# Phosphorus Removal in a Vertical Up-Flow Constructed Wetland

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# Foreword

**The Road Not Taken**

Two roads diverged in a yellow wood,
And sorry I could not travel both
And be one traveler, long I stood
And looked down one as far as I could
To where it bent in the undergrowth;

Then took the other, as just as fair,
And having perhaps the better claim
Because it was grassy and wanted wear,
Though as for that the passing there
Had worn them really about the same,

And both that morning equally lay
In leaves no step had trodden black.
Oh, I kept the first for another day!
Yet knowing how way leads on to way
I doubted if I should ever come back.

I shall be telling this with a sigh
Somewhere ages and ages hence:
Two roads diverged in a wood, and I,
I took the one less traveled by,
And that has made all the difference.

Robert Frost

# Dedication

Je dédie ce travaille à ma grand-mère Gilberte Lavigne;
merci pour ton sourire, for the graceful exit.

# Acknowledgements

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# Statement of the role of the authors

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Michel Duteau is responsible for all parts of the work presented herein and is the main author of all parts of this thesis. He designed and carried out the experiments, organizing and leading the field work. He also conducted all lab analyses, prepared the buffers, reagents and standards, as well as calibrated the instruments and performed the measurements. Finally, he performed all data analyses and interpreted the observations with due statistical scrutiny. Dr. Clark commented on all preliminary versions of the thesis, and provided insights throughout the writing process. Dr. Prasher gracefully provided the experimental site and lab facilities and provided guidance in the experimental design. The final version was corrected by Dr. Dominic Frigon (McGill U., Department of Civil Engineering).

# Abstract

Accelerated eutrophication of freshwater ecosystems led by agricultural activities has raised concerns in Southern Quebec and other industrialized locales. Phosphorus being the main culprit, effort has been made to rationalize application and curtail exports of this nutrient with agricultural best management practices as first and second lines of defense. Still, concentrations of phosphorus and nitrogen in typical tile drainage return flow wastewater exceeds the eutrophication-prevention criterion set by the Quebec Ministry of Environment (0.030 mg TP $\cdot L^{-1}$; MDDEP, 2009) and the ecosystem safeguard criterion suggested in the literature (1.10 mg TN $\cdot L^{-1}$; Chambers et al., 2012), with cumulative loads becoming a major contributor to the poor quality of downstream aquatic ecosystems, especially when poorly diluted, as is the case with heavily drained agriculture-dominated watersheds.

As a third line of defense in a best management practices package, constructed wetlands (CWs) for the interception of phosphorus are proposed. These wetlands can also mitigate nitrogen and contribute other ancillary benefits. They can be implemented at the mouth of tile drainage or at the confluence of a few outlets, i.e. drainage ditches or first order streams.

The main phosphorus removal mechanisms in a CW are adsorption and precipitation with positively charged ions contained in the substrate (e.g., $Ca^{2+}$, $Fe^{3+}$, $Al^{3+}$). Physico-chemical conditions prevailing in the system – especially redox potential – are major factors influencing these reactions. A sub-surface vertical up-flow system seems most appropriate, as it maximizes potential interaction of pollutant-charged water with the substrate constituents, allowing full radial contact and deterring preferential flow. These wetlands also are efficient longer into the cold season, given the underground nature of the flow.

An experiment was conducted on McGill's CW research site, situated in Ste-Anne-de-Bellevue, Québec, so as to ascertain the efficiency of a vertical up-flow constructed wetland in treating tile drainage return flow wastewater. During 14 weeks, the capacity to remove the different forms of phosphorus was evaluated, as was the removal of nitrogen compounds. The effluent quality was also compared to the criteria (Chambers et al., 2012; MDDEP, 2009). The wetland had a dimension of 9.15 $m^2$ and the target flow rate was 1 $L \cdot min^{-1}$, which is representative of a drainage system serving a 3 ha field in typical Southern Quebec conditions (wetland:watershed ratio: 0.03%; hydraulic loading rate: 0.16 $m \cdot d^{-1}$; hydraulic retention time: 2.99 days). The target influent concentrations were 0.300 mg TP $\cdot L^{-1}$, and 10.00 mg TN $\cdot L^{-1}$, which – again – is typical of Southern Quebec tile drainage return flow.

The wetland was efficient at removing 84% TP and 86% TN, but the treated wastewater was still above the criteria in 76% and 69% of the cases for TP and TN, respectively.

Recommendation is made to supplement the wetland with a dedicated phosphorus-removal substrate so as to further enhance its performance, and to increase the wetland:watershed surface ratio to abate more nitrogen compounds. Community support is key to the implementation of agricultural best management practices. Hence, suggestion is made to include third-line-of-defense structures such as constructed wetlands in the set of initiatives that are financially aided through governmental programs, such as Prime-Vert (MAPAQ, 2009) of Québec.

# Résumé

L’eutrophisation accélérée des écosystèmes aquatiques dû aux activités agricoles donne lieu à des inquiétudes tant dans le Québec méridional que dans d’autres pays industrialisés. Le phosphore étant le principal coupable, des efforts importants ont été consentis à la réduction des exportations de ce nutriment, avec l’instauration de première et deuxième lignes de défense dans une série de pratiques de gestion agricole optimales. Néanmoins, les concentrations de phosphore et d’azote dans les eaux usées de retour de drainage agricole typiques sont, à ce jour, encore au-dessus des critères pour la prévention de l’eutrophisation (0.030 mg TP $\cdot L^{-1}$; MDDEP, 2009) et de maintien de la santé des écosystèmes aquatiques (1.10 mg TN $\cdot L^{-1}$; Chambers et al., 2012), la charge cumulative étant un contributeur majeur à la piètre qualité des écosystèmes aquatiques situés en aval, en particulier lorsque peu diluée, comme c’est le cas par exemple dans les bassins versants à dominante agricole où le drainage est fortement présent.

À titre de troisième ligne de défense dans la série de pratiques de gestion agricole optimales, les marais filtrants ciblant l’interception du phosphore sont proposés. Ces marais peuvent également atténuer l’azote et apporter des bénéfices collatéraux. Ils peuvent être installés à l’embouchure de drains agricoles, ou bien à la confluence de plusieurs sorties, comme par exemple dans un fossé agricole ou un cours d’eau d’ordre un.

Les deux principaux mécanismes d’enlèvement du phosphore sont l’adsorption et la précipitation avec des ions à charge positive qui sont contenus dans le substrat (e.g., $Ca^{2+}$, $Fe^{3+}$, $Al^{3+}$). Les conditions physico-chimiques qui règnent dans le système – en particulier le potentiel d’oxydo-réduction – sont des facteurs importants pouvant influencer ces réactions. Le système à flux vertical ascendant sous-surfacique est celui qui semble le plus approprié, puisqu’il maximise les interactions entre l’eau chargée de polluants avec les constituants du substrat, permettant un plein contact radial et prévenant les flux préférentiels. Ce type de marais est aussi efficace plus longtemps pendant la saison froide, étant donné la nature sous-surfacique du flux.

Une expérience a été menée au site de recherche de l'Université McGill, situé à Sainte-Anne-de-Bellevue, au Québec, afin de vérifier l'efficacité d'un marais à flux vertical ascendant pour traiter les eaux usées de retour de drainage agricole. Pendant quatorze semaines, la capacité d'enlèvement du phosphore sous ses différentes formes a été évaluée, de même que l'enlèvement des composés azotés. La qualité de l'effluent traité a aussi été comparée aux critères de qualité (Chambers et al., 2012; MDDEP, 2009). Le marais avait une surface de 9.15 $m^2$ et le débit cible était de 1 L $\cdot min^{-1}$, ce qui est représentatif d'un système de drainage desservant un champ de 3 ha dans les conditions typiques du Québec méridional (ratio bassin versant:marais filtrant : 0.03%; charge hydraulique : 0.16 $m \cdot d^{-1}$; temps de rétention hydraulique : 2.99 jours). Les concentrations cibles dans l'affluent étaient de 0.300 mg TP $\cdot L^{-1}$ et 10.00 mg TN $\cdot L^{-1}$, ce qui – encore là – correspond à un retour de drainage agricole dans les conditions du Québec méridional.

L'efficacité du marais est telle qu'un enlèvement de 84% du phosphore total et 86% de l'azote total a été observé, mais l'effluent traité outrepassait encore les critères dans 76% et 69% des cas pour ce qui est du phosphore total et de l'azote total, respectivement.

Il est recommandé d'ajouter au marais un substrat dédié à l'enlèvement du phosphore, afin de renforcer la performance, ainsi que d'augmenter le ratio surfacique marais filtrant:bassin versant, afin de diminuer davantage les composés azotés. Le support par la communauté est un élément clé dans l'instauration de pratiques de gestion agricole optimales. Ainsi donc, il est suggéré d'inclure les structures de troisième ligne de défense telles les marais filtrants dans l'ensemble d'initiatives qui sont financièrement appuyées par les programmes gouvernementaux, tels le programme Prime-Vert (MAPAQ, 2009) au Québec.

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# Abbreviations and symbols

| | |
|---|---|
| $NH_4^+ + NH_3$ | Ammonia Nitrogen |
| $NH_3$ | Ammonia |
| $NH_4^+$ | Ammonium |
| BMP | Best Management Practices |
| BOD | Biochemical Oxygen Demand |
| CEC | Cation Exchange Capacity |
| CW | Constructed (treatment) Wetland |
| DAHP | Dissolved Hydrostable Phosphorus |
| DO | Dissolved Oxygen |
| SP | Soluble Phosphorus |
| SRP | Soluble Reactive Phosphorus |
| FWS | Free Water Surface |
| HRT | Hydraulic Retention Time |
| HLR | Hydraulic Loading Rate |
| HDPE | High Density Poly Ethylene |
| IDL | Instrument Detection Limit |
| $N_i$ | Inorganic Nitrogen |
| $P_i$ | Inorganic Phosphorus |
| K-M | Kaplan-Meier (estimator) |
| LOQ | Limit of Quantitation |
| MDL | Method Detection Limit |
| $mg \cdot L^{-1}$ | Milligrams per Liter ($=g \cdot m^{-3}$, Grams per cubic meter) |
| MDDEP | Ministry of Environment |
| $NO_2^-$ | Nitrates |
| $NO_3^-$ | Nitrites |
| NPS | Non-Point Sources (pollution) |
| OM | Organic Matter |
| $N_{org}$ | Organic Nitrogen |
| $P_{org}$ | Organic Phosphorus |
| ORP | Oxidation-Reduction (Redox) Potential |
| Eh | Oxidation-Reduction (Redox) Potential |
| rep | Replicate |
| SSF | Sub-Surface Flow |
| SShF | Sub-Surface Horizontal Flow |
| SSvUF | Sub-Surface Vertical Up-Flow |
| SSvDF | Sub-Surface Vertical Down-Flow |
| SS | Suspended Particles |
| XP | Particulate Phosphorus |

# Chapter 1 Introduction

## 1.1 Context

### The problem: excessive phosphorus in freshwater ecosystems

Southern Quebec is faced with increasing surface water quality problems: in the last few years, an increasing number of freshwater ecosystems have persistently been plagued with nutrient imbalance, triggering accelerated eutrophication, characterized by cyanobacterial blooms. Season 2007 saw the cyanobacterial bloom burden increase to unprecedented levels, with 156 water bodies stricken in the province (> 20, 000 cells per mL water) (MDDEP, 2012b). Over the 2007-2011 period, the tally varied between 108 and 156 (MDDEP, 2011b). With time, affected lakes tend to get blooms that are more frequent and more extensive (MDDEP, 2011a). The problem is not expected to disappear anytime soon, as the impetus leading to this problem is slow to be curbed, much less to be reversed.

It is generally accepted that concentrations of phosphorus (P) higher than the carrying capacity of a freshwater ecosystem is the main trigger of cyanobacterial blooms and that cyanobacterial blooms are symptomatic of accelerated eutrophication, sometimes marking a regime shift (Carlson, 1977; Carpenter et al., 1998; Correll, 1999; Vollenweider, 1971; Wetzel, 1983). Eutrophication can be described as the gradual enrichment of a watercourse (Schindler, 1977). Overgrowth of plants is the single most visible symptom of this endowment (Anderson, 2005), but the vegetation increase is only the first in a cascade of detrimental effects brought about by excessive P (Vollenweider, 1968). The consequential alteration of ecosystem services has a tremendous impact on the economy, public health and general human well-being (Dodds et al., 2009; Pretty et al., 2003; Walker Jr, 1983; Wilson and Carpenter, 1999). In cases of cyanobacterial overgrowth, suitability of water for any usage is compromised, for these photosynthetic organisms can release powerful toxins that are capable of causing significant harm or death to wildlife as well as human beings (Hoppu, 2005; Izaguirre et al., 1982; Kotak et al., 1994; Leflaive and Ten-Hage, 2007; Soares et al., 2005).

The median concentration of total phosphorus (TP) in rivers and lakes of Southern Quebec is consistently found to be two to six times higher than Quebec Ministry of Environment's 0.030 mg TP $\cdot L^{-1}$ criterion for the prevention of eutrophication of surface water (Gangbazo et al., 2005). Thus, Quebec's Office of Environmental Public Hearing (BAPE – "Bureau d'audiences publiques en environnement") recognized phosphorus as the pollutant that causes the greatest impairment of surface waters in Southern Quebec (BAPE, 2000).

In the St. Lawrence River, the TP concentration in the main river increases from 0.008 mg TP $\cdot L^{-1}$ at its entrance to Quebec from Ontario/New York State – at Cornwall island (7800 $m^3 \cdot s^{-1}$) –, to 0.014 mg TP $\cdot L^{-1}$ before Montreal, and 0.036 mg TP $\cdot L^{-1}$ at Quebec city (12,600 $m^3 \cdot s^{-1}$; Rondeau et al., 2005). In a fluvial lake situated halfway between Montreal and Quebec city (Lac St-Pierre: ~300 $km^2$), the surface water quality criterion (0.030 mg TP $\cdot L^{-1}$) is exceeded on over 40% of the surface area (Hudon and Carignan, 2008). St. Lawrence River traverses meridional Quebec West to East and drains the whole area, on top of carrying all waters exiting the Great Lakes. Half the population of Quebec (total: 8 million people) uses the St. Lawrence as a drinking water source and it supports a plethora of leisure and industrial activities, representing an essential habitat for a number of species (MDDEP, 2012b). Two major rivers that flow into Lac St-Pierre, draining most of the Montérégie (agricultural) area (R. Yamaska and R. Richelieu), show chronic excess of the 0.030 mg TP $\cdot L^{-1}$ eutrophication prevention criterion (Roy, 2002).

The situation prevailing in Southern Quebec is similar to that encountered in many other locales, with eutrophication being the most ubiquitous water quality impairment on the planet (Carpenter et al., 1998; Schindler et al., 2008; Sharpley et al., 2001; Smith, 2003). In North America, the Gulf of Mexico, Lake Erie (Beeton, 1961; Stumpf et al., 2012), Chesapeake Bay (Kemp et al., 2005), Missisquoi Bay of Lake Champlain (Manley and Manley, 1999) and Petit-Lac-St-François (MDDEP, 2011b) are all examples of heavily eutrophication-plagued ecosystems. The Baltic Sea in Europe (Conley et al., 2007) and the Rotura Lakes of New Zealand (Bourke, 2006) face the same situation. Rapidly developing areas are not left out; for instance, eutrophication and cyanobacteria outbreaks are augmenting tremendously in the Yunan Province's Lake Region of China (e.g., Dianchi Lake, Taihu Lake, Guanting Reservoir, etc.; Lu et al., 2010). Van Ginkel (2011) expresses the same concerns for South Africa. Overall, an estimated 48% of lakes in North America, 41% in South America, 53% in Europe, 54% in Asia, and 30% in Africa are eutrophic (World Resources Institute, 2012).

### The cause: continuous exports of agricultural phosphorus through runoff

Phosphorus pollution sources are numerous, but the greatest impairment of Southern Quebec surface waters is led by agricultural non-point sources (NPS), among which agricultural runoff is the chief contributor (BAPE, 2000). NPS is also referred to as "diffuse pollution" or "non-discrete pollution". Runoff comprises all waters moving over and through the soil. In the agricultural realm, agricultural runoff is viewed as the combination of all waters that leave an agricultural field, whether through surface flow or through tile drainage return flow. Thereby, agricultural runoff is somewhat similar to "agricultural stormwater" (USEPA, 1993). Pollution coming from tile drainage systems sometimes is referred to as "distributed non-point pollution", as the drain outlets are specifically located, but scattered over the territory and often difficult to locate. The P that is found in agricultural runoff comes from fertilizers applied onto fields to upkeep agriculture production, in the form of liquid or solid chemical fertilizers and manure (USEPA, 1993). The water comes from precipitation, snowmelt and aquifer resurgence. When the conditions meet, water carries P away from the field into the hydric system through erosion, leaching and runoff. The conditions and factors leading to P-export will be explored further on. Unlike nitrogen (N) or carbonaceous biological oxygen demand (BOD) pollution, P cannot be transformed into a gaseous form that could escape the system; the only way to locally remove it is through transport. When a continuous stream of P gets into the hydric system, it can accumulate in the environment.

Hudon and Carignan (2008) found that the reason for the sharp rise in P concentration between Montreal and Quebec City in the St. Lawrence River is that 50% of Quebec's total cropland drains and discharges in the St. Lawrence over that stretch (1.85 million ha in 2001; Statistics Canada, 2001). As a matter of fact, 85% of the total P load present in the fluvial Lac St-Pierre of the St. Lawrence River is of agricultural origin, the remainder being from municipal effluents (Hudon and Carignan, 2008). In general, it is estimated that in Quebec, upwards of 70% of excess P in cyanobacteria-plagued lakes and streams comes from agricultural non-point sources (Beauchemin et al., 2003; Chambers et al., 2012; Michaud et al., 2005). In fact, a majority of Quebec's agricultural watercourses are considered *degraded*, with median summer TP concentrations superior to the 0.030 $mg \cdot L^{-1}$ water quality criterion (Simard, 2004).

In the USA, many studies have attested to the dominance of NPS pollution as a main contributor to current water quality impairment, with agricultural runoff as a major culprit (e.g., Baker, 1992; Kellogg et al., 1994; Parry, 1998; Reinhardt et al., 2005; USEPA, 1988). In Taiwan, Kao et al. (2001) similarly finds that NPS is among the major causes of freshwater degradation. Still, Kokik (2010) estimates that agriculture provides 45% of the net Swedish P load to the eutrophication-plagued Baltic Sea. Kronvang et al. (2005) have shown that in most Northwestern and Southern European countries, P-export from small agricultural watersheds is significantly higher than that from similar non-agricultural watersheds. Heathwaite et al. (1996) claim that eutrophication of many European rivers and lakes is mainly led by agricultural NPS.

### Legislation evolution

Point sources of P, including farm effluents and industrial discharges through pipes or domestic and municipal wastewaters, are easily identified and are now somewhat under control, following the application of stringent regulations and huge capital investments in recent years so as to cap and diminish the amount of nutrients that get into waterways. This effort is still ongoing, with for instance a strengthening of P requirements for Quebec municipal wastewater treatment plants to come into force by 2017 (MDDEP, 2012c) and 40% reduction of P release from fish farms in the 2004-2014 period (Comeau et al., 2006). It has to be noted that P pollution was much worse before inception of this effort, with several portions of major rivers being subject to anoxic conditions and large scale fish kills, with ominous cyanobacterial blooms. Over the past few decades, it can certainly be said that water quality did improve in Quebec (Painchaud, 1997a; 1997b).

The gist now is on NPS, given that it has come to constitute the greater part of P sources (Kronvang et al., 2005; Sharpley et al., 1994). However, this NPS pollution is relatively more difficult to monitor, regulate and control, as it is derived from huge areas of land (Kronvang et al., 2005; Reinhardt et al., 2005). In Quebec, the “Règlement sur les exploitations agricoles (REA)” which was enacted in 1991 to replace the former anti-pollution act, called for a diminution of agricultural NPS. Ultimately, the “Politique nationale de l’eau” (MDDEP, 2002a) proposed water quality criteria that apply to the agricultural realm and everywhere else. Already in 1997, Gangbazo advocated for agricultural wastewater TP discharge limits, but as of 2013, no such discharge limits have been implemented in Quebec or anywhere else in North America.

### Proposed solution: constructed wetlands for the treatment of agricultural tile drainage return flow

Constructed treatment wetlands (CWs) are proposed as a tool to remediate excessive P-export from agricultural tile drainage. CWs can also treat a multitude of other pollutants that are susceptible to being conveyed in the return flow (e.g., nitrates, pharmaceuticals, etc.). Moreover, they can bring ancillary benefits such as flood control and biodiversity support. CWs are particularly well adapted to the treatment of large volumes of low-concentration wastewaters (Kovacic et al., 2000), such as those expelled through drainage return flow (Raisin and Mitchell, 1995). Moreover, they can sustain the high variability and unpredictability of the stochastic flow rate and quality that is inherent to tile drainage return flow wastewater. CWs can be implemented at the outlet of tile drains or in collector ditches or first order agricultural streams. They are relatively economical, requiring low initial investment capital and minimal maintenance, plus they are easily adoptable.

CWs can be considered as a third line of defense in a global Best Management Practices (BMP) package. The two first lines of defense (reduced P-application and in-field measures) are effective and can potentially bring the concentrations in agricultural streams back to background levels (Broussard and Turner, 2009). However, given the legacy P concentrations (Kleinman et al., 2007) in many situations, these results will be felt only in the mid- to long-term, if at all (Grimvall et al., 2000). On the other hand, a CW's results can be seen in the first weeks and will last as long as the device is maintained efficient. However, it is essential that CWs installation be accompanied by proper nutrient reduction and retention measures – the contrary would be counterproductive. Given the urgency of the situation, especially in heavily impaired watersheds, CWs are a must.

CWs such as those that are proposed here are likely to be first implemented in watersheds where the downstream lake would already be affected by accelerated eutrophication – this is where they are most needed, and there are plenty of such situations.

## 1.2 State of the science

A strong body of literature exists on CWs as a wastewater treatment system. For instance, Kadlec and Knight (1996) and Kadlec and Wallace (2009) offer syntheses of CWs usage and research in the North American context. Vymazal et al. (1998) and Vymazal and Kröpfelová (2008) offer thorough reviews of CW technologies in the European context, where sub-surface flow systems are common. Other monographs include Tchobanoglous (1993), and a number of fact-sheets, reports and design manuals provide useful insights for the conception of CWs, such as USDA-NRCS (1995) and Melbourne Water (2010). An Ontario (Canada) institution is particularly active in the domain of CW research and innovation: the Centre for Alternative Wastewater Treatment, at Fleming College (Lindsay, ON). For a number of years, researchers have been maintaining, updating and using the North America Data Base on CW performance (Knight et al., 1993; USEPA, 2000a).

However, CWs meant to treat nonpoint sources, such as stormwater or agricultural runoff, have not received as much attention as CWs for point sources. The reason is that these wastewaters are highly variable in concentrations, and dependant on land usage and environmental stochasticity. Nevertheless, a number of studies have illustrated their capacity in treating agricultural runoff, including phosphorus, sometimes focussing on drainage return flow, and covering specific aspects such as operation in cold climates or the type of flow regime. Although emerging, the whole sector of end-of-field water treatment technologies, such as CWs, is a very active one, for agriculture-induced eutrophication needs to be addressed urgently (Buda et al., 2012).

Still, the functioning of CWs for treating agricultural drainage return flow is not well understood yet. The normalisation of their efficiency will come through the development of proper design criteria, which lies in the improvement of the comprehension of their functioning (Mitsch and Gosselink, 2000).

Since 2004, McGill University's Bioresource Engineering Department has been conducting research on CWs treating agricultural drainage wastewaters, with the objective of developing such guidelines for optimal design. For this purpose, an experimental site was built on the Macdonald Campus and has since been used for a number of experiments and studies, including studies by Yates (Yates, 2008; Yates, 2010; Yates and Prasher, 2009) and by Hussain (Hussain et al., 2011a; Hussain, 2011; Hussain and Prasher, 2011; Hussain et al., 2011b; Hussain et al., 2012).

## 1.3 Purpose and objectives

The purpose of the research conducted as part of this project is to bring together elements of information concerning the performance of CWs in the reduction of water pollution coming from agricultural tile drainage, especially P, in view of contributing to the development of design guidelines.

The specific objectives are:

- To ascertain the performance of a sub-surface vertical up-flow (SSvUF) CW in the removal of P
- To understand the P-removal mechanisms involved

In order to meet these objectives, a pilot-scale experiment was conducted at McGill's CW experimental site.

## 1.4 Intended audience

This thesis is intended in part for policy-makers, who hold the key to the implementation of CWs for the treatment of agricultural tile drainage return flow. Indeed, the main limitation is cost, for agricultural producers currently are not required to pay the costs of damages inflicted on aquatic ecosystems through non-point pollution. When public programs are in place to support agriculture, along with consequent legislation, then the right best management practices are implemented (D'Arcy and Frost, 2001). Consequentially, pollution decreases, and water usage and services can return and last. In Norway and Finland, for instance, 70% of the cost of construction of CWs to treat agricultural runoff (surface and tile drainage return flow) is sponsored by the national agricultural authorities; this initiative is based on the positive results of CWs, even in the rugged landscape of Northern Europe (Braskerud et al., 2005b; Liikanen et al., 2004).

## 1.5 Format (overview)

The first part of the thesis is intended as an introduction to the topic, with the rationale for the experiment that was conducted. After introducing the water quality situation in Southern Quebec and beyond, the P dynamics will be explored, along with the polluting potential of tile drainage return flow wastewaters and an overview of agriculture practices in Southern Quebec. A presentation of the CW technology follows, with a special emphasis on P removal. The third part of the thesis is an article reporting on an experiment accounting for P removal in a SSvUF CW. At the end of the thesis the findings are summarized and conclusions are presented.

## 1.6 Scope

The costs incurred by the implementation, maintenance and operation of CWs are not considered in this thesis, nor are the materials that can be used to build them. Neither addressed is their production of wastes, such as contaminated substrates, green-house gases, plant material, etc., or P recovery from wastes. The whole issue of dedicated substrates is also left to future research. The legal aspects of P release and P treatment, as well as the financing of CWs are only mentioned, as is the topic of Best Management Practices (BMPs).

# Chapter 2 Literature review

## 2.1 Phosphorus dynamics

### What is phosphorus?

Phosphorus (P) is the 11th most abundant chemical element in the Earth's crust (Valsami-Jones, 2004). To the contrary of the other elements involved in major biogeochemical cycles (CHNOPS), P virtually has no gas phase and its cycle thus involves no significant atmospheric flux (CRAAQ, 2008). Furthermore, P exists in only one valance state, tending to form three bonds; it is never found as an element in nature, but as an ion, which immediately bonds to another (Stevenson and Cole, 1986). It mainly occurs as an oxide (orthophosphates: $PO_4^{3-}$, $HPO_4^{2-}$, $H_2PO_4^-$, $H_3PO_4$). Phosphorus can also combine with carbon to form a multitude of organic compounds. As orthophosphates are highly (negatively) charged, they can easily form inorganic complexes or adsorb onto positively charged surfaces, such as the anion exchange sites present in the soil matrix. In water chemistry (and the present research work), P measures are expressed in terms of elemental P, while in agronomy, it is accounted for as $P_2O_5$.

Phosphorus is essential to life and is present in all ecosystems. Its presence is thus ubiquitous in soils as much as in water ecosystems. However, being the limiting nutrient, excess P is recognized as the main trigger to accelerated eutrophication of freshwater ecosystems (Carlson, 1977; Carpenter et al., 1998; Correll, 1999; Schindler, 1977; Vollenweider, 1968; 1971; Wetzel, 1983). Unlike nitrates or pharmaceuticals, the polluting potential of P is not eliminated by any degradation mechanism – it can only be prevented from entering the ecosystem, otherwise it accumulates locally or is moved away downstream, and thus can be said to be persistent.

The vast majority of P that is now used in agriculture comes from phosphate rock (calcium phosphate rocks, i.e. apatite). Phosphate rock, like oil, is a finite, non-renewable resource. To the contrary of nitrogen (N) fertilizer, it cannot be synthesized, and there is no substitute for P in crop growth. However, P can be recovered and re-used.

Modern agriculture depends heavily on P as fertilizer. This element is essential to current food production levels, and the waning of reserves definitely casts gloom over prospective food security (Schröder et al., 2010; Van Vuuren et al., 2010). The loss of agricultural P to water ecosystems represents the loss of a valuable resource that could have been otherwise used by the growing crops, whether now or in the future. Therefore, its sound management is essential, for now and for generations to come.

