | Density (kg/m³) | Mass (kg) |
|-------------------------------|-------------------------------|-----------------------------------|----------------------|
| Roots | 10×10^{-6} | 830 | 8.3×10^{-3} |
| Stem | 9.82×10^{-6} | 830 | 8.2×10^{-3} |
| Leaf (20) | 25×10^{-6} | 820 | 2.1×10^{-2} |

Table A-4: Estimated surface area for the modeled illustrative plant system

| Vegetation Compartment | Volume (m³) | FWS Surface Area (m²) | SSF Surface Area (m²) |
|-------------------------------|-------------------------------|--|---|
| Roots | 10×10^{-6} | n.c. | n.c. |
| Stem | 9.82×10^{-6} | E: 3.92×10^{-3} S: 3.92×10^{-3} | 7.85×10^{-3} |
| Leaf (20) | 25×10^{-6} | *E: 0.05 | 0.05 |
| Surface Area:Volume | -- | E: 800 S: 1803 | 1662 |

E – Emergent fraction (50% for FWS; 100% for SSF).

S – Submerged fraction (50% for FWS; 0% for SSF).

n.c. – not calculated, roots not included in submerged area/volume of vegetation.

*Leaves are not present in submerged fraction of vegetation.

Table A-5: Parameterization of the Model – Recommended Values

| Parameter | Recommendation | Notes | References |
|--|---|---|---|
| Vegetation Type | <i>Typha latifolia</i> (cattail), <i>Phragmites australis</i> (reed), <i>Scirpus acutus</i> (bulrush) | Emergent aquatic plant species typical in North American wetlands. | U.S. EPA, 1999. |
| Water Depth | 0.1m to 1.0m | Aquatic macrophytes prefer water depths between 0.1 and 1.0 metre to allow to the emergence of plant out of the water phase. | U.S. EPA, 1999. Conservation Halton, (n.d.) |
| Depth of Rooting Medium | Up to 1.0m | Extensive rhizome network and roots extend to depths up to 1 metre for mature <i>Typha latifolia</i> . | Conservation Halton, (n.d.) |
| Weight of Rhizomes | ~ 0.008kg (8g) | Trapp and McFarlane (1995) illustrative plant system. | Trapp and McFarlane, 1995. |
| Weight of Submerged plant | ~ 0.004kg (4g) | ~ see <i>Weight of Rhizomes</i> Assumes 50% submerged. Stem only, no leaves submerged. | Trapp and McFarlane, 1995. |
| Weight of Emergent plant | ~ 0.0024kg (2.4g) | ~ see <i>Weight of Rhizomes</i> Assumes 50% emergent. Stem and leaves. | Trapp and McFarlane, 1995. |
| Surface Area to Volume Ratio (submerged) | ~ 800 | Trapp and McFarlane (1995) illustrative plant system. SA/V (submerged stem). Assumes 50% submerged. | Trapp and McFarlane, 1995. |
| Surface Area to Volume Ratio (emergent) | ~ 1803 (FWS) ~ 1662 (SSF) | Trapp and McFarlane (1995) illustrative plant system. SA/V (emergent stem+ leaves). Assumes 50% emergent for FWS and 100% emergent for SSF. | Trapp and McFarlane, 1995. |
| Number of Plants (plant density) | <i>Typha latifolia</i> : 40 – 50 stems/m ² <i>Scirpus acutus</i> : 100 – 300 stems/m ² | Ibekwe et al. (2006) report enhanced microbial diversity from 50% wetland plant coverage. It is suggested these plant densities are reduced accordingly for average | United States Environmental Protection Agency, 1999. Legace et al. (n.d.). |

| | | | |
|--------------------------|---|---|---|
| | | bulk plant density of wetland (i.e. by up to 50%). | |
| Water Transport in Xylem | 10 cm ³ /h (0.24 L/day) per plant | Crank et al. (1981) illustrative plant with total foliage area of 0.05m ² . | Crank et al. (1981) Paterson and Mackay (1994) Trapp and McFarlane, 1995. |
| Evapotranspiration MTC | 2.6mm/day (annual daily average) 3.1mm/day (wet subarctic coastal marsh) | Stannard et al. (2013) reports USGS results for 3-year annual average ET rates for wetlands and open-surface water. Lafleur (1990) describes summertime mean daily ET rates for aquatic macrophytic vegetation in an Ontario, CA subarctic coastal marsh (3.1mm/day). | Stannard et al., 2013). Lafleur, 1990. |

Appendix B. Free Water Surface Flow Wetland Model Output Data

Appendix B.1: Parameterization of the FWS flow wetland model

Table B-1: Full Parameterization of FWS flow wetland model

| Input Parameter | Pyrene | Arsenic | Naphthenic Acid |
|---|---------------|----------------|------------------------|
| molecular weight (g/mol) | 202.26 | 74.92 | 170.25 |
| contaminant is an organic substance (Y or N) | Y | N | Y |
| transformation half life time in water (day) | 60 | 15 | 15 |
| transformation half-life time in submerged vegetation (day) | 600 | 150 | 150 |
| transformation half-life time in emergent vegetation (day) | 600 | 150 | 150 |
| LC ₅ or EC ₅ (water) in micro-organisms (g/L water) | na | na | na |
| LC ₅ or EC ₅ (water) in vegetation (g/L water) | na | na | na |
| LC ₅ (water) in fish (g/L water) | 0.002 | na | na |
| LC ₅ (sediment) in benthic invertebrates (g/kg sediment dw) | 0.024 | na | na |
| concentration in water inflow (g/L) | 1.00E-03 | 1.00E-03 | 1.00E-03 |
| water solubility of contaminant (g/L) | 1.35E-04 | 1.00E-06 | 4.78E-01 |
| density of pure contaminant (kg/L) | 1.27E-03 | 5.78E+00 | 9.15E-01 |
| initial mass of contaminant in water (g) | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| initial mass of contaminant in sediment (g) | 0.0E+00 | 0.0E+00 | 0.0E+00 |

-- For Organic Substances (neutral or ionic) --

| | | | |
|---|----------|--------------|----------|
| Henry's Law Constant (Pa.m ³ /mol) | 1.21E+00 | Do Not Enter | 2.36E-01 |
| log K _{ow} (for neutral organic) or log D (for organic acid or base) of the contaminant (unitless) | 4.88 | Do Not Enter | 0.83 |
| Solids organic carbon to octanol equivalency factor (unitless) | 0.226 | Do Not Enter | 0.35 |
| DOC-octanol proportionality constant (unitless) | 0.08 | Do Not Enter | 0.08 |
| Vegetation organic carbon to octanol equivalency factor (unitless) | 0.35 | Do Not Enter | 0.35 |

-- For Non-Organic Substances --

| | | | |
|---|--------------|-------|--------------|
| Air-Water Distribution Coefficient (L/L) | Do Not Enter | na | Do Not Enter |
| Rooting Solids-Water Distribution Coefficient (L/kg dw) | Do Not Enter | 6190 | Do Not Enter |
| Suspended Solids Water Distribution Coefficient (L/kg dw) | Do Not Enter | 6190 | Do Not Enter |
| Vegetation-Water Distribution Coefficient (L/kg ww) | Do Not Enter | 2096 | Do Not Enter |
| Phytoplankton-Water Distribution Coefficient (L/kg ww) | Do Not Enter | 0.286 | Do Not Enter |

| | | | |
|--|--------------|-------|--------------|
| Zooplankton-Water Distribution Coefficient (L/kg ww) | Do Not Enter | 0.286 | Do Not Enter |
| Benthos-Water Distribution Coefficient (L/kg ww) | Do Not Enter | 1.7 | Do Not Enter |
| Fish One-Water Distribution Coefficient (L/kg ww) | Do Not Enter | 1.7 | Do Not Enter |
| Fish Two-Water Distribution Coefficient (L/kg ww) | Do Not Enter | 1.7 | Do Not Enter |
| Fish Three-Water Distribution Coefficient (L/kg ww) | Do Not Enter | 1.7 | Do Not Enter |

-- System-Specific Characteristics --

| | | | |
|--|------------------------|------------------------|------------------------|
| wetland name | FWS Flow Wetland | FWS Flow Wetland | FWS Flow Wetland |
| name of vegetation | <i>Typha latifolia</i> | <i>Typha latifolia</i> | <i>Typha latifolia</i> |
| name of phytoplankton or algae species | Phytoplankton | Phytoplankton | Phytoplankton |
| name of zooplankton species | Zooplankton | Zooplankton | Zooplankton |
| name of benthic invertebrate species | Benthos | Benthos | Benthos |
| name of fish species 1 | Small fish | Small fish | Small fish |
| name of fish species 2 | Medium fish | Medium fish | Medium fish |
| name of fish species 3 | Large fish | Large fish | Large fish |
| water body surface area (m ²) | 1.00E+04 | 1.00E+04 | 1.00E+04 |
| rooting medium surface area (m ²) | 1.00E+04 | 1.00E+04 | 1.00E+04 |
| average water depth (m) | 1 | 1 | 1 |
| depth of rooting medium (m) | 1 | 1 | 1 |
| weight of rhizomes of one plant (kg/plant) | 0.2 | 0.2 | 0.2 |
| weight of submerged part of one plant (kg/plant) | 0.3 | 0.3 | 0.3 |
| weight of emerged part of one plant (kg/plant) | 0.5 | 0.5 | 0.5 |
| surface area-volume ratio for submerged vegetation (m ² /m ³) | 800 | 800 | 800 |
| surface area-volume ratio for emergent vegetation (m ² /m ³) | 1803 | 1803 | 1803 |
| Number of plants per m ² (1/m ²) | 2.50E+01 | 2.50E+01 | 2.50E+01 |
| water inflow (L/day) | 2.00E+06 | 2.00E+06 | 2.00E+06 |
| Concentration of particles in water (kg/L) | 3.00E-05 | 3.00E-05 | 3.00E-05 |
| Concentration of DOC in water (kg/L) | 1.00E-06 | Do Not Enter | 1.00E-06 |
| concentration of solids in rooting medium (kg/L) | 1.80E-01 | 1.80E-01 | 1.80E-01 |
| density of suspended solids (kg/L) | 1.50E+00 | 1.50E+00 | 1.50E+00 |
| density of rooting medium solids (kg/L) | 1.85E+00 | 1.85E+00 | 1.85E+00 |
| density of vegetation (kg/L) | 8.50E-01 | 8.50E-01 | 8.50E-01 |
| organic carbon content of suspended solids (unitless) | 5.00E-02 | Do Not Enter | 5.00E-02 |
| organic carbon content of rooting medium solids (unitless) | 5.00E-02 | Do Not Enter | 5.00E-02 |
| organic carbon content of | 8.00E-02 | Do Not Enter | 8.00E-02 |

| | | | |
|---|--------------|--------------|--------------|
| vegetation (unitless) | | | |
| density of organic carbon (kg/L) | 1.00E+00 | Do Not Enter | 1.00E+00 |
| water-side evaporation mass transfer coefficient (m/day) | Do Not Enter | Do Not Enter | Do Not Enter |
| air-side evaporation mass transfer coefficient (m/day) | Do Not Enter | Do Not Enter | Do Not Enter |
| water-to-sediment diffusion mass transfer coefficient (m/day) | 9.60E-03 | 9.60E-03 | 9.60E-03 |
| solids settling velocity (m/day) | 1 | 1 | 1 |
| sediment burial rate (m/day) | 0 | 0 | 0 |
| atmospheric pressure (atm) | 1.00 | 1.00 | 1.00 |
| pH of water | 7.00 | 7.00 | 7.00 |
| water temperature (°C) | 1.20E+01 | 1.20E+01 | 1.20E+01 |
| plant-side evapotranspiration mass transfer coefficient (m/day) | Do Not Enter | Do Not Enter | Do Not Enter |
| air-side evapotranspiration mass transfer coefficient (m/day) | Do Not Enter | Do Not Enter | Do Not Enter |
| water-side submerged vegetation-water mass transfer coefficient (m/day) | 1.00E-01 | 1.00E-01 | 1.00E-01 |
| plant-side submerged vegetation-water mass transfer coefficient (m/day) | 1.00E-02 | 1.00E-02 | 1.00E-02 |
| water transport in xylem (L/day) | 2.40E+00 | 2.40E+00 | 2.40E+00 |
| growth submerged vegetation (1/day) | 1.00E-03 | 1.00E-03 | 1.00E-03 |
| growth emergent vegetation (1/day) | 1.00E-03 | 1.00E-03 | 1.00E-03 |

Appendix B.2: Output data from the FWS model contaminant illustrations

Figure B-1: FWS temporal removal efficiency – pyrene, arsenic, and a naphthenic acid

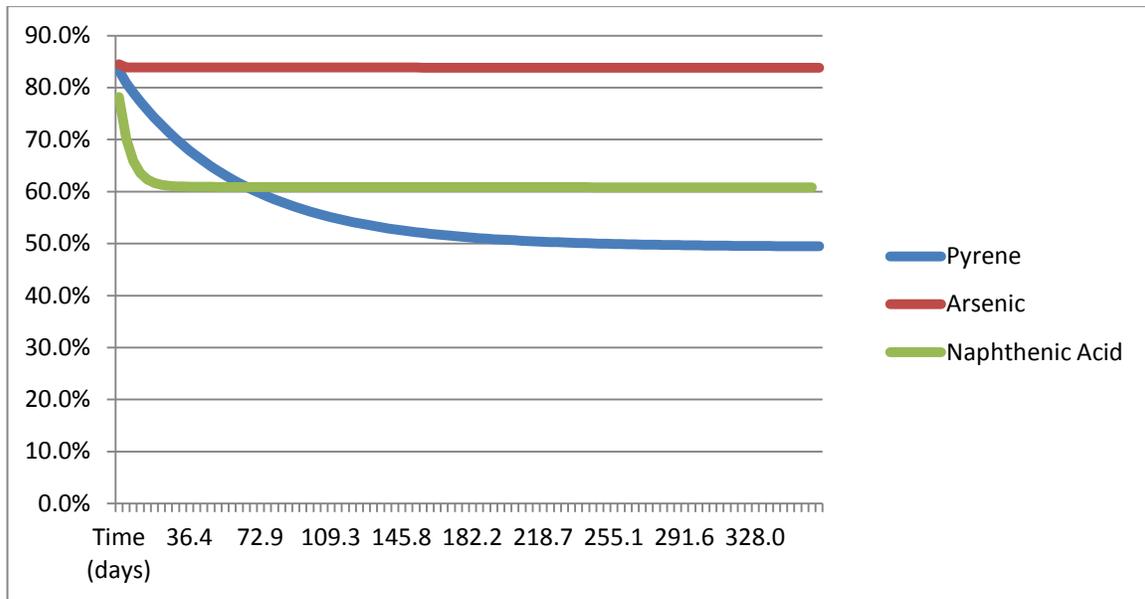


Table B-2: FWS and SSF steady state removal efficiency – pyrene, arsenic, and a naphthenic acid

| Contaminant | Removal Efficiency (E, %) | |
|-----------------|---------------------------|------|
| | FWS | SSF |
| Pyrene | 41 | 7.3 |
| Arsenic | 83 | 23.2 |
| Naphthenic Acid | 31 | 23.2 |

Figure B-2: FWS temporal contaminant flux – pyrene [Pyr], arsenic [As], and a naphthenic acid [N.A.]

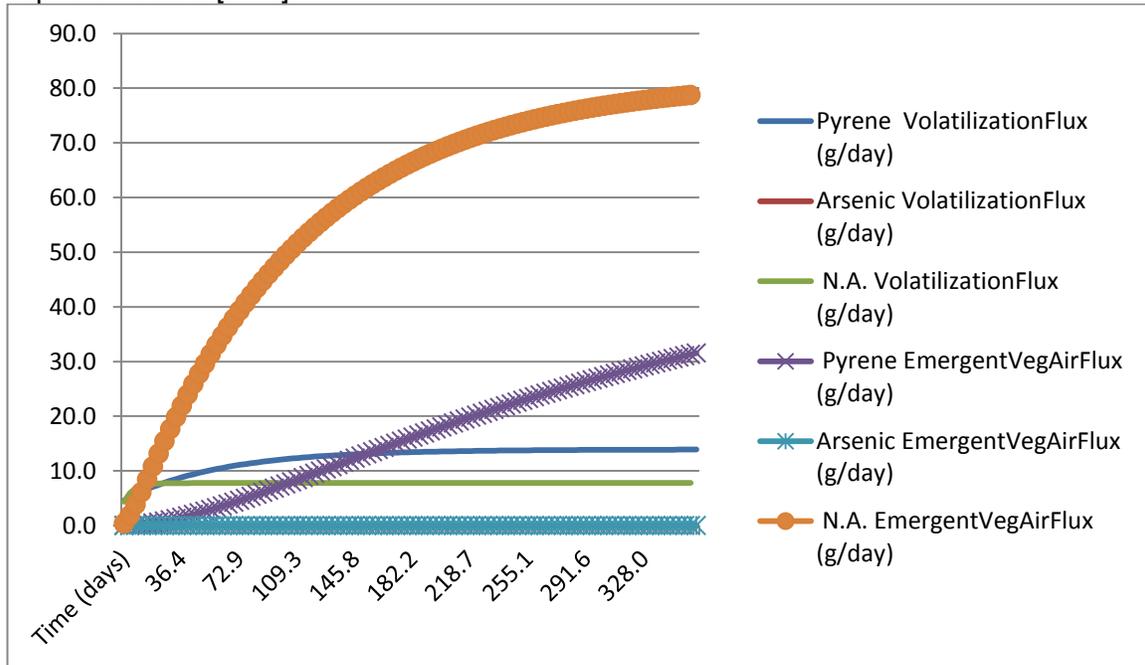


Figure B-3: FWS temporal overall flux of contaminant removal mechanisms – pyrene [Pyr], arsenic [As], and a naphthenic acid [N.A.]

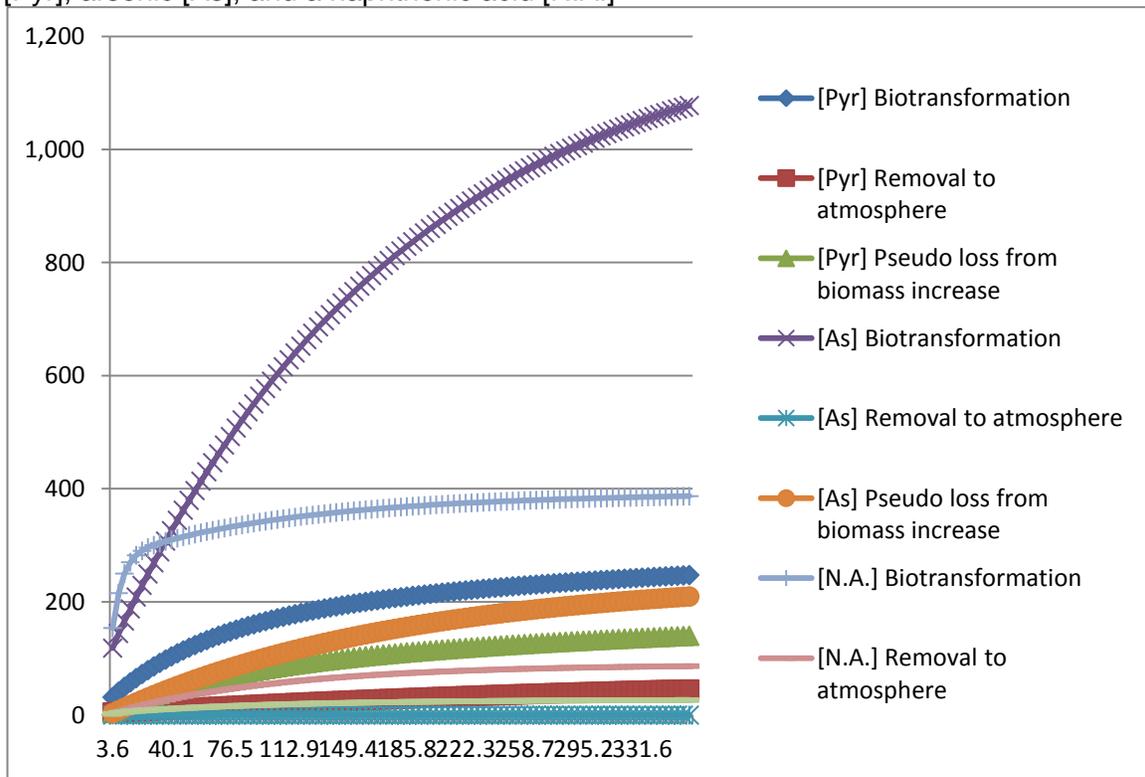


Table B-3: Estimated time to reach 95% of steady state

| | <i>t</i> _{95%} (days) | <i>t</i> _{95%} (days) | <i>t</i> _{95%} (days) |
|------------------------|--------------------------------|--------------------------------|--------------------------------|
| PYRENE | FWS | HSSF | VSSF |
| Water | 3.5 | na | na |
| Rooting Medium | 67112 | 13154 | 10562 |
| Submerged Vegetation | 57.9 | na | na |
| Emergent Vegetation | 48.2 | 1089 | 48.3 |
| Phytoplankton | 0.36 | 0.36 | 0.36 |
| Zookplankton | 0.42 | 0.42 | 0.42 |
| Benthos | 4.74 | 4.74 | 4.74 |
| Small Fish | 2.21 | na | na |
| Medium Fish | 4.13 | na | na |
| Large Fish | 7.40 | na | na |
| | <i>t</i> _{95%} (days) | <i>t</i> _{95%} (days) | <i>t</i> _{95%} (days) |
| ARSENIC | FWS | HSSF | VSSF |
| Water | 3.44 | na | na |
| Rooting Medium | 49348 | 18502 | 18502 |
| Submerged Vegetation | 0.48 | na | na |
| Emergent Vegetation | 534 | 534 | 534 |
| | <i>t</i> _{95%} (days) | <i>t</i> _{95%} (days) | <i>t</i> _{95%} (days) |
| NAPHTHENIC ACID | FWS | HSSF | VSSF |
| Water | 3.48 | na | na |
| Rooting Medium | 66487 | 28586 | 22874 |
| Submerged Vegetation | 5.2 | na | na |
| Emergent Vegetation | 7.9 | 321 | 321 |
| Phytoplankton | 0.2 | 0.2 | 0.2 |
| Zookplankton | 0.03 | 0.03 | 0.003 |
| Benthos | 0.37 | 0.37 | 0.37 |
| Small Fish | 1.19 | na | na |
| Medium Fish | 3.14 | na | na |
| Large Fish | 6.08 | na | na |

na – not applicable for the specified wetland design (i.e. HSSF or VSSF)

Figure B-5: FWS temporal biota concentration - pyrene

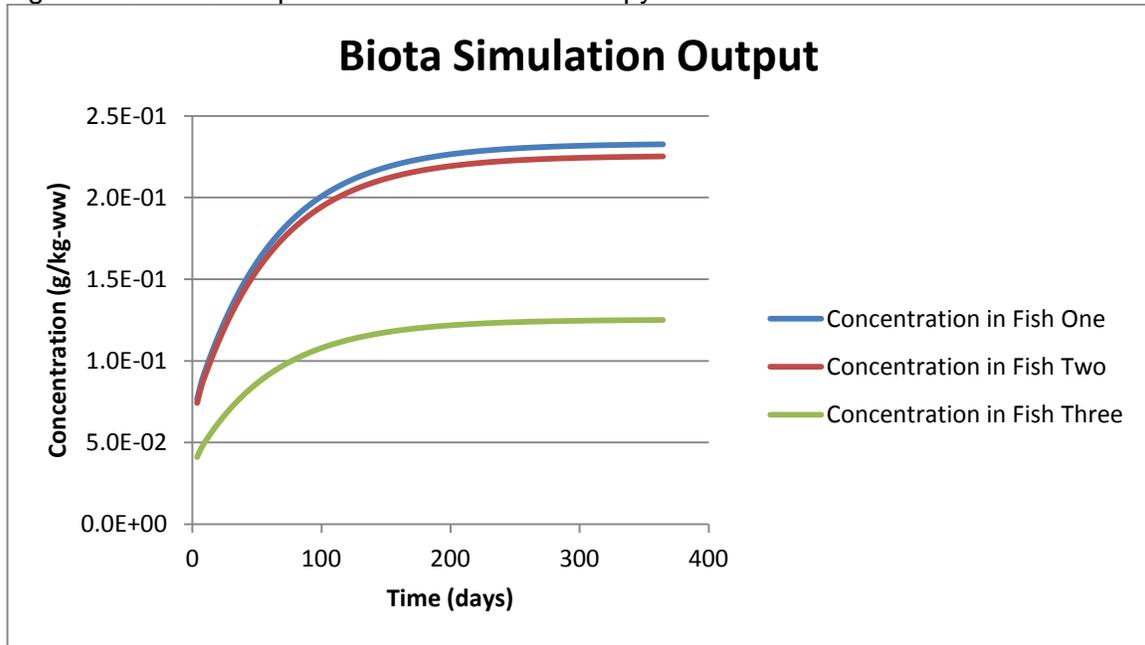


Figure B-5: FWS temporal biota concentration – arsenic

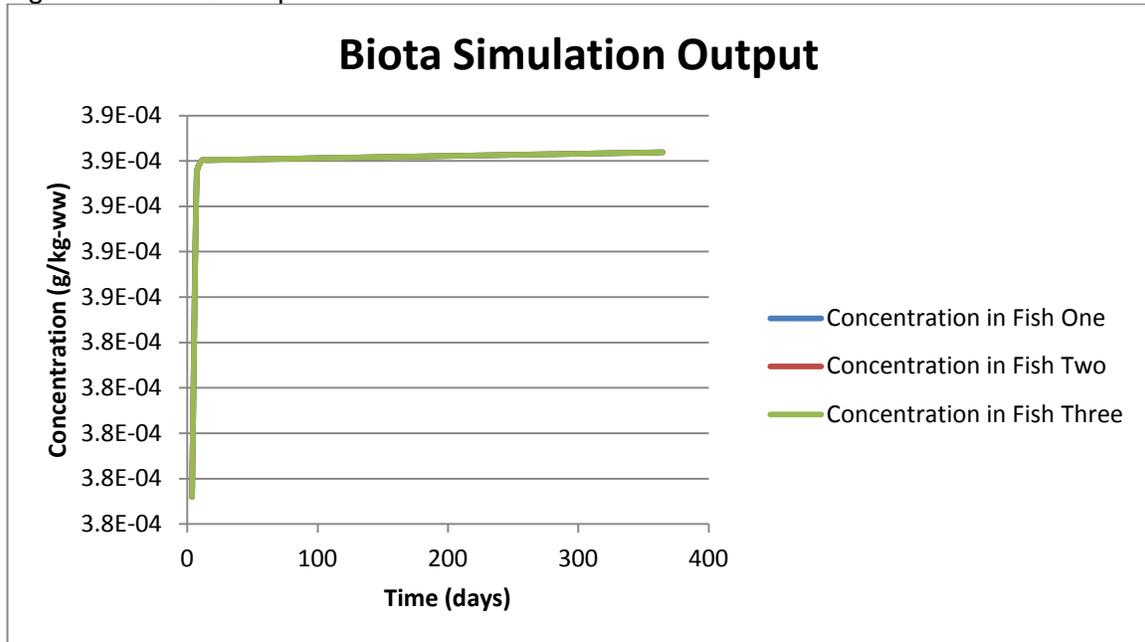
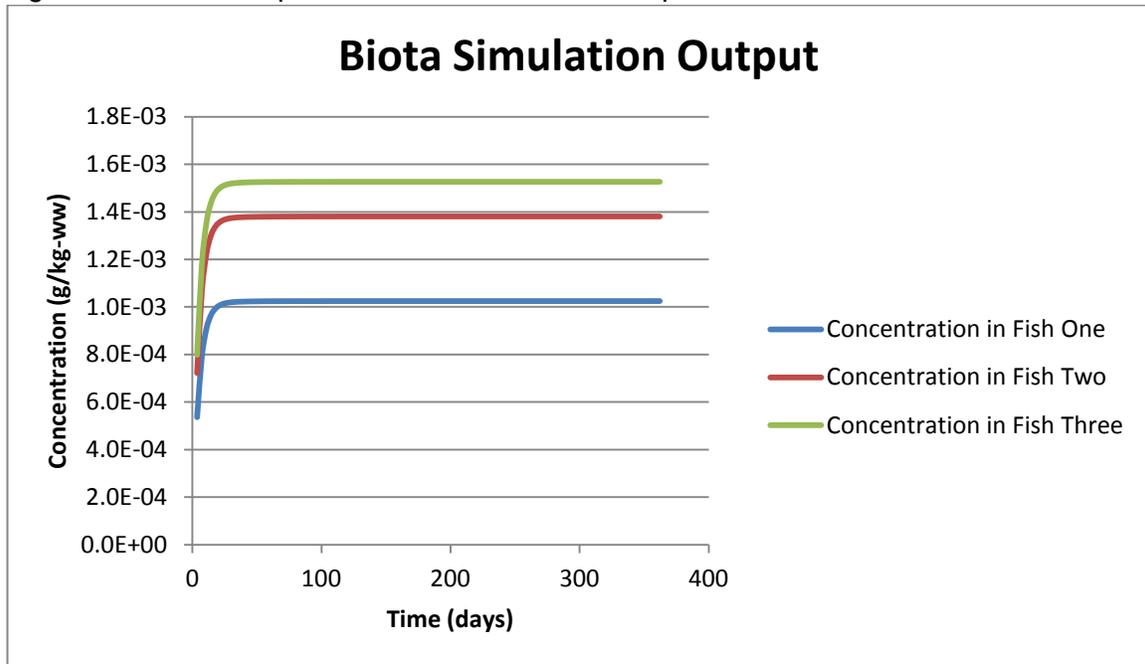