## Phosphorus thresholds in relation to eutrophication

All ecosystems are different, yet nutrient availability is what most often limits plant growth. In a terrestrial ecosystem, it is the concentration of nutrients contained in the water dwelling in the soil pores that determines vegetation productivity; conversely, the same is true of free water for a freshwater ecosystem – in this case, it is the concentration of nutrients that is contained in the free water that determines vegetation productivity. In the free water of a freshwater ecocystem, P and N generally are present at background or natural levels below 0.050 mg·L$^{-1}$ and 0.30 mg·L$^{-1}$, respectively (USEPA, 1993). Recent work has shown that in Southern Quebec (Canadian Shield and Appalachia), the background total phosphorus (TP) concentration is 0.007 mg·L$^{-1}$ (Berryman, 2006). In P limited situations, the soluble reactive fraction of P should be low to undetectable (<0.005 mg·L$^{-1}$) (Sharpley et al., 1992).

In the early work of Sawyer (1947) and Vollenweider (1968), it was demonstrated that in general, from a total phosphorus (TP) concentration of 0.020 mg·L$^{-1}$ or higher in running waters (rivers, streams, etc.), and 0.030 mg·L$^{-1}$ or higher in still waters (lakes, ponds, etc.), P stimulates the growth of algae, therefore accelerating eutrophication; if entirely inorganic and soluble ($SP_i$), a concentration of 0.010 mg·L$^{-1}$ is sufficient to have the same effect (Sharpley and Smith, 1989; Sharpley et al., 1992; Vollenweider and Kerekes, 1980). This is an order of magnitude less than what plants need to grow in a terrestrial ecosystem (0.200-0.300 mg TP ·L$^{-1}$ in the soil solution) (Tisdale et al., 1985). This disparity underlines the importance of limiting P-export from agricultural fields to downstream aquatic ecosystems (Daniel et al., 1998).

Unlike toxic chemicals, it is impossible to identify exact thresholds beyond which P concentration leads to impairment of an ecosystem, because P increase does not directly lead to measurable endpoints, such as death or behavioral change. Yet, through eutrophication, it induces significant changes in aquatic ecosystems which might be catastrophic and irreversible, and often are hysteretic. Those changes however do not occur at specific, universally-applicable concentrations, the eutrophication process being a continuum that evolves in a unique fashion for each waterbody. Nevertheless, using probabilistics, Carlson (1977) devised a system whereby lakes can be classified into trophic states, based on critical levels of key variables: the Trophic State Index (TSI) (MDDEP, 2012a). This index can be used to make a rough estimate of the lake's biological condition, or health, but the idea is to describe the lake productivity in relation to the thresholds that are likely to lead to regime shifts. The single most important threshold that comes out of this model is 0.030 mg TP $\cdot L^{-1}$, as measured in the surface-middle water of a lake, beyond which a lake is likely to move into a eutrophic state.

This knowledge brought USEPA (1986) to issue a first set of P concentration criteria for the prevention of eutrophication. Quebec's Ministry of Environment (MDDEP) built on this science to develop its own national water quality criteria for P (measured in the ice-free period) (MDDEP, 2009):

- For watercourses discharging into lakes where the environmental context is not problematic (i.e. not facing eutrophication yet), TP should not exceed 0.020 $mg \cdot L^{-1}$.
- In any lakes, TP should not exceed 0.030 $mg \cdot L^{-1}$.
- For oligo- and meso- trophic lakes, the water streams discharging into these should never exceed the lake's natural P level.

However, the goal of these P concentration criteria was arbitrarily determined: keeping or returning water to a condition established by informal judgement, without any consideration of local conditions (Boesch, 2002; D'Elia et al., 2003). The development of water quality criteria benefits from the integration of knowledge about reference conditions, which depend on geological history, food web interactions, biogeochemical processes, as well as wind and currents, etc. (Chambers et al., 2012).

A number of physical factors influence the potential effect of P in a freshwater ecosystem, such as type of substrate, depth, transparency, water temperature, flow speed and shading. These are not taken into account by the current quality criteria. Neither are additional stressors such as suspended sediments, pesticides, other nutrients, climate change, or the interactions among them and with P itself and the combined and possibly synergistic effects. Hence, the quality criteria for P have to be wisely used by expert judgment, taking into account the environment at hand. This is especially true for small agricultural streams, where a number of stressors are often present all at once (Chambers et al., 2012).

It is interesting to note that the current environmental objectives for wastewater discharge in Quebec are a complete order of magnitude more lax: 0.300 mg TP $\cdot L^{-1}$ – rather than the 0.030 mg TP $\cdot L^{-1}$ eutrophication-inducing threshold (MDDEP, 2007). These objectives are still guided by the dilution-is-the-solution principle, where the overall effect of discharge is hoped to be attenuated by mixing with a large water volume of lower concentration, which does not always happen. It has to be kept in mind that in the Canadian Shield or Appalachian conditions of Southern Quebec, the natural P concentration is estimated to be 0.007 mg TP $\cdot L^{-1}$ (Berryman, 2006). In any case, as of 2013, no wastewater discharge objective applies to agriculture yet.

Ideally, the water quality criteria would be applied on an adaptive approach (Holling, 1978), where the current status of the receiving freshwater ecosystem would continuously determine the level of control that need be exerted on the nutrient concentration of the discharged water (Chambers et al., 2012). The next step should be to develop P criteria that attempt to match the hydrosystem input to the hydrosystem output, in order to maintain reasonable balance. This way, it is the amount to be removed that would be calculated, and not the amount allowed to be exported. A promising avenue is the calculation of a Total Maximum Daily Load (TMDL) for a specific watershed, e.g., the Chesapeake Bay (Obama, 2009) .

## What are the different forms of phosphorus?

As seen above, P is ubiquitous and it has the particularity of having no gaseous phase – all forms are either solid or dissolved into liquid. In water environments as much as soils, only the forms that are less than 250 μm in size are usually accounted for in the calculation of total phosphorus (TP) content, disregarding fish, larger zooplankton, invertebrates, root debris and living plants, even though these can make up a sizeable fraction of the P that is contained in the ecosystem (Kitchell et al., 1975; Prepas, 1982).

As can be seen in Figure 2-1, the different TP forms are first classed according to their solubility in water: XP vs. SP. The latter is further separated into its mineral (SRP) vs. organic ($SP_{org}$) parts. These different forms have different levels of bioavailability – the speed at which it can be taken up by vegetation, plants and cyanobacteria alike – and hence different time-related eutrophication-inducing potential (Nürnberg and Peters, 1984; Rigler, 1964). P forms are rather non-conservative, as they can undergo many biogeochemical changes, i.e. even though the total quantity of P (TP) is stable, the pools are not static.

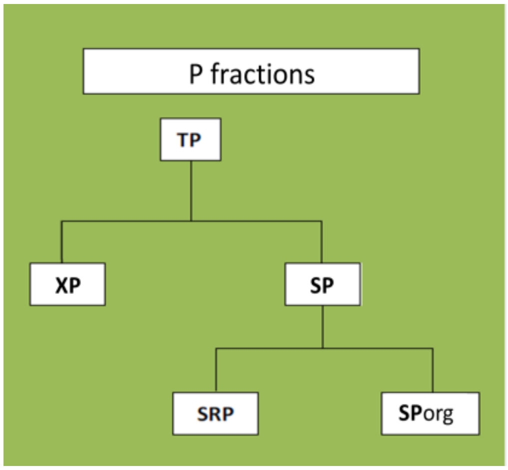

Figure 2-1: Phosphorus pools as commonly considered:
particulate phosphorus (XP), soluble phosphorus (SP), soluble reactive phosphorus (SRP) and soluble organic phosphorus ($SP_{org}$)
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Phosphorus pools in relation to their bioavailability

Particulate phosphorus (XP) can be divided into its inorganic ($XP_i$) and organic ($XP_{org}$) contents, but is usually considered as a whole, as both have a similar character in terms of bioavailability. Inorganic particulate phosphorus typically reflects the P which is adsorbed onto or precipitated with inorganic particulates, such as suspended sediments (clays and silts smaller than 250 µm in size), and primarily involves the association of P with Al, Fe or Ca. Organic particulate phosphorus, on the other hand, is part of minute organic components, such as bacteria, detritus and smaller zooplankton (smaller than 250 µm in size), and includes such compounds as phospholipids, nucleic acids, and humic acids (Nelson and Logan, 1983). In water, as XP is carried with a solid particle, it is less likely to sorb onto native minerals than SP.

For XP to be available for vegetation growth it has to go through decomposition and/or desorption and dissolution, whereby it is transformed into $SP_i$; these processes are rather slow

(Auer et al., 1998; Young, 1982). For this reason, XP was long said to be *non-bioavailable*. The bioavailability of XP actually is variable, the labile portion ranging from 10-90%, depending on the nature of the solid particle it is part of, its size and degree of P saturation, as well as the surrounding chemical environment, such as the redox potential and the presence of competing anions (e.g., $NO_3^-$) (Sharpley and Sisak, 1997). Thus, XP can be considered as *ultimately bioavailable*. As it is a long-term P pool, it has lower immediate eutrophication-inducing potential.

For technical reasons, SP is considered as all P contained in the solution after the sample has been passed through a 0.45 µm membrane filter (Reynolds and Davies, 2001). It thus includes all the $SP_i$ and $SP_{org}$ (<0.001 µm) but also colloidal P (0.001-0.45 µm). The SP pool is considered to be entirely *bioavailable*. The soluble inorganic phosphorus ($SP_i$) represents all P forms that are *readily bioavailable*. It can be further partitioned into soluble reactive phosphorus (SRP) and dissolved hydrostable phosphorus (DAHP). The first is a measure of all SP that can react with molybdate – it includes all the fully dissociated orthophosphates ($PO_4^{3-}$). Its ease of uptake by vegetation is better than DAHP, as it is less sorbed onto soil. SRP is typically much more prevalent than DAHP; $SP_i$ can thus be rightly assimilated to SRP only. In many studies, SP is approximated to SRP (disregarding $SP_{org}$, colloidal P, and DAHP), i.e. all P passing through a 0.45 µm sieve and being able to react with molybdate.

SRP is the only P pool that is considered as *immediately bioavailable* and likewise has a very high immediate eutrophication-inducing potential (Auer et al., 1998; Nürnberg and Peters, 1984). As a matter of fact, it has been established that the $SP_i$ group plays the main role in eutrophication and that in P limited situations, the concentration of SRP should be low to undetectable ($<0.005\ mg \cdot L^{-1}$) (Sharpley et al., 1992). The rest of the SP pool ($SP_{org}$) can be *made bioavailable* through enzymatic hydrolysis and mineralization processes, which reactions are rather slow (Auer et al., 1998; Young, 1982). A distinction is made between labile $SP_{org}$ and stable $SP_{org}$, as the labile fraction can speedily go through the hydrolysis and mineralisation processes when the right pH conditions are met (Sharpley, 2003). Much like $XP_{org}$, $SP_{org}$ is comprised of un-decomposed residues and microbes – the distinction is made along a particle size criterion.

The SP:TP ratio reflects how much the P is *rapidly bioavailable*; higher values indicate rapid bioavailability. Similarly, $SP_i$:SP ratio indicates what proportion of the SP pool is *readily bioavailable* (Sharpley, 2003).

## 2.2 Tile drainage

### Why draining?

Southern Quebec receives more rainfall than is evaporated, plus the water table often is close to the surface. Moreover, a major part of agricultural lands are flat (e.g., Montérégie region), and the vast majority are poorly drained. This situation is compounded by a rather short growing season, and snow accumulation during winter. In these conditions, crop productivity is greatly enhanced when lands are artificially drained (BAPE, 2000). In the spring, rapid water evacuation soon after snow thaw enables earlier seedbed preparation and planting, stretching ever so little the growing season. Tile drainage also diminishes the potential for soil compaction and assures trafficability. By abating the water table, drainage allows better crop conditions, most of the time: it minimizes the stress that could be incurred by plants due to the poor soil aeration that accompanies waterlogging, plus the plants can grow longer roots, making use of a larger soil matrix volume and bigger nutrient pool. Drained croplands are thus some of the most productive in the world – hence, crop production, food security, and surface water quality are intimately intertwined.

On the other hand, Southern Quebec's summer conditions vary such that conventional artificial drainage at times turns out to be a stressor for plants, because less precipitation is allowed to infiltrate to the deeper ground water, reducing the soil water reserves that would have been salutary during drier periods, which leads to reduced yields (Doty et al., 1986).

### What are the potential environmental impacts of tile drainage?

Tile drainage reduces surface runoff, which is associated with erosion and particulate phosphorus (XP) export; up to 30% of the surface runoff can be mitigated this way (Haygarth et al., 1999; Uusitalo et al., 2001). However, the presence of drainage –

especially surface drainage – drastically modifies the hydrology of the watershed. As the water-retention capacity of a field is compromised, water is rapidly sent to the watercourse, which shortens the response to precipitation, and increases the peak flow in the receiving watercourses (Needelman et al., 2007). This phenomenon can multiply into a throng of negative effects. For instance, flash floods can trigger bank erosion, sending great quantities of sediments downstream, which will degrade fish spawning grounds when settling out, alter the watercourse's hydrology by reducing its depth and shifting its banks, etc. These risks are further exacerbated by inability of streams and rivers to spill over their banks, as they are often disconnected from their floodplains by channelization and entrenchment for drainage purposes (USEPA, 1993).

Tile drains also provide a direct migration route for nitrate-rich water coming from the surface, which by-passes the potential denitrification zones that may occur in riparian environments and in deeper anaerobic groundwater (David et al., 1997; Gentry et al., 2000; Hill, 1996; Kovacic et al., 2000; Mehnert et al., 2007; Patni et al., 1996). Similarly and more important to the subject of this thesis, tile drainage increases the export of soluble phosphorus (SP), even if P is not easily solubilized (Baker et al., 1999; Monaghan and Smith, 2004; Randall and JA Huffman, 2003; Sims et al., 1998; Tomer et al., 2003) – mechanisms involved shall be explored further. Nevertheless, due to the reduction of surface runoff, which usually has higher P concentrations, tile drains overall diminish the global P-export from agricultural fields to the hydric system.

### Prevalence of tile drainage

Installation of modern drainage systems has been ongoing worldwide for over 100 years (McIsaac and Hu, 2004; Tomer et al., 2003), and expanded rapidly with the invention of slotted high density poly ethylene (HDPE) drains in the 1960s. It peaked in the 1980s and still is ongoing, but at a slower pace, as most drainable land has already received treatment. However, installation of tile drainage is no longer subsidized by agricultural authorities, as it once was during the heydays of drainage (70s-80s).

This type of system is very widespread in Southern Quebec, covering 40% of agricultural lands, or 700 000 ha (BAPE, 2000). This is typical of other agricultural regions of North America, but specific smaller watersheds can have much higher tile drain distribution. For instance, in the Upper Embarras River watershed (Illinois), 70-85% of croplands are artificially drained, and contribute up to 59% of the SP load to the river (Kovacic et al., 2000). In the US Midwest as a whole, it is said that up to 50% of all croplands are drained (Fausey et al., 1995) and in the Corn Belt and the Great Lakes regions, the estimate is at 37% (Kovacic et al., 2000).

## Nature of tile drainage return flow wastewater: what does it contain?

Tile drainage return flow is a very dilute, yet variable, type of wastewater, much like surface runoff or stormwater. Unless it is mixed with surface runoff, it is virtually devoid of suspended particles (sediments). As water has to percolate through the ground to get to the drain, only dissolved pollutants can reach it. Thus, nitrates can certainly be found there. It is also likely to contain ammonia, pathogenic bacteria and viruses, as well as agricultural endocrine disrupters, such as pesticide residues or antibiotics, especially those used as prophylactics. It does not convey organic matter, and thus has very low biochemical or chemical oxygen demand (BOD or COD). Nevertheless, it does transport dissolved organic carbon (DOC).

Because P is relatively insoluble, the quantities found in tile drainage return flow are relatively low, but still significant (Daniel et al., 1998). Most of it is in an inorganic form, as orthophosphates ($PO_4^{3-}$). In a study conducted in England, Heckrath et al. (1995) found that 66-86% of the total P load exported through tile drainage was in the soluble reactive phosphorus (SRP) form. In a study conducted on tile drainage in the Parkhill Creek watershed of Southwestern Ontario, Fleming (1990) found an average TP concentration of 1.300 $mg \cdot L^{-1}$ and nitrate-N concentration of 10.60 $mg \cdot L^{-1}$. In a refined study trying to elucidate the factors influencing P-export, the team found an average TP concentration of 0.480 $mg \cdot L^{-1}$ (Fleming et al., 1998). At the outlet of tile drains draining three intensively grazed pastures in New Zealand, Tanner and Sukias (2011) found flow-proportional TP concentrations of 0.210-0.340 $mg \cdot L^{-1}$, 0.030-0.120 $mg \cdot L^{-1}$ and 0.220-0.430 $mg \cdot L^{-1}$.

Over the course of a year, the concentration of drainage return flow is highly variable, and correlated with the intensity of precipitation. Most P-export by tile drainage return flow happens at snowmelt (early spring) and during winter thaw events (late winter) (Lazzarotto et al., 2005) with fall runoff being less concentrated than in the spring. Still, high P losses are detected throughout the year in connection to intensive rainfall, especially just after fertilizer application. Heathwaite and Dils (2000) measured P concentrations that were six times greater in stormflow than baseflow. The "first flush" is always much more concentrated then what comes after. In corollary, a tile drain's baseflow seldom is problematic, as it is mainly fed by aquifer resurgence.

### How does that wastewater quality compare to other wastewater streams?

Tile drainage wastewater and secondary wastewater effluents share similar characteristics with respect to TN concentration. But they differ markedly over the TP concentration: secondary wastewater is 5 times more TP concentrated than tile drainage return flow. The latter is, however, very close to fish farm effluents (i.e. 0.23 mg TP $\cdot L^{-1}$; Ouellet, 1998). Fish farm effluent nevertheless carries much more DOC than tile drainage return flow.

When comparing tile drainage return flow to surface runoff counterpart, the striking difference is the balance of particulate and soluble forms. Surface runoff can carry quantities of XP in addition to SP, which can amount to a higher TP content, but more importantly, a higher XP:TP ratio (Hansen et al., 2002). For instance, in a study conducted in an agricultural part of the Thames catch basin (England), Gardner (2002) found that at high flow, the XP and SRP concentrations were up to 1.3 and 0.3 $mg \cdot L^{-1}$, respectively. Hence, the greater part of P-export from agricultural fields still is through surface runoff, and mainly as XP (Kokic, 2010). In a study conducted in the Pike River watershed (Southern Quebec), Gollamudi (2007) found that 61.2% and 87.7% of the total P-export from an agricultural field was in the particulate form (XP), indicating that most P-exports occur via sediment transport, thus surface runoff. In the surface runoff of fields draining to the Boyer River (Southern Quebec), the same author (2002) found a TP concentration of 0.12-0.21 $mg \cdot L^{-1}$, with the major fraction being particulate. Similarly, Sharpley (1992) posits XP export by surface runoff amounts to 60-90% of the total P-export.

In soils that already have very low erosion potential, such as pastureland or fields with reduced tillage, the relative importance in carrying P is more important for tile drainage than surface runoff (whereby the export is in the form of SP) (NRCS, 2005). Still, significance and importance of tile drainage return flow P-export should not be underrated, as will be developed in other sections.

### Quantity: how much tile drainage return flow wastewater is produced per unit space?

The quantity of water that is evacuated through tile drainage per unit space of catch basin area is extremely variable, depending on a throng of factors. It typically is pulse-produced, in relation with rain events, which are stochastic by nature. However, it also is dependent on climatic conditions, which follow nonetheless an annual pattern of rainfall distribution (intensity, duration, and interval between events) and temperature (above or below freezing point). In a humid continental climate like the one prevailing in Southern Quebec, the flow can be nonexistent for part of the year, during the dry summer weeks and when soil is frozen for months. But it can be very heavy at snow thaw (spring), during storm events and when autumn rains arrive. For an equivalent precipitation, the generated return flow is lower in the summer than in any other season, considering the higher interception by vegetation and evapotranspiration (Eastman et al., 2010).

Site characteristics such as the soil type (texture) and topography (field slope and slope length) also influence the quantitative production of tile drainage return flow. Management practices, such as the cropping system, timing and type of tillage, crop residue coefficient and ground cover, are all agronomic factors that also influence the quantity of return flow production. The combination of all abovementioned factors is what determines the soil structure. In turn, the structure is what defines the proportion of runoff that infiltrates into the ground to the tile drains, the rest staying at the surface to form surface runoff. The structure also influences how will the water circulate when going down the soil profile to the drain: either matrix flow (evenly distributed), or preferential and macropore flow (channel-conveyed).

In a study conducted in the Pike watershed of Montérégie, Southern Quebec, Eastman et al. (2010) observed tile drainage discharge depths of 358 mm and 737 mm for the 2004-2005 and 2005-2006 hydrologic years, respectively. Taking into account the yearly precipitation, this is a drainage:precipitation ratio of 0.57 and 0.37 for a clay loam and a sandy loam, respectively. From this information, it can be roughly estimated that in a clayey soil, the combination of surface runoff and tile drain return flow, at summer peak flow in Southern Quebec conditions, is in the order of 0.25 $L{\cdot}min^{-1}{\cdot}ha^{-1}$. Therefore, the annual TP loss is approximately 2.9 $kg{\cdot}ha^{-1}{\cdot}yr^{-1}$, of which circa 50% exit through the tile drainage system (Eastman et al., 2010). In comparison, Kyllmar (2006) found a long-term average annual TP export load of 0.1-0.9 $kg{\cdot}ha^{-1}{\cdot}yr^{-1}$ in Swedish agricultural runoff. When monitoring the influence of rain events on a tile-drained field, Laubel (1999) found XP exports of 0.71 to 5.92 g XP $\cdot ha^{-1}{\cdot}mm^{-1}$,

## Why is this wastewater quality problematic?

However low in comparison with other wastewaters, the P concentrations that are carried in tile drainage return flow are still 1-2 orders of magnitude above the 0.030 $mg{\cdot}L^{-1}$ water quality criterion (MDDEP, 2009) for the prevention of accelerated eutrophication. By comparison, it can be said that in Southern Quebec conditions, the "natural" watercourse background concentrations for P is 0.007 mg TP $\cdot L^{-1}$ (Berryman, 2006) and for N, it is below 0.30 $mg{\cdot}L^{-1}$ (USEPA, 1993).

Plus, the major part of P in tile drainage return flow is in the soluble form. Bearing in mind that, for the most part, SP can readily be assimilated by plants, while XP has to undergo desorption and/or mineralization before being usable, SP has a much higher immediate eutrophication potential (Nürnberg and Peters, 1984). Nonetheless, XP (carried mostly by sediments) can be a long-term source of P (Carignan and Kalff, 1980).

More importantly, tile drainage systems being so widely spread and covering so much ground, drainage return flow does not get diluted much, and can account for a significant proportion of the streamflow, especially in highly agricultural areas (Macrae et al., 2007). Thus, beyond the concentration, it is the cumulative effect of large volumes of low concentration waters that is problematic, for it accrues to an impressive cumulative load (Eastman et al., 2010). On top of contributing to the eutrophication status of lakes or rivers collecting the watershed's runoff, the tile drain effluent highly influences the quality of the local habitat where it exits; in the case of agricultural ditches or first order streams (Horton, 1945), where it can compose at times up to 100% of the flow, this can be catastrophic. Water quality of the upper parts of a watershed will also have an impact all along the length of its pathway, and thus over a much larger area, as P cannot evaporate and remains in the ecosystem, unless it is immobilized in the sediments.

## Mechanics of phosphorus export to tile drainage

Water that percolates through a soil by matrix flow is virtually devoid of P, since this element has high adsorption affinity for the positively charged minerals that are present in the soil, such as $Fe^{3+}$, $Al^{3+}$ and $Ca^{2+}$. In theory, P is thus intercepted and retained en route, before it reaches the drain. However vastly abundant they may be in a soil's top layer, these cations are nonetheless finite. Hence, past a certain P saturation level, any supplemental P will simply pass through and possibly reach the tile drain.

In the case of preferential flow, macropores route water directly from the surface to the drain, accompanied by the pollutant burden it contains (Armstrong and Garwood, 1991; Blann et al., 2009; Skaggs et al., 1994). This short-circuiting now is recognized to be a major pathway for agricultural P-export from field to tile drains (Grant et al., 1996; Kovacic et al., 2000; Sims et al., 1998). This observation has been noted for a wide range of types of soil and management practices (Beauchemin et al., 2003; Gardner et al., 2002). In a tracer test using $^{137}Cs$, Laubel (1999) found that the particles accompanying P-exports in the tile drainage return flow came from the top soil. Moreover, mainly SP can be exported this way. As mentioned above, SP has a higher immediate eutrophication-inducing potential then XP, given its higher bioavailability.

Deep, sandy soils are particularly prone to P-export, because they have a low cation content, which is reflected in a low Cation Exchange Capacity (CEC) (Vadas et al., 2005). The same is observed in organic or peaty soils, where the $Fe^{3+}$ and $Al^{3+}$ cations are complexed with organic matter. These phenomena (low CEC) are exacerbated at low pH (Sims et al., 1998). When inundated or water-saturated, a soil can lose its P-retention capacity, since an anaerobic environment leads to conversion of insoluble $Fe^{3+}$ to soluble $Fe^{2+}$ and mineralization of organic P, destroying potential adsorptions sites, and even releasing the P that once was stored (Sharpley, 2003). Clayey ("heavy") soils that are susceptible to cracking are also prone to P-export, especially when a certain saturation threshold is passed – cracks induce macropores and preferential flow, which can become direct routes for P. For instance, Heckrath et al. (1995) frequently measured TP concentrations of 1 $mg \cdot L^{-1}$ and up to 2.75 $mg \cdot L^{-1}$ in tile drainage wastewaters in an alkaline clay soil. Macropores can also be initiated by earthworm activity (Simard et al., 2000a).

P-export also depends on the timing of fertilizer application. The period between application and rainfall, as well as the intensity and amount of precipitation, highly influence the export of P, especially if the fertilizer is not incorporated in the soil (DeLaune et al., 2004; Harmel et al., 2006; Maguire et al., 2004). The vegetative cover and growth stage, which determine plant uptake, also are important factors, for what is not taken up by the plant or immobilized one way or another is available for export. For instance, plant uptake is much lower late in the fall than in early spring. Of course, P-export to tile drainage also depends on the method and rate of fertilizer application, as well as the P content and saturation of the soil, as shall be explored further down.

## 2.3 Agriculture portrait

### Agriculture in Quebec: production, territory, history and trends

In Quebec, agriculture is practiced on 8.6 million hectares (Statistics Canada, 2001). Though this is a mere 2% of the territory, they are all situated in the Southern fringe. The type of agriculture that is practiced in the vast majority of the territory can be described as conventional and intensive (Gangbazo, 2005). The prime agricultural region is Montérégie, where monocultures of corn and soya are typical. There, the main production is hogs and milk. These clayey lowlands have excessive P concentrations in the plow layer area (Simard et al., 2000b; Tabi et al., 1990), which is a major P-export factor, exacerbated by flat topography (slopes ranging from 0 to 3%) and widespread tile drains (Beauchemin et al., 1998). Other important agricultural regions of Québec are Lanaudière, Beauce, Cantons-de-l'Est, and Lac-Jean, all characterized with more important slopes and colder climate than Montérégie.

In the second half of the 20th century, Quebec agriculture followed the same trend as the rest of the Western industrialized world: shift from extensive pastureland agriculture, with dairy production in the vanguard, to intensive corn production (14 fold rise), so as to support a heavy rise in hog and chicken production (4 and 3 fold rise, respectively) (MDDEP, 2003; Statistics Canada, 2001). With the development of adapted strains, agricultural land now is mainly used for cash crop production of corn (*Zea mays* L.) and soybeans (*Glycine max* L. Merrill). This intensification of agriculture is correlated with mechanization, and with the installation of tile drainage. In the same period, Quebec attained 150% self-sufficiency for milk and pork, but 100, 000 of the 1950s' 135, 000 farms disappeared, with the agriculturally-used area passing from 3.4 million ha to 1.9 million ha (BAPE, 2000).