Figure B-6: FWS temporal biota concentration – naphthenic acid



Appendix B-3: Output data from the FWS model chemical universe illustration

Figure B-7: Chemical universe removal efficiency (%) contour plot (Log K_{OW} vs. Log K_{OA})

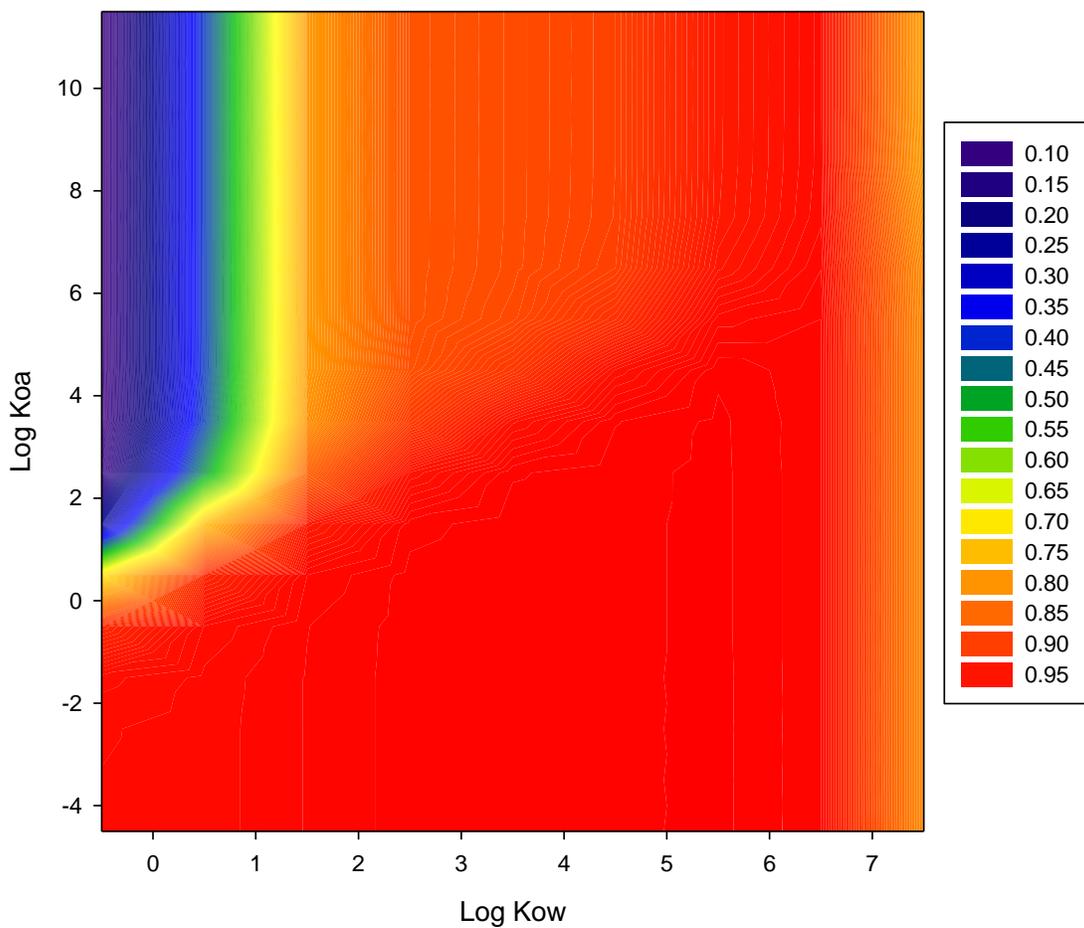


Table B-4: Chemical universe emergent vegetation to air flux ($\text{g}\cdot\text{day}^{-1}$) representation

| | | Log K _{ow} | | | | | | | | |
|---------------------|----------|---------------------|----------|----------|----------|----------|----------|----------|----------|----------|
| | | -0.5 | 0.5 | 1.5 | 2.5 | 3.5 | 4.5 | 5.5 | 6.5 | 7.5 |
| Log K _{oa} | -4.5 | 5.96E-01 | 5.34E+00 | 2.62E+01 | 4.31E+01 | 4.60E+01 | 4.59E+01 | 3.91E+01 | 1.05E+01 | 9.70E-01 |
| | -3.5 | 5.97E-01 | 5.34E+00 | 2.62E+01 | 4.31E+01 | 4.60E+01 | 4.59E+01 | 3.91E+01 | 1.05E+01 | 9.70E-01 |
| | -2.5 | 6.01E-01 | 5.35E+00 | 2.62E+01 | 4.31E+01 | 4.60E+01 | 4.59E+01 | 3.91E+01 | 1.05E+01 | 9.70E-01 |
| | -1.5 | 6.50E-01 | 5.39E+00 | 2.63E+01 | 4.31E+01 | 4.60E+01 | 4.59E+01 | 3.91E+01 | 1.05E+01 | 9.70E-01 |
| | -0.5 | 1.12E+00 | 5.82E+00 | 2.64E+01 | 4.31E+01 | 4.60E+01 | 4.59E+01 | 3.91E+01 | 1.05E+01 | 9.70E-01 |
| | 0.5 | 4.46E+00 | 9.83E+00 | 2.83E+01 | 4.34E+01 | 4.60E+01 | 4.59E+01 | 3.91E+01 | 1.05E+01 | 9.70E-01 |
| | 1.5 | 1.13E+01 | 3.47E+01 | 4.43E+01 | 4.61E+01 | 4.63E+01 | 4.59E+01 | 3.91E+01 | 1.05E+01 | 9.70E-01 |
| | 2.5 | 1.36E+01 | 7.09E+01 | 1.07E+02 | 6.82E+01 | 4.92E+01 | 4.62E+01 | 3.91E+01 | 1.05E+01 | 9.70E-01 |
| | 3.5 | 1.38E+01 | 8.02E+01 | 1.50E+02 | 1.35E+02 | 7.18E+01 | 4.89E+01 | 3.93E+01 | 1.05E+01 | 9.70E-01 |
| | 4.5 | 1.35E+01 | 8.10E+01 | 1.57E+02 | 1.69E+02 | 1.38E+02 | 7.01E+01 | 4.09E+01 | 1.05E+01 | 9.69E-01 |
| | 5.5 | 1.07E+01 | 7.88E+01 | 1.57E+02 | 1.73E+02 | 1.69E+02 | 1.27E+02 | 5.16E+01 | 1.07E+01 | 9.68E-01 |
| | 6.5 | 3.51E+00 | 6.16E+01 | 1.49E+02 | 1.69E+02 | 1.69E+02 | 1.49E+02 | 6.93E+01 | 1.12E+01 | 9.53E-01 |
| | 7.5 | 4.54E-01 | 1.93E+01 | 1.00E+02 | 1.33E+02 | 1.35E+02 | 1.22E+02 | 6.02E+01 | 9.68E+00 | 8.02E-01 |
| | 8.5 | 4.68E-02 | 2.45E+00 | 2.34E+01 | 4.23E+01 | 4.52E+01 | 4.09E+01 | 2.04E+01 | 3.30E+00 | 2.84E-01 |
| | 9.5 | 4.69E-03 | 2.52E-01 | 2.70E+00 | 5.41E+00 | 5.89E+00 | 5.35E+00 | 2.66E+00 | 4.32E-01 | 3.75E-02 |
| 10.5 | 4.69E-04 | 2.53E-02 | 2.74E-01 | 5.57E-01 | 6.08E-01 | 5.52E-01 | 2.75E-01 | 4.46E-02 | 3.87E-03 | |
| 11.5 | 4.69E-05 | 2.53E-03 | 2.74E-02 | 5.59E-02 | 6.10E-02 | 5.54E-02 | 2.76E-02 | 4.47E-03 | 3.89E-04 | |

Figure B-8: Chemical universe emergent vegetation to air flux ($\text{g}\cdot\text{day}^{-1}$) contour plot (Log K_{OW} vs. Log K_{OA})

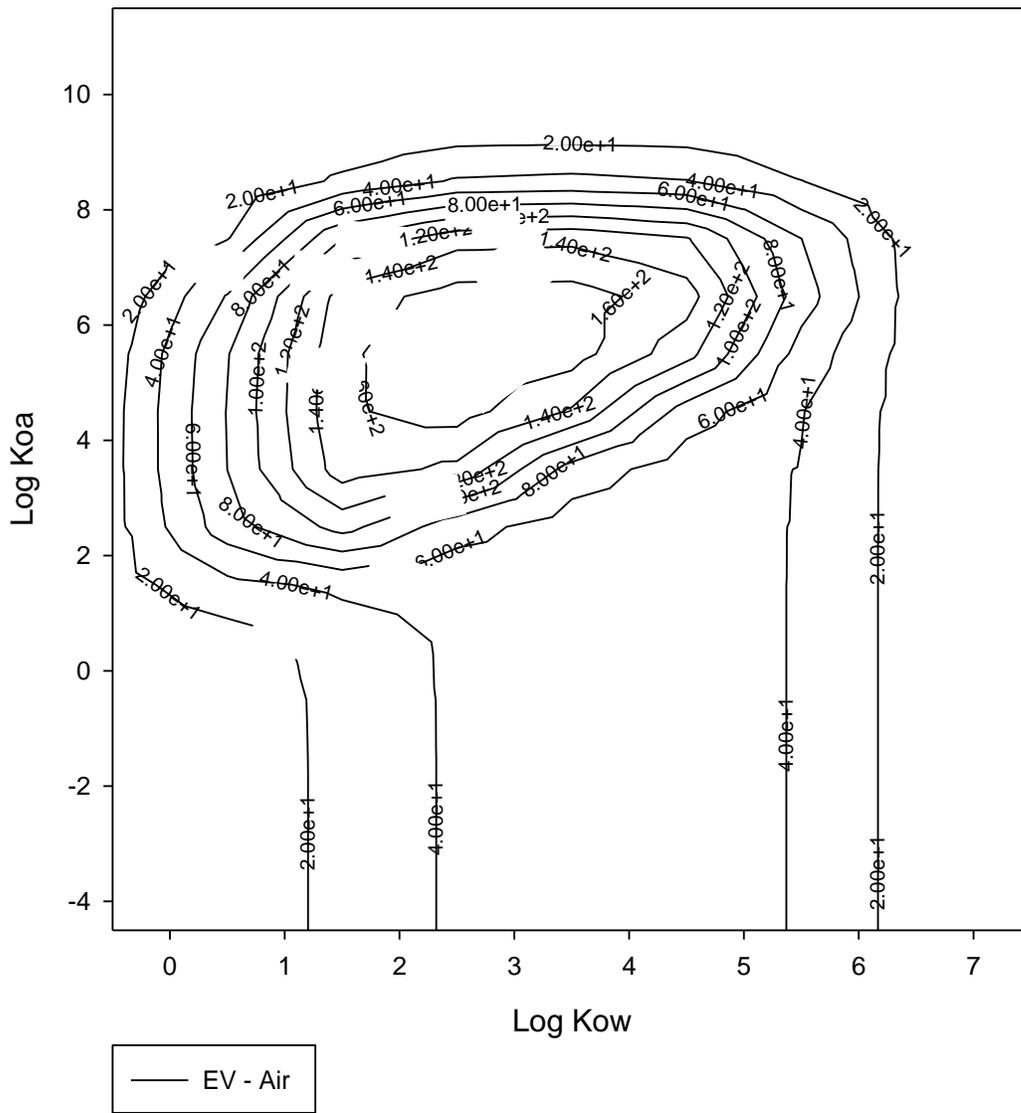
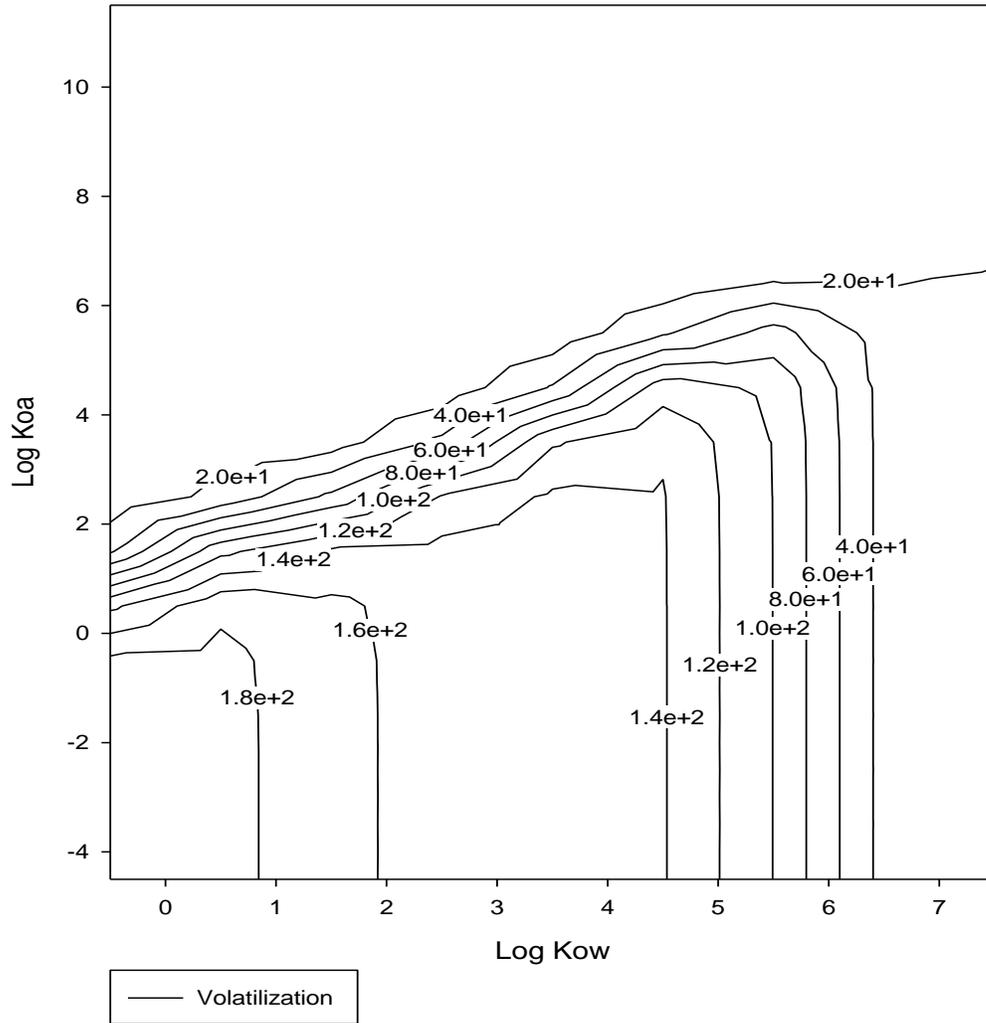


Table B-5: Chemical universe volatilization flux (g·day⁻¹) representation

| | | Log K _{ow} | | | | | | | | |
|---------------------|----------|---------------------|----------|----------|----------|----------|----------|----------|----------|----------|
| | | -0.5 | 0.5 | 1.5 | 2.5 | 3.5 | 4.5 | 5.5 | 6.5 | 7.5 |
| Log K _{oa} | -4.5 | 1.91E+02 | 1.87E+02 | 1.67E+02 | 1.51E+02 | 1.47E+02 | 1.41E+02 | 9.97E+01 | 3.35E+01 | 2.36E+01 |
| | -3.5 | 1.91E+02 | 1.87E+02 | 1.67E+02 | 1.51E+02 | 1.47E+02 | 1.41E+02 | 9.97E+01 | 3.35E+01 | 2.36E+01 |
| | -2.5 | 1.91E+02 | 1.87E+02 | 1.67E+02 | 1.51E+02 | 1.47E+02 | 1.41E+02 | 9.97E+01 | 3.35E+01 | 2.36E+01 |
| | -1.5 | 1.91E+02 | 1.87E+02 | 1.67E+02 | 1.51E+02 | 1.47E+02 | 1.41E+02 | 9.97E+01 | 3.35E+01 | 2.36E+01 |
| | -0.5 | 1.84E+02 | 1.86E+02 | 1.67E+02 | 1.51E+02 | 1.47E+02 | 1.41E+02 | 9.97E+01 | 3.35E+01 | 2.36E+01 |
| | 0.5 | 1.36E+02 | 1.76E+02 | 1.64E+02 | 1.50E+02 | 1.47E+02 | 1.41E+02 | 9.97E+01 | 3.35E+01 | 2.36E+01 |
| | 1.5 | 3.76E+01 | 1.15E+02 | 1.44E+02 | 1.47E+02 | 1.47E+02 | 1.41E+02 | 9.97E+01 | 3.35E+01 | 2.36E+01 |
| | 2.5 | 4.56E+00 | 2.57E+01 | 6.45E+01 | 1.22E+02 | 1.44E+02 | 1.41E+02 | 9.96E+01 | 3.35E+01 | 2.36E+01 |
| | 3.5 | 4.66E-01 | 2.93E+00 | 9.89E+00 | 4.48E+01 | 1.18E+02 | 1.38E+02 | 9.92E+01 | 3.35E+01 | 2.36E+01 |
| | 4.5 | 4.67E-02 | 2.97E-01 | 1.04E+00 | 6.12E+00 | 4.18E+01 | 1.11E+02 | 9.51E+01 | 3.33E+01 | 2.35E+01 |
| | 5.5 | 4.67E-03 | 2.98E-02 | 1.05E-01 | 6.35E-01 | 5.61E+00 | 3.73E+01 | 6.74E+01 | 3.11E+01 | 2.34E+01 |
| | 6.5 | 4.67E-04 | 2.98E-03 | 1.05E-02 | 6.37E-02 | 5.81E-01 | 4.88E+00 | 1.72E+01 | 1.87E+01 | 2.17E+01 |
| | 7.5 | 4.67E-05 | 2.98E-04 | 1.05E-03 | 6.37E-03 | 5.83E-02 | 5.04E-01 | 2.04E+00 | 3.75E+00 | 1.28E+01 |
| | 8.5 | 4.67E-06 | 2.98E-05 | 1.05E-04 | 6.37E-04 | 5.83E-03 | 5.06E-02 | 2.07E-01 | 4.16E-01 | 2.50E+00 |
| 9.5 | 4.67E-07 | 2.98E-06 | 1.05E-05 | 6.37E-05 | 5.83E-04 | 5.06E-03 | 2.08E-02 | 4.21E-02 | 2.76E-01 | |
| 10.5 | 4.67E-08 | 2.98E-07 | 1.05E-06 | 6.37E-06 | 5.83E-05 | 5.06E-04 | 2.08E-03 | 4.22E-03 | 2.79E-02 | |
| 11.5 | 4.67E-09 | 2.98E-08 | 1.05E-07 | 6.37E-07 | 5.83E-06 | 5.06E-05 | 2.08E-04 | 4.22E-04 | 2.79E-03 | |

Figure B-9: Chemical universe volatilization flux ($\text{g}\cdot\text{day}^{-1}$) contour plot (Log K_{ow} vs. Log K_{oa})

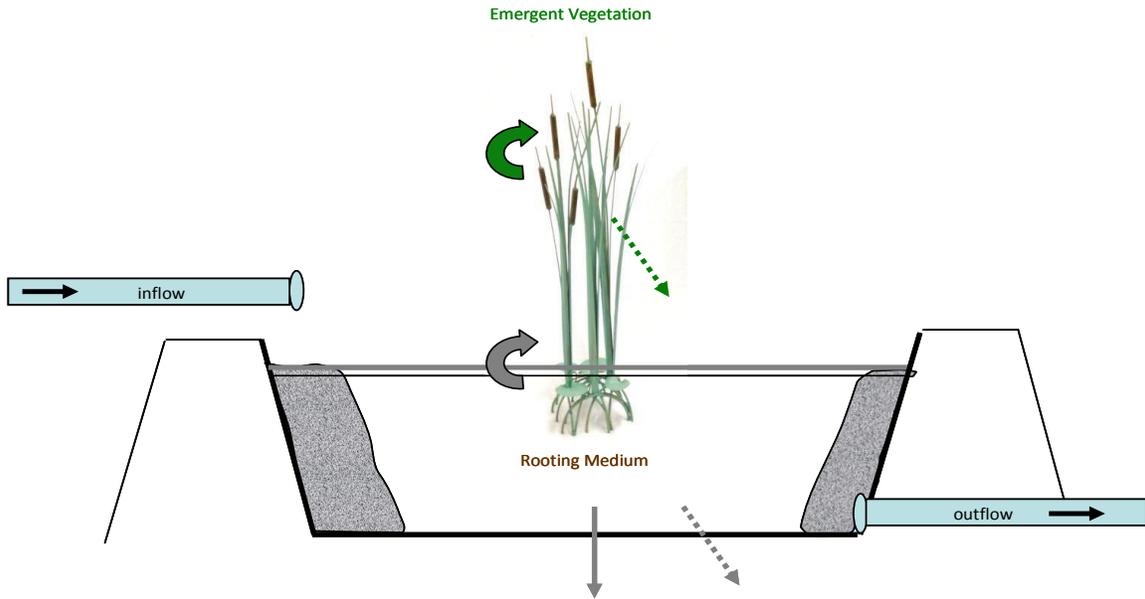


Appendix B-4: Output data from the FWS model U.S. EPA TRI list evaluation (refer to Word file in Appendix E)

Appendix C. Horizontal Subsurface Flow Wetland Model Output Data

Appendix C.1: Parameterization of the HSSF wetland model

Figure C-1: Conceptual diagram of the distribution of a contaminant in a HSSF wetland model



Solid arrows represent transport processes between wetland media. Dashed arrows represent transformation processes. Vegetation growth dilution is not shown.

For the HSSF wetland models, the mass balance equations were derived for the rooting medium and the emergent vegetation only. This wetland configuration does not include freestanding water and therefore no submerged vegetation in water. The wastewater influent is introduced to the system through the rooting medium, which has been defined as the bulk-phase with pore water and rhizomes of vegetation. The mass balance equations are therefore:

$$dM_{RM}/dt = L - (k_O + k_B + k_{RM-SV} + k_{RMT}) \cdot M_{RM}$$

$$dM_{EV}/dt = k_{RM-EV} \cdot M_{RM} - (k_E + k_{EVT} + k_{EVG}) \cdot M_{EV}$$

Table C-1: Parameterization of the HSSF wetland model

| Input Parameter | Pyrene | Arsenic | Naphthenic Acid |
|---|------------------------|------------------------|------------------------|
| molecular weight (g/mol) | 202.26 | 74.92 | 170.25 |
| contaminant is an organic substance (Y or N) | Y | N | Y |
| transformation half life time in water (day) | 60 | 15 | 15 |
| transformation half-life time in emergent vegetation (day) | 600 | 150 | 150 |
| LC ₅ or EC ₅ (water) in micro-organisms (g/L water) | na | na | na |
| LC ₅ or EC ₅ (water) in vegetation (g/L water) | na | na | na |
| LC ₅ (sediment) in benthic invertebrates (g/kg sediment dw) | 0.024 | na | na |
| concentration in water inflow (g/L) | 1.00E-03 | 1.00E-03 | 1.00E-03 |
| water solubility of contaminant (g/L) | 1.35E-04 | 1.00E-06 | 4.78E-01 |
| density of pure contaminant (kg/L) | 1.27E-03 | 5.78E+00 | 9.15E-01 |
| initial mass of contaminant in sediment (g) | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| -- For Organic Substances (neutral or ionic) -- | | | |
| Henry's Law Constant (Pa.m ³ /mol) | 1.21E+00 | Do Not Enter | 2.36E-01 |
| log K _{ow} (for neutral organic) or log D (for organic acid or base) of the contaminant (unitless) | 4.88 | Do Not Enter | 0.83 |
| Solids organic carbon to octanol equivalency factor (unitless) | 0.226 | Do Not Enter | 0.35 |
| DOC-octanol proportionality constant (unitless) | 0.08 | Do Not Enter | 0.08 |
| Vegetation organic carbon to octanol equivalency factor (unitless) | 0.35 | Do Not Enter | 0.35 |
| -- For Non-Organic Substances -- | | | |
| Air-Water Distribution Coefficient (L/L) | Do Not Enter | na | Do Not Enter |
| Rooting Solids-Water Distribution Coefficient (L/kg dw) | Do Not Enter | 6190 | Do Not Enter |
| Vegetation-Water Distribution Coefficient (L/kg ww) | Do Not Enter | 2096 | Do Not Enter |
| Phytoplankton-Water Distribution Coefficient (L/kg ww) | Do Not Enter | 0.286 | Do Not Enter |
| Zooplankton-Water Distribution Coefficient (L/kg ww) | Do Not Enter | 0.286 | Do Not Enter |
| Benthos-Water Distribution Coefficient (L/kg ww) | Do Not Enter | 1.7 | Do Not Enter |
| -- System-Specific Characteristics -- | | | |
| wetland name | HSSF Wetland | HSSF Wetland | HSSF Wetland |
| name of vegetation | <i>Typha latifolia</i> | <i>Typha latifolia</i> | <i>Typha latifolia</i> |

| | | | |
|---|---------------|---------------|---------------|
| name of phytoplankton or algae species | Phytoplankton | Phytoplankton | Phytoplankton |
| name of zooplankton species | Zooplankton | Zooplankton | Zooplankton |
| name of benthic invertebrate species | Benthos | Benthos | Benthos |
| rooting medium surface area (m ²) | 1.00E+02 | 1.00E+02 | 1.00E+02 |
| depth of rooting medium (m) | 1 | 1 | 1 |
| weight of rhizomes of one plant (kg/plant) | 0.2 | 0.2 | 0.2 |
| weight of emerged part of one plant (kg/plant) | 0.8 | 0.8 | 0.8 |
| surface area-volume ratio for emergent vegetation (m ² /m ³) | 1803 | 1803 | 1803 |
| Number of plants per m ² (1/m ²) | 2.50E+01 | 2.50E+01 | 2.50E+01 |
| water inflow (L/day) | 2.00E+04 | 2.00E+04 | 2.00E+04 |
| concentration of solids in rooting medium (kg/L) | 1.80E-01 | 1.80E-01 | 1.80E-01 |
| density of suspended solids (kg/L) | 1.50E+00 | 1.50E+00 | 1.50E+00 |
| density of rooting medium solids (kg/L) | 1.85E+00 | 1.85E+00 | 1.85E+00 |
| density of vegetation (kg/L) | 8.50E-01 | 8.50E-01 | 8.50E-01 |
| organic carbon content of rooting medium solids (unitless) | 5.00E-02 | Do Not Enter | 5.00E-02 |
| organic carbon content of vegetation (unitless) | 8.00E-02 | Do Not Enter | 8.00E-02 |
| density of organic carbon (kg/L) | 1.00E+00 | Do Not Enter | 1.00E+00 |
| sediment burial rate (m/day) | 0 | 0 | 0 |
| atmospheric pressure (atm) | 1.00 | 1.00 | 1.00 |
| pH of water | 7.00 | 7.00 | 7.00 |
| water temperature (°C) | 1.20E+01 | 1.20E+01 | 1.20E+01 |
| plant-side evapotranspiration mass transfer coefficient (m/day) | Do Not Enter | Do Not Enter | Do Not Enter |
| air-side evapotranspiration mass transfer coefficient (m/day) | Do Not Enter | Do Not Enter | Do Not Enter |
| water transport in xylem (L/day) | 2.40E+00 | 2.40E+00 | 2.40E+00 |
| growth emergent vegetation (1/day) | 1.00E-03 | 1.00E-03 | 1.00E-03 |

Appendix C.2: Output data from the HSSF model contaminant illustrations

Figure C-2: HSSF temporal removal efficiency – pyrene, arsenic, and a naphthenic acid

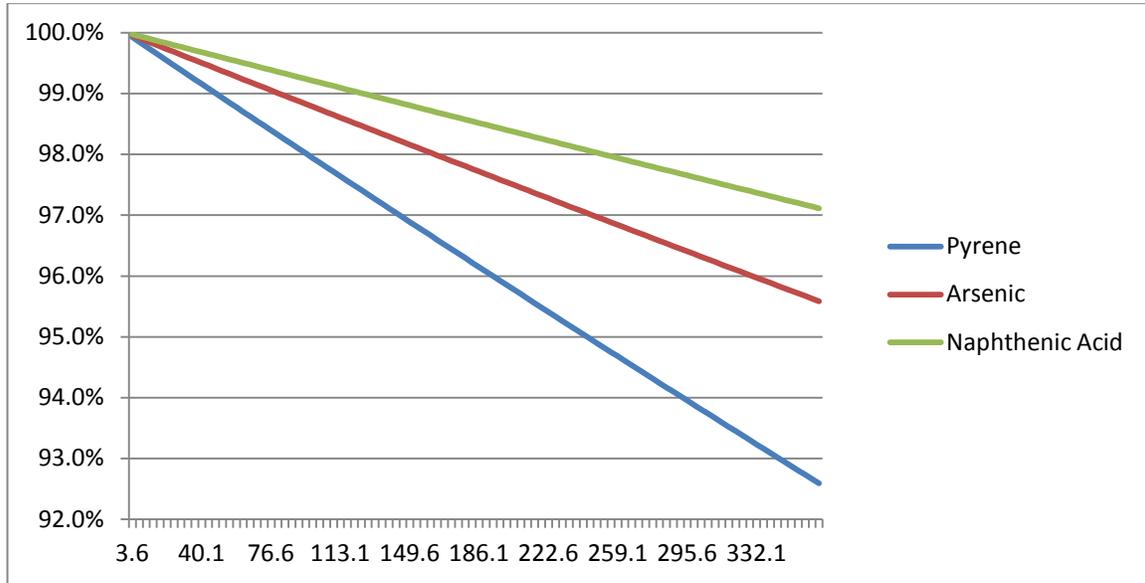


Figure C-3: HSSF temporal contaminant removal flux – pyrene [Pyr], arsenic [As], and a naphthenic acid [N.A.]