### Phosphorus saturation of agricultural soils

When P-fertilizers are continuously applied to agricultural fields above crop utilization and rate of extraction through agricultural produce harvest, P can accumulate in soils; this build-up often is referred to as *legacy P* (Kleinman et al., 2007). This accumulation leads to increased P-saturation of agricultural soils (Beauchemin et al., 2003; Simard and Beauchemin, 2002). As seen above, the P-saturation of an agricultural field is positively correlated with P-export to tile drainage (Breeuwsma et al., 1995; Brookes and Hesketh, 2000; Daniel et al., 1998; Pote et al., 1996; Sims et al., 1998; Vadas et al., 2005). P-saturation is a measure of the proportion of P-adsorption sites that already are occupied by P.

This over-application of P has been ongoing for decades in many intensive cropping and livestock production locales (Sharpley et al., 1996), including Southern Quebec (BAPE, 2000; Beauchemin et al., 2003; MDDEP, 2003), Florida (Elrashidi et al., 2001), and Europe (Behrendt and Boekhold, 1993; Kronvang et al., 2005). In these conditions, soil P loads now are much more of an environmental concern rather than an agronomic concern, given P's potential to accelerate freshwater ecosystem eutrophication (Sharpley, 1995).

This over-application of fertilizers has been possible because fertilizers are cheap in comparison to the pecuniary gain of over-fertilization, and expectations are for producers to maximize their productivity, instead of producing at an optimum that would take into account the potential damage to water quality. They are asked to produce always more, cheaper food. Those that don't follow the dogma have an economic disadvantage, for all competitors in the globalized market strive for maximum, and not the optimum. The demand for more, cheaper, food is led by the augmentation of food wastage throughout the food chain, a shift in diet tastes towards more meat, as well as the ever increasing population (Schröder et al., 2010; Van Vuuren et al., 2010). In the last few years, production of agricultural goods for fiber and energy has come to exacerbate the situation.

The situation is often worsened by an imbalance between available crop lands and the quantities of manure that are produced at the local scale (Sharpley, 2003). This is particularly true for regions with little crop production and lots of animal husbandry, such as the Beauce region of Southern Quebec with pork production.

The tenet has now changed in the governing instances (e.g., MAPAQ), with the obligation of farmers to apply P only up to the needs of the plants so that it doesn't accumulate further in the soil, or worse, be exported (Bolinder et al., 2000; Lemunyon and Gilbert, 1993; NRCS, 2005). This newer philosophy is instilled into the farm industry using such tools as the phosphorus budget-sheet ("Bilan phosphore") in Quebec (MDDEP, 2002b; Michaud et al., 2008). This is a good first step, part of the first line of defense in the Best Management Practices package, but the saturation brought about by decades of over-application is not yet addressed by this measure (Berka et al., 2001; USEPA, 1993).

### How to measure phosphorus saturation of agricultural soils?

In Quebec, two methods are recognized to determine the P-saturation index of a soil: either the soil P concentration is contrasted with the soil Al content only, in Mehlich III extracts (Giroux and Tran, 1996) or it is compared to the Al + Fe content (Van der Zee et al., 1988). In Quebec and the rest of North America, the first is more commonly used.

Simard and Beauchemin (2002) assert that the first is only good for coarse-textured soils, with the latter being a better choice for clayey ones.

The agricultural soil is said to be P-saturated when it has attained a P content that renders it available to plants; this is expressed by the critical value for P fertilizer response. The soil is said to be over-saturated when it has attained a P content whereby potential P-export exceeds the agronomic benefits. The determination of an over-saturation threshold is however very perilous, considering the number of factors to take into account; yet it is time and site-specific. In Quebec, a P-saturation of 20% or more is generally considered as very risky for P-export, and a 5-10% saturation is said to bear moderate risk (Beaudet et al., 1998; Bolinder et al., 2000). As a gross generalization, it can be said that excessive P content starts from 112 mg Mehlich-III extractable P $\cdot kg^{-1}$ (Conseil des productions végétales du Québec, 1996). In a study conducted on a clayey soil, Heckrath et al. (1995) has shown that past the 60 mg Olsen-P $\cdot kg^{-1}$ threshold, P-exports were much more closely related to P additions than at lower saturation.

## Best management approach

In Quebec and many other North American jurisdictions, the concept of Best Management Practices (BMPs) is favoured in the struggle against P from agricultural run-off and its detrimental effects. A BMP can be defined as the "economically achievable measure that reflects the best available technology for reducing pollutants" (USEPA, 1993). It is often described as a 3-fold package, with 3 lines of defense. The first efforts go to limiting the pollutant at the source: fine-tuning fertilizer application so that it is not applied in excess of the gap between crop needs and what is already available in the soil. The second line is to prevent its export into the hydric system, constraining it to the field with measures such as erosion control. Last, if those preventive measures have failed, mitigation procedures might be necessary, whereby the pollutant is intercepted and removed (Crumpton et al., 2006; Jordan et al., 2003). CWs fall within the third category. In Quebec, many BMPs are directly subsidizable, under the *Prime-Vert* (MAPAQ, 2009) program, and some of the prevention BMPs are mandatory to receive governmental paybacks (ecoconditionnality). However, up to now, in Quebec, the construction of CWs does not receive any financial support whatsoever.

## Third-line-of-defense: mitigation strategies

The third line of defence is a supplemental one, in the sense that if the first two worked well, it shouldn't be needed. However, in areas where soil P-saturation is endemic, it seems that they will not be able to abate P concentrations in agricultural runoff below the eutrophication threshold of 0.030 mg TP $\cdot L^{-1}$ (Beauchemin, Simard et al. 2003); hence, additional measures are needed. Depending on the pollutant burden, focus can be kept onto surface runoff, because it is much simpler and still carries the major part of the total P load, but the contribution of tile drainage return flow should nonetheless be pondered. It always is best to treat the water as close as possible to the pollutant source, so treating tile drainage return flow might be profitable where its quality is problematic.

The third line of defence consists in an array of end-of-field treatment structures that can trap potential pollutants such as P before they reach a natural waterway. This is a very active field of research, as no perfect technology exists (Buda et al., 2012). Michaud et al. (2005) suggest such structures as riparian buffer strips, catch basins along stream channels and constructed wetlands (CWs) in ditches, but other structures such as detention ponds (Desmarais, 2009; Savoie, 2009) or bioreactors (Christianson et al., 2009) can be considered. These structures all have the advantage of blending well into the agricultural production environment.

The efficacy of detention basins is affected by the fluctuating water levels in soil; research has shown that it can result in the release of stocked pollutants back into the water column (e.g., desorption of P from sediments, release of P from biomass). The anaerobic (low oxidation-reduction potential) conditions that build after a few hours of ponding can also send P back into the water column. In the same way, buffer strips have limited P-removal capacity, for they often are flooded or waterlogged, plus their soil has a limited quantity of available P-sorption sites. Nonetheless, buffer strips have proven their efficiency in removing nitrates and bringing ancillary benefits (e.g., biodiversity support, biomass production, etc.).

Thus, CWs seem most appropriate as an end-of-field third line of defense for the treatment of both surface and tile drainage runoff. They indeed have a capacity to remove a broad range of pollutants, – including P –, plus they can aptly deal with unpredictable and variable loading inherent to agricultural runoff production, with occasional extremes (Kovacic et al., 2000). It should be remembered that, taken individually, the P-load removal of a lone structure, although statistically significant, may not look very important. It is the implementation of many of these throughout a watershed that provides an impressive global P reduction (USEPA, 1993).

## 2.4 Constructed wetlands

### What is a constructed wetland?

A constructed wetland (CW) is a man-made ecosystem designed to emulate natural wetlands in their passive water treatment capacity (Hammer, 1992). It is an engineered ecosystem, in the sense of a task-oriented mesocosm (Mitsch and Jørgensen, 1989; Odum, 1971; Todd and Josephson, 1996). It basically consists of a holding structure through which water passes, with a specific soil, and in which a wetland flora and fauna are established. Yet these constituents can be arranged in a multitude of combinations, making this technology very versatile and adaptable to local conditions and the water that must be treated.

Designing an efficient CW is all about specifying the appropriate components. The four main aspects of a CW are (i) the hydrology, (ii) the substrate (iii) the microbial community and (iv) the vegetation (Hammer, 1992; Maehlum et al., 1995; Mitsch and Gosselink, 1993). All aspects have to be scaled and harmonized with one another according to the quantity of wastewater that is produced as well its production pattern, the climate, the type and concentration of pollutants that may be present, the water's physico-chemical conditions, as well as the desired water quality in the effluent.

### What kind of wastewater and pollutants can a constructed wetland treat?

CWs have been proven to be efficient in removing a broad range of pollutants, conveyed in all kinds of wastewaters (Sundaravadivel and Vigneswaran, 2001). They are best at treating high volumes of low-concentration wastewaters (Baker, 1992; Verhoeven and Meuleman, 1999). They are useful in treating non-point sources, such as mine drainage, urban stormwater, agricultural runoff and tile drainage return flow (Braskerud, 2002a), which are highly dilute. They also often are used as a polishing, tertiary treatment after a more conventional wastewater treatment train.

A wetland is typically geared up to treat one specific pollutant (e.g., P), but many others will be removed, given the range of physico-chemical conditions occurring in specific micro-environments within the wetland. Depending on the design, CWs can remove bacteria, viruses, suspended solids, heavy metals, biological oxygen demand, endocrine disrupters such as antibiotics or pesticide residues, N (ammonia and nitrates), and P (Kadlec and Wallace, 2009). The means by which these pollutants are removed are different, and sometimes incompatible. Hence, the design of the wetland has to correspond to one specific target pollutant. Other pollutants – the removal mechanisms for which are compatible with that of the target pollutant – may also be removed, along with other ancillary benefits. For instance, P removal is best performed at high oxidation-reduction potential (ORP) conditions, which also are needed for nitrification of ammonia nitrogen ($NH_4^+$+$NH_3$).

If more than one pollutant must be removed and their removal mechanisms are incompatible, a multi-stage CW system can be designed, whereby different conditions prevail in different cells. This way, the CW system as a whole is efficient in removing multiple target pollutants. For instance, ammonia can be nitrified in a first *aerobic* cell, and nitrates transformed into nitrogen gas in a second *anaerobic* cell. The cells are often staged in series and gravity usually drives the flow, but water can be recirculated with pumps.

Some wastewaters have to be pre-treated before entering a CW in order to assure adequate treatment and preserve the hydraulic conductivity and useful life of the CW (Braskerud et al., 2005a). In any case, solids and suspended particles need be attenuated, either mechanically, or with the help of a septic tank, settling pond, sedimentation basin, decanting tower, or pre-filter, etc.

### How does this passive technology compare to more conventional wastewater technologies?

In comparison to conventional wastewater treatment technologies, CWs offer a robust, reliable, low-energy, technologically simple, aesthetically pleasing and cost-effective alternative, with low maintenance and operating costs (Brix, 1993; Drizo et al., 1999; Sundaravadivel and Vigneswaran, 2001). CWs might also partly boast functional values similar to natural wetlands, such as wildlife habitat, production of biomass, fish and shell-fish, ground-water recharge, recreation, aesthetics, shore protection, or peak flow buffering. A CW can be tweaked for ancillary benefits, but focus should be kept on water treatment.

CWs have the disadvantage of requiring more space than conventional wastewater treatment technologies for the same level of treatment (Drizo et al., 1997; Sundaravadivel and Vigneswaran, 2001). Thus they are less suitable where land is scarce and expensive, as for the treatment of large cities' wastewaters. CWs also need long run-up periods before being fully functional, typically two to three growing seasons (Sundaravadivel and Vigneswaran, 2001). Also, their functioning is still somewhat elusive, thus far poorly understood, leading to imprecise design criteria and operating instructions (Ladegaard et al., 2001; Sundaravadivel and Vigneswaran, 2001). If not well designed or operated, CWs can be a breeding ground for mosquitoes. Like any water treatment technology, they need to be monitored and maintained.

For the specific case of P, municipal wastewater treatment plants usually count on chemical precipitation techniques to partly remove P (USEPA, 2000c). In the last few years, biological P removal techniques have also been implemented, despite the complexity of the required pathways (Tchobanoglous and Burton, 1991). Both the chemical and biological techniques require a decantation device, and large volumes of sludge are generated, which must be appropriately disposed of (Jiang et al., 2005).

Chemical methods might possibly be adapted to agricultural runoff using system automation, but biological P-removal techniques are categorically unsuitable, given their inadaptability to variable hydraulic loading rates and low BOD content in this type of wastewater, notwithstanding the inhibitory costs. In treating tile drainage return flow, the only alternative to CWs are prevention and the other Best Management Practices depicted previously.

### Where can constructed wetlands be used?

CWs are very cost effective, and therefore are suitable for adoption in any kind of economical setting (Sundaravadivel and Vigneswaran, 2001). They are the favoured choice for the treatment of wastewater in isolated places, for instance small communities, off-grid houses, remote industrial plants, or scattered agricultural fields.

This is true for tropical and temperate regions, but also for hemiboreal regions such as Southern Quebec, and even for boreal regions (Jenssen et al., 1993; Jenssen et al., 2005; Koskiaho et al., 2003; Mander and Jenssen, 2002a; 2002b; Smith et al., 2005). In cold climates performance will vary with season following the Arrhenius principle, where reactions operate faster when temperature is warmer (Anderson and Rosolen, 2000; McCarey et al., 2004).

### How do constructed wetlands operate?

In a CW, physical, chemical and biological pathways combine to reduce the pollutant load (Hammer, 1989; Kadlec and Knight, 1996; Moshiri, 1993). A CW can thus be considered as a “biogeochemical filter” (Kosolapov et al., 2004). Pollutants are captured and transformed, and either released in the environment in an altered form or accumulated over time (Jordan et al., 2003), leaving the wetland effluent with a lower pollutant load than the influent. It is important to note that many of the microorganisms that transform and remove pollutants in a CW are the same as those in conventional biological treatment systems (Faulwetter et al., 2009).

Key to the wetland operation and efficiency are the physico-chemical conditions prevailing in the system: pH, T, dissolved oxygen (DO) and redox potential (ORP), the latter being of utmost importance (Braskerud et al., 2005c; Patrick Jr, 1981; Pratt et al., 2007). Treatment performance is also influenced by seasonal variability and wetland maturity.

## Redox potential

Redox potential is a metric reflecting the availability and thermodynamic strength of electron acceptors that are present in a solution, or oxidation level of the system (Water Analytics, 2011). It is also known as reduction potential or oxidation-reduction potential and is abbreviated as ORP or Eh. It is measured in units of mV, and generally stays within the +600 mV to –200 mV range (Figure 2-2). The higher the ORP, the greater the availability of strong electron acceptors; e.g., oxidation reaction in the presence of free oxygen. A low negative ORP is indicative of a low availability of strong electron acceptors, such as in the absence of oxygen and nitrates, although weak electron acceptors might be present; e.g., methanogenic reaction in presence of $CO_2$.

ORP is related to dissolved oxygen (DO) in so far as it reflects the availability of $O_2$ as a terminal electron acceptor, when present. In a water-logged environment such as the wetland matrix, $O_2$ generally is a limited resource, as it diffuses 10, 000 times more slowly than in air. ORP is also negatively correlated to pH, which can be calculated through the Nernst equation, and graphed on a Eh-pH Pourbaix diagram (1945).

A solution where Eh > 300 mV is termed an oxidized environment, because dissolved oxygen is available as a terminal electron acceptor (Kadlec and Knight, 1996). In the 100-300 mV interval, the ORP conditions are designated as moderate. If nitrate or nitrite are present but not oxygen, the environment is termed anoxic. The solution is deemed “reduced” when ORP conditions drop below 100mV. Because neither oxygen nor nitrates are present, such an environment is termed anaerobic (Kadlec and Knight, 1996).

## Influence of redox potential on constructed wetland operation

ORP conditions are paramount in the operation and efficiency of a wetland because it determines the possibility and rate of biological and/or chemical cleansing processes to occur (Figure 2-2). Distribution of the different types of bacteria mainly depends on the oxidation level: strict (obligate) aerobes are active at high Eh, and strict anaerobes thrive at negative Eh values. Facultative bacteria can live in both kinds of environments, having the capacity of utilizing different electron donors and acceptors for respiration. The ORP conditions also determine the sense and rate of chemical reactions.

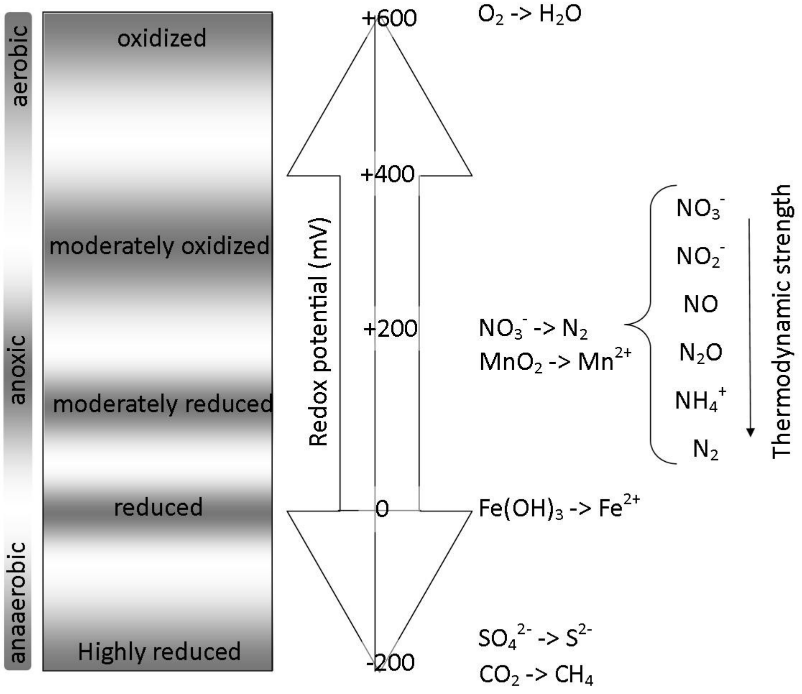

Figure 2-2: Relation between oxygenation, redox potential and thermodynamic favourability of electron acceptors in the water-logged environment of a constructed wetland.
Figure adapted from Patrick Jr (1981).

The ORP scale is a continuum, but decrease of Eh goes by steps, due to poising, whereby the system stays at a given level as long as the electron acceptor is present, along with the microorganism operating the electron acceptance. When this electron acceptor all is depleted, it is the next lower-energy electron acceptor that is favoured – this is when the system passes at a lower Eh level. For instance, as long as there is oxygen, ORP conditions will not drop beneath 300mV and organic matter mineralisation will be possible, and denitrification will not; in the same manner, as long as there are nitrates, ORP conditions will not drop beneath 100mV, preventing reduction of Al or Fe. In a recently flooded soil, the system will go through a series of Eh drop steps as different receptors are exhausted (Hendershot, 2010, comm. pers.). It should be noted that soils being a multitude of microenvironments, the electron accepting could be at different steps of the poising phenomenon from one microenvironment to another i.e. the redox sequence is a continuum in space, although step-hampered. This is what allows a wetland to achieve processes that need contrasted ORP conditions (e.g., nitrification vs. denitrification).

Depending on the wetland design and the DO content of influent wastewater, oxidized conditions are encountered in a more or less limited proportion of the wetland, as oxygen cannot diffuse rapidly in water. Hence, oxidizing reactions are the limiting steps of many cleansing reactions. This is the case with most pharmaceutical's degradation (Hussain and Prasher, 2011). This also is the case with nitrogen removal i.e. the oxidation of ammonia (nitrification) is the limiting process, whereas reduction of nitrates can operate in a greater proportion of the water-logged wetland (Henze, 2008; Ye and Li, 2009).

A severely reduced wetland might see methane ($CH_4$) be produced by anaerobic methanogenic microorganisms that ferment organic matter, whereby $CO_2$ or the carboxyl group of acetate is the terminal electron acceptor (Patrick et al., 1996; Szogi et al., 2004). Incomplete denitrification is also typical of a severely reduced environment, releasing nitrous oxide ($N_2O$). Both are potent greenhouse gases (GHGs).

### Plants' contribution to redox conditions, and treatment efficiency, in turn

The rationale for employing CWs to treat wastewater is the ability of plants to "pump" oxygen down into a water-logged soil substrate, allowing oxidation reactions to take place in an otherwise anaerobic environment (Brix, 1987; 1997; Sundaravadivel and Vigneswaran, 2001). Indeed, small though crucial quantities of $O_2$ ooze through lenticles on the rootlets, raising the ORP in the rhizosphere (Armstrong et al., 1988). This is especially true for plants that have lacunae or aerenchymous tissues, such as cattails (*Typha sp.*). The presence of plants thus stimulates the decomposition of organic matter, the nitrification of ammonia into nitrates and the precipitation and adsorption of P.

Contradicting claims have been made about the magnitude of oxygen supplied by wetland plants' roots. Of course, it certainly varies with the species. Some authors have found very little oxygen outflow (e.g., Armstrong and Armstrong, 1988), while others claim they observed up to 4.3 g $O_2 \cdot m^{-2} \cdot d^{-1}$ with *Phragmites sp*. (Lawson, 1985). With emergent plants, Brix and Schierup (1990) found 0.02 g $O_2 \cdot m^{-2} \cdot d^{-1}$, and Gries et al. (1990) measured a range of 1-2 g $O_2 \cdot m^{-2} \cdot d^{-1}$.

## What are a wetland's hydrology alternatives?

The hydrology of the CW system is determined by the way water is supplied to the system, the way water moves through the CW space, and the residence time.

The CW supply possibilities are threefold: the water can be fed regularly, intermittently, or irregularly. If the water is not fed continuously, the system may be allowed to drain between influxes, letting portions of the soil matrix to aerate in the interval, elevating the ORP.

The main alternative flow regimes are to let water pass over the surface (free water surface; FWS) or to force it to flow within the soil matrix (sub-surface flow; SSF). When passing through the matrix, water can flow horizontally, ascend or descend. Figure 2-3 depicts the main flow patterns possible. Sometimes a hybrid wetland can be useful, combining aspects of two or more flow patterns.

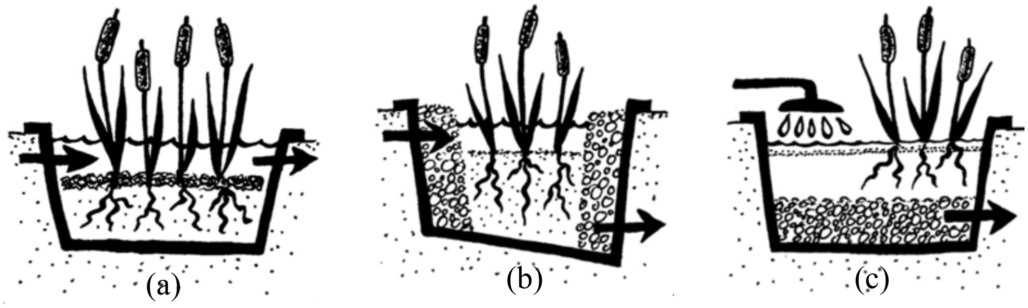

Figure 2-3: The three main constructed wetland flow regimes:
a) Free water surface b) Sub-surface horizontal flow c) Sub-surface vertical down-flow
Figure adapted from Akvopedia (2012).

The residence time (RT) is a measure of the time it takes for water to go from one end to the other. It thus reflects the size of the wetland relative to the loading rate. A longer residence time is generally correlated to higher cleansing performance for most pollutants (e.g., $NO_3^-$) (Stern et al., 2001). However, a longer residence time diminishes the ORP conditions, which might have a negative influence on certain pollutant removal processes, including P removal (Braskerud et al., 2005c). Residence time can be estimated by calculating the *bed volume* Hydraulic Retention Time (HRT): wetland volume divided by the flow rate. Alternatively, the *void* HRT is calculated as: wetland volume multiplied by porosity of the substrate, divided by the flow rate. Flow through a CW is complex and deviates somewhat from plug flow. The plug-flow model is a useful approximation when the concentration of contaminants gradually decreases along the CW's length (Levenspiel, 1999).

### Characteristics of the different flow regime alternatives for a constructed wetland

Historically, CWs were designed as free water surface (FWS) systems, as they closely mimic natural wetlands (Hammer, 1992). In any case, a wetland should be designed so as to maximize the contact between water and the soil, favouring matrix flow and deterring preferential channelling, with consideration for space footprint and costs. Table 2-1 shows the advantages and disadvantages of the different possible flow regimes regarding a number of issues.

In a FWS, or "surface flow" CW, there is very little matrix flow. The substrate usually has low permeability and is permanently saturated (Mitsch and Gosselink, 2000). The depth of water ponded over the surface is controlled with a weir, typically at less than 0.4 m (Sundaravadivel and Vigneswaran, 2001).

In the case of a sub-surface horizontal flow (SShF) CW, or "infiltration wetland", the water is forced to pass horizontally through the matrix. This way, the performance per unit space can greatly be enhanced, because the surface area where contaminant-laid water comes into contact with the soil particles and microfauna is multiplied many-fold (USEPA, 1995). The water level is maintained just below the surface of the bed (Verhoeven and Meuleman, 1999). The bed depth typically is in the range of 2-3 m (Sundaravadivel and Vigneswaran, 2001). The bottom of the bed is sloped to allow a slow but steady movement of the incoming water and to minimize flow above the surface (Kadlec, 1995). The key difference between the two first types of systems resides in the height of the outlet compared to the inlet.

In a sub-surface vertical down-flow (SSvDF) system, water is usually trickled over the surface and collected at the bottom; it can also enter the system through distribution pipes installed below the soil surface, typically at depths of 60-100 cm (Sundaravadivel and

Vigneswaran, 2001). The matrix can be maintained saturated or not, depending on the type of outlet, as well as the supply pattern and the residence time.

In the sub-surface vertical up-flow (SSvUF) CW option, the water is introduced at the bottom and forced against gravity towards the surface. This is the only type of CW that needs pressure to enable water movement, usually provided by an elevation difference between the wetland and the source.

In general, sub-surface flow (SSF) CWs more closely resemble wastewater treatment plants, with boosted surface contact, thence higher biofilm growth and possibility for adsorption and precipitation reactions to occur. SSF CWs have better protection against hydraulic failure in sub-zero temperatures. They also offer a greater assimilation potential per unit of land area. In Europe, SSF CWs definitely are more popular than in the Americas, given the contrasted land availability (Kadlec and Knight, 1996).