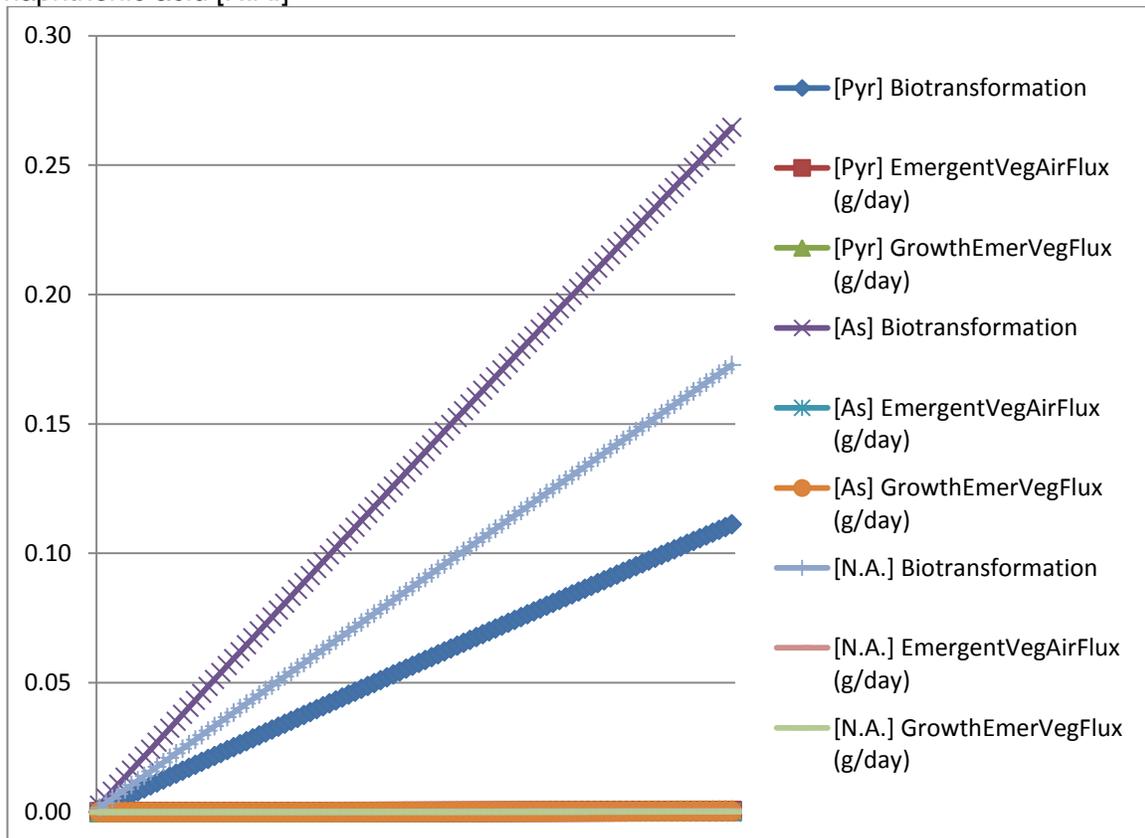


Figure C-4: Flux diagram of contaminant fate through HSSF flow wetland – Pyrene
**All values in g·day⁻¹*

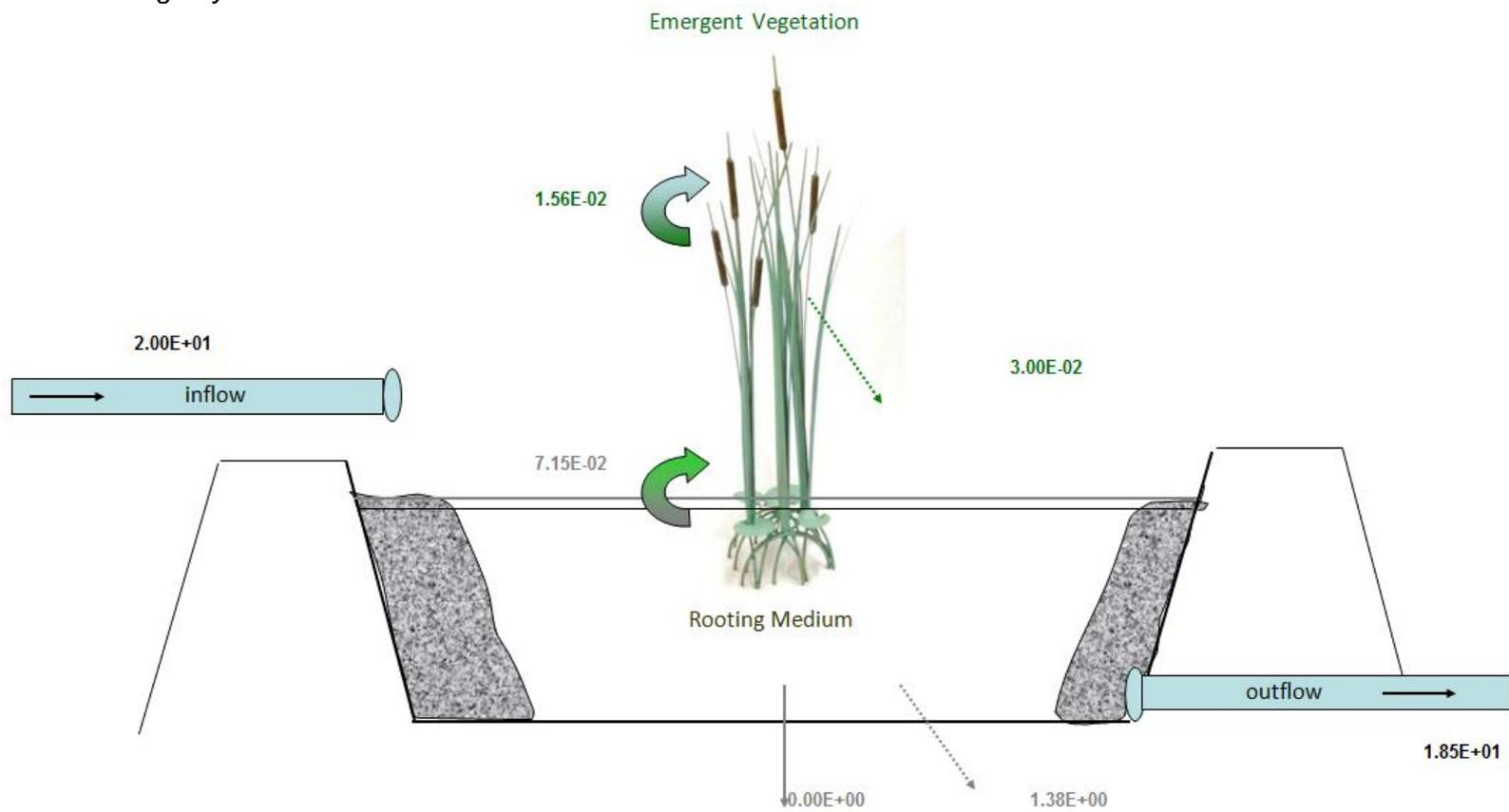


Figure C-5: Flux diagram of contaminant fate through HSSF flow wetland – Arsenic
*All values in $g \cdot day^{-1}$

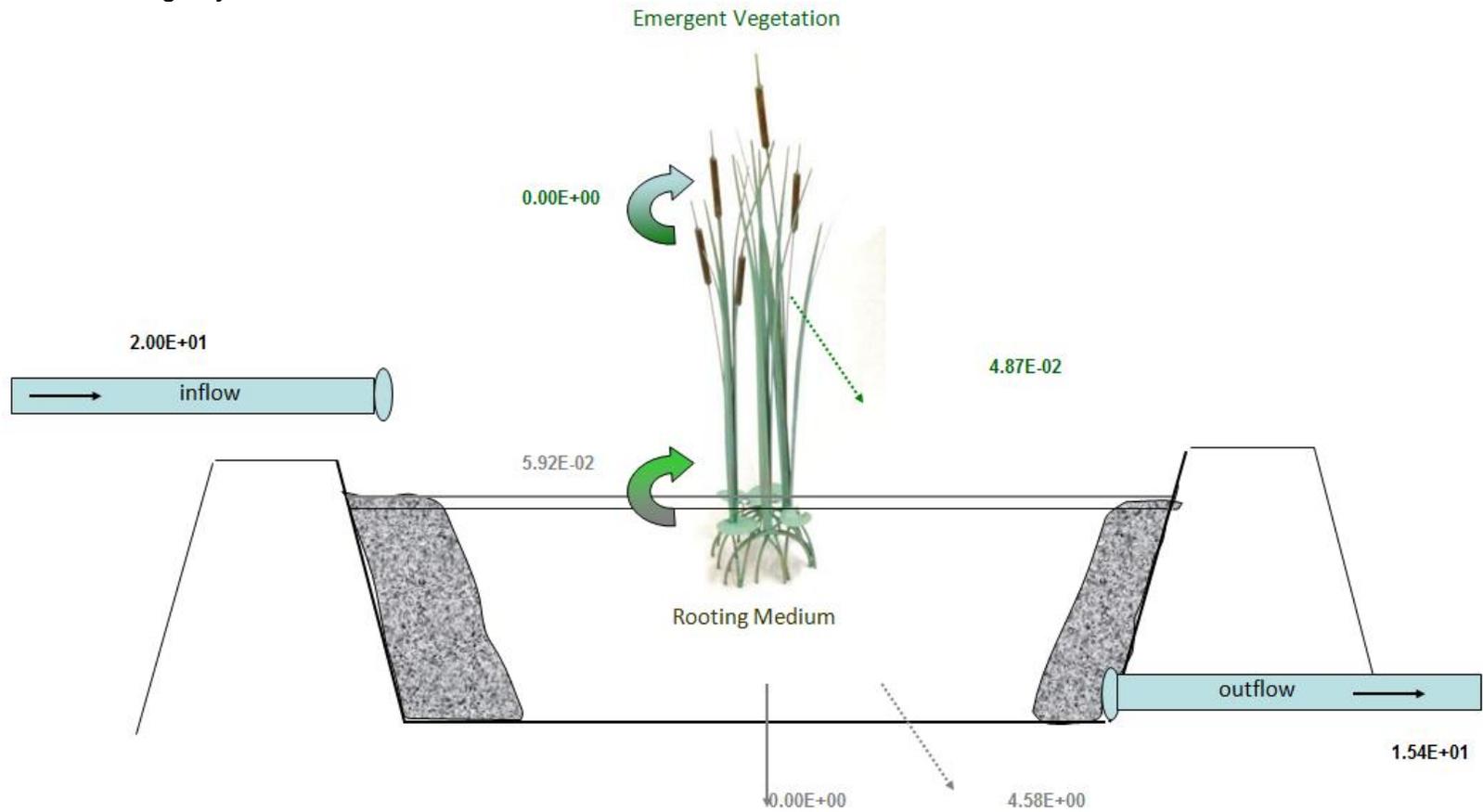


Figure C-6: Flux diagram of contaminant fate through HSSF flow wetland – Naphthenic Acid
*All values in $g \cdot day^{-1}$