Table 2-1: Flow regime comparison regarding specific issues.

| Free water surface (FWS) | Sub-surface horizontal flow (SShF) | Sub-surface vertical flow (SSvF) |
|---|---|---|
| **Hydraulic complexity** | | |
| - Simplest in terms of engineering. | | - vUF are the most hydrologically complicated, requiring an elevation difference and are thus topographically limited. |
| **Preferential channelling and usage of matrix volume** | | |
| - Often subject to saturation and standing water (Mitsch and Gosselink, 2000; USEPA, 1995).<br>- Plants can help to prevent standing waters and to better distribute water throughout.<br>- Very little matrix flow and contact. | - Prone to preferential flow – along the sides of the basin and within the matrix – which diminishes the residence time and hampers interaction of water with the substrate matrix, with rapid saturation of the over-used channel zones.<br>- Using a free-water basin at the inlet of a SShF reduces the chance of short-circuit routes (Lightbody et al., 2009). | - Less prone to short-circuits in the matrix than SShF; can still happen, especially when the matrix is not fully saturated.<br>- vUF have the edge over all CWs, as the *whole* water volume uses every horizon of the wetland matrix (full radial contact).<br>- In a vUF, the water movement constantly works against gravitational settlement of the soil particles and packing of the matrix, rendering the residence time less susceptible of diminishing with time of operation. |
| **Usage of the root zone** (This zone is particularly propitious to phosphorus removal, given the higher ORP conditions) | | |
| - Very restrained | - Only a very small fraction of the water load is forced to pass in this zone; assuming plug-flow, only the top layer of the moving water mass have access to this zone (Breen and Chick, 1995). | - Encourage the passage of water in the root zone, which is further enhanced in a vUF, whereby the axial water distribution is more even (Farahbakhshazad and Morrison, 2003; Farahbakhshazad et al., 2000). |
| **Biofilm growth** | | |
| - Very little surface area is available for biofilm growth. | - High | - High |
| **ORP conditions** | | |
| - Oxidized conditions can prevail throughout the water column, if well mixed.<br>- In the soil matrix, only the first centimeters beneath the soil surface typically have oxidized conditions – the rest is relatively reduced. | - Diffusion of oxygen is limited.<br>- Oxidized conditions are more or less restricted to a small space at the soil-air interface and in the rhizosphere.<br>- The water-saturated soil is increasingly oxygen-poor with depth. | - Have the highest potential for oxidized conditions, even when fed on a continuous basis, as the matrix is not necessarily always water-saturated<br>- In a vUF, oxidized conditions can be both encountered at the inlet – near the bottom – and near the soil surface, depending on the wastewater's BOD:DO ratio. |

| | | |
|---|---|---|
| **Operation in cold climates** | | |
| - Will freeze in sub-zero °C conditions.<br>- Less efficient into the cold season. | - Less prone to freezing; as long as the water line is kept low enough and there is sufficient insulation at the air-soil interface (with a plant mat, mulch, etc.), it will not completely freeze.<br>- Recommended in cold climate conditions (USEPA, 1995). | - *Idem* as SShF |
| **Removal of particulate pollutants and clogging** | | |
| - Least prone to clogging and best particulate pollutant removal (USEPA, 1993).<br>- Particles settle through sedimentation and/or decantation and are let to accumulate at the bottom, much like in a retention pond, without risk of clogging; plants do ameliorate this feature. | - Sediments can accumulate close to the entrance, which might lead to hydraulic failure. | - Clog less easily then SShF (Sundaravadivel and Vigneswaran, 2001).<br>- vUF can easily be backwashed. |
| **Removal of soluble phosphorus (SP)** | | |
| - Very little surface area is available for adsorption and precipitation. | - Better SP removal than FWS (USEPA, 1993). | - Have the edge on SShF.<br>- vUF champions all CWs. |
| **Stripping of pollutants (e.g., ammonia) and photodegradation** | | |
| - Possible | - Impossible | - *Idem* as SShF. |
| **Pests and odours** | | |
| - When well-managed, a CW should not bear any pest or odour problem (Knight et al., 2003). | - Cannot be a breeding ground for mosquitoes. | - *Idem* as SShF. |
| **Ancillary flood control** | | |
| - Easy, by accumulating a higher water column. | - Less easily adaptable. | - *Idem* as SShF. |
| **Costs** | | |
| - Cheapest type, with lower costs and straightforward construction, operation, maintenance and repair (USEPA, 1995). | - Generally more expensive. | - vUF are the most expensive to construct. |
| **Space footprint** | | |
| - Substantial. | - Lower. | - vUF is the most efficient per unit space among all CWs. |
| **Preferred usage** | | |
| - High flow rate (USEPA, 1995).<br>- Low concentration wastewater. | - Small flow rate (USEPA, 1995).<br>- Limited space (e.g., urbanised context). | - *Idem* as SShF. |

## 2.5 Phosphorus removal in a sub-surface flow constructed wetland

### How is phosphorus cycled in a sub-surface flow constructed wetland?

As seen above, particulate inorganic P ($XP_i$) is virtually absent from tile drainage return flow, but all other forms of P are susceptible of being present. Soluble inorganic forms ($SP_i$), mainly of the reactive kind (SRP), form the majority. To a much lesser extent, particulate organic phosphorus ($XP_{org}$) can be present; it can simply be accounted as XP, because $XP_i$ is absent.

Between its entrance in the wetland and final removal, P is cycled through complex biogeochemical processes (Figure 2-4) (McCarey et al., 2004). A reasonable simplification is to assume that in a sub-surface flow constructed wetland, only $SP_i$ is removed. Organic P, whether particulate ($XP_{org}$) or soluble ($SP_{org}$), has to be mineralized into $SP_i$ by the soil microorganisms before removal (Brookes et al., 1984). Thus, CWs are less responsive to XP and $SP_{org}$ than to $SP_i$ (Reinhardt et al., 2005).

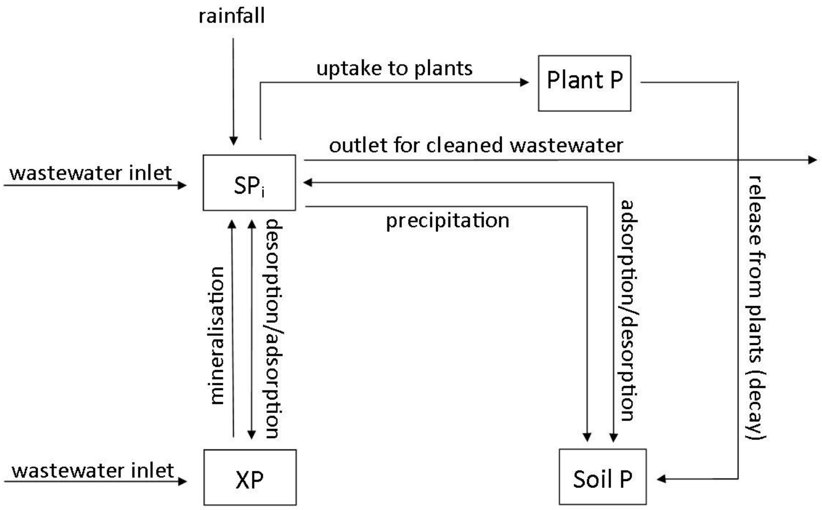

Figure 2-4: Conceptual model of phosphorus cycling in a constructed wetland.
Figure adapted from Ladegaard et al. (2001).

Bacterial uptake can be considered as a P removal process, but any biological uptake is only temporary, thus would be more precisely ascribed to a mere SP cycling mechanism (Vymazal, 2007). Bacterial P uptake is stimulated by the presence of biologically available carbon (Khoshmanesh et al., 1999).

In a case where tile drainage return flow wastewater would contain contributions from surface runoff, provision should be made for XP and suspended sediments to be removed prior to wastewater passage in the sub-surface flow CW, for instance with the help of a sedimentation basin, a filter pre-treatment or a free water surface CW, as the particles could clog the system (Blackwell et al., 2002; Syversen and Borch, 2005).

In such a pre-treatment, some of the $XP_i$ would simply fall out to the bottom with the sediments, but some would be dissolved and added to the $SP_i$ that already is present in the water. Resolubilization would especially be favored if the conditions were anoxic. No sediment-removal mechanisms can take out all particles – a compromise has to be found between efficiency, and space footprint and costs. For instance, Melbourne (2010) recommends sediment ponds to be designed so as to remove 95% of the 125 µm sediment, while being deep enough to accumulate particles over a 5 year period without resuspension, before having to be excavated.

## How is phosphorus removed in a sub-surface flow constructed wetland?

### *Precipitation and adsorption*

The main P removal mechanisms in a CW are precipitation with and adsorption onto soil minerals. Unlike plant uptake, these two mechanisms can operate year round (Liikanen et al., 2004). The two mechanisms involve surface reactions and so are dependent on the matrix's specific surface area: in a given volume, smaller particles have a higher adsorption and precipitation potential. However, smaller particles also result in a lower hydraulic conductivity, precluding the contact between water and soil particles that is essential for adsorption and precipitation. Hence, it is important to choose a substrate with a particle size that optimizes surface area and hydraulic conductivity.

The adsorption and precipitation mechanisms are limited by the availability and nature of mineral content in the soil substrates, i.e. they are finite (Calder et al., 2006; McCarey et al., 2004). This relative availability is estimated as the Cation Exchange Capacity (CEC) (Hendershot and Duquette, 1986). Adsorption and precipitation capacities diminish and eventually stop as the substrate becomes saturated (Blackwell et al., 2002; Liikanen et al., 2004; Reddy et al., 1999). It was established that P uptake efficiency of wetlands is greater in the initial stage of operation but decreases after a few years of operation (Richardson, 1995).

These complex phenomena are dependent on the physico-chemical conditions prevailing in the substrate, especially the oxidation-reduction potential (ORP) (Calder et al., 2006; McCarey et al., 2004). Following Arrhenius principle, the rate of reaction is directly proportional to temperature (Akratos and Tsihrintzis, 2007). They are also influenced by co-solutes, microbial metabolism and vegetation (Calder et al., 2006; Dunne and Reddy, 2005; McCarey et al., 2004; Moore and Reddy, 1994; Reddy et al., 2005). Adsorption and precipitation are fast reactions that do not need a long contact time i.e. hydraulic retention time (HRT). Aeration of the substrate, can enhance adsorption and/or precipitation of P, by keeping the ORP conditions high (oxidized environment) (Kumar, 2007). Actually, precipitation is slightly slower than adsorption, but is not as dependant on ORP conditions as adsorption is (Lantzke et al., 1999).

A main distinction between the two mechanisms is that adsorption is fully reversible, while precipitation is virtually permanent, given that the bonds formed by adsorption are generally weaker than the stable and insoluble complexes formed during precipitation (Liikanen et al., 2004). It is a useful approximation to say that precipitated P will not be released when the conditions become unfavourable (e.g., reduced environment), while adsorbed P might be released in such adverse conditions.

Quantitatively, adsorption of P is the single most important mechanism for P removal in a CW (Jamieson et al., 2003; Kadlec and Knight, 1996; Liikanen et al., 2004; Prochaska and Zouboulis, 2006; Reddy et al., 2005; Sakadevan and Bavor, 1998). Adsorption happens when phosphate ($PO_4^{3-}$) is bound to a positively charged surface. Adsorption-desorption reactions are in equilibrium, governed by the amount of elements at hand, their P-saturation, and the prevailing physico-chemical conditions (Kokic, 2010; Uusi-Kämppä et al., 2000).

The cation usually involved in adsorption is Fe under neutral conditions, but Al cations can bind P when the conditions are basic (e.g., 7.5), as can Mn when the conditions are acidic (e.g., 6.5). Note that pH and ORP are connected by an inverse correlation. Adsorption onto CaO is also possible through either iron or ligand exchange.

Some silts, kaolinite and calcite clays, and some organometallic complexes also have chemically active surfaces that, if positively charged, can bind P (Liikanen et al., 2004; Uusi-Kämppä et al., 2000). By contrast, sand is relatively inert (Yates and Prasher, 2009), which also hampers its capacity to support plant growth. High organic matter content often reduces amount of active sorption sites, by complexing with Fe and Al (Liikanen et al., 2004).

Adsorption can operate only if the conditions are aerobic enough and it is fully reversible if the conditions become too reduced (Blackwell et al., 2002; Reddy et al., 1999). At 300 mV or over, Fe is present in its oxidized and P-binding, immobile form: $Fe^{3+}$. Below this threshold, it is – at least partially –, reduced in its mobile form ($Fe^{2+}$), which is unable to retain P; any previously adsorbed P will be released: e.g., $FePO_4$ is reduced into soluble $Fe^{2+}$ and mobile $PO_4^{3-}$ (Drizo et al., 2002; Mann, 1997). Part of this P can resorb onto Al oxides, which can sustain lower Eh before being reduced (80-100 mV) (Liikanen et al., 2004). Also, because pH tends to rise when ORP conditions go down, $OH^-$ ions can replace P onto the aluminum complex, hindering P adsorption and compounding desorption (Liikanen et al., 2004). Low salt concentrations can also favour desorption of P (Uusi-Kämppä et al., 2000), as can flooding-drying cycles.

At pH > 8 and in the presence of $Ca^{2+}$ ions, the main P removal mechanism is precipitation of P (orthophosphate or hydrogen phosphate) to form calcium phosphates, mainly hydroxyapatite (Equations 2-1 and 2-2; Wiechers, 1987).

$$5Ca^{2+} + 3PO_4^{3-} + OH^- \rightarrow Ca_5(OH)\,(PO_4)_3 \qquad \text{(Equation 2-1)}$$

$$5Ca^{2+} + 4OH^- + 3HPO_4^{2-} \rightarrow Ca_5OH(PO_4)_3 + 3H_2O \qquad \text{(Equation 2-2)}$$

When a solution is exposed to air, atmospheric $CO_2$ can dissolve and form carbonate ($CO_3^{2-}$) (Equation 2-3). When $Ca^{2+}$ ions is present in the solution, they can precipitate as calcium carbonate ($CaCO_3$) (Equation 2-4), as the solubility of $CaCO_3$ in water at normal atmospheric pressure is relatively poor (47 mg·L$^{-1}$). This phenomenon takes $Ca^{2+}$ out of solution and renders it unavailable for precipitation with P. In addition, $CaCO_3$ can diminish the hydraulic conductivity of the matrix. Hence, precipitation is more efficient in the absence of air. The importance of $CaCO_3$ formation depends on pH, as bicarbonate, and carbonate ($CO_3^{2-}$) ions are in equilibrium in water according to pH.

$$CO_2 + H_2O \leftrightarrow H_2CO^3 \leftrightarrow H^+ + HCO_3 \leftrightarrow 2H^+ + CO_3^{2-} \qquad \text{(Equation 2-3)}$$

$Ca^{2+} + HCO_3^- + OH^- \rightarrow CaCO_3 + H_2O$ (Equation 2-4)

Magnesium can also easily precipitate P, the reaction product being magnesium ammonium phosphate (struvite) (Equation 2-5). A number of other minerals can be formed as P precipitates with other ions, such as strengite (Fe) and variscite (Al).

$Mg^{2+} + NH_4^+ + H_nPO_4^{n-3} + 6H_2O \rightarrow MgNH_4PO_4x6H_2O + nH^+$ (Equation 2-5)

*Uptake by vegetation*

Vegetation does take up P for its own tissue accretion when growing. As P is converted into additional plant material, it is immobilized where most plant biomass is: the leaves. Most authors ascribe the plants' contribution to 17-20% of the CW P removal during the growing season (Barker and Maltby, 2009; Kokic, 2010; Uusi-Kämppä et al., 2000). However, P removal by plants is only significant on a short term basis (Kadlec and Knight, 1996). When senescence sets in, plants translocate part of their nutrients, including P, to their roots, then leaves die and fall to the ground (Verhoeven and Meuleman, 1999). As the leaf litter decay, the remaining P is released into the water (Uusi-Kämppä et al., 2000). For plants that do not have lignified structural tissues, such as herbaceous helophyte species, more than 80% of the P stored in the tissues is released at the end of the season (Simpson et al., 1978).

In cold climates, this P can easily be washed out during snow melt (McCarey et al., 2004). With lignified plants, the structural tissues do not die off at the end of the season, but P will eventually be released. Thus, the turnover time varies according to the plant species and the environmental conditions, but P removal and storage by plants is ultimately temporary, unless the biomass is harvested. Overall, plants are considered to be an insignificant sink for P in a CW (Howell et al., 2005; Lu et al., 2006a; Reddy et al., 1999; Wang and Mitsch, 2000).

The uptake rate follows the plants' growth pattern, with a maxima in the summer (Liikanen et al., 2004; Moore and Reddy, 1994). For CWs treating – agricultural or other – runoff, this implies that in many areas, including boreal climates such as that of Southern Quebec, that the plants' capacity to take up P is completely out of phase with its availability: The highest P load is in the spring with the snow melt, when the growth of plants is negligible, while the highest capacity for plants to take P is in the summer, when P load is less (Koskiaho et al., 2003; Liikanen et al., 2004; Uusi-Kämppä et al., 2000). The capacity of plants to take up P still is in phase with the vulnerability of the freshwater ecosystem, however, which is most sensitive to P pollution in the midst of the summer. Thus, CW plants prevent overloading of the receiving waterbodies by buffering the summer flow of P (Gottschall et al., 2007; Kao et al., 2004; Kroger et al., 2007).

Proportionately, P removal by plants is highest when nutrient availability is low (Shaver and Melillo, 1984). This suggests that plants might be especially useful when the incoming P concentrations already are relatively low (i.e. $< 0.100\ mg \cdot L^{-1}$) (Lu et al., 2006b). It has been observed that intermittent "starvation" of plants increases their P-removal capacity, as in intermittently-fed CWs (Farahbakhshazad and Morrison, 2003). Another aspect is the fact that as CW age, plant contribution to P removal diminishes (Shaver and Melillo, 1984; Tanner et al., 1995; Vymazal, 2004).

Nevertheless, plants contribute indirectly to P removal by maintaining ORP conditions up, as seen previously. Several studies have shown vegetated CWs to be superior in terms P removal and retention (Chazarenc et al., 2003; Kadlec and Knight, 1996; Tanner et al., 1995).

### *Accumulation in sediments*

In some conditions, as much as 25% of leaf litter might persist, thus sequestering P (Dunne et al., 2005; Liikanen et al., 2004; Pant et al., 2001). However, most of this stored litter is labile and will eventually decompose, releasing its P content (Reddy et al., 1999). A small fraction will form humus and sequester P over a longer term. Another minute fraction is made of very recalcitrant organic matter, and stays as is in the wetland sediments, forming peat. Under natural conditions, sediment burial is considered as the main long-term P storage in wetlands (Liikanen et al., 2004), but less so in a CW.

## Expected phosphorus removal in a sub-surface flow constructed wetland

### *Reported performance*

Much literature reports experiments in which CWs remove pollutants from wastewaters, but the reported performance is widely variable. Comparisons are further complicated because authors report efficiency using various indices: absolute removal ($mg \cdot L^{-1}$), relative removal (%), removal rate ($g \cdot m^{-1}$), mass removal rate ($g \cdot m^{-2} \cdot y^{-1}$), removal rate constant (k, $m \cdot y^{-1}$), etc.

The vast majority of published studies involve initial P concentrations that are much higher than what is found in tile drainage wastewaters in Southern Quebec, with consequentially higher P removal efficiency, as it is more difficult to reduce P concentrations that are already low. For instance, in the North American Data Base (NADB), the average TP removal performed by CWs is 57%, but this is based on an average influent concentration of 3 $mg \cdot L^{-1}$, at a hydraulic loading rate (HLR) of 3.30 $cm \cdot y^{-1}$ (Knight et al., 1993).

Dealing with surface runoff and tile drainage return flow increases the variability of pollutant removal in general, due to highly variable flow rates and concentrations (Tanner and Sukias, 2011). This is especially true in regards to P removal, and even more so in cold climates, where environmental conditions change dramatically (McCarey et al., 2004). Retention time, which reflects the size of the wetland, definitely is a main driver, as well as the type of substrate (Calder et al., 2006; Drizo et al., 2000; Jenssen et al., 1993; Reed and Brown, 1995).

For sub-surface flow systems treating agricultural runoff, reported P removal ranges from 30-98%. USEPA (1993) reports relative TP removal of 50-90% when treating this kind of wastewater with CWs in general, with typical efficiency around 65%. Braskerud (2002b), Tonderski et al. (2005) and Uusi-Kämpä et al. (2000) reported the performance of Scandinavian CWs in comparable agroclimatic conditions with removal rates of 2.26, 48.2 and 63 g TP $\cdot m^{-2} \cdot y^{-1}$, respectively. Still for the same kind of wastewater, Lu et al. (2010) found that 59% of the incoming TP was removed in CWs receiving 12.7 $cm \cdot d^{-1}$ of 0.87 mg TP $\cdot L^{-1}$, with a hydraulic retention time (HRT) of 2 days. When monitoring the performance of a CW built in the agriculture-dominated Pike River watershed, Southern Quebec, Kroeger (2008) found that it removed 44% TP over 4 seasons (May-Nov., 2003-2006).

Melbourne Water (2010) defined a fair objective as “45% TP load removal on an annual basis”. This might mean 80% removal in optimum conditions, during the summer’s low-flow, dry conditions, but a large part of the load is sent when the wetland cannot work at optimum, e.g., during peak flows and winter thaws.

Carleton et al. (2001) found removal rate constants (k, $m \cdot y^{-1}$) of 11.3-17.6 $m \cdot y^{-1}$ when evaluating the P-removal performance of CWs treating storm water in the USA. Kadlec (2000) found a median k value of 10 $m \cdot y^{-1}$ for natural non-forested wetlands. In Norway, very high P-related k values (e.g., 214 $m \cdot y^{-1}$) are reported for CWs treating agricultural runoff, probably due to high hydraulic loading rates (HLRs) (Kadlec and Knight, 1996).

*Calculating expected performance*

Predicting the performance of a CW is challenging (McCarey et al., 2004). Some attempts have been made to model P removal, but none of them are successful over a broad range of wetlands (Kadlec and Wallace, 2009). All models require the influent TP concentration to be known – if it cannot be measured, it has to be estimated from local standards.

One option is the pseudo first-order “mass balance” approximation developed by Kadlec and Knight (1996) for SSF CWs , based on empirical observations made on 90 such wetlands reported in the North American data base (Equation 2-6). Whether or not this model applies to SSvUF CWs is still unclear.

$$P\_out = 0.51xTP\_in^{1.1} \qquad \text{(Equation 2-6)}$$

where
TP_out is the effluent P concentration (applicable to a range of 0.1-15 mg TP $\cdot L^{-1}$)
TP_in is the influent P concentration (applicable for a range of 0.5-20 mg TP $\cdot L^{-1}$)

When the hydraulic loading rate (HLR) is known, Kadlec and Knight (1996) suggest another first order “mass balance” model, using a removal rate constant (k) of 12

$m \cdot y^{-1}$. This model assumes plug-flow (Kadlec, 2000; Persson et al., 1999; Braskerud, 2002) and a k that does not depend on flow rate (Q) and influent concentration (TP_in). There is growing awareness, however, that these two factors do influence the k (Braskerud, 2002b; Kadlec, 2000). In this equation, TP* is the background TP concentration that is present in the soil matrix that was used in the wetland (Equation 2-7); a conservative value of zero is commonly used (Kadlec and Knight, 1996) (Equation 2-8).

$$TP\_out = TP^{*} + (TP\_in - TP^{*})^{(-k/HLR)}) \qquad \text{(Equation 2-7)}$$
$$TP\_out = TP\_in^{(-k/HLR)}) \qquad \text{(Equation 2-8)}$$

where
HLR = Q/A
i.e. hydraulic loading rate = flow rate / surface area of the wetland

## Sizing the constructed wetland, with phosphorus as a target pollutant

Typically, P is the one pollutant that has the highest demand in terms of footprint, because its removal is performed through interaction with the surfaces of the matrix particles, and high reserves of suitable substrate particle surface area are needed for long-term efficiency (Carty et al., 2008; Kadlec and Knight, 1996). Thus, designing for P removal may be problematic when land availability is limited (McCarey et al., 2004).

### *First approach to wetland surface area calculation: hydraulic retention time*

The bigger the wetland, the higher is the hydraulic retention time (HRT). In general, the higher the HRT, the better the pollutant removal capacity (Jing et al., 2002; Knight et al., 2000; Liikanen et al., 2004); however HRT has an influence on ORP, with negative feedback on cleansing performance of certain pollutants when the HRT is above a certain level.

Empirical data can help in the choice of a HRT. In a free water surface (FWS) CW treating agricultural runoff in China, Shaoyong et al. (2010) reported that the water temperature, influent P load and concentration, and hydraulic load rate did not significantly correlate with P removal efficiency, but HRT did. Koskiaho et al. (2003) reported CWs to be a net source of $SP_i$ when HRT is too short. Another author reported a significant direct correlation between HRT and P removal efficiency in the 1.7-3.8 days spectrum (Lu, Zhang, and Xiang, 2006). Over 10 days HRT, Reinhardt et al. (2005) observed a 50-90% TP removal efficiency, but low to negative removal if HRT fell beneath 5 days. Also, more than 50% $SP_i$ was removed when HRT exceeded 7-10 days (Reinhardt et al., 2005).

For P removal, typical design HRT is 72 hours; it can be lower in retrofitting situations, but not shorter than 48 hours (Melbourne, 2010). In the case of biochemical oxygen demand (BOD) charged wastewaters (e.g., primary or secondary urban wastewaters), the USEPA (1988) recommends a rather longer theoretical HRT of 6-7 days. Desired HRT can also be found using Kadlec and Knight's (1996) hydraulic loading rate (HLR) pseudo-first order model.

The HRT expresses the time that a parcel of water takes to go from one end of the wetland to the other (Q/V), so the volume of the wetland can be derived from it by integrating the flow rate of wastewater that is meant to be treated over a given time period. Treating maximum 20% of the 2 years average recurrence interval flow seems to be a fair objective (Christianson et al., 2011b). If the flow rate is not known, it can be estimated by taking into account the size of the drainage basin (the surface area that is drained, or watershed) and the agroclimatic conditions prevailing in this specific watershed: climate (rainfall intensity and frequency, snow accumulation, possibility of soil freeze), land slope, soil type, crop, proportion of the watershed that is drained by a tile drainage system, etc. When the CW is to be installed in-line to treat return flow only, the peak flow can be estimated from the diameter of the drain outlet (Christianson et al., 2011a).

In the case of tile drainage return flow, which is stochastically produced, another way of determining the CW volume would be that of Reinhardt et al. (2005): the volume of the wetland should be equal to the desired HRT multiplied by the expected maximum daily discharge generated by a 2 years recurrence rain event.

After the necessary volume is known, the surface area can be determined, dividing for the height. Height (depth) generally hovers around 60 cm for sub-surface flow (SSF) CWs (Vymazal and Kröpfelová, 2008). In a cold climate, depth should be more important, at about 90 cm, so that water circulation can continue even when the first few top centimeters are frozen (Mander & Jenssen, 2003).

*Second approach to calculating wetland surface area: watershed to wetland ratio*

In the context of a CW treating runoff, the wetland's surface area can be determined based on recommendations of the ratio of the wetland size compared to the watershed area, bypassing the need to calculate expected efficiency and HRT. The efficiency of pollutant removal is usually inversely proportional to this ratio (Kovacic et al., 2000). When dealing with runoff, the wetland:watershed ratio is the single most important dimensioning issue CW designers should focus on, as it dictates the HRT, which highly influences the performance (Knight, 2000; Koskiaho, 2006). Schueler (1992) recommends the wetland to represent at least 1% of the watershed, but recommendations usually hover around ratios of 4-5% (Kovacic et al., 2000; Larson et al., 2000; Reinhardt et al., 2005). Mitsch et al. (2001) suggest that returning 3-5% of agricultural watersheds back to wetlands would be sufficient to substantially impact water quality. Norwegian CWs treating agricultural runoff are rather small, often only 0.1 % of the watershed surface area, but still have proven useful as a third line of defense in the BMP package (Braskerud, 2002b).

*Third approach to calculating wetland surface area: models*

A commonly used model for the calculation of a sub-surface horizontal flow (SShF) CW's surface area is the empirical one developed by Rousseau et al. (2004), taking into account the target pollutant, influent concentration and desired effluent concentration. Computer programs have also been developed to help in the design of CWs, using higher-order modeling languages (e.g., STELLA$^{TM}$; Richmond et al., 1987). These are based on mass-balance water budgets and branching off from conventional wastewater treatment plant design (Ladegaard et al., 2001; Mitsch and Wilson, 1996; Zhang and Mitsch, 2005). The hydrology of CWs is far from ideal (i.e., plug-flow vs. completely mixed), but these models can still provide useful approximations.

### *Adjustment of the wetland dimensions*

The length:width ratio (aspect ratio) also is of prime importance, as it dictates the velocity of the water in the wetland (Shaoyong et al., 2010). For SSF CWs, the L:W ratio usually is within the 2-4 bracket (Crites et al., 2006), but Kadlec and Wallace (2009) suggest that a ratio of up to 10 is reasonable. Free water surface (FWS) CWs might have ratios as low as 1, as the lateral distribution is more important in such system (USEPA, 2000b).

Anywhere in a SSF CW, the velocity has to stay within a certain limit, in order to prevent scouring, whereby accumulated pollutants could be re-suspended, or biofilm be detached, due to excessive shear-stress. As wetlands usually are longer then wide, maximum velocity is usually attained in the vertical length plane; thus, maximum velocity is calculated by dividing the flow rate by the cross-section. All consulted authors recommend that maximum velocity be kept under 0.5 $m \cdot s^{-1}$ (e.g., Jones, 1995; Melbourne Water, 2010), with the ideal being 0.2 $m \cdot s^{-1}$ (Jones, 1995). If velocity cannot be kept in check by tweaking the L:W ratio, this is when the CW has to be separated into more than one parallel cell.

## What substrate to use in a sub-surface constructed wetland targeting phosphorus?

As the vast majority of pollutant removal processes engage the substrate, this CW component is of a paramount importance. When P is the target pollutant, the optimum substrate has a maximal adsorption and precipitation potential for a minimal cost and space and this, on the long term, while enabling ancillary benefits. The substrate's capacity to retain P thus has to be balanced over its other functions: plant growth and water circulation.

For the plants to grow, the substrate particles have to be chemically active enough to be able to retain nutrients, which – like the adsorption and precipitation potential –, is reflected in the cation exchange capacity (CEC). Clay particles are generally positively charged, and so are sand particles, but to a much lesser extent. The higher the CEC (Al, Fe and Ca content, etc.) in the soil, the greater the P-binding capacity. A soil that has a high adsorption capacity, however, might also be a high source of P when the conditions permit desorption (Yates and Prasher, 2009).

Sufficient organic content also is necessary for plant growth, but too much (negatively charged) organic matter would occupy the positively charged P-adsorption mineral sites (Fe, Ca, etc.), diminishing the P removal capacity. Melbourne (2010) recommends that the top 150 mm layer contain at least 5% organic matter, but the rest can be totally mineral. In a trial preceding the experiment reported herein, it was observed that an amendment of 5% peat to a sandy soil gravely affected the hydraulic conductivity of the matrix, to the point of virtually stopping all water circulation.

Indeed, the substrate also has to be sufficiently permeable and coarse enough to sustain water movement and thereby limit the land requirement, which is reflected by the hydraulic conductivity ($k_s$). This feature is determined by the substrate's porosity ($\eta$), which results from the particle size ($D_{10}$ and $D_{60}$). The coarser the particle, the higher the porosity and hydraulic conductivity (Table 2-3, adapted from Chen et al., 1993), but the lower the specific surface area and chemical activity. Sand can be a suitable candidate, but fine or coarse gravel are more common, while fine and soil-based substrates are to be proscribed, especially when space is limited (Hammer 1992b; Tchobanoglous, 1997). According to the Danish Environmental Protection Agency (1999 in Arias et al., 2001), the ideal sand particle size distribution goes as follow: $D_{10}$ of 0.3-2.0 mm , $D_{60}$ of 0.5-8.0 mm and $D_{60}/D_{10}$ of <4.

Sub-surface flow CWs' matrix is often built using an amalgam of contrasted particle sizes in successive layers, so as to optimize overall pollutant removal while safeguarding plant growth and hydraulic conductivity; bigger particle sizes in the bottom, finer ones on top. For instance, HG Environment uses a patented coarse substrate mix (QV PHRAGMIX-01) covered by a sand layer in their *Roseau Épurateur*® sub-surface horizontal flow CW technology. In the design of a 70 cm-deep vertical down-flow (VdF) CW, Biang (2011) used the substrate amalgam described in Table 2-2.

Table 2-3: Hydraulic conductivity in relation to particle size for wetland substrate media usable in a constructed wetland.

| Media type | Particle size ($D_{10}$, mm) | Porosity (η) | Hydraulic conductivity ($k_s$, $cms^{-1}$) |
|---|---|---|---|
| Coarse sand | 2 | 0.32 | 1.2 |
| Gravelly sand | 8 | 0.35 | 5.8 |
| Fine gravel | 16 | 0.38 | 8.7 |
| Medium gravel | 32 | 0.40 | 10.6 |
| Coarse rock | 128 | 0.45 | 115.7 |

Table 2-2: Particle size distribution in a vertical down-flow constructed wetland.

| Thickness (cm) | Media size (mm) |
|---|---|
| 30 | 2.5-5.0 |
| 10 | 10.0–12.0 |
| 10 | 14.0–20.0 |
| 20 | 20.0–40.0 |

The substrate matrix of the CW has to be replaced when the soil is saturated with P. The lack of empirical information over long-term performance of CWs precludes accurate measurements of longevity, but it can be estimated at 15-20 years (Comeau et al., 2006; Drizo et al., 2002).

# Chapter 3 The experiment

## Phosphorus Removal in a Vertical Up-Flow Constructed Wetland Treating Agricultural Tile Drainage Return Flow

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### Abstract

An experiment was conducted to ascertain the performance of a vertical up-flow constructed wetland in treating agricultural tile drainage return flow wastewater. The 2010 experiments were conducted in triplicate, at an experimental site situated in Sainte-Anne-de-Bellevue, Quebec, on a young, newly established sandy matrix wetland (9.15 $m^2$). The influent was tightly controlled and measured (1 $L·min^{-1}$, 0.300 mg TP $·L^{-1}$, 10.00 mg TN $·L^{-1}$), and the effluent was monitored weekly over the summer period (14 weeks), tracking for nutrients – phosphorus and nitrogen – in their different species, as well as related physico-chemical parameters. The wetland was able to reduce both TP and TN efficiently, at 84% and 86%, respectively, but the treated wastewater still surpassed the water quality criteria: 0.030 mg TP $·L^{-1}$ for the prevention of eutrophication (MDDEP, 2009) and 1.10 mg TN $·L^{-1}$ for the safeguard of aquatic ecosystems (Chambers et al., 2012). Such a treatment system has to be further improved so as to mitigate this type of wastewater's impact on the environment, especially when it constitutes a significant proportion of the

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stream flow. Recommendation is made to upgrade the wetland with a dedicated P-removal substrate.

## 3.1 Introduction

### Context

Agricultural tile drains wastewater can be an important source of distributed non-point pollutants, especially when this type of wastewater constitutes a major part of the stream flow. This is especially true in regards to phosphorus, which is the main trigger to eutrophication acceleration. Compounding the situation, tile drainage return flow's phosphorus composition is highly soluble (SP), therefore bioavailable, with SPi – the majority fraction – being immediately bioavailable to plants and cyanobacteria alike.

Constructed wetlands (CWs) can be used to intercept and treat this wastewater before it reaches surface waters. CWs only find their utility as a third line of defense within a best management approach (Hammer, 1992; Mitsch et al., 1995). If P was the very exclusive potential problem, a simple P trap would do (e.g., slag filter). However, tile drainage return flow usually contains other pollutants, such as nitrates, as well as antibiotics pesticides residues, and potential pathogens, which can all be taken care of simultaneously in a CW.

In a cold climate like the one in Quebec, sub-surface CWs can be efficient throughout the year, and has a maximum P removal efficiency in the midst of the summer, when the freshwater ecosystems are particularly vulnerable to phosphorus. CWs for the treatment of agricultural tile drainage return flow can be built directly in-line, at the outlet of a drainage pipe, or at the confluence of a few tile drains, in agricultural collector ditches or first order streams.

The pulse-induced and stochastic, yet seasonally modulated production of tile drainage return flow definitely is a challenge to CWs' efficiency (Chikhaoui et al., 2008; Eastman et al., 2010; Kyllmar et al., 2006; Sims et al., 1998). Still, a number of studies have demonstrated that this technology can perform very well in terms of P removal under the variable volumes and varying contaminant levels that are typical of agricultural tile drainage runoff (e.g., Crumpton et al., 2006; Hammer, 1992; Kovacic et al., 2000; Tanner et al., 2005; Tanner and Sukias, 2011).

Some sort of equalization sometimes is necessary, so as to buffer the flow rate and reduce peak flow, which helps in maintaining the predicted efficiency; however, steady state can certainly not be expected. If the CW is installed at the outlet of a tile drain, equalization can be provided by a flow restrictor on the inlet pipe, repulsing water in the field's soil profile (Melbourne Water, 2010). Care should be taken, however, not to keep the field wet for too long. A retention basin can also temporarily retain and buffer the admission of water into the wetland, much like the septic tank of a conventional domestic wastewater treatment system.

Flow rates exceeding a certain level need be by-passed, so as to limit the size of the wetland and prevent scouring. The treatment of 20% of the 2 years average recurrence interval flow is a fair objective (Christianson et al., 2011b). The first flush is much more concentrated than what comes after, and it is not necessary to treat the base flow, as it is caused by groundwater resurgence, which is generally clean. If the tile drainage return flow is mixed with surface runoff (e.g., CW built in a ditch), appropriate measures have to be taken to account for the presence of suspended sediments. Hence, a pre-filter might be necessary, but a retention pond could provide for the bulk of suspended sediments removal (Blackwell et al., 2002; Syversen and Borch, 2005).

In a cold climate environment, special provisions have to be made for the wetland not to completely freeze during the cold months, and keep a minimum performance. The growth of plants and the addition of a thick mulch layer onto the substrate help in isolating the CW substrate matrix from the outside temperature. Building the wetland basin beneath the surrounding ground level also is advantageous, as it allows a better heat exchange with the soil's warmth. The wetland might have to be made deeper (e.g., 90 cm), so as to account for the inevitably frozen top portion during the winter months (Mander and Jenssen, 2002a).

Unlike domestic, barn, or barnyard effluents, no aeration pre-treatment is needed, since runoff (surface and tile drainage alike) contains relatively low concentrations of ammonia ($NH_4^+$), organic matter (carbonaceous biochemical and chemical oxygen demand – BOD and

COD) and particulate P (XP). Still, the presence of pesticides, antibiotics and other pharmaceuticals' residues could possibly influence the wetland's microfauna in the cleansing performance (Hussain et al., 2011b; Kim et al., 2011).

### Problem

Design guidelines for sub-surface vertical up-flow (SSvUF) CWs treating agricultural tile drainage return flow wastewaters, or CWs generally, are scarce. It is not known whether a SSvUF CW can efficiently remove P from agricultural tile drainage wastewaters and the water quality response has never been documented.

### Aim and objectives

The aim of this research was to provide information for the design of CWs. The general objective was to assess the efficiency of nutrient (N and P) removal and the processes involved. Here, the target pollutant was P, the wastewater was tile drainage wastewater, and the wetland type was a vertical up-flow system. The specific objectives of this study were:

1) Appraise the efficiency of the CW in terms of P removal.
2) Determine if, on a weekly average, the wetland can reduce P concentrations below eutrophication-related thresholds.

To the best of the authors' knowledge, this study represents the first attempt to evaluate the P removal performance of a vertical up-flow (vUF) CW treating agriculture runoff. Assessment of the contribution to eutrophication of a CW-treated tile drainage return flow wastewater was never reported either.

## 3.2 Material and methods

### Experimental site

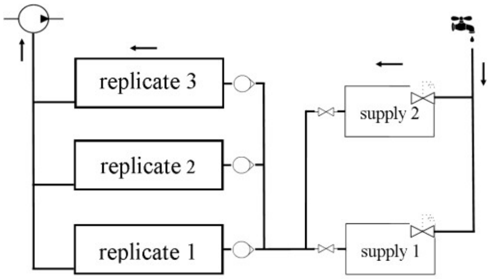

Figure 3-1: Configuration of McGill’s experimental site in 2010.

A constructed wetland (CW) research site is situated in Sainte-Anne-de-Bellevue, Quebec (45°25’21.47”N 73°56’24.06”W) (Figure 3-1 and Appendix I). The experimental site includes CW replicates that can be configured for different flow regimes (e.g., free water surface, sub-surface flow, etc.). Each basin is made up of elongated (6.1 m long) black high-density polyethylene (HDPE) half-pipes, (Ø: 1.5 m), laid on the ground with a 1% downward slope (surface area: 9.15 $m^2$). The cylindrical shape and diameter of these basins emulate that of a typical agricultural ditch or first order agricultural stream in Southern Quebec conditions, where such CWs could easily be implemented. Supply tanks made of white high-density poly ethylene (HDPE; 9 000 L capacity each; 2 m × 3 m) are situated at a higher elevation (1.7 m), from which a pressurized synthetic wastewater can be fed to the basins (maximum pressure of 3.50 psi when full and minimum pressure of 2.45 psi when near-empty.

Three CW replicates were set up as vertical up-flow systems (Figure 3-2); they were simultaneously fed from one of two elevated supply tanks, used alternatively on 24 hour periods (Figure 3-3).

The site is equipped with an automatic refrigerated autosampling system (custom-built, *Avensys Solutions*®, St-Laurent, Qc) with built-in sample storage maintained at 4 °C. The programmable system allows for sequential sampling from different points.

The site was first commissioned in 2004 and became fully operational in the summer of 2006. A number of experiments have been conducted on this site, including Yates (2008; 2009) and Hussain (2011, 2011b, 2012).

The experiment ran from July 12 to October 18, 2010 (99 days, or 14 weeks), with an acclimation period from May 31st, 2010. Observations were made at regular time intervals, once a week on Monday mornings.

### Experimental units (treatments)

The CWs were established (plumbing, matrix and vegetation) at the end of May, 2010, therefore can be described as young, newly established. To induce vertical up-flow, water was introduced along the bottom length of the wetland through a perforated agricultural drain (Ø: 10.16 cm, 4”) running on 75% of the basin`s bottom length, and was pushed up through the soil matrix by the pressure generated by the elevated supply tank. It exited the system at an outlet 20 cm beneath the soil surface. The inlet perforated drain (®Soleno, St-Jean-sur-Richelieu, Quebec) was 4.58 m long, with perforations width and area of 2 mm max and 32 $cm^2 \cdot m^{-1}$, respectively. The outlet was protected with a filter made of coarse gravel (amalgam of 1.9 cm and 0.6 cm granulates), enclosed in geotextile so as to prevent substrate wash-out.

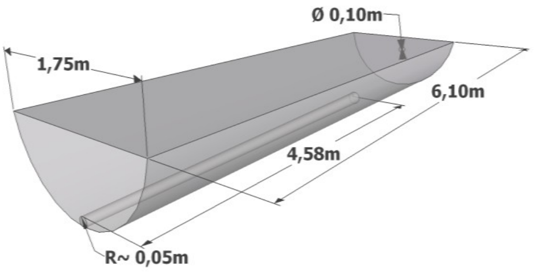

Figure 3-2: Model representation of a vertical up-flow constructed wetland replicate.

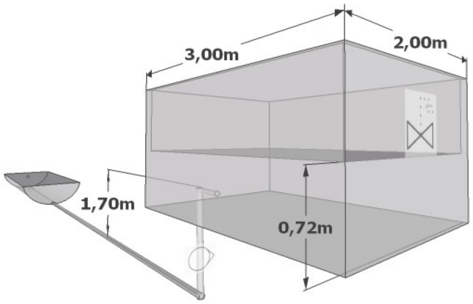

Figure 3-3: Model representation of the wastewater supply system.

The basins were filled to 80% depth with coarse sandy soil (max depth: 0.6 m; cross section: 0.71 $m^2$; volume: 4.31 $m^3$). This is the type of matrix material recommended by Yates and Prasher (2009) in light of their experiments, as it has fair hydraulic conductivity and low Al and Fe content, so as to lose less P should oxidation-reduction potential (ORP) conditions become low enough to reduce iron. The quality of this sand was assumed to be similar to that of two sand batches quarried from the same region that had been used in previous CW experiments (Hussain et al., 2012; (Table 3 1); Yates and Prasher, 2009).

Table 3-1: Characteristics of the sand matrix that was used in the wetland

| **Sand characteristics** | **(Hussain et al., 2012)** | **(Yates and Prasher, 2009)** |
|---|---|---|
| Sand (53µm < Ø < 2mm) % | 99 | 96 |
| Silt (2µm < Ø < 53µm) % | 0.2 | 3 |
| Clay (Ø < 2µm) % | 0.8 | 1 |
| OM % | 4.7 | 0.8 |
| Al (mg·kg$^{-1}$)* | 335.3 (SD: 9.5) | 232.7 (SD : 4.6) |
| Fe (mg·kg$^{-1}$)* | 57.6 (SD: 5.1) | 108.9 (SD : 4.5) |

* Al and Fe determined on Mehlich III extracts
Ø: diameter

The fresh sandy soil was virtually devoid of organic matter (circa 0.8-4.7%), so carbon was added to the influent water to emulate wetland maturity. Among other chemical reactions important to the good functioning of a wetland, denitrification needs C as a fuel (Vymazal, 2005b). Sucrose was used, at a concentration of 20 mg·L$^{-1}$, based on experiments conducted by Ugwuegbu (1996).

The vegetation growing in the basins was a type of biomass willow crop, *Salix miyabeana* Seemen (Agro-Énergie, St-Roch-de-l'Achigan, Quebec). The willows were planted as two-meter shoots in early June 2010, in a checkered, 30 cm pattern at an approximate density of 11 shoots ·m$^{-2}$.

### Synthetic wastewater

The system had been drained in the fall of 2009, and controlled water circulation was begun again on May 31st, 2010. The synthetic wastewater was produced by dissolving a specific quantity of salts of the target pollutants in a known volume of water. The water was municipal tap water that sat at least 24 h in order to evaporate $Cl_2$. A 24 h supply of water was prepared every day in one of the two supply tanks, alternatively. The synthetic wastewater was conveyed to the vUF CWs by gravity.

Throughout the 4-month experiment period, about 1 440 L·d$^{-1}$ of synthetic wastewater was released through each wetland. The target flow rate was 1 L·min$^{-1}$, representing a hydraulic load rate (HLR) of 0.16 m·d$^{-1}$ and a (bed volume) hydraulic retention time (HRT) of 2.99 days. The flow rate was controlled by ball valves and fine-tuned with rotameters (FL-2068, ®OMEGA, Laval, Quebec). It was adjusted to a little less than 1 $L\cdot min^{-1}$ when the supply tank was at maximum level (maximum pressure). This flow was chosen so as to be close to the maximum capacity of the sand matrix, given the sand's porosity and estimated hydraulic conductivity, and taking into account the size of the wetland. From Eastman et al.'s (2010) work, it was estimated that this flow rate was representative of a typical summer flow for a tile drain in Southern Quebec serving a 3 ha drainage basin (wetland-to-watershed ratio: 0.03%).

Every night, the valve from the active supply tank was shut and the alternate tank was turned on. If any water was left in a supply tank at the end of the day, it was saved and subtracted from the volume of water that needed to be mixed for the next 24 h.

It was assumed that evapotranspiration counterbalanced precipitation, which is standard practice in pilot-scale CW experiments – even in humid climates (McCarey et al., 2004). The integral validity of this assumption is debatable, but fact is that those two forces counteract one another to a certain extent, and estimation is made that this assumption induces sufficient approximation to enable comparison of the effluent concentrations to the influent concentrations. In any case, because all replicates were exposed to the same rain quantities, precipitation can be considered as controlled for.

The target concentration for P was 0.300 $mg\cdot L^{-1}$ as ortho-P ($PO_4^{3-}$) and was 10.00 $mg\cdot L^{-1}$ for N as nitrate ($NO_3^-$). In other words, the target load for each basin was 43.2 mg $P \cdot d^{-1}$ and 14.400 g $NO^3$ -N $\cdot d^{-1}$. These P and $NO_3^-$ concentrations reflect the summer flow concentrations for a typical tile drainage system in conditions similar to Southern Quebec agriculture setting (Daniel et al., 1998; Fleming, 1990; Fleming et al., 1998; Tanner and Sukias, 2011). They are the same concentrations that were used on this site by Hussain et al. (2012) and Yates and Prasher (2009). P was provided by the dissolution of potassium phosphate ($KH_2PO_4$) and N by the dissolution of potassium nitrate ($KNO_3$). For complete recipe details, see Appendix I.

### Data acquisition

The flow rate out of the three CW replicates was tracked with the help of custom built tipping buckets monitored with a *SmartReader Plus 9* (ACR Systems®) pulse data logging cartridges. The data were retrieved once a week.

Water samples (1 000 mL) were pumped every 42 hours from the effluent of each vUF CW basin by the auto sampler, and immediately refrigerated. Every Monday morning, a 120 mL composite sample was formed for each CW replicate by mixing equal proportions (30 mL) from each of the 4 samples that were taken during the week, in order to produce a sample representative of the conditions encountered at different time of the day throughout the week (Yates and Prasher, 2009). A 120 mL grab sample was also taken from the effluent of the mixing tank currently in use.

The samples were put in 120 mL white plastic HDPE bottles (®Nalgene, Rochester, NY). All containers involved in sample handling were pre-washed with a detergent (*Sparkleen*®, Fisher Scientific, Waltham, MA), acid-bathed (HCl) and rinsed with distilled, deionised water (*Milli-Q system*®, Millipore, Molsheim, France). All samples were put on ice in a cooler upon retrieval from the autosampler and transported to the lab, where they were stored at 4 °C until analysis (for up to two weeks). The samples were then conditioned and analysed in accordance with USEPA-approved standard methods (APHA et al., 2005). For detailed lab procedures, see Appendix III.

TP and TN concentrations were evaluated in the weekly composite samples. To get an indication of the composition of TP and TN, the different soluble (S) and particulate (X) forms were evaluated according to their organic (org) and mineral (i) fractions. The P and N concentrations were measured by colorimetry following APHA's (2005) methods on an automated spectrophotometer (*Quickchem Model 8500*®, Lachat Instruments, Milwaukee, WI, methods 10-115-01-1-A, 10-107-04-1-a and 10-107-06-2-C). From these concentrations, removal efficiencies and ratios were calculated. For detailed lab procedures, see Appendix III. TP, SP, TN and SN, concentrations were determined on persulfate-digested samples, following Ebina et al.'s (1983) method. The Lachat instrument was calibrated to an accuracy of $r \geq 0.995$ and less than 10% residual error for every calibration standard.

Dissolved organic carbon (DOC) concentrations were analysed according to APHA (2005) on a TOC/VCSN analyzer (®Shimadzu Scientific Instruments, Columbia, MD, method 415.1, USEPA, 1974), in the weekly composite samples. Again, the detailed lab procedures can be found in Appendix III. DOC is indicative of the carbon loading, which is related to the biochemical oxygen demand (BOD).

Measurements of pH, temperature and ORP were taken from every sample bottle before it was sent to the lab. The readings were made with a Horiba multimeter (model D-52®, Horiba Ltd., Tokyo, Japan). All probes were calibrated and stored according to Horiba's specifications (Horiba, 2003). The ORP electrode was calibrated with a 250 mV solution before the first seasonal reading and was verified every three weeks. The pH electrode was calibrated every week.

### Reporting censored data

Table 3-2: Concentration of the standards used for calculating the method detection limits and the limits of quantitation.

| Analyte ($mg\cdot L^{-1}$) | Low-range standard | MDL | LOQ |
|---|---|---|---|
| $PO_4^{3-}$–P | 0.200 | 0.011 | 0.027 |
| $NO_2^-$+$NO_3^-$ – N | 1.00 | 0.04 | 0.10 |
| $NH_4^+$+$NH_3$–N | 0.08 | 0.021 | 0.052 |

Given that some observations were close to the Instrument Detection Limits (IDLs), the Method Detection Limits (MDLs) and Limits of Quantitation (LOQ) were determined (Table 3-2). The MDL represents the minimum concentration of a substance that can be measured and reported with 99% confidence that the concentration of analyte is greater than zero (Huston and Juarez-Colunga, 2009). The MDL takes into account the variance brought about by the observer as well as the whole set of lab procedures, including the chemicals and the solutes (Ripp, 1996). The LOQ is the threshold from which the value can be considered as true within reasonable doubt, and thereof reported as a single value of right accuracy (Antweiler and Taylor, 2008).

Values lying beneath the MDL were expressed here as an interval with lower bound of 0 and the upper bound being the MDL and are said to be "censored". The values between the MDL and the Limit of Quantitation (LOQ) were reported as single values, but are more likely to be inaccurate than those greater than the LOQ. The MDLs and LOQs were calculated following one of USEPA's (1982) recommended methods. The MDL was computed by multiplying the standard deviation obtained from the analysis of 7-10 replicates (n) of a low-range standard by the one-tailed Student's T value at α=0.01 and n-1 degrees of freedom. The LOQ was computed by multiplying the MDL by 2.5.

### Data processing

Preliminary verification indicated a number of erroneous data (e.g., $NO_2^- + NO_3^- > TN$), which were rejected based on USEPA's (1996) quality control guidelines (see Appendix IV). In this experiment, there was a clear difference between the SP and TP concentrations, and between $SP_i$ and SP. The P fractions were therefore reported independently. $NO_2^-$ being easily oxidized into $NO_3^-$, these two compounds were reported together.

The median was used to estimate central tendency, because it is less influenced by extreme values, skewed data or censored data (Huston and Juarez-Colunga, 2009). The interquartile range (IQR) was used in expressing the statistical dispersion, i.e. the range which can be reasonably assumed to include the true value (Miller and Miller, 1993). The boxplots used herein to depict variability were built following Tukey's (1977) style: any value smaller than 1.5 × 25th percentile and bigger than 1.5 × 75th percentile is considered as outliers and plotted with asterisks (Figure 3-4). The relative width of the boxplot expresses the relative size of the sample (width= $\sqrt{n}$) (Chambers, 1983). When possible, the log scale was used so as to be able to better appreciate the extent of the spread, and make comparisons. Where necessary, the censoring level was depicted with a line through the schematic.

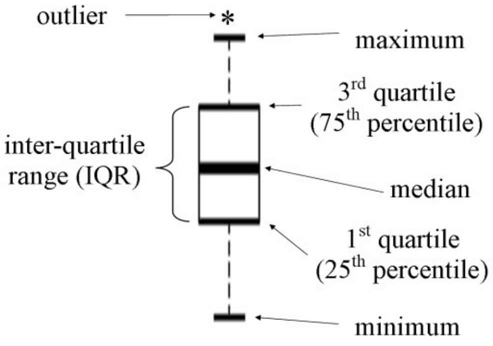

Figure 3-4: Boxplot schematic.

When the set of observations included censored data, the summary statistics (median and IQR) were computed using Kaplan-Meier (K-M)'s survival analysis estimator (i.e. product limit estimator; Kaplan and Meier, 1958). This non-parametric estimator is based on the reliability theory and generates a likelihood (step) function with a confidence interval of 90%. The K-M estimator was developed to estimate survival (S) up to a certain time (t) for the i$^{th}$ individual (Equation 3-1). In left-censored water quality analysis, t can be construed to MDL.

$$\hat{S}(t) = \prod_{t_i<t} \frac{n_i - d_i}{n_i} \qquad \text{(Equation 3-1)}$$

This method is recognized to give the best results when dealing with small samples (i.e. n <20), among the alternatives recommended by She (1997) and the USEPA (2006) (see Appendix V). For the data sets that included censored data ($SP_i$ and $NH_4^+ + NH_3$), comparison was made between the results obtained by different "classical" methods (substitution and exclusion), and the "alternative" (robust) K-M estimator, so as to provide insight into the reliability of the conclusions.

Statistical analysis

All the experiments were conducted in triplicate on pilot-scale wetlands. The basins were exposed to the same environmental conditions: sun, wind, rain, etc. All experimental variables were tightly controlled, so that the experimental units would be subjected to the same experimental factors: flow rate, influent concentrations, vegetation, etc. Our design was balanced (same number of observations on all basins, every week), but for a number of reasons, the sample sizes were unequal: equipment failures and inclement weather prevented the data sets from being complete. The locations of the replicates on the experimental site were originally chosen randomly, in order to separate the effects of the locations of the replicates. As the CW replicates were randomly chosen, the conclusions, based on 14 week experiments in the summer conditions of a hemiboreal climate, can be extended to the whole statistical population: all vertical up-flow constructed wetlands (vUF CWs) operating in similar conditions (Miller and Miller, 1993).

Statistical analysis was done using R (*version 2.13.0, 2011*© The R Foundation for Statistical Computing, Vienna, Austria). R can readily accommodate left-censored data, with the NADA package, which is not yet the case with any commercially-available statistical packages (Huston and Juarez-Colunga, 2009). In this study, statistical significance was *a priori* attributed at a significance level (α) of 0.10. If the same data were used more than once in the same test, a Bonferroni correction was applied: α'

(Huston and Juarez-Colunga, 2009). This was the case when comparing the response of the three replicates among each other, because all three received their influent water from the same stream (influent was non-independent among the CW replicates); in these cases, α' = 0.033.

All statistical tests used throughout this study were non-parametric, which is generally recommended for water quality analysis (Berryman et al., 1988; Hirsch et al., 1982; Lettenmaier, 1976). In any case, sample sizes were small (max 14 observations) and could not be assumed to be normally distributed, nor homoscedastic, which precluded the use of parametric tests (Conover, 1971; Hirsch et al., 1993; Marascuilo and McSweeney, 1977). Nevertheless, the data sets often appeared right skewed, which is an indication that the underlying distribution might be log-normal, which is typical of environmental data that have a lower limit (i.e. zero) (Antweiler and Taylor, 2008; Helsel and Hirsch, 1992; Vega et al., 1998). Another advantage of non-parametric tests is that censored data (i.e. non-zero data that are below a certain threshold, for instance the MDL) can be included in the computation of the test statistic. Among the compared sets of observations, the variance, however, was similar, which is required for non-parametric tests.

In trying to discern response differences in between replicates, simple visual observations on the distributions were made. When the medians of two samples are encompassed within one another's IQRs, it can be considered that there is no indication that there would be a statistical difference between the two distributions, or that the two samples would come from different populations (McLeod et al., 1991). It, however, does not confirm that this statistical difference be absent, which can be assessed through statistical tests. As the sample sizes involved herein (max 14) were too little to perform such tests, examination of boxplots was the best that could be done. In this exercise, "any peculiarities (e.g., outliers) should be cautiously considered" (McLeod et al., 1991).