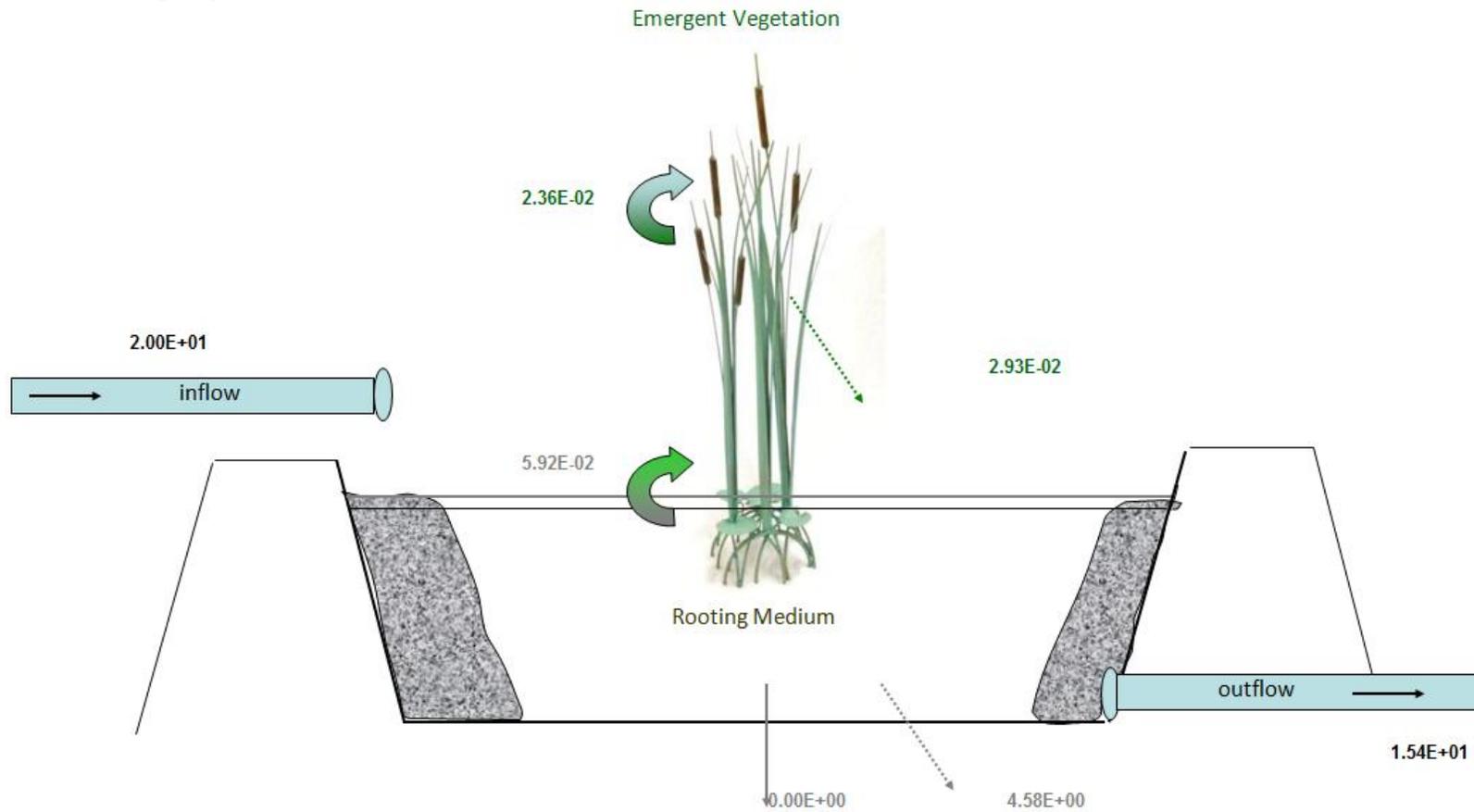


Figure C-7: HSSF temporal biota concentration – pyrene

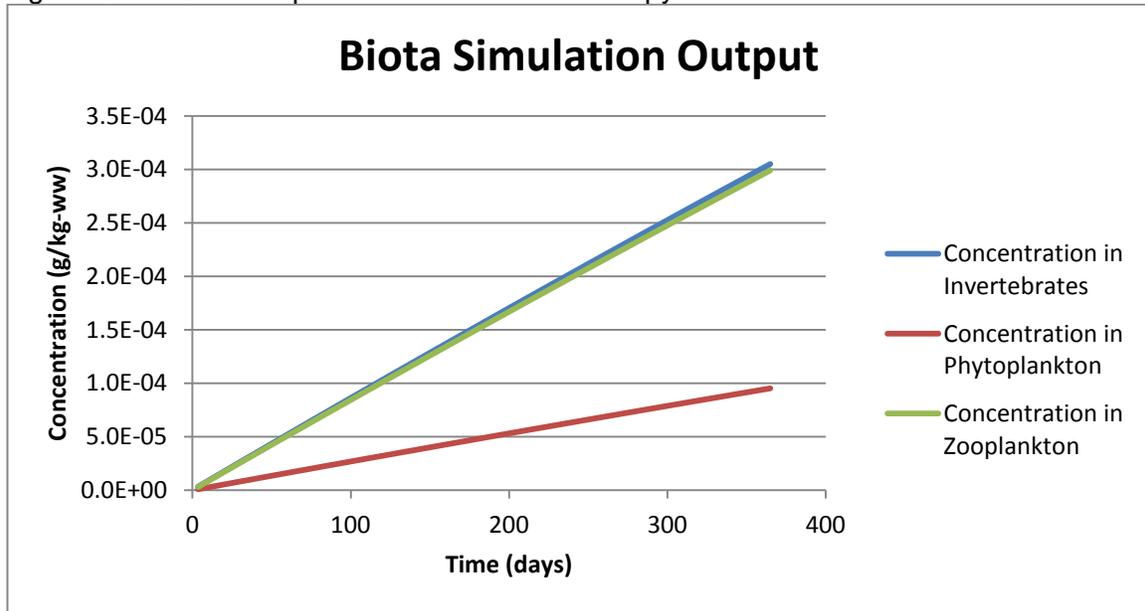


Figure C-8: HSSF temporal biota concentration – arsenic

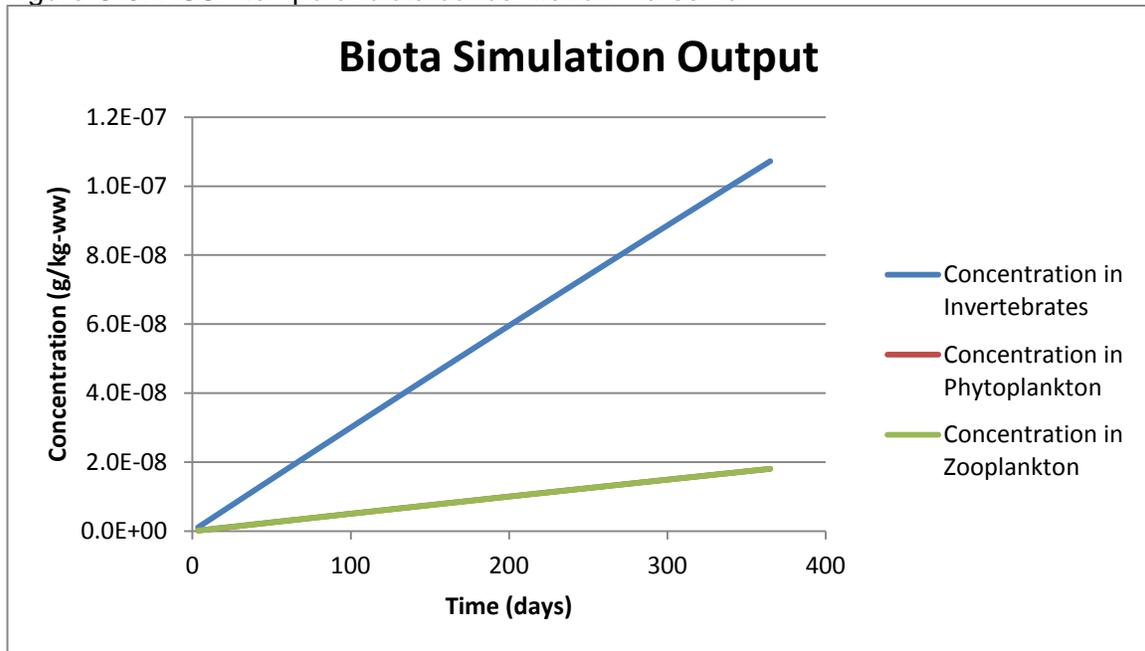
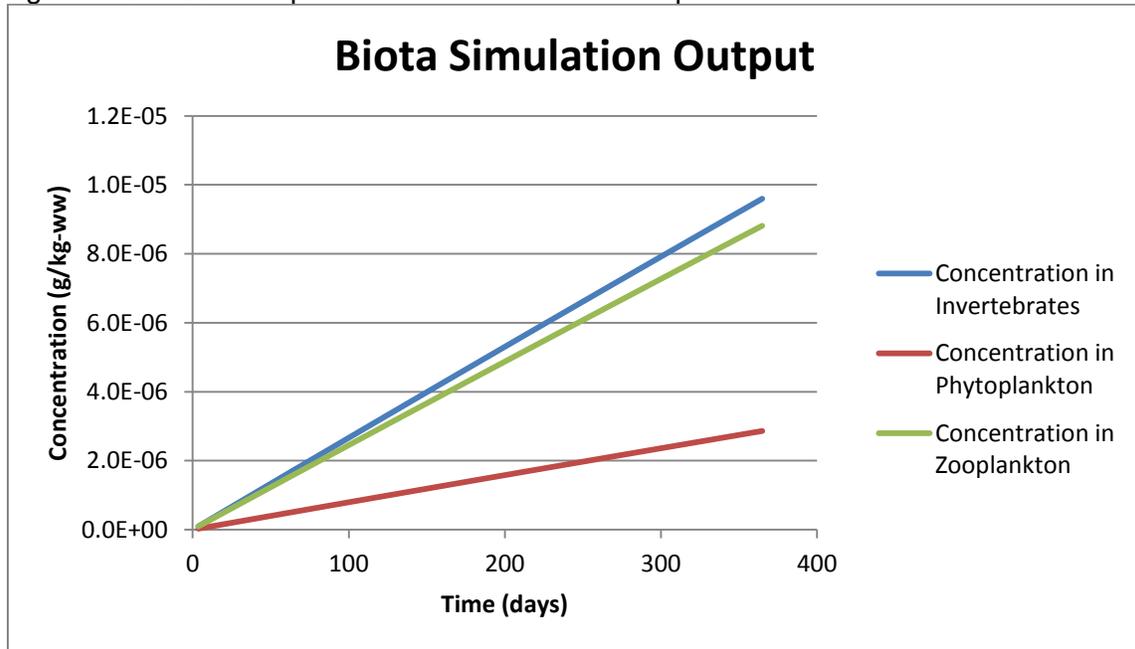


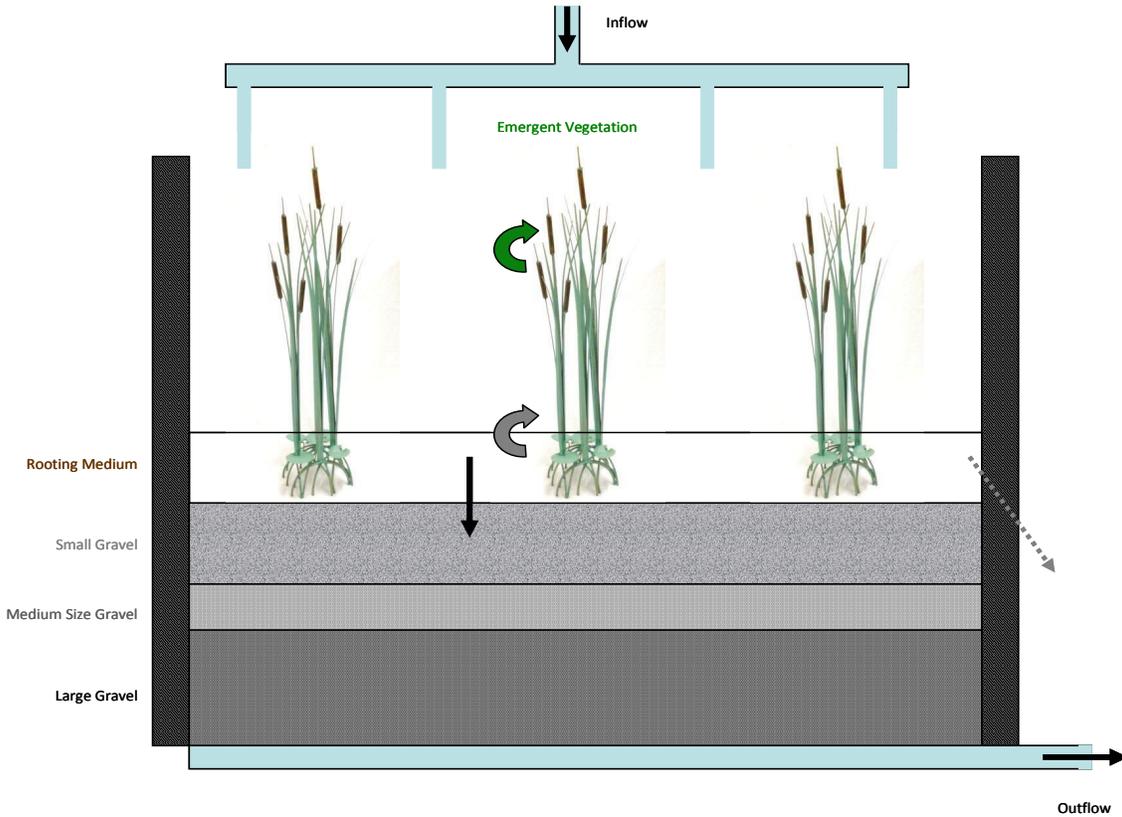
Figure C-9: HSSF temporal biota concentration – naphthenic acid



Appendix D. Vertical Subsurface Flow Wetland Model Output Data

Appendix D.1: Parameterization of the VSSF wetland model

Figure D-1: Conceptual diagram of the distribution of a contaminant in a VSSF wetland model



Solid arrows represent transport processes between wetland media. Dashed arrows represent transformation processes. Vegetation growth dilution is not shown.

For the VSSF wetland models, the mass balance equations were derived for the rooting medium and the emergent vegetation only. This wetland configuration does not include freestanding water and therefore no submerged vegetation in water. The wastewater influent is introduced to the system through the rooting medium, which has been defined as the bulk-phase with pore water and rhizomes of vegetation. The mass balance equations are therefore:

$$dM_{RM}/dt = L - (k_O + k_B + k_{RM-SV} + k_{RMT}) \cdot M_{RM}$$

$$dM_{EV}/dt = k_{RM-EV} \cdot M_{RM} - (k_E + k_{EVT} + k_{EVG}) \cdot M_{EV}$$

Table D-1: Parameterization of the VSSF wetland model

| Input Parameter | Pyrene | Arsenic | Naphthenic Acid |
|---|---------------|----------------|------------------------|
| molecular weight (g/mol) | 202.26 | 74.92 | 170.25 |
| contaminant is an organic substance (Y or N) | Y | N | Y |
| transformation half life time in water (day) | 60 | 15 | 15 |
| transformation half-life time in emergent vegetation (day) | 600 | 150 | 150 |
| LC ₅ or EC ₅ (water) in micro-organisms (g/L water) | na | na | na |
| LC ₅ or EC ₅ (water) in vegetation (g/L water) | na | na | na |
| LC ₅ (sediment) in benthic invertebrates (g/kg sediment dw) | 0.024 | na | na |
| concentration in water inflow (g/L) | 1.00E-03 | 1.00E-03 | 1.00E-03 |
| water solubility of contaminant (g/L) | 1.35E-04 | 1.00E-06 | 4.78E-01 |
| density of pure contaminant (kg/L) | 1.27E-03 | 5.78E+00 | 9.15E-01 |
| initial mass of contaminant in sediment (g) | 0.0E+00 | 0.0E+00 | 0.0E+00 |

-- For Organic Substances (neutral or ionic) --

| | | | |
|---|----------|--------------|----------|
| Henry's Law Constant (Pa.m ³ /mol) | 1.21E+00 | Do Not Enter | 2.36E-01 |
| log K _{ow} (for neutral organic) or log D (for organic acid or base) of the contaminant (unitless) | 4.88 | Do Not Enter | 0.83 |
| Solids organic carbon to octanol equivalency factor (unitless) | 0.226 | Do Not Enter | 0.35 |
| DOC-octanol proportionality constant (unitless) | 0.08 | Do Not Enter | 0.08 |
| Vegetation organic carbon to octanol equivalency factor (unitless) | 0.35 | Do Not Enter | 0.35 |

-- For Non-Organic Substances --

| | | | |
|---|--------------|-------|--------------|
| Air-Water Distribution Coefficient (L/L) | Do Not Enter | na | Do Not Enter |
| Rooting Solids-Water Distribution Coefficient (L/kg dw) | Do Not Enter | 6190 | Do Not Enter |
| Vegetation-Water Distribution Coefficient (L/kg ww) | Do Not Enter | 2096 | Do Not Enter |
| Phytoplankton-Water Distribution Coefficient (L/kg ww) | Do Not Enter | 0.286 | Do Not Enter |
| Zooplankton-Water Distribution Coefficient (L/kg ww) | Do Not Enter | 0.286 | Do Not Enter |
| Benthos-Water Distribution Coefficient (L/kg ww) | Do Not Enter | 1.7 | Do Not Enter |

-- System-Specific Characteristics --

| | | | |
|--|------------------------|------------------------|------------------------|
| wetland name | VSSF Wetland | VSSF Wetland | VSSF Wetland |
| name of vegetation | <i>Typha latifolia</i> | <i>Typha latifolia</i> | <i>Typha latifolia</i> |
| name of phytoplankton or algae species | Phytoplankton | Phytoplankton | Phytoplankton |

| | | | |
|---|--------------|--------------|--------------|
| name of zooplankton species | Zooplankton | Zooplankton | Zooplankton |
| name of benthic invertebrate species | Benthos | Benthos | Benthos |
| rooting medium surface area (m ²) | 1.00E+02 | 1.00E+02 | 1.00E+02 |
| depth of rooting medium (m) | 1 | 1 | 1 |
| weight of rhizomes of one plant (kg/plant) | 0.2 | 0.2 | 0.2 |
| weight of emerged part of one plant (kg/plant) | 0.8 | 0.8 | 0.8 |
| surface area-volume ratio for emergent vegetation (m ² /m ³) | 1803 | 1803 | 1803 |
| Number of plants per m ² (1/m ²) | 2.50E+01 | 2.50E+01 | 2.50E+01 |
| water inflow (L/day) | 2.00E+04 | 2.00E+04 | 2.00E+04 |
| concentration of solids in rooting medium (kg/L) | 1.80E-01 | 1.80E-01 | 1.80E-01 |
| density of suspended solids (kg/L) | 1.50E+00 | 1.50E+00 | 1.50E+00 |
| density of rooting medium solids (kg/L) | 1.85E+00 | 1.85E+00 | 1.85E+00 |
| density of vegetation (kg/L) | 1.00E+00 | 1.00E+00 | 1.00E+00 |
| organic carbon content of rooting medium solids (unitless) | 4.00E-02 | Do Not Enter | 4.00E-02 |
| organic carbon content of vegetation (unitless) | 8.00E-02 | Do Not Enter | 8.00E-02 |
| density of organic carbon (kg/L) | 1.00E+00 | Do Not Enter | 1.00E+00 |
| sediment burial rate (m/day) | 0 | 0 | 0 |
| atmospheric pressure (atm) | 1.00 | 1.00 | 1.00 |
| pH of water | 7.00 | 7.00 | 7.00 |
| water temperature (°C) | 1.20E+01 | 1.20E+01 | 1.20E+01 |
| plant-side evapotranspiration mass transfer coefficient (m/day) | Do Not Enter | Do Not Enter | Do Not Enter |
| air-side evapotranspiration mass transfer coefficient (m/day) | Do Not Enter | Do Not Enter | Do Not Enter |
| water transport in xylem (L/day) | 2.40E+00 | 2.40E+00 | 2.40E+00 |
| growth emergent vegetation (1/day) | 1.00E-03 | 1.00E-03 | 1.00E-03 |

Appendix D.2: Output data from the VSSF model contaminant illustrations

Figure D-2: VSSF temporal removal efficiency – pyrene, arsenic, and a naphthenic acid

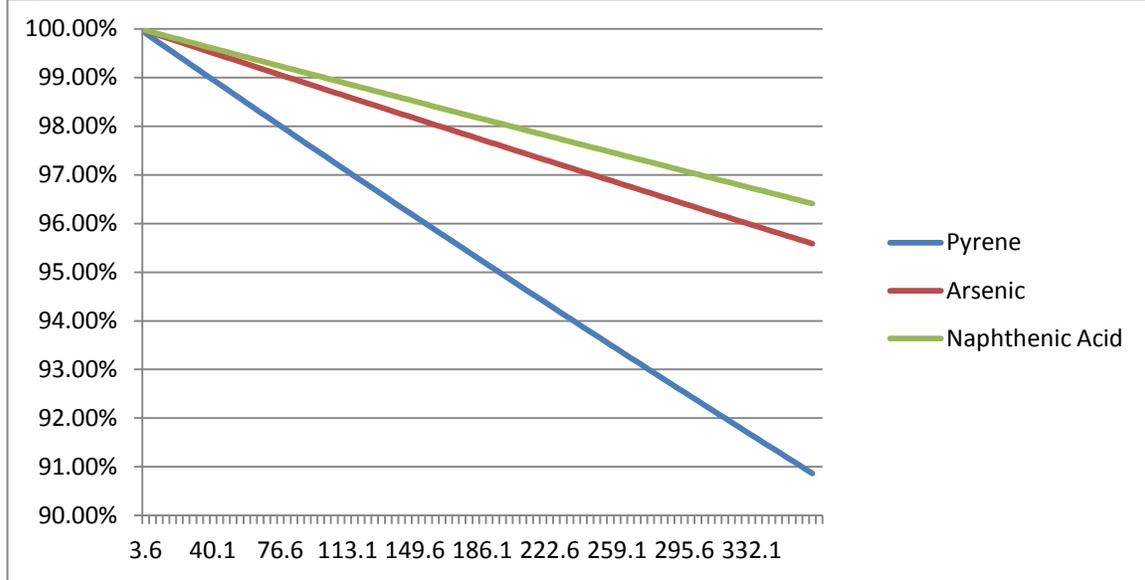


Figure D-3: VSSF temporal contaminant removal flux – pyrene [Pyr], arsenic [As], and a naphthenic acid [N.A.]

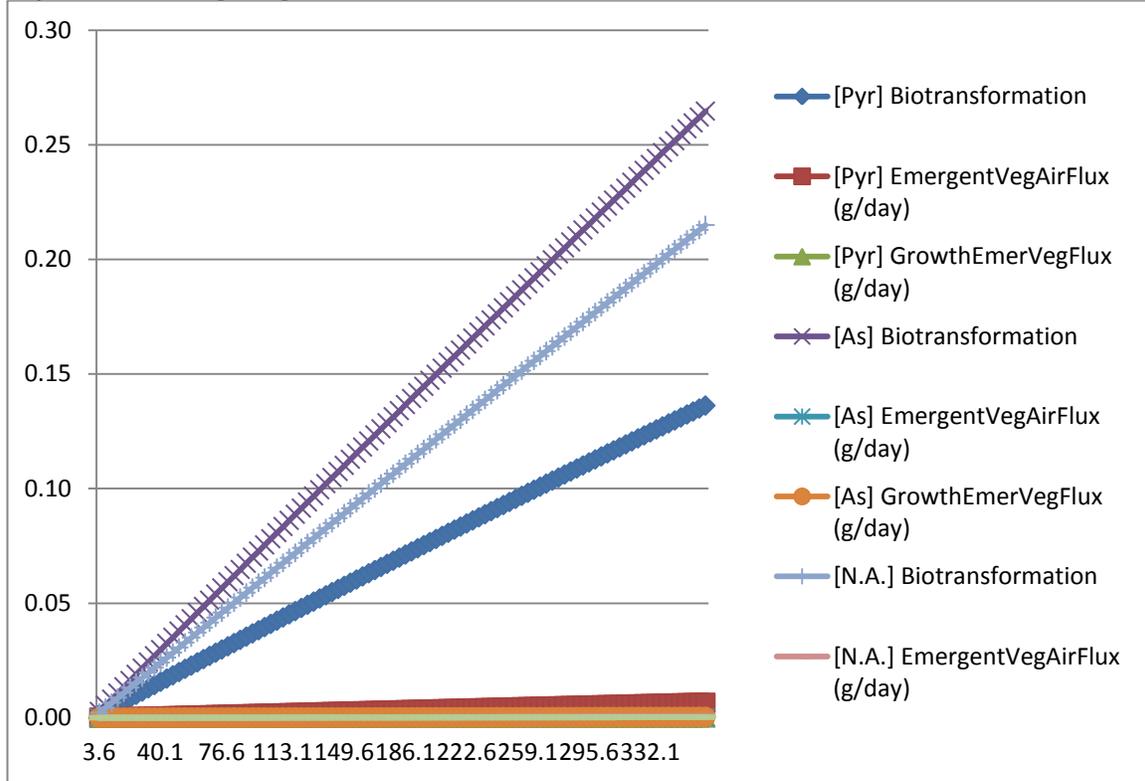


Figure D-4: Flux diagram of contaminant fate through VSSF flow wetland – Pyrene

*All values in $g \cdot day^{-1}$

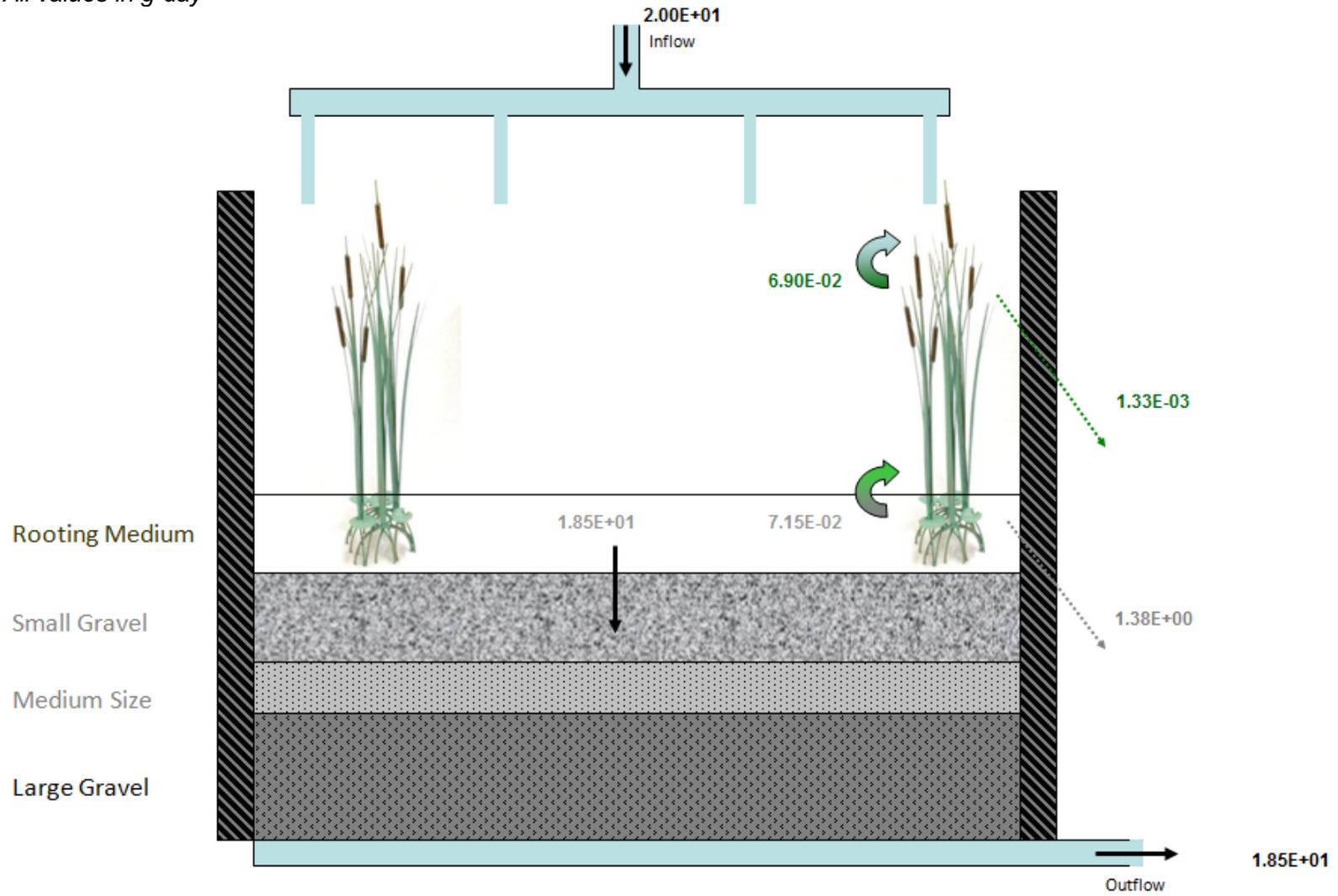


Figure D-5: Flux diagram of contaminant fate through VSSF flow wetland – Arsenic

*All values in $g \cdot day^{-1}$

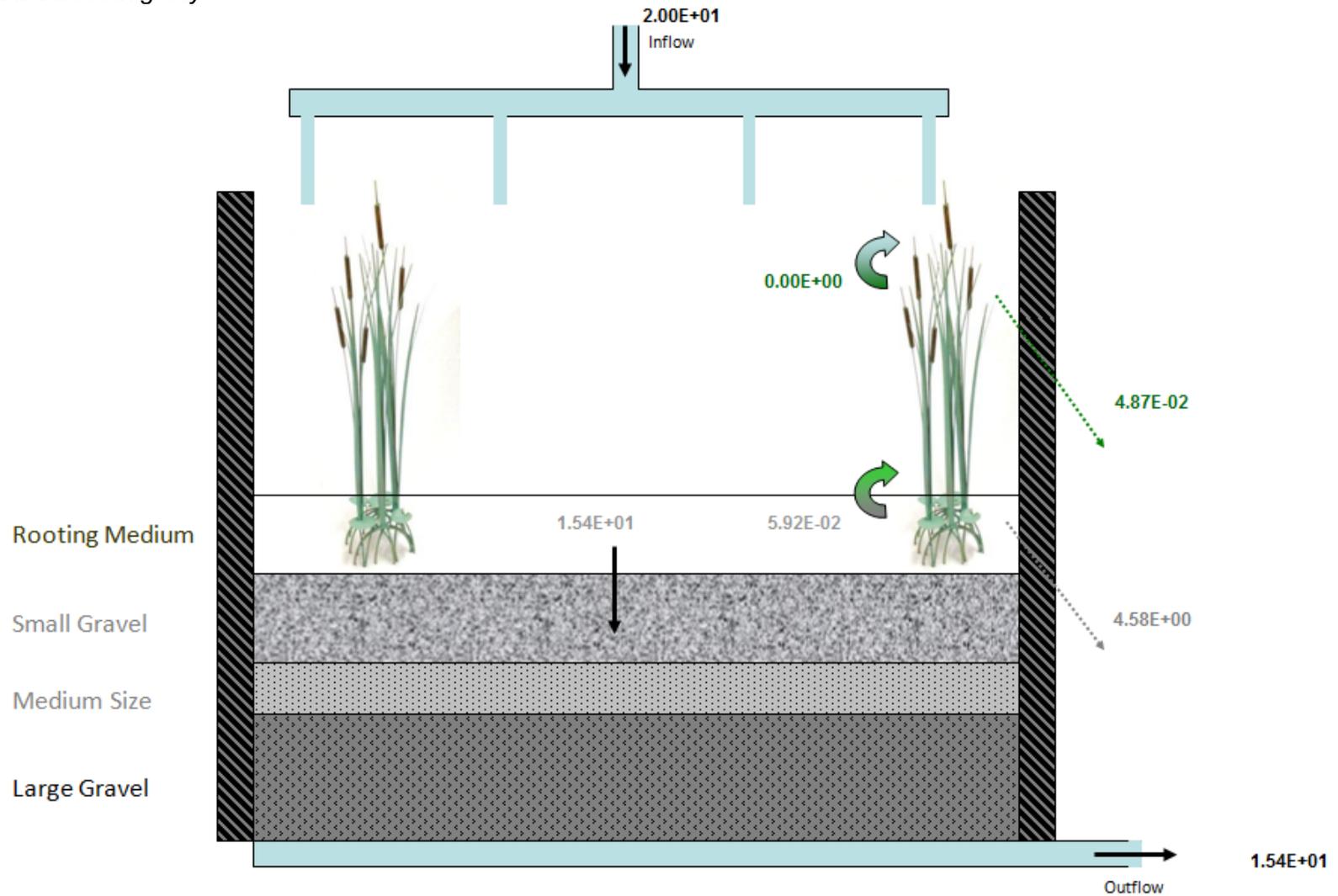


Figure D-6: Flux diagram of contaminant fate through VSSF flow wetland – Naphthenic Acid
 *All values in $g \cdot day^{-1}$