A first statistical test was conducted to determine whether the effluent concentration of total phosphorus (TP _out) was significantly lower than the influent concentration (TP_in).

$H_0^1$: TP_out ≥ TP_in
$H_1^1$: TP_out < TP_in

Here, the *paired* version of the two-sample unilateral (i.e. one-tailed) Wilcoxon (1945) signed rank tests with continuity was used. This test can compare medians even when samples have different number of observations (Huston and Juarez-Colunga, 2009), which often was the case in this experiment. Note that it is not the difference in medians that is computed (a common misconception), but rather the median of all of the midpoints of pairs of observations (the pseudo-median), which is calculated using Hodges-Lehman statistic (Hodges Jr and Lehmann, 1963) with a confidence interval of 95%. In order to be able to compare the results with those obtained by other authors, the results were normalized and expressed in terms of different indices, such as the absolute efficiency, relative efficiency, removal rate constant, etc.. As a complement, the evolution of different ratios (e.g., SP:TP; $NH_4^+$+$NH_3$:TP) was tracked, in order to determine which P and N forms were best removed by the wetland.

Another statistical test was conducted to determine whether, on a weekly average, the wetland can reduce P concentrations below eutrophication-related thresholds.

$H_0^2$: Concentration_out ≥ criterion
$H_1^2$: Concentration_out < criterion

Here, it is the *unpaired* version of Wilcoxon's that was used – which sometimes is referred to as *Mann-Whitney's*. The TP criterion was set at 0.030 mg TP $\cdot L^{-1}$, which is the ultimate criterion for lakes or streams in Southern Quebec to prevent eutrophication (MDDEP, 2009). The soluble inorganic phosphorus ($SP_i$) criterion was set at 0.010 mg$\cdot L^{-1}$, which is the concentration from which P can cause the same effect if entirely inorganic and soluble (Sharpley and Smith, 1989; Sharpley et al., 1992; Vollenweider and Kerekes, 1980).

For data sets that included censored observations, the Peto-Prentice test (Peto and Peto, 1972) was performed on Kaplan-Meier fits, which is a slightly more robust improvement to Gehan's (1965) generalized Wilcoxon. Here, the tests' results were compared with those that would have been obtained by processing the observations through substitution and elimination procedures.

In order to be able to evaluate the eutrophication-inducing potential of the water coming out of the wetland, calculation was made of the proportion of weekly samples that can be categorized as oligotrophic (< 0.010 mg TP $\cdot L^{-1}$), mesotrophic (0.010-0.030 mg TP $\cdot L^{-1}$), eutrophic (0.030-0.100 mg TP $\cdot L^{-1}$) and hyper-eutrophic (> 0.100 mg TP $\cdot L^{-1}$). These levels were determined following Carlson's (1977) Trophic State Index (TSI) for freshwater ecosystems.

As a complement, the effluent N concentrations were evaluated. The total nitrogen criterion was set at 1.10 mg TN $\cdot L^{-1}$, following Chambers et al. (2012) recommendations for the protection of ecological condition of agricultural streams in the "Mixed woodplains" region, which encompasses Southern Quebec. The ammonia nitrogen ($NH_4^+$+$NH_3$) criterion was set at 0.5-1.5 mg$\cdot L^{-1}$, which is the pH-dependent toxicology criterion used in Quebec by the Ministry of Environment (MDDEP, 2009) for freshwater ecosystems.

## 3.3 Results

### Influent wastewater

The quality of the influent water was assumed to be the same as the seasonal median of the observations made of the influent, because it was the best estimate at hand (Figure 3-5 to Figure 3-8). Accordingly, the comparison tests (Wilcoxon*s*) between effluent wastewater quality and influent wastewater quality was performed between the aggregated effluent observations and the (unique) influent seasonal medians. The influent seasonal measured total phosphorus (TP) median concentration was very close to the influent experimental target concentration (0.322 and 0.300 mg $\cdot L^{-1}$). The total nitrogen (TN) concentration was also very close to the target, but actually a bit higher (10.56 and 10.00 mg$\cdot L^{-1}$). The latter is rather surprising because if anything, it should have been a little lower, given the occurrence of biological activity in the supply tanks that could have denitrified some nitrogenous compounds. In any case, most N entering the wetland was already in the oxidized form: 70% of TN was nitrites and nitrates ($NO_2^-$+$NO_3^-$), while ammonia nitrogen ($NH_4^+$+$NH_3$) only accounted for 1% of TN.

The high $SN_{org}$ concentration in the influent was not expected ($SN_{org}$:TN = 11.55%, results not shown), as the synthetic wastewater was composed with mineral forms of N ($KNO_3$), but this $N_{org}$ may have derived from the growth of plankton in the supply tanks. Plankton growth was kept in check with a tarp covering the supply tank to block the sunlight, but it was still present. The addition of sugar (i.e. carbon) to the synthetic wastewater mixture seems to have promoted plankton growth, as less plankton was observed in supply tanks used for a simultaneous experiment with same nutrient concentration but no additional carbon.

Note that soluble inorganic phosphorus ($SP_i$) and $NH_4^+$+$NH_3$ were censored, with the values lying below the MDL represented as intervals (0-MDL)[b], and the central tendencies were computed using K-M estimator. The medians were situated above the MDL and were estimated to be 0.018 mg$\cdot L^{-1}$ for $SP_i$ and 0.120 mg$\cdot L^{-1}$ for $NH_4^+$+$NH_3$.

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[b] In the case of $NH_4^+$+$NH_3$, the minimum lying at zero, it cannot be represented on a log scale.

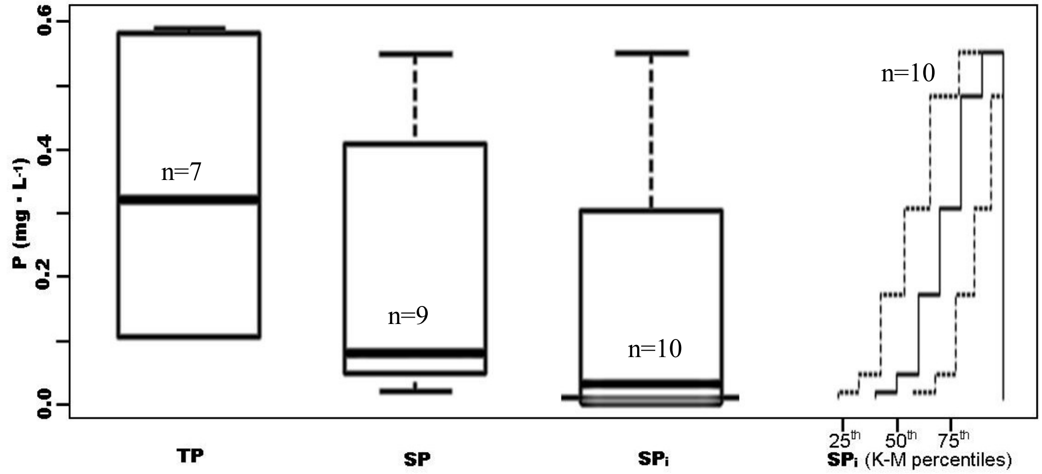

Figure 3-5: Phosphorus concentrations in the influent.
On the $SP_i$ likelihood function, the dashed lines indicate a confidence interval of 90%.

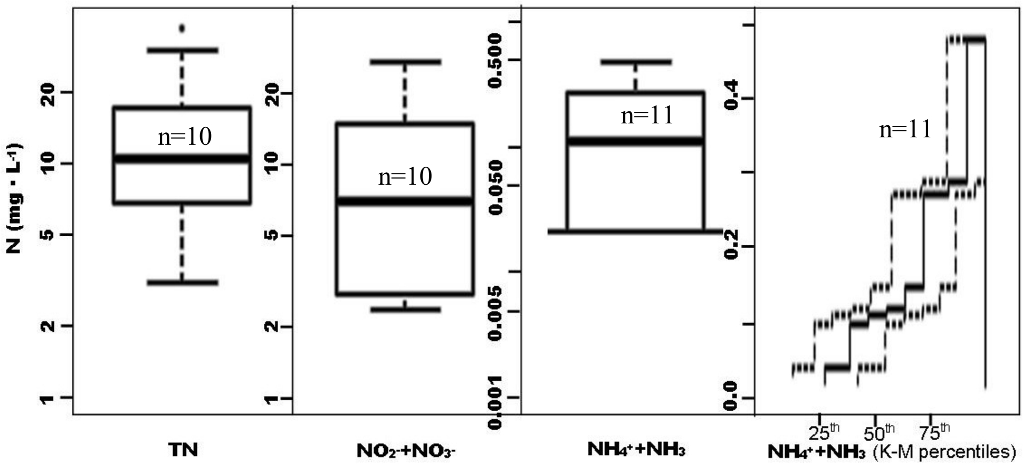

Figure 3-6: Nitrogen concentrations in the influent.
Note that the vertical axes for the first three sub-figures are logarithmic. On the $NH_4^+$+$NH_3$ likelihood function, the dashed lines indicate a confidence interval of 90%.

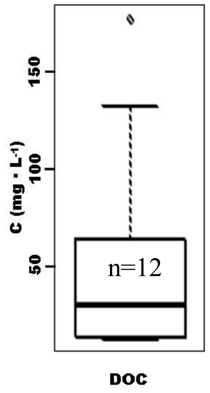

Figure 3-7: Soluble organic carbon concentration in the influent.

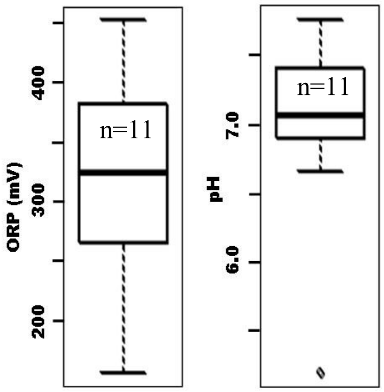

Figure 3-8: Physico-chemical conditions in the influent.

The K-M method was used to determine influent median $SP_i$ and $NH_4^+$+$NH_3$ concentrations because it is the most robust method (She, 1997). For instance, if a substitution method had been used for the estimation of the influent $SP_i$ concentration, the median would had been calculated as 0.031 mg $SP_i \cdot L^{-1}$, which is higher than what was obtained by K-M (0.018 mg $SP_i \cdot L^{-1}$), no matter the proxy used (0.5 × MDL, 1 × MDL or other). The similarity of the substitution methods' results is due to the fact that less than 50% of the influent $SP_i$ concentrations were censored (4 out of 10) and this, at a low censoring level (of 0.003 $mg \cdot L^{-1}$). The apparent big difference between 0.018 $mg \cdot L^{-1}$ and 0.031 $mg \cdot L^{-1}$ and is due to the fact that there was only a small, even, number of observations (n=10), with 0.018 and 0.045 occupying the 5th and the 6th rank. Thus computation of a "classical" median renders 0.031 $mg \cdot L^{-1}$ ((5th rank + 6th rank)/2), but using a K-M fit, the median is estimated to have more chances falling onto 0.018 rather than 0.031 (or anything else). Note that the median obtained by K-M, rather than being the middle occurrence, is the value associated with the first case to have a cumulative "survival" probability of $\geq 0.5$. If the censored values had been excluded, the median would had been evaluated to be 0.237 mg $SP_i \cdot L^{-1}$, which is much higher than that rendered by the K-M estimator (0.018 mg $SP_i \cdot L^{-1}$) or the "classical" substitution method (0.031 mg $SP_i \cdot L^{-1}$), as the 4 lower values would have been discarded. In the same way, if the 0.5 × MDL substitution method had been retained for estimating the $NH_4^+$+$NH_3$ seasonal influent median, it would had been evaluated to be 0.111 mg $NH_4^+$+$NH_3 \cdot L^{-1}$, which is lower than what was obtained by K-M (0.120 mg $NH_4^+$+$NH_3 \cdot L^{-1}$). Had the non-detects been excluded, the $NH_4^+$+$NH_3$ influent concentration would had been thought to be 0.137 mg $NH_4^+$+$NH_3$ $\cdot L^{-1}$, which also is higher than the median obtained by K-M. These observations confirm that exclusion induces an undue upward shift onto the data set – all quartiles are bumped up –, even at low censored proportions. This comes as a clear plea against exclusion, even when the censored proportion is modest.

The flow could not be appraised with confidence because the flow meters frequently stopped functioning. This malfunction was due to the growth of algae in the tipping buckets and adjoining pipes, despite being covered with aluminum foil. The high nutrient content (especially carbon) and the warm temperatures did little to lessen the problem. The data loggers also frequently malfunctioned. However, the volume of water that was sent to the wetland on a daily basis was strictly controlled and the flow was regulated with valves and a flow-meters. Therefore, it can be assumed that the flow was close to the design flow of 1 L·min$^{-1}$.

In all sub-surface flow (SSF CWs), aerobic (high oxydo-reduction potential – ORP) conditions typically only occur in the few centimeters beneath the contact zone with air and in the vicinity of the roots (rhizosphere). In the vertical up-flow (vUF) version, high ORP conditions are also likely in the distribution zone, depending on the quality of the influent water. With a median ORP of 324 mV (IQR: 117 mV) in the influent wastewater (Figure 3-8), oxidized conditions may have occurred at the bottom of this vUF CW as well.

### Total phosphorus evolution

The wetland attenuated the TP concentration by a median proportion of 84% ($p=1.3 \times 10^{-6}$)[c] from 0.322 mg·L$^{-1}$ in the influent to 0.052 mg·L$^{-1}$ in the effluent (Figure 3-9). The median absolute TP removal thus amounts to 0.270 mg·L$^{-1}$. Bearing in mind the 9.15 m$^{2}$ surface area of the wetland, it can be said that this wetland's median TP removal rate is 0.030 g·m$^{-1}$. When controlling for the hydraulic loading rate (i.e. the volumetric flow per unit area: 57.44 m·y$^{-1}$), the median TP mass removal rate is 15.51 g TP ·m$^{-2}$y$^{-1}$.

The variability of the TP concentration in the effluent was high (Figure 3-9). For instance, the aggregated response shows a relative inter-quartile range (IQR) of 162%. More worrying, the median effluent TP concentrations are not all encompassed within one another's IQRs;

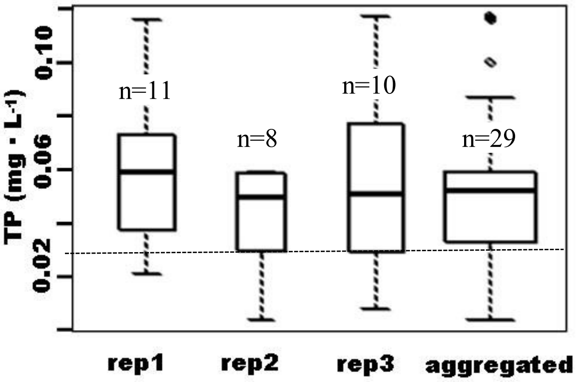

Figure 3-9: TP concentration in the effluent, by detail replicates and aggregated, in relation to the criterion as indicated by the dotted line. The median influent TP concentration was 0.322 mg·L$^{-1}$.

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[c] n=21 and 29, pseudo-median= 0.272

in particular, replicate 1's median is higher than replicate 2's 75th percentile. This indicates that the replicates behaved differently. Given the small number of observations, these apparent differences were not statistically significant. When the replicates were analyzed independently, however, the TP attenuation was statistically significant in all cases.

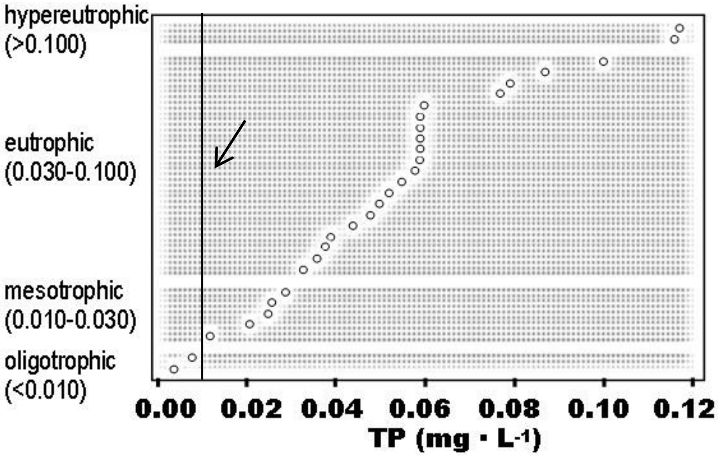

Figure 3-10: TP concentration in the constructed wetland effluent in relation to the Carlson (1977) Trophic State Index groupings, with Method detection limit (MDL).

The CW reduced the effluent TP concentration to below the eutrophication criterion of 0.030 mg·L$^{-1}$ ($p \leq 0.001$) in only 24% of the cases. Similar results were obtained when analyzing the 3 replicates independently (18%, $p=0.003$; 25%, $p= 0.004$; 30%, $p \leq 0.001$). As can be appreciated from the dotchart in Figure 3-10, the effluent water could be deemed as oligotrophic (<0.010 mg TP ·L$^{-1}$) in 7% of the cases and 17% of the samples can be considered as mesotrophic (0.010-0.030 mg TP ·L$^{-1}$). The rest (76%, or 22/29 observations) has a high eutrophication-inducing potential, with 69% comprised between 0.030-0.100 mg TP ·L$^{-1}$ (eutrophic) and a sheer 7% still being hyper-eutrophic (> 0.100 mg TP ·L$^{-1}$). What can be said is that the CW was able to bring the water down from a hyper-eutrophic state (median influent: 0.322 mg TP ·L$^{-1}$) to a eutrophic state (median effluent: 0.052 mg TP ·L$^{-1}$); however, this was not achieved on a permanent basis, as 2 out of 29 observations were still above the hyper-eutrophic bar (0.100 mg TP ·L$^{-1}$).

## Soluble phosphorus evolution

The wetland decreased the SP concentration by 89% ($p=1.3 \times 10^{-7}$)[d] from a median of 0.083 mg·L$^{-1}$ in the influent to 0.009 mg·L$^{-1}$ in the effluent. A decrease occurred

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[d] n=21 and 35, pseudo-median=0.069

in 100% of the cases, although the variability of the effluent SP concentration was very high (Figure 3-11). The aggregated replicates' relative IQR was 267%, but the medians were all encompassed within the IQRs of the other basins, which mean that there is no indication the replicates behaved differently in terms of SP removal. XP declined 82% ($p=1.3 \times 10^{-7}$)[e], from 0.239 $mg \cdot L^{-1}$ in the influent to 0.043 $mg \cdot L^{-1}$ in the effluent.

It should be remembered that SP concentrations lower than the censorship level (MDL: 0.011 $mg \cdot L^{-1}$) were possible. This is because the SP values were calculated by subtracting the P concentration of the (digested) blank from the P concentration of the digested sample. If the difference between the P concentration of the blank and the MDL was greater than the difference between the P concentration of the digested sample and the MDL, then the final result could be less than the MDL.

In general, the wetland did not change the SP:TP ratio. The wetland may have abated the SP:TP ratio by 22% (Figure 3-12), from a median value of 0.28 in the influent to 0.22 in the effluent, but the difference was not statistically significant ($p= 0.22$)[f]. There were instances in which the SP:TP ratio increased – this can be seen from effluent ratios being higher than the influent ratio. Because the effluent's 75th percentile is higher than the influent's median value, it can be said that SP:TP ratio augmentation happened in more than 25% on the cases. Any decrease in the SP:TP ratio may have been masked by the high variability of the SP and TP concentrations in the effluent. The moderate size of the apparent decrease (22%) compounded this difficulty.

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[e] n=21 and 35, pseudo-median=0.069

[f] n=15 and 24 , pseudo-median= 0.030

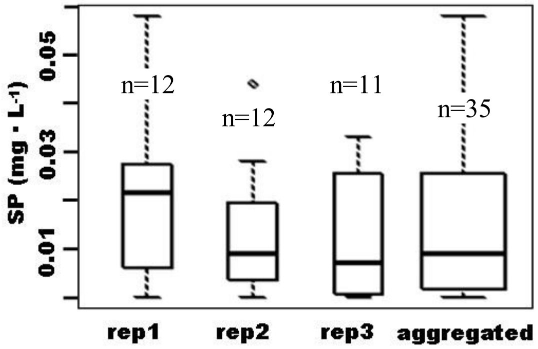

Figure 3-11: SP concentration in the effluent, by detail replicates and aggregated.
The median influent SP concentration was 0.083 mg·L$^{-1}$.

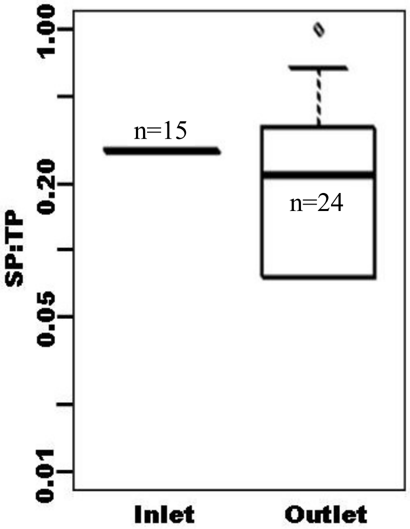

Figure 3-12: SP:TP ratio in the influent and effluent of the wetland.
Note the log scale on the vertical axis.

## Soluble inorganic phosphorus evolution

The $SP_i$ decreased by 83-100%, the concentration in the influent being 0.018 mg·L$^{-1}$ and 0-0.003 mg·L$^{-1}$ in the effluent. As all $SP_i$ data were censored, rendering robust methods such as K-M unusable, the effluent $SP_i$ was estimated using substitution. Table 3-3 summarizes the removal extents that would have been rendered using different proxies. The choice of a proxy of 0-0.5 x MDL is based on the fact that environmental data are commonly right-skewed (Antweiler and Taylor, 2008; Helsel and Hirsch, 1992; Vega et al., 1998). However, no science can back up the choice of a proxy comprised in this bracket (0-0.5 x MDL) over another – "Substitution between zero and the MDL is arguably as valid as another (Helsel, 2005b)" – but nonetheless common practice. Note that had a different proxy value been substituted for estimating the effluent $SP_i$

Table 3-3: $SP_i$ removal efficiency as estimated using different proxy values for censored data.

| Substitute | $SP_i$ removal | p-value |
|---|---|---|
| 1 × MDL | 65% | 0.0002[g] |
| 0.5 × MDL | 83% | $9.877 \times 10^{-6}$[h] |
| 0.25 × MDL | 85% | $3.416 \times 10^{-8}$[i] |
| 0 × MDL | 100% | |

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[g] n=10 and 31, pseudo-median=0.143
[h] n=10 and 31, pseudo-median= 0.143
[i] n=10 and 31, pseudo-median= 0.015

concentration, the removal efficiency would still have been significant, but of a different magnitude (Table 3-3). If the censored data had been excluded, no results could have been obtained at all.

From this example, it is recommended that care be taken to ensure the greatest accuracy possible in lab protocols. As well, researchers should re-examine their use of "classical" statistical methods in favour of methods for analysis of censored data. In this case, for instance, the MDL (0.011 mg $SP_i \cdot L^{-1}$) is close to the criterion (0.010 mg $SP_i \cdot L^{-1}$); in a regulatory decision context, compliance might be erroneously granted with one substitution method but refused with the other. It is thus recommended that, when possible, robust methods such as K-M be used.

Overall, the $SP_i$:SP ratio did not change. It may have decreased by 36%, passing from a median 0.22 in the influent to 0.14 in the effluent, but this difference was not statistically significant ($p= 0.71$)[j]. Here, the variability was very high as well, with a relative IQR of 200% for the aggregated replicates' $SP_i$:SP ratio in the effluent (Figure 3-13). In more than 25% of the cases, the $SP_i$:SP ratio apparently increased, which is expressed as a "negative reduction". Here, the replicates behaved differently from one another, so the median of each was not encompassed within the IQRs of the others.

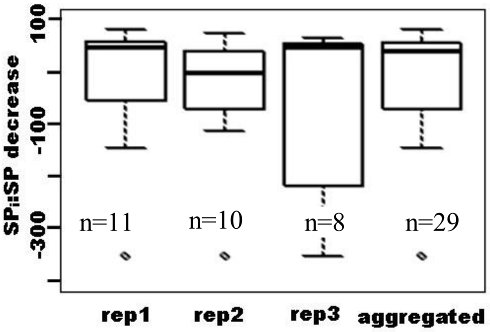

Figure 3-13: $SP_i$:SP reduction, by detail replicates and aggregated.
The median influent $SP_i$:SP ratio was 0.22 (n=24).

The $SP_i$:SP ratios in the effluent were not censored data because they were calculated by dividing the median effluent $SP_i$ (computed using K-M estimator) by the median effluent SP (computed using the traditional method). This resulted in an underestimate of the variability, because K-M does not give statistical dispersion. Still, the variability of the SP was large enough to mask any change in the $SP_i$:SP ratio. Had the effluent $SP_i$ been calculated using another proxy, the difference between the influent and effluent $SP_i$:SP ratios would have been different, but never significant.

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[j] n= 24 and 29, pseudo-median= 0.020

## Total nitrogen evolution

The median TN concentration diminished 86% ($p = 2.1 \times 10^{-5}$)[k], from 10.56 $mg \cdot L^{-1}$ in the influent to 1.52 $mg \cdot L^{-1}$ in the effluent, with an absolute removal of 9.04 $mg \cdot L^{-1}$ and mass removal rate at 519.26 $g \cdot m^{-2} \cdot y^{-1}$. Important intra-basin variability was present (Figure 3-14), with relative IQR for the aggregated replicates at 312%. The medians were not encompassed within one another's IQRs, shedding doubts over the inter-basin constancy; this last observation, however, has to be mitigated by the fact that the distributions all appear to be highly right-skewed, leaving little chance for the median to run the 25th percentile. The small number of observations precluded any statistical assertion of the among-replicates difference in the TN removal response. As can be seen from Figure 3-14, the effluent TN concentrations were lower than the water quality criterion (1.10 $mg \cdot L^{-1}$) in only 31% of the cases.

The TN:TP ratio did not change. Figure 3-15 shows that the median TN:TP ratio may have decreased by 14%, from 29.3 in the influent to 25.3 in the effluent, but this observation was not significant ($p = 0.31$)[l]. In more than 25% of the cases, the ratio apparently increased. Had the TN:TP ratio decreased significantly, it would have meant that the wetland was better at removing TN than TP. Again, the variability of the TN removal, along with its TP counterpart, would have masked the TN:TP ratio evolution.

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[k] n=21 and 29, pseudo-median= 11.35

[l] n=21 and 23, pseudo-median= 9.27

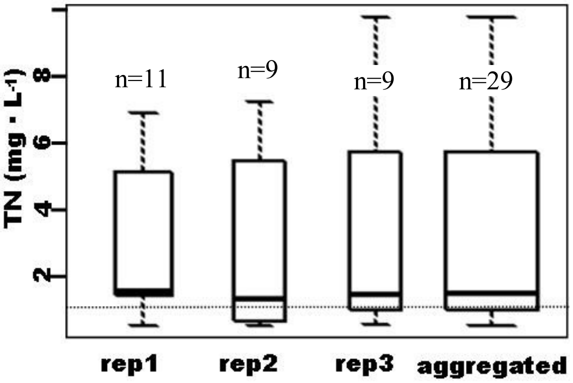

Figure 3-14: TN concentration in the effluent in relation to the criterion, by detail replicates and aggregated.
The influent concentration was 10.56 mg TN $\cdot L^{-1}$.

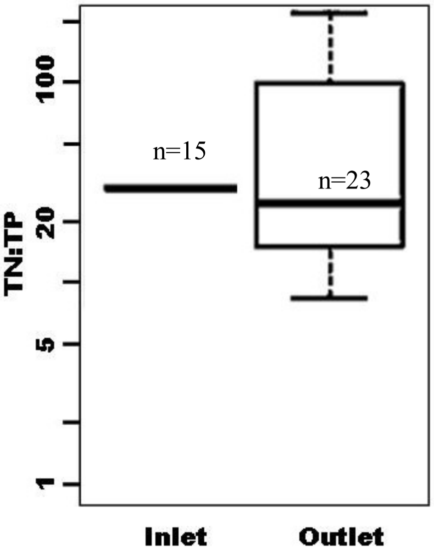

Figure 3-15: TN:TP ratio in the influent and effluent of the wetland.
Note the log scale on the vertical axis.

## Ammonia nitrogen evolution

The $NH_4^+$+$NH_3$ concentration did not change from one end of the wetland to the other. It actually may have increased 17%, but this change was not statistically significant ($p= 0.81$)[m], the median concentration passing from 0.120 mg$\cdot L^{-1}$ in the influent (obtained by K-M estimator) to 0.140 mg$\cdot L^{-1}$ in the effluent (obtained by K-M estimator). Again, the variability of the $NH_4^+$+$NH_3$ concentration in the effluent was high (Figure 3-16), with a relative IQR of 127% for the aggregated replicates, which would have masked the significance of the apparent augmentation. The distribution seems to be particularly right-skewed, with a few very large observations (max: 0.316 mg $NH_4^+$+$NH_3$ $\cdot L^{-1}$) and the rest at a much lower level.

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[m] n= 21 and 36, pseudo-median=0.030

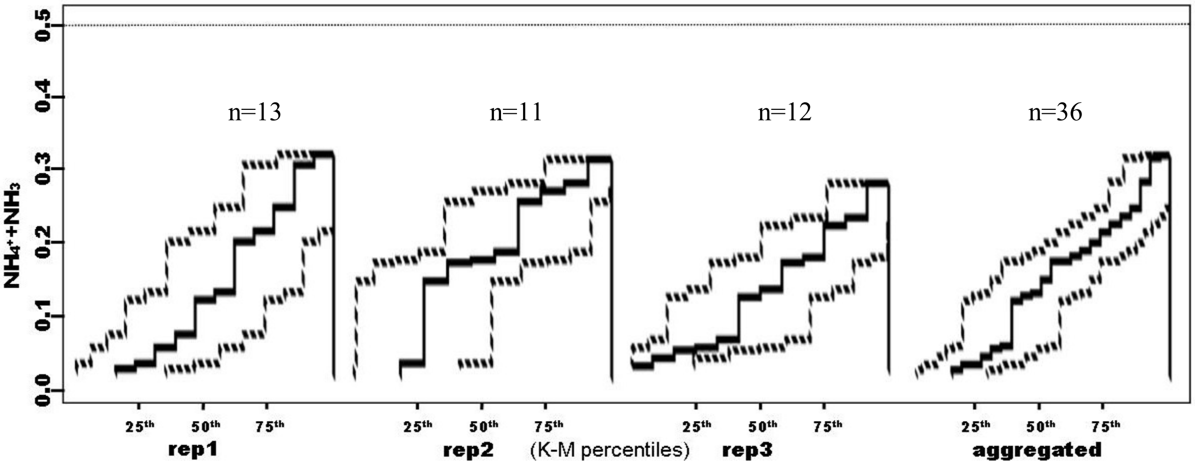

Figure 3-16: $NH_4^+$+$NH_3$ concentration in the effluent in relation to the criterion, by detail replicates and aggregated, in relation to the criterion.

Although the $NH_4^+$+$NH_3$ concentration did not change, the effluent concentration still was far less than the criterion value of 0.500 mg·L$^{-1}$ (MDDEP, 2009) in all weekly samples, at a median effluent concentration of 0.140 mg·L$^{-1}$ (Figure 3-16).

The ratio of $NH_4^+$+$NH_3$:TP increased 250% (p= 0.0002)[n], from 0.84 (obtained by K-M estimator) in the influent to 2.9 (obtained by K-M estimator) in the effluent (Figure 3-17). As the aggregated replicates' 25th percentile is situated higher than 0.84 (1.09), there were less than 25% of the cases where the ratio did not increase.

The $NH_4^+$+$NH_3$:$NO_2^-$+$NO_3^-$ ratio was 0.017 in the influent, and 0.13 in the effluent, i.e. roughly an order of magnitude higher, which means that the wetland was better at removing $NO_2^-$+$NO_3^-$ than $NH_4^+$+$NH_3$.

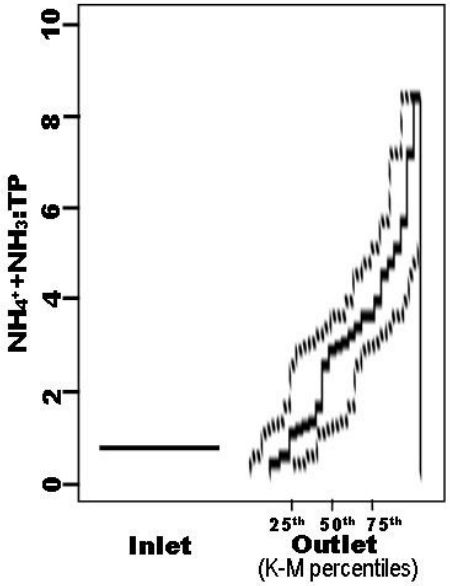

Figure 3-17: $NH_4^+$+$NH_3$:TP ratio in the influent and outlet of the wetland.
On the likelihood function, the dashed lines indicate a confidence interval of 90%.

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[n] n=21 and 26, pseudo-median= 1.156

## 3.4 Discussion

### First objective: efficiency of the wetland

*Total phosphorus removal*

Efficient phosphorus removal (84% TP and 15.51g TP $m^{-2} \cdot y^{-1}$) confirms the effectiveness of the experimental wetland in removing the target pollutant. Direct comparisons of CWs is often misleading, with the slightest difference in operating conditions influencing the P removal (Lu et al., 2010). Nevertheless, this relative TP removal is much higher than what is typically reported for CWs operating in similar conditions (Braskerud et al., 2005b; Farahbakhshazad and Morrison, 2003; Fink and Mitsch, 2004; Hammer, 1992; Kroeger et al., 2009; Liikanen et al., 2004; Lu et al., 2009; McCarey et al., 2004; Mitsch et al., 1995; Pries et al., 1996; Reinhardt et al., 2005; Yates and Prasher, 2009). For instance, Yates and Prasher (2009) reported TP removal of 41%, which is already in the high range. Congruent with our results, Liikanen (2004) reported a removal rate of 68% for an *in situ* CW. But many authors actually report net P release (Bass, 2000; Tanner and Sukias, 2011).

The TP mass removal rate of the experimental CW (15.51 g TP $\cdot m^{-2} \cdot y^{-1}$) is similar to reported values. For instance, Braskerud (2002b), Reinhardt (2005) and Fink and Mitsch (2004) reported mass removal rates of 26-71, 1.1, and 6.2 g TP $\cdot m^{-2} \cdot y^{-1}$, respectively. However, the wetland did not respond to Kadlec and Knight's (1996) so-called general first order "mass-balance" for SSF CWs, which projected an effluent TP concentration of 0.146 mg TP $\cdot L^{-1}$. This is likely due to both the influent and effluent concentrations being out of the suggested applicable ranges (0.5-20 and 0.1-15 mg TP $\cdot L^{-1}$ for the influent and effluent, respectively). This suggests the need for an improved model that can take into account low P concentrations.

The good performance of the wetland may be due to the nature of its hydrology. Vertical up-flow (vUF) systems make better use of the whole substrate matrix, with a better axial distribution – every horizon is fully used – , and deter preferential flow, as the whole volume has to be flooded before circulation begins (Breen and Chick, 1995). Water is better distributed to the root zone, where oxidized conditions can allow for P adsorption and plants can uptake P (Farahbakhshazad et al., 2000). Moreover, depending on the influent wastewater quality (biochemical oxygen demand to dissolved oxygen ratio – BOD:DO ratio, and ORP conditions), oxidized conditions can also be encountered at the bottom of the wetland, close to the inlet, which is unique to vUF systems (Farahbakhshazad and Morrison, 2003).

In conjunction, the good performance may be due to the type of plants growing on the wetland, and the interaction of the two parameters might be synergistic. *Salix miyabeana* is a biomass willow crop bred for its fast growth; therefore, the rate at which it draws nutrients (including P) from the soil is particularly high, especially in the establishment period (Tanner, 1996).

*Ratio of soluble phosphorus to total phosphorus*

In this study, the SP:TP ratio did not increase. This means that the wetland removed soluble phosphorus (SP) just as well as it removed particulate phosphorus (XP). SP removal is expected, but wetlands are usually reported to be better at removing particulate phosphorus than its soluble counterpart (e.g., Braskerud, 2002b). The former is easily removed by physical mechanisms, such as filtration or sedimentation, and part of it is then cycled into SP by desorption and/or mineralisation and adds to that which is already present in the influent. On the other hand, SP is mainly removed through adsorption; precipitation and plant uptake remove a lesser amount. Since adsorption requires particular ORP conditions to operate (high Eh), which occur in only a fraction of the wetland's total volume, SP is said to be more difficult to remove than XP.

In this study, the non-superiority of the XP removal is postulated to be caused by the effluent sampling apparatus: the sample was taken from the top margin of the "U" shaped device collecting the effluent waters, but phytoplankton could have been growing in the effluent sampling apparatus, increasing measured XP in the effluent. The device was opaque, so phytoplankton growth could not be assessed directly, but green particles were observed in the sample water.

Even though USEPA-approved Standard Methods (APHA et al., 2005) were used and samples were stored at 4 $^{o}$C, SP may have sorbed onto particles ($XP_i$) or cycled into organics ($SP_{org}$ and $XP_{org}$). This would have increased XP, which would have led to an underestimation of the SP:TP ratio at the time of sampling (Braskerud, 2002b). Desorption is also possible. The use of different kinds of filtration media may result in different measures of SP, which hampers rigorous comparison between studies (Carlson, 1996). The use of glass fibre filters, for instance, could lead to an overestimation of SP.

*Ratio of soluble inorganic phosphorus to soluble phosphorus*

The stability of the $SP_i$:SP ratio means that the wetland was not better at removing $SP_{org}$ than $SP_i$. Although not significant statistically in this experiment, this ratio typically decreases (e.g., Pant et al., 2001).

*Ratio of total nitrogen to total phosphorus*

The ratio of TN:TP did not augment, which implies that the wetland was not better at removing phosphorus than nitrogen. In this study, the difference was not statistically significant, but it still is clear that the CW was able to reduce TP (84%) while also offering other benefits, such as TN removal (86%). The wetland operated at a much higher removal rate (519.26 g TN $\cdot m^{-2} \cdot y^{-1}$) than usually reported, with typical values at 39 $g \cdot m^{-2} \cdot y^{-1}$ (Fink and Mitsch, 2004).

The TN:TP is typically observed to decrease in a wetland, as the conditions necessary to $NO_2^-$+$NO_3^-$ removal (low ORP) are much easier to encounter than the conditions leading to TP removal; $NO_2^-$+$NO_3^-$ are removed when denitrified into $N_2$ gas by anaerobic microorganisms or by dissimilatory reduction into $NH_4^+$+$NH_3$ in anaerobic conditions (DNRA). It is interesting to note that some authors argue that in a flooded ecosystem such as this experimental wetland, DNRA is the dominant $NO_2^-$+$NO_3^-$ removal process (Rütting et al., 2011).

The fact that most N was already in the oxidized form when entering the wetland precluded the limitation of TN removal by ammonia nitrification (which needs high ORP), which typically is the case in a wetland (Henze, 2008; Vymazal, 2005a; Ye and Li, 2009). In other words, the $NO_2^-$+$NO_3^-$ evolution defined the direction of TN evolution. Although not significant in this experiment, an $NH_4^+$+$NH_3$ augmentation would only lessen the importance of TN removal in a minor way.

*Ratio of ammonia nitrogen to total phosphorus*

The wetland was significantly better at removing TP than $NH_4^+$+$NH_3$, as expressed by the higher ratio in the effluent: the concentration of $NH_4^+$+$NH_3$ did not change significantly, while TP was significantly reduced. This, because TP adsorption continues at lower ORP conditions than does nitrification of $NH_4^+$+$NH_3$, and ORP tends to be generally low in a wetland. Nitrification of $NH_4^+$+$NH_3$ might also have been counteracted by DNRA. The degradation of organic N from plant and microbial growth in the wetland and from influent may also have contributed to $NH_4^+$+$NH_3$. The organic nitrogen ($N_{org}$) that was present in the influent is due to the growth of phytoplankton in the supply tanks. Had $N_{org}$ not been that high in the influent, there probably would have been less $NH_4^+$+$NH_3$ in the effluent. Plus, oxygen was consumed in the wetland by the respiration process of microorganisms mineralising $N_{org}$ into $NH_4^+$+$NH_3$; oxygen was also consumed by the nitrifying microorganisms oxidizing $NH_4^+$+$NH_3$ into $NO_2^-$+$NO_3^-$. This oxygen consumption further lowered the ORP conditions, hampering to some extent the TP removal.

## Second objective: attaining the criteria

*Phosphorus criteria*

No matter how efficient the wetland is at removing TP, the effluent concentration should not exceed the criterion. The median effluent concentration (0.052 mg TP $\cdot L^{-1}$) and the eutrophication-inducing potential of the wetland effluent (76% of the observations were above the criterion) were still too high. This CW did not perform enough to eliminate the full impact of agricultural tile drainage return flow on the eutrophication of freshwater ecosystems, especially where this constitutes a major part of the flow.

Since no increase in the SP:TP and $SP_i$:SP ratios were detected, the bioavailability of each P unit present in the effluent was not found to be higher than the bioavailability of those present in the influent. As bioavailability is an indicator of the speed at which a P unit can foster eutrophication (Nürnberg and Peters, 1984; Rigler, 1964), it can be said that the time-related character of the eutrophication-inducing potential of those P units present in the effluent was not found to be higher than that of the ones present in the influent.

It would have been accurate to evaluate the time-related character of the eutrophication-inducing potential of the effluent water using the $SP_i$ observations, with 0.010 mg $SP_i \cdot L^{-1}$ as the criterion from which P can immediately foster eutrophication if entirely inorganic and soluble. However, all the effluent $SP_i$ observations were below the censoring level (MDL: 0.011 mg P $\cdot L^{-1}$), therefore had to be estimated using substitution. Hence, the agreement to the $SP_i$ eutrophication-prevention criterion that was found (0% of the observations was above the criterion) is dubious. It has to be noted that the MDL (0.011 mg P $\cdot L^{-1}$) inherent to this experiment is very close to the eutrophication-inducing threshold (0.010 mg $SP_i \cdot L^{-1}$). No matter what, in P-limited situations, the $SP_i$ concentration should be <0.005 mg $\cdot L^{-1}$ (Sharpley et al., 1992); in the Canadian Shield and/or Appalachian context of Southern Quebec, the TP "natural" background noise in streams and rivers is 0.007 mg TP $\cdot L^{-1}$ (Berryman, 2006).

*Nitrogen criteria*

Just as in the case of TP, the TN removal efficiency of the wetland seemed admirable when looking up relative removal, but compared to the water quality criterion, the performance of the wetland in terms of TN is just as slim as in the case of TP removal – the TN criterion was respected in only 31% of the cases, with a median effluent concentration of 1.52 mg TN $\cdot L^{-1}$. This means that the ecological conditions in the receiving stream are not safeguarded (Chambers et al., 2012). Nitrogen not being the limiting nutrient in the freshwater eutrophication process, this failure to meet the water quality criterion should not be a major problem in the upper parts of these ecosystems; however, when this kind of N concentration reaches a saline environment (e.g., St. Lawrence estuary), it is likely to foster the on-going eutrophication process, N rather than P being the rate limiting nutrient in this kind of an environment (Gibson et al., 1997).

It is worth noting that although studies have shown that freshwater eutrophication can happen at TN concentrations as low as 0.40 mg TN $\cdot L^{-1}$ (e.g., Casey and Klaine, 2001), Quebec's Ministry of Environment (MDDEP, 2009) still suggests a criterion that is much more lax (2.90 mg $NO_2^-$+$NO_3^-$ –N ·$L^{-1}$), based on the Canadian Council of Ministers of the Environment's (CCME, 2003) recommendations for the protection of aquatic life. As of 2013, no TN or $NO_2^-$+$NO_3^-$ criterion exist for the prevention of eutrophication in the Quebec legislation, even though MDDEP recognizes that concentrations of ≥ 1.00 mg TN ·$L^{-1}$ are indicative of overabundance (MDDEP, 2012b); yet, this criterion is currently still under revision (MDDEP, 2009). From the foregoing, it appears that the development of TN and/or $NO_2^-$+$NO_3^-$ criteria specifically applicable to Southern Quebec conditions is urgent.

### *Interaction of phosphorus and nitrogen criteria*

Thence, not only does the wetland system need to abate TP further, but TN (especially $NO_2^-$+$NO_3^-$) has to be better taken care of as well – firstly for the protection of freshwater ecosystems and secondly for the sake of saline environments.

Because an excellent removal was already attained (84% TP and 86% TN), further amelioration is dubious, which would come from adjustments in the wetland design (hydrology of the system, soil matrix composition, plants, etc.). Anyway N and P need contrasting physico-chemical conditions to be removed – the bulk of P removal (by adsorption) is performed at high ORP conditions, while denitrification needs low ORP. As a matter of fact, the effluent concentrations that were obtained seem to be very low compared to the literature, and might be at a floor line.

### "Messy" data

Our observations perfectly corresponded to the definition of a ''messy'' data set that often is characteristic of environmental monitoring (McLeod et al., 1991), which greatly complicates their statistical analysis. For one, the variability observed in the results of this study was substantial. This has a lot to do with the fact that the mesocosms were exposed to environmental factors that are unstable and stochastic by nature – indeed, there always is a lot of variability inherent in environmental observations such as water quality data (Miller and Miller, 1993). Some weaknesses were also noted in the control of experiment factors, (e.g., hydraulic failures in specific pipes), the sampling scheme (e.g., missing samples), and the lab procedures. The data sets were also, more often than not, right-skewed, and transformations (e.g., log) did little to shape up the distribution into a normal curve, given the small sample sizes, compounded by the variability discussed above. Therefore, non-parametric tests were required. Likewise, given the lab procedures at hand, some observations comported censored values, which called for alternative, robust methods when trying to determine the central tendencies and spread. Moreover, the complex interactions sustaining the CW ecosystem masked the possibility of detecting correlations among observed variables. Varying flow rates would have compounded this situation. Lastly, missing values prohibited time series analysis in trying to discern trends, notwithstanding possible autocorrelations such as lagging and cyclic patterns that are typical of environmental data – autocorrelation invalidates many statistical methods (Hirsch et al., 1991; Lettenmaier, 1976; Van Belle and Hughes, 1984).

## 3.5 Conclusion and recommendations

A pilot-scale investigation was carried out to estimate the phosphorus removal efficiency of a vertical up-flow constructed wetland in treating agricultural tile drainage return flow wastewater, using a sandy soil substrate. The hydraulic loading rate was 0.16 $m \cdot d^{-1}$, which is representative of a 0.03% wetland:watershed ratio in typical Southern Quebec summer conditions, given the size of the wetland (9.15 $m^2$) and flow rate (1 $L \cdot min^{-1}$).

An average 84% total phosphorus removal was found. However, the average effluent 0.052 mg TP $\cdot L^{-1}$ concentration still had a high eutrophication-inducing potential, with only 24% of the samples meeting the eutrophication prevention criterion (0.030 $mg \cdot L^{-1}$; MDDEP, 2009). This wetland performed a TP absolute removal of 0.270 $mg \cdot L^{-1}$, with the removal rate standing at 0.030 g $\cdot m^{-1}$, and mass removal rate of 15.51 $g \cdot m^{-2} \cdot y^{-1}$. The wetland removed a similar total nitrogen (86%), and the difference between TN and TP removal was not significant. The effluent TN concentration was 1.52 $mg \cdot L^{-1}$, but the TN criterion for protection of ecological condition of agricultural streams (1.10 $mg \cdot L^{-1}$;

Chambers et al., 2012) was met in only 31% of the cases. TN absolute removal rate was 9.04 mg$\cdot$L$^{-1}$, and mass removal rate amounted to 519.26 g $\cdot$m$^{-2}\cdot$y$^{-1}$.

The removal trends were in the higher-range of the findings made by other authors for constructed wetlands operating in similar conditions. Thus, a vertical up-flow constructed wetland system appears to be an effective technology for removing P form agricultural tile drainage wastewater, but further cleansing is necessary so as to curtail the eutrophication-inducing potential of the discharge. Our findings apply to vUF CWs treating tile drainage wastewater with similar substrate and hydraulic loading rate (HLR) operating in a hemiboreal summer climate (15 $^{o}$C $\leq$ Temp $\leq$ 35 $^{o}$C and related precipitation). Extrapolation to other types of CWs, wastewaters, or environments may necessitate supplementary investigation.

Recommendation is made for increasing the size of the wetland to further remove nitrates, and supplement the wetland with a dedicated substrate, either added in the soil matrix or as a supplementary treatment step, in order to remove phosphorus some more. Among the materials that are currently under scrutiny for P removal, mention can be made of Fe- and Ca-rich slags (Chazarenc et al., 2007), activated alumina (Neufeld and Thodos, 1969), Mg-activated biochar (Yao et al., 2011), gypsum (Bryant et al., 2011), dewatered alum sludge (Babatunde et al., 2011), and Fe-activated woodchips, which value is compared, along with those of other materials, in a few reviews (e.g., Ballantine and Tanner, 2010; Boyer et al., 2011; Buda et al., 2012; De-Bashan and Bashan, 2004; Drizo et al., 1999; Hylander et al., 2006; Johansson Westholm, 2006; Mortula et al., 2007; Penn et al., 2007; Vohla et al., 2011).

# Chapter 4 General summary and conclusions

Increases in phosphorus levels in the freshwater ecosystems of Southern Quebec have given rise to concern over eutrophication. Agricultural runoff, including tile drainage return flow, is a major contributor of phosphorus. This situation is similar to that in many industrialized and developing countries. Constructed wetlands were investigated as part of a third line of defence in a Best Management Practices package to reduce phosphorus in water. The vertical up-flow configuration seems suitable to agricultural conditions and, as with all sub-surface systems, it can function year-round in a hemiboreal climate such as that of Southern Quebec and is known to have a better soluble phosphorus removal rate than free-water surface constructed wetlands.

A pilot-scale experiment was conducted to assess the efficiency of a vertical up-flow constructed wetland to reduce phosphorus in tile drainage return flow wastewater. A young, newly established system made of a 9.15 $m^2$ sandy soil matrix was tested in triplicate. The influent was tightly controlled, and the effluent was monitored for nutrient content. The target flow rate and influent total phosphorus and total nitrogen concentrations were 1 $L \cdot min^{-1}$, 0.030 mg TP $\cdot L^{-1}$ and 0.10 mg TN $\cdot L^{-1}$, respectively. This is representative of a typical tile drainage effluent serving a 3 ha agricultural watershed in Southern Quebec conditions. The following results were obtained:

- The wetland removed 84% total phosphorus (0.030 g TP $\cdot m^{-1}$ or 15.51 g TP $\cdot m^{-2} \cdot y^{-1}$).
- The wetland removed 86% total nitrogen (9.04 mg TN $\cdot L^{-1}$ or 519.26 g TN $\cdot m^{-2} \cdot y^{-1}$).
- The median effluent concentration of total phosphorus (0.052 $mg \cdot L^{-1}$) exceeded the eutrophication-prevention criterion (0.030 mg TP $\cdot L^{-1}$; MDDEP, 2009) in 76% of the cases.
- The median effluent concentration of total nitrogen (1.52 $mg \cdot L^{-1}$) exceeded the criterion for protection of ecological conditions (1.10 $mg \cdot L^{-1}$; Chambers et al., 2012) in 69% of the cases.

The removal rate of TP was higher than usually reported by other authors. This experimental constructed wetland efficiently removed phosphorus while also removing nitrites and nitrates. The effluent water could still have contributed to eutrophication and degradation of ecological conditions, however, so the constructed wetland system might be improved by using a dedicated substrate to further remove phosphorus, and by increasing the retention time (enlarging the wetland) to remove more nitrites and nitrates.

It is generally recognised that the key to improving agricultural water quality is to adopt best management practices. Although proven to be effective, best management practices are seldom adopted unless financially subsidized. It is recommended, therefore, that constructed wetlands be added to the list of subsidized practices through programs such as *Prime-Vert* (MAPAQ, 2009), in Quebec.

# Chapter 5 Suggestions for further research

## 5.1 Monitoring other possibly significant factors

The experiment described here was conducted following a “black-box” approach; performance was assessed with little provision to monitor factors that could help explain the internal processes. A few suggestions follow that could help to address this need.

First, as Yates (2008) suggested, mass balance studies would be needed, as pollutants and their derivatives either are evacuated in the water or air, or accumulate in different portions of a CW system (e.g., vegetation, substrate, litter).

Oxidation-reduction potential (ORP) conditions are the main physico-chemical determinant to all reactions occurring in a wetland. As ORP conditions can vary significantly over 24-h periods, they should be monitored regularly, or better, continually, with *in-situ* probes installed throughout the system. Alternatively, ORP conditions could be measured from samples taken at short intervals (e.g., 6 h). When in contact with air, the ORP conditions start changing from the very moment the water sample is taken – the conditions in a sample that was taken hours before the reading are completely unrepresentative. In order to refine the understanding of spatial distribution of the reactions, piezometers could be installed throughout the wetland. Yates (2008) suggested that $Fe^{2+}$ content in water might be correlated with the prevailing ORP conditions, $Fe^{2+}$ release being caused by reducing conditions, which could account for P release.

Vegetation should be monitored by taking weekly measurements of such parameters as plant height, maturity or chlorophyll content of the leaves, because plants become an important nutrient pool as they grow.

Regarding carbon content in the water, a non-filtered sample could be analysed in addition to the filtered one, to obtain Total Organic Carbon, and get a better overall picture of carbon fractions, including particulate organic carbon (e.g., phytoplankton).

The understanding of mechanisms underlying nutrient dynamics requires the monitoring of soil conditions, before and throughout the experiment. Variables such as soil organic matter (SOM), Fe, Al, and Ca content are essential to understand P cycling and removal. To analyse minerals in a soil sample, they first have to be leached out, and then gaged in an aqueous phase. For instance, the Olsen, Bray-1 and Mehlich III extraction methods are conventionally used to perform P extraction. Hence, such analyses should be conducted.

Characterization of the residence time would help to understand the nutrient dynamics. Tracers such as isotopes and food color have proven useful for this purpose. Alternatively, bromide or salt could be used at the end of the experimental period. These tests should be performed in triplicate to provide sufficient statistical power (Yates, 2008).

## 5.2 Representativity issues

The constructed wetland (CW) experiment presented herein included a number of design features that drove the pilot-scale experiment away from real-life field conditions, reducing its representativity. Here are a few suggestions to improve representativity.

Experiments pertaining to tile drainage should account for the variability of flow that is inherent to this type of wastewater. Tile drainage return flow is a function of precipitation – which is stochastic – and is somewhat hysteretic, and the variability of flow can influence the efficiency of nutrient removal in a wetland. The supply of influent water could be varied to simulate the natural variability of tile drainage return flow. This could be done by sending water to the wetland only for limited periods and allowing the wetland to drain between these periods. Periods of different lengths and variability could be used to more closely approximate field conditions.

The results of the present experiment only apply to summer base-conditions of a hemiboreal climate. It does not represent either storm-flow or winter and spring conditions, which is when most P is exported. At spring time and during wintery snow-thaw events, the concentration of nutrients (and other pollutants) conveyed by agricultural runoff (including tile drainage) is known to be much higher than during summer conditions, influencing the performances of wetlands. As a matter of fact, an ill-designed constructed wetland might not be functional at all at spring time, when it would be most beneficial. For instance, Fink and Mitsch (2004) found in an experiment with a CW treating agricultural runoff that the P concentrations and loads that were exported from the wetland during precipitation events were significantly higher than at base-flow. Any further experiment should strive towards enhancing representativity throughout the year, for instance by extending the experimental season into the spring.

The reconstituted synthetic wastewater used in this experiment was a good surrogate of tile drainage wastewaters, but could be improved. It did not contain any suspended solids, which can influence the forms of P conveyed, and its removal. It did not contain any organic matter, which can also influence the forms of P or N conveyed, and their removal. It did not contain any pesticide or antibiotic residues, which can influence the microbiota. As a matter of fact, a wetland is a complex ecosystem, where a multitude of factors interact with one another and can all influence the cycling and removal of pollutants.

In order to get closer to real-life field conditions, future pilot-scale experiments would benefit from the addition of other constituents to the synthetic wastewater fed to the system. On top of typical concentrations of P and N, antibiotic and pesticide (residues) could be added to the wastewater. Trace elements, heavy metals, surfactants, and surrogates of potentially pathogen microorganisms could also be taken into account. If accounting for surface runoff in addition to tile drainage return flow, suspended solids (SS) should be added as well; in this case, a stirring mechanisms would be needed, to assure even SS distribution.

CWs typically need 2-3 growing seasons to be fully functional (Sundaravadivel and Vigneswaran, 2001). As wetlands mature, less soluble nutrients (e.g., SP) are taken up by the plants, but the particulates (e.g., XP) usually keep on being removed with the same efficiency (Braskerud et al., 2005b). Hence, it would be relevant to compare results obtained from a new CW with those obtained from a mature one.

## 5.3 Manipulations, lab procedures and analysis

Variability of the response would be reduced by better control of hydraulic loading rates (HLRs) among the replicates. As a matter of fact, the piping scheme used in this study induced a number of hydraulic failures, possibly inducing variability in the performance response. First, avoiding the introduction of air into the pipes (which interrupted flow) could be done by permanently maintaining the inflow submerged; to do so, the intake could be raised, with a longer pipe reaching down to the bottom of the supply tank (avoiding swirls that introduce air into the pipes). A bleed valve could also be added near each wetland, so as to help purge eventual air locks. To evacuate these, the influent pressure could be enhanced by elevating the supply tanks or with a pump.

Also, the validity of the assumption that evapotranspiration counterbalances precipitation (McCarey et al., 2004) could be assessed by measuring the effluent volume or through statistical analysis, nesting precipitations obtained by a local weather station into time in a time series analysis.

Variation in the removal efficiency and relative abundance of the chemical species (e.g., $SP_i$ vs. XP) could be assessed by time series analysis to discern trends and correlations with physico-chemical conditions (e.g., ORP, pH, DO) or rainfall. Pearson's correlation coefficient or Kendall's (1948) tests are particularly suitable to the analysis of water quality through time (Berryman et al., 1988; Van Belle and Hughes, 1984). Auto-correlation should be removed by de-trending so that the remaining error terms are independent – a basic requirement of many statistical tests.

The lab methods used for nutrient analysis should introduce less variability than those used in this study, to improve the statistical power of the experiments. This would also reduce dependency on unconventional statistical methods such as survival analysis to analyze censored data. For instance, the P analysis procedures used herein introduced a detection limit that is somewhat higher that what is used in most labs, at 0.011 mg TP $\cdot L^{-1}$. This situation was likely caused by the high variability experienced in this lab, discussed previously. The limit of detection that is obtained by the soil lab of McGill's MacDonald campus (spectrophotometer (*Quickchem Model 8500®*, Lachat Instruments, Milwaukee, WI, method 10-115-01-1-A, ) is ≤ 0.005 (Lalande, H., 2010, pers. comm.). Carlson and

Simpson (1996) report that a detection limit ≥ 0.005 mg TP$\cdot$L$^{-1}$ is not adequate for typical limnological studies (lakes, streams and wetland monitoring), even though this might be ok for soils or sewage analysis. The public health implications of pollutants' presence in water at low but chronic concentrations bolster the need to accurately measure and account for small concentrations, as in the case of P. Use of branded reagents and standards, replicate measurements of each sample, and timely analysis are critical for accurate measurement (APHA et al., 2005).

For ammonia nitrogen ($NH_4^+$+$NH_3$), the Indephenol Blue (Berthelot reaction – Lachat 10-107-06-1-J ) method has a much lower instrument detection limit (IDL) than the Emerald Green method (Lachat 10-107-06-2-C) (Bogren and Stieg, 1999). For comparison, the method that Quebec's MDDEP uses for determination of $NH_4^+$+$NH_3$ concentrations has a method detection limit (MDL) of 0.02 mg ($NH_4^+$+$NH_3$) $\cdot$L$^{-1}$ (Berryman and Blais, 2006), and that of the methods used in this work was similar, at 0.0208 mg ($NH_4^+$+$NH_3$) $\cdot$L$^{-1}$. All $NH_4^+$+$NH_3$ analysis were conducted in Macdonald's soil lab, in this study.

Alternatively, nutrients could be analyzed by ion chromatography, using an Inductively-Coupled Plasma Mass Spectrometer (ICP-MS), instead of colorimetry, which uses a spectrophotometer. The measurement method has to be adapted to the lowest concentrations expected, so that to ensure accuracy even at low concentrations. Specific phosphate minerals could be examined using TEM-EDXS (Transmission Electron Microscopy coupled with Energy-Dispersive X-Ray Spectroscopy). Analysis of water samples in an external lab with standardized low MDLs would enhance the precision of results, especially at low concentrations.

As seen in the results section, eliminating or substituting non-detects with a proxy can greatly skew the data and lead to unjustified conclusions. Substitution of censored water quality data is still common practice, however, though it is difficult to defend, especially when the proportion of censored data approaches 25%. Moreover, given the right-skewed, non-normal and incomplete nature of typical water quality data sets, their statistical analysis should only be done using non-parametric tests (Helsel and Hirsch, 2002; Hirsch et al., 1993).

The understanding of nutrient dynamics would benefit from increased sampling frequency. This would enable the observation of weekly and daily variations. However, increasing the sampling frequency increases auto-correlation (Berryman et al., 1988).

The addition of sugar to the supply water appears to be unnecessary after the first year, as the matured wetland has accumulated enough labile carbon to allow carbon-dependant reactions to occur. This carbon is assimilated by plants through photosynthesis and is secreted by their roots, enriching the rhizosphere and thereby enhancing the nutrient removal process (Platzer, 1999; Shackle et al., 2000).

## 5.4 Size of the wetland

The CW studied herein had an elongated, half-cylindrical shape (Ø: 1.5 m), based on the configuration of agricultural ditches or first order streams where it could be implemented. Hence, changing the size of the wetland would be a matter of making it longer or shorter, but not changing the shape. However, the aspect ratio (length:width) should stay within recommended values: the current aspect ratio is 4.1, and Kadlec and Wallace (2009) suggest a range of 2-10, with typical values being 0.4-3.0.

The wetland:watershed ratio (0.03%) in this study was rather small, compared to typical reported values. For instance, Schueler (1992) recommends it to be at least 1%, and most authors strive for 4-5%. Still, Braskerud (2002b) reported a very good TP removal (21-44%) with CWs making up only 0.06-0.4% of the watershed. Experimenting with a wetland closer to recommended sizes would be interesting.

Increasing the wetland:watershed ratio (bigger wetland) decreases the hydraulic loading rate (HLR) and increases the retention time (HRT). A higher HRT (bigger wetland) generally increases a wetland's pollutant removal performance (Kovacic et al., 2000). However, it can sometimes decrease the ORP conditions (less dissolved oxygen inflow per unit volume of wetland); in such a case, the P removal would actually be diminished, with probable instances of P release (Braskerud et al., 2005c). In the present study, it actually seems like the relatively high HLR that was supplied to this rather small wetland was sufficient to keep the ORP conditions at a satisfactory level (enough DO supply) to enable P retention, and forestall periods with P loss.

Increasing the wetland:watershed ratio (bigger wetland for same flow or lower flow for same wetland area) might increase nitrate removal, given the more wide-spread denitrification biofilm, but as far as P goes, it seems like it would be no use. The only advantage of making the wetland bigger might be an enhancement of the long-term P storage capacity, as it is dependent on the number of adsorption and precipitation sites, which is finite. But as far as the instantaneous P-removal capacity, it is unlikely that it would be improved; it is likely that this wetland is operating at a maximum capacity in terms of P removal, as the effluent TP concentration is as low as any reported in the literature.

Rather, it seems that the only solution in abating TP further resides in the utilization of a dedicated P-removal substrate; either as an amendment to the soil matrix, or in a supplementary treatment cell.

## 5.5 Possibly interesting comparisons to make

The vertical up-flow regime could be compared with other flow patterns, such as horizontal flow or vertical down-flow. Finally, the performance of a vertical up-flow constructed wetland filled with sandy soil could be compared with that of wetlands with different media. The soil matrix should be able to sustain plant growth, support competing removal processes, such as denitrification alongside phosphorus immobilization, and have sufficient hydraulic conductivity. In addition to aggregate-based materials (e.g., gravel), dedicated natural or artificial substrates could be used, such as slags or activated alumina. It is not recommended to use soils that simply have higher CEC, because any supplementary P that might be adsorbed could potentially be released if ORP conditions were to change (Yates and Prasher, 2009).

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# Appendix I. Experimental site

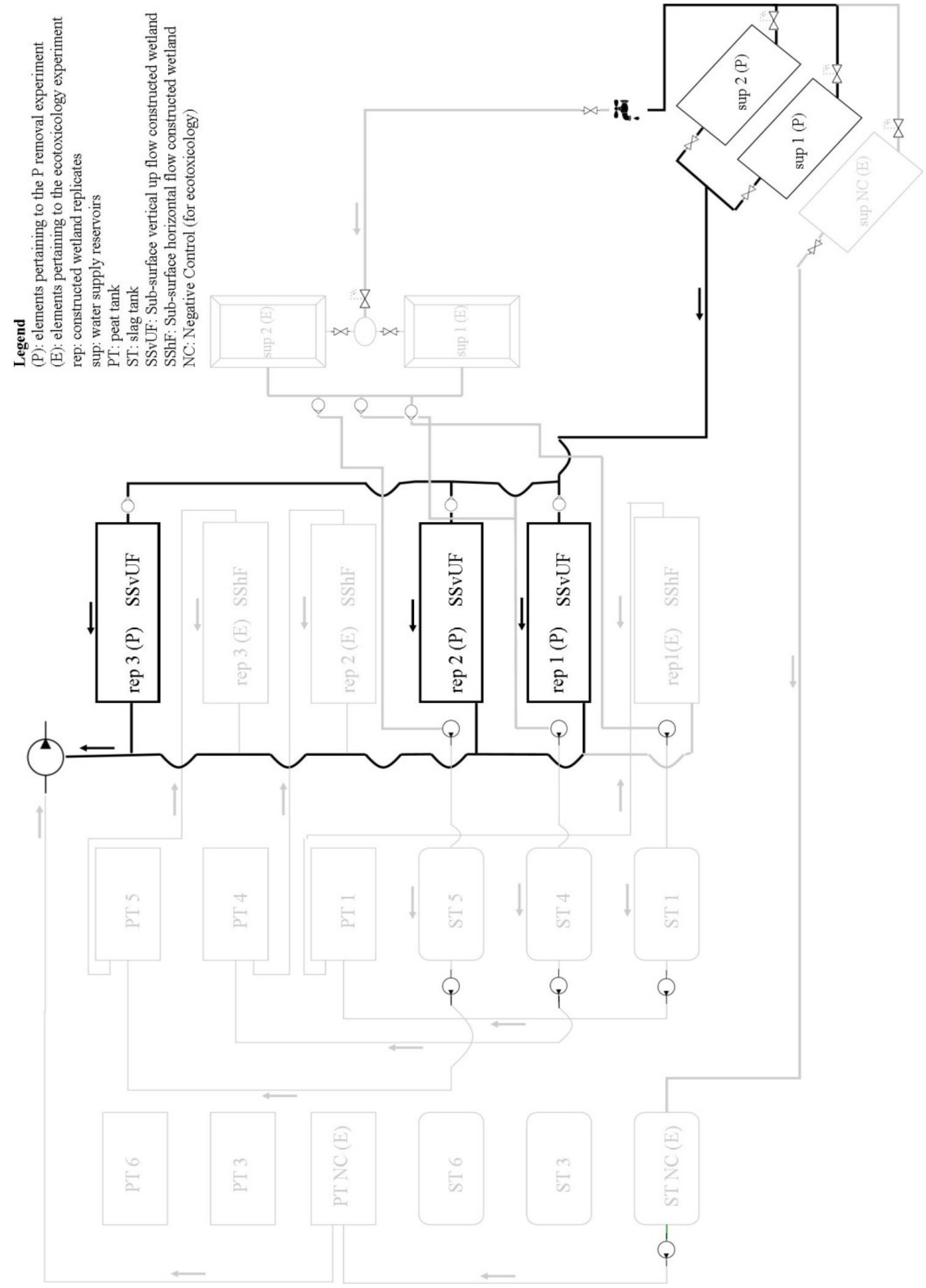

Figure AI-1: Schematic of the constructed wetland experimental site in 2010.
Macdonald campus of McGill University, Ste-Anne-de-Bellevue, Quebec, Canada (not to scale) © Michel Duteau and Kate McGregor. Details of components used in this experimental work are shown in Materials and Methods.

# Appendix II. Reconstituted (synthetic) wastewater composition

### Context

The three CW replicates receive a constant 1 L·min$^{-1}$ flow of evenly concentrated reconstituted wastewater. A 24 hours need of reconstituted wastewater is prepared every day in a single supply tank: 4 320 L for the three replicates altogether. The specific quantities of pollutant-emulating salts are dissolved in a $Cl_2$-evaporated municipal tap water base. The municipal tap water flows into the tank through a float valve until the desired level is attained.

### Target concentration

- 0.300 mg $PO_4^{3-}$—P ·L$^{-1}$
- 10.00 mg $NO_3^{-}$N ·L$^{-1}$
- 20.00 mg $C_{12}H_{22}O_{11}^{-}$C ·L$^{-1}$

### Flow

- 1 L·min$^{-1}$ for 24 h·day$^{-1}$

### Volume of water

- Three lines/system
- Volume per supply tank:
  1 L· (min·(line)$^{-1}$)$^{-1}$ × 3 lines · system$^{-1}$ × 24 h·day$^{-1}$ × 60 min·day$^{-1}$ = 4320 L· (day·(system)$^{-1}$)$^{-1}$

### Level of water in the supply tank (total capacity, 9 000 L):

- Width: 2 m
- Length: 3 m
- Height: 1.5 m
- Level of water: 0.72m

### Quantities of chemicals to dissolve in cocktails

Potassium nitrate ($KNO_3$) for N content (molecular weight: 101.102 g·mol$^{-1}$)

Weight = 4 320 L × 10 mg N ·L$^{-1}$ × (101.102 g $KNO_3$ × (14.007 g N)$^{-1}$)
= 311 815.97 mg $KNO_3$
= 311.82 g $KNO_3$

Potassium phosphate ($KH_2PO_4$) for P content (molecular weight: 136.0838 g·mol$^{-1}$)

Weight = 4 320 L × 0.3 mg P ·L$^{-1}$ × (136.0838 g $KH_2PO_4$ × 30.974 g P$^{-1}$)
= 5 693.96 mg $KNO_3$
= 5.69 g $KNO_3$

Table sugar (sucrose; $C_{12}H_{22}O_{11}$) for C content (molecular weight: 342.30 g·mol$^{-1}$)

Weight $= 4\,320 \text{ L} \times 20.0 \text{ mg}\cdot\text{L}^{-1} \times (342.30 \text{ g } C_{12}H_{22}O_{11} \times 144.12 \text{ g } C^{-1})$
$= 205\,208.99 \text{ mg } C_{12}H_{22}O_{11}$
$= 205.21 \text{ g } C_{12}H_{22}O_{11}$

## Lab Procedures

- Once a week, prepare 7 bottles of cocktail, to be used in the coming week
- Weigh proper amounts of potassium nitrate and potassium phosphate.
- Add both amounts to a large, square, plastic bottle.
- Fill with distilled water; leaving about 1 inch clearance.
- Add stir bar and place the bottle on a stir plate, until all of the chemicals have dissolved.
- Remove stir bar, replace lid.
- Mark down the date the solution was prepared
- Put on the shelf (no need to refrigerate)

## Field procedure

- Every day, shut the valve from the previous supply tank and let it refill for use the next day
- Pour a pollutant cocktail bottle in the filled supply tank and open the valve leading to the wetland

# Appendix III. Sample conditioning and analysis

## Conditioning

### *Filtration*

Sample filtrations occurred within 48h of collection. A 50 mL sub-sample was filtered on a 0.45 µm prewashed nylon sieve (type Whatman binder-free GF/F). If the sample was very dirty, a first filtration was performed with a 1.2 µm cellulosic sieve (type Whatman binder-free GF/A). The filtrations were executed with a 20 cc white HDPE syringe equipped with a filter holder. It was assumed that all soluble matter passes free through the 0.45 µm sieve and that all particulate matter is retained. It now however is generally accepted that particles smaller than 0.45 µm are present in water samples, passing free through this kind of a membrane, and being account for as SP – interpretation of results should accordingly be made with care (Spinakov, 1999).

### *Digestion*

Digestion of organic matter in the water sample was performed according to USEPA's 4500-P J Persulfate method (1999), which is based on Ebina et al.'s (1983) work, whereby alkaline oxidation for TN and acid oxidation for TP is carried in turn during a single autoclaving (pH sweeping from approx. 12.57 to approx. 2.0). The digestion mixture was prepared by dissolving 20g of potassium persulfate ($K_2S_2O_8$) and 3g of NaOH in 1l of DI. A 1:1 ratio of sample and digestion mixture was autoclaved at $120^0$C for 20 min. Digestion is meant to liberate the organic fraction of nutrients ($XP_{org}$, $SP_{org}$ and $N_{org}$), and the digested solution is read for $PO_4^{3-}$ and $NO_2^-$+$NO_3^-$. A 20 mL non-filtered sub-sample was digested off for total organic matter. A 20 mL filtered sub-sample was digested off for Dissolved organic matter.

## Lab analysis

Every analysis was conducted on 10 mL sub-samples (only one replicate). For N and P dosage, a *Lachat Quickchem*® autoanalysing spectrophotometer unit, Model 8500 was used for all analysis (Lachat Instruments, Milwaukee, WI, USA). The principle is flow injection analysis colorimetry, whereby the absorbance of a colour-induced sample is linearly related to concentrations by Beers Law.

### *Phosphorus*

All P analysis were performed on the Lachat autoanalyser, following QuickChem Method 10-115-01-1-A (Diamond, 2000), reading for P as $PO_4^{3-}$, based on the Blue molybdenum colour reaction involving ascorbic acid that was developed by Murphy and Riley (1962). This method is based on USEPA's SM 4500-P (E) (USEPA, 1999). The applicable range is 0.01 to 2.00 mg P $\cdot L^{-1}$ and the instrument detection limit (IDL) is 0.01 mg P $\cdot L^{-1}$. For all P analysis, the zero was forced.

In this test, the molybdate reagent reacts with orthophosphates, producing phosphomolybdic acid, which forms the colored molybdenum blue upon reduction with ascorbic acid. While the compound appears blue, the peak absorbance at 885 nm is in the infrared region.

A non-digested filtered sample was analysed for (total soluble) orthophosphate ($PO_4^{3-}$), while a digested non-filtered sample was analysed for total phosphorus (TP) and a digested filtered sample was analysed for total soluble phosphorus (SP).

*Nitrogen*

$NO_2^-$+$NO_3^-$, TN and SN analysis were performed on the Lachat autoanalyser, following method 10-107-04-1-a, based on the Sulphanilamide color reaction, whereby a cadmium reduction channel is used to reduce nitrates into nitrites and the latter are dosed. It should be noted that the nitrite:nitrate ratio usually is very low. The applicable range is 0.2 to 20 mg N $\cdot L^{-1}$ as $NO_2^-$ or $NO_3^-$ and the instrument detection limit (IDL) is 0.01 mg N $\cdot L^{-1}$ as $NO_2^-$ or $NO_3^-$ (Egan, 2003).

A non-digested filtered aliquot was analysed for nitrite + nitrate ($NO_2^-$+$NO_3^-$), while a digested non-filtered sample was analysed for Total nitrogen (TN) and a digested filtered sample was analysed for Total soluble nitrogen (SN).

A non-digested filtered aliquot was analysed for ammonia nitrogen ($NH_4^+ + NH_3$) on the Lachat autoanalyser, following method 10-107-06-2-C, whereby salycilate ammonium develops an Emerald green color that can be dosed at 660nm. This method is based on USEPA's method 350.1 (O'Dell, 1993). The applicable range is 0.02 to 2.00 mg-N (as NH3) $\cdot L^{-1}$ and the instrument detection limit (IDL) is 0.02 mg N $\cdot L^{-1}$ (Bogren, 2003).

*Dissolved organic carbon (DOC)*

A non-digested filtered (45 µm) aliquot adjusted at pH 3-4 was analysed for dissolved organic carbon (DOC) on a Shimadzu TOC/VCSN analyzer (Shimadzu Scientific Instruments, Columbia, Maryland), according to USEPA's method 415.1 (1974), based on a combustion catalytic oxidation method (APHA et al., 2005) and involving a colour reaction with absorbance at 440 nm. The applicable range is 0 to 25 000 mg TC $\cdot L^{-1}$ and the instrument detection limit (IDL) is 50µg $\cdot L^{-1}$.

# Appendix IV. Data discards and calculations

## Discards

The following data were rejected (discarded), based on the provided rationale:

TP_out for rep2 on 19 juillet (0.003)
- The seasonal median for that replicate is much higher, at 0.038 (rk = 10/10)
- The seasonal median for the aggregated replicates is much higher, at 0.050 (rk= 31/31)
- The available value for the other replicate (rep1) on that date is much higher, at 0.036
- Measured SP value is higher, which does not make sense, at 0.02 (and the latter does make sense, compared to the seasonal median for this replicate, to the seasonal median for the aggregated replicates and to other replicates on that day)

TP_out for rep2 on 30 août (0.042)
- Measured SP value is higher, which does not make sense, at 0.044 (and the latter does make sense, compared to the seasonal median for this replicate, to the seasonal median of the aggregated replicates and to other replicates on that day)

SP_in on 2 août and 27 sept (1.431 mg $\cdot L^{-1}$ and 1.914 mg $\cdot L^{-1}$, respectively)
- The measured TP_in values are lower, which does not make sense (and the latter do make sense, compared to the seasonal median for these replicates, to the seasonal median for the aggregated replicates and to other replicates on that day)

SP_out for rep2 on 20 sept. 2010 (0.000)
- The seasonal median for that replicate is much higher, at 0.009 (rk = 11/11)
- The seasonal median for the aggregated replicates is much higher, at 0.017 (rk= 30/30)
- The available values for the other replicates (rep1 and rep3) on that date is much higher, at 0.005 and 0.002, respectively
- The $SP_i$ estimate is higher, which does not make sense, at 0.00275 (and the latter does make sense, see ”censored data” above)

$NH_4^+$+$NH_3$_in on 30 août 2010 (0.88 mg$\cdot L^{-1}$)
- Calculated $SN_i$ (28.08) is higher than TN (27.33), which does not make sense (and the latter does make sense, compared to the seasonal median for this replicate, to the seasonal median for the aggregated replicates and to other replicates on that day)

$NH_4^+$+$NH_3$_out for rep2 on 13 sept. 2010 (0.59 mg$\cdot L^{-1}$)
- It is a clear outlier
- The $NH_4^+$+$NH_3$_out:TP_out ratio calculated with this was totally out of range (157.91, which is a 42 079,64% augmentation from the entrance 0.373 ratio.!!)
- The seasonal median for that replicate is much lower, at 0.22 (rk = 1/14)
- The seasonal median for the aggregated replicates is much lower, at 0.17 (rk= 1/41)

$NH_4^+$+$NH_3$_out for rep3 on 13 sept. 2010 (0.43 mg$\cdot L^{-1}$)
- It is a clear outlier
- The $NH_4^+$+$NH_3$_out:TP_out ratio calculated with this was totally out of range (34.784, which is a 9233.59% augmentation from the entrance 0.373 ratio.!!)

- The seasonal median for that replicate is much lower, at 0.14 (rk = 1/14)
- The seasonal median for the aggregated replicates is much lower, at 0.17 (rk= 2/40)

$NH_4^+$+$NH_3$_out for rep1 on 13 sept. 2010 (0.59 mg·$L^{-1}$)

- It is a clear outlier
- The $NH_4^+$+$NH_3$_out:TP_out ratio calculated with this was totally out of range (27.799, which is a 7359.39% augmentation from the entrance 0.373 ratio.!!)
- The seasonal median for that replicate is much lower, at 0.13 (rk = 1/14)
- The seasonal median for the aggregated replicates is much lower, at 0.17 (rk= 1/39)

$NH_4^+$+$NH_3$_out for rep2 on 20 sept. 2010 (0.44 mg·$L^{-1}$)

- The seasonal median for that replicate is much lower, at 0.19 (rk = 1/13)
- The seasonal median for the aggregated replicates is much lower, at 0.16 (rk= 1/38)

$NH_4^+$+$NH_3$_out for rep2 on 23 août 2010 (0.43 mg·$L^{-1}$)

- The seasonal median for that replicate is much lower, at 0.18 (rk = 1/12)
- The seasonal median for the aggregated replicates is much lower, at 0.15 (rk= 1/37)

TN_out and $NO2^-$+$NO3^-$ for rep1 on 11 oct. 2010 (1.25 mg·$L^{-1}$ and 1.78 mg·$L^{-1}$, respectively)

- Measured $NO2^-$+$NO3^-$ value is higher than TN_out value, which does not make sense, and it was impossible to determine which one made more sense.

TN_out and $NO2^-$+$NO3^-$ for rep2 on 11 oct. 2010 (0.88 mg·$L^{-1}$ and 1.60 mg·$L^{-1}$, respectively)

- Measured $NO2^-$+$NO3^-$ value is higher than TN_out value, which does not make sense, and it was impossible to determine which one made more sense.

TN_out and $NO2^-$+$NO3^-$ for rep3 on 11 oct. 2010 (1.28 mg·$L^{-1}$ and 1.79 mg·$L^{-1}$, respectively)

- Measured $NO2^-$+$NO3^-$ value is higher than TN_out value, which does not make sense, and it was impossible to determine which one made more sense.

TN_out and $NO2^-$+$NO3^-$ for rep2 on 26 juillet 2010 (5.98 mg·$L^{-1}$ and 7.48 mg·$L^{-1}$, respectively)

- Measured $NO2^-$+$NO3^-$ value is higher than TN_out value, which does not make sense, and it was impossible to determine which one made more sense.

TN_out and $NO2^-$+$NO3^-$_out for rep3 on 27 sept. 2010 (3.76 mg·$L^{-1}$ and 3.98 mg·$L^{-1}$, respectively) respectively)

- Measured $NO2^-$+$NO3^-$ value is higher than TN_out value, which does not make sense, and it was impossible to determine which one made more sense.

SN_in on 23 août 2010 (8.02 mg·$L^{-1}$)

- Measured $NO2^-$+$NO3^-$ value is higher, which does not make sense, at 8.96 (and the latter does make sense, compared to the seasonal median for this replicate, to the seasonal median for the aggregated replicates and to other replicates on that day)

SN_in on 30 août 2010 (3,47 mg·$L^{-1}$)

- Measured TN value is lower, which does not make sense, at 3.17 (and the latter does make sense, compared to the seasonal median for this replicate, to the seasonal median for the aggregated replicates and to other replicates on that day)

SN_out for rep1 on 9 août 2010 (1.61 mg·$L^{-1}$)

- Measured $NO2^-$+$NO3^-$ is higher, which does not make sense, at 2.92 (and the latter does make sense, compared to the seasonal median for this replicate, to the seasonal median for the aggregated replicates and to other replicates on that day)

SN_out for rep2 on 26 juillet 2010 (7.42 mg·$L^{-1}$)

- Measured $NO_2^-+NO_3^-$ value is higher, which does not make sense, at 7.48 (and the latter does make sense, compared to the seasonal median for this replicate, to the seasonal median for the aggregated replicates and to other replicates on that day)

SN_out for rep1 on 19 juillet 2010
for rep3 on 26 juillet 2010
for rep1 and rep3 on 16 août 2010
for rep1, rep2 and rep3 on 30 août 2010
for rep1, rep2 and rep3on 6 sept. 2010
for rep1, rep2 and rep3 on 13 sept. 2010
for rep1 and rep2 on 27 sept. 2010
for rep1, rep2 and rep3 on 11 oct. 2010
for rep2 and rep3 on 18 oct. 2010

- Measured TN values are lower, which does not make sense (and the latter do make sense, compared to the seasonal median for these replicates, to the seasonal median of the aggregated replicates and to other replicates on that day)

SN_out for rep1, rep2 and rep3 on 11 oct. 2010

- There is no TN or $NO2^-+NO3^-$ value to compare to

## Digested samples' concentration

In order to obtain the analytes' concentrations in digested samples (TN, SN, TP and SP), the digestion blank's value was subtracted from the value obtained when reading for the sample itself, multiplying this result by two, if not otherwise specified.

$[D]_p = 2([D]_b - [D]_{db})$

where p is the processed concentration
b is the blunt concentration
db is the digestion blank concentration

In many cases, the digestion blank's P value had to be estimated from the lowest reading obtained in that batch, because of obvious