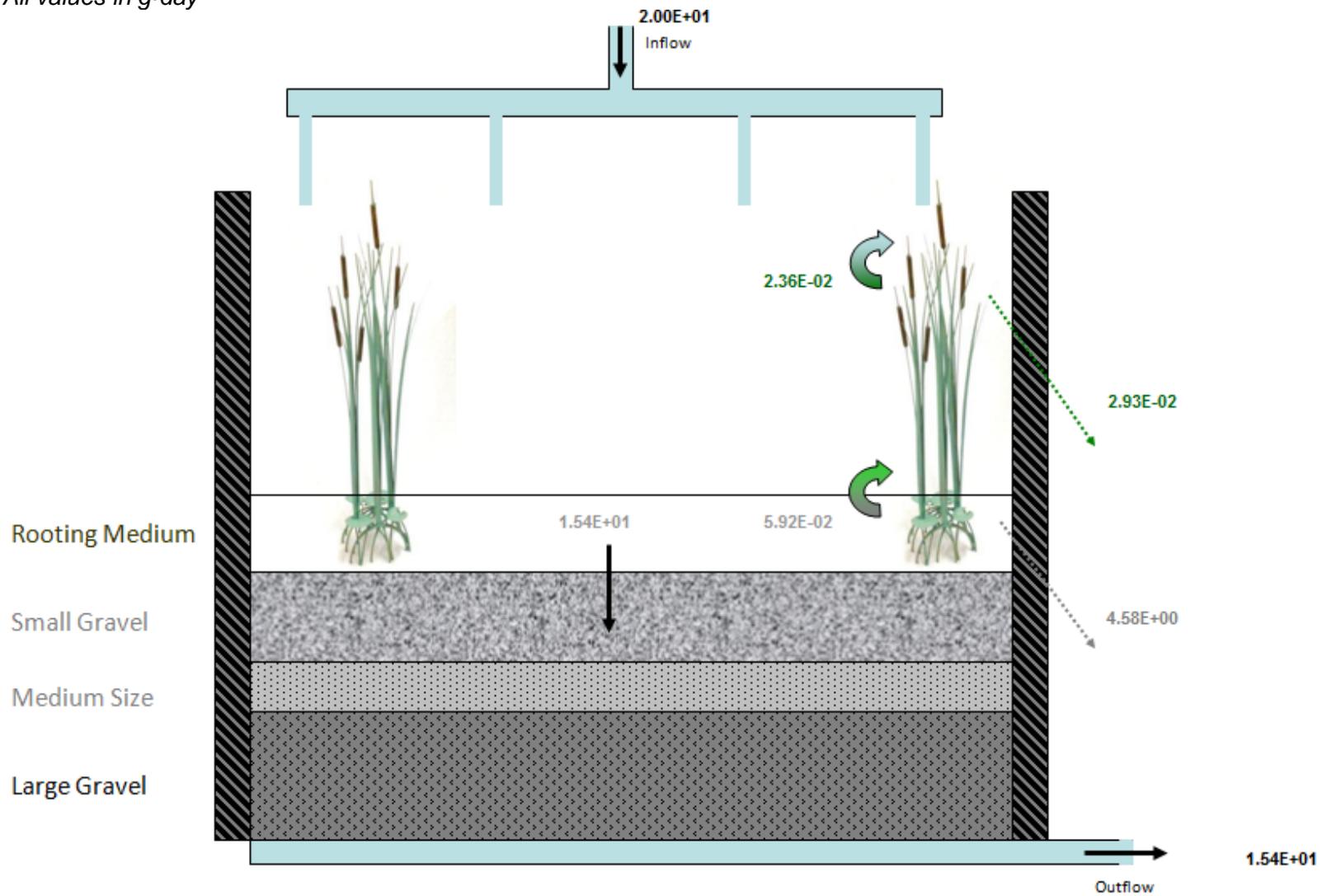


Figure D-7: VSSF temporal biota concentration – pyrene

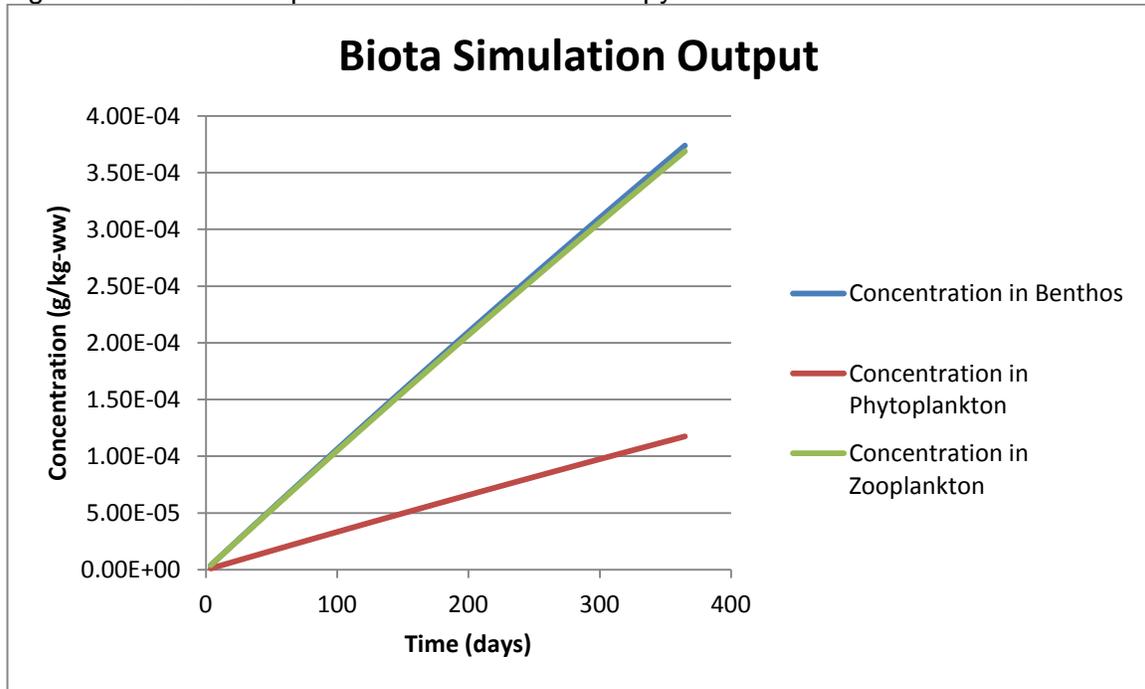


Figure D-8: VSSF temporal biota concentration – arsenic

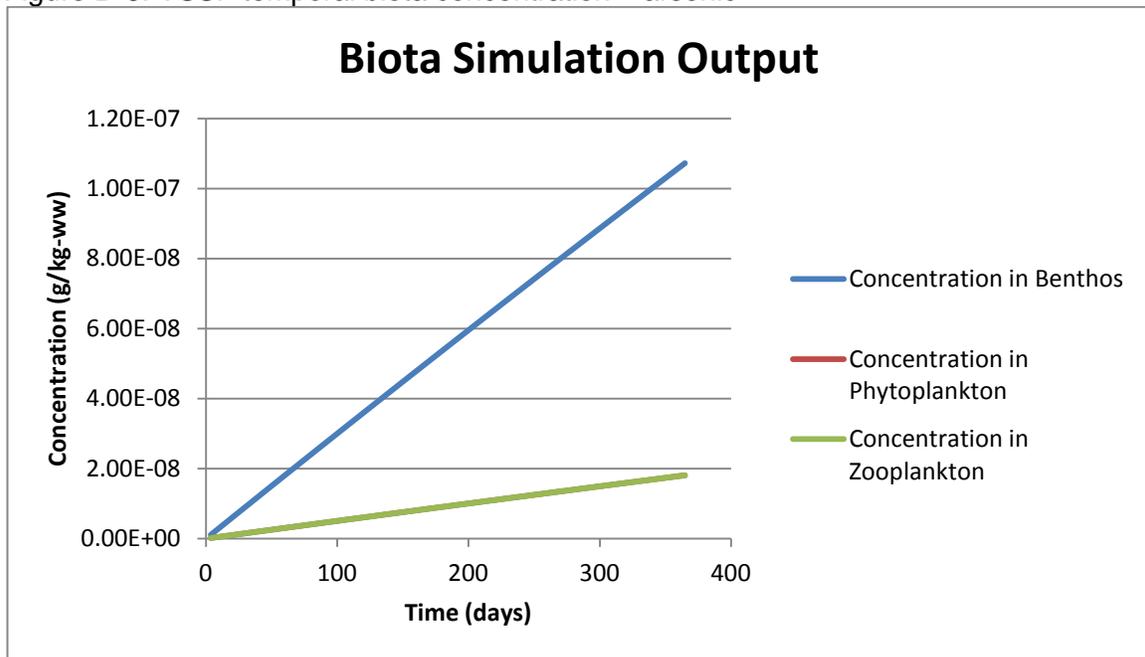
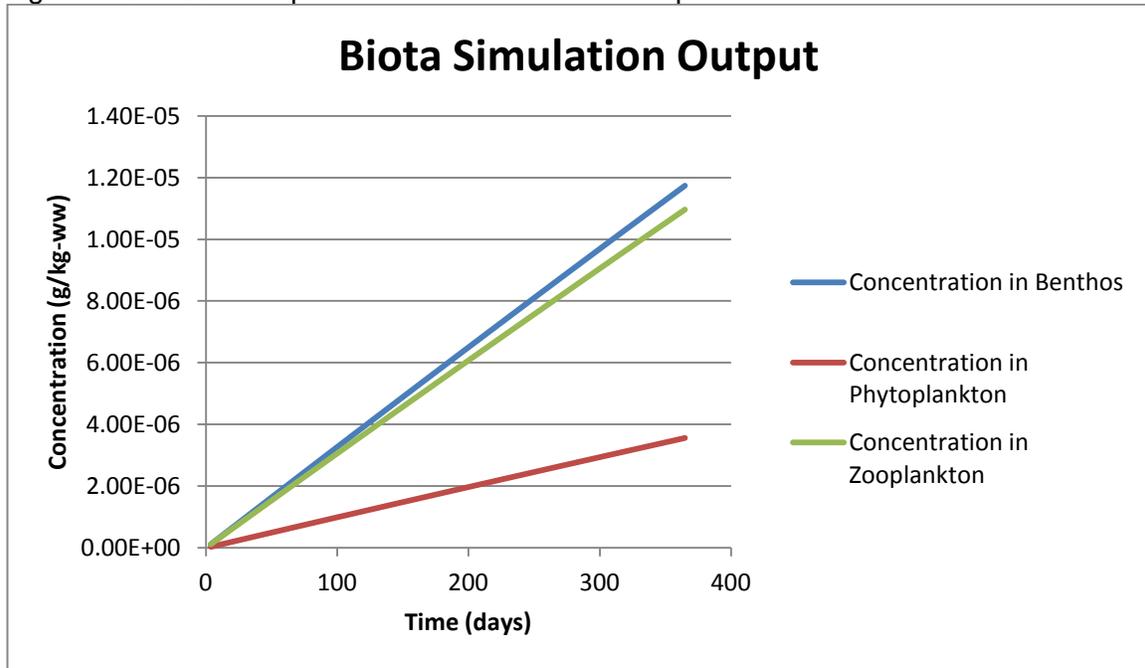


Figure D-9: VSSF temporal biota concentration – naphthenic acid



Appendix E: Data File Index

Please refer to folders:

- Alex.Cancelli – Engineered Wetland Models
- Alex.Cancelli – Model output for U.S. EPA TRI list evaluation

The USB memory-drive referred to in this appendix forms a part of this work.

Excel data files are intended to be opened with MS Excel or similar spreadsheet interface programs.

Data files:

| | |
|--|----------|
| • †Alex.Cancelli – FWS Model (Pyrene) | 4,228 KB |
| • †Alex.Cancelli – FWS Model (Arsenic) | 4,226 KB |
| • †Alex.Cancelli – FWS Model (Naphthenic Acid) | 4,229 KB |
| • †Alex.Cancelli – FWS Model (Chemical Universe and TRI List) | 4,584 KB |
| • †Alex.Cancelli – HSSF Model (Pyrene) | 3,667 KB |
| • †Alex.Cancelli – HSSF Model (Arsenic) | 3,677 KB |
| • †Alex.Cancelli – HSSF Model (Naphthenic Acid) | 3,667 KB |
| • †Alex.Cancelli – VSSF Model (Pyrene) | 4,335 KB |
| • †Alex.Cancelli – VSSF Model (Arsenic) | 4,362 KB |
| • †Alex.Cancelli – VSSF Model (Naphthenic Acid) | 4,421 KB |
| • ‡Alex.Cancelli – Appendix B.4 (Model output for U.S. EPA TRI list evaluation) | 2,501 KB |

†MS Excel file (.xls)

‡Adobe file (.pdf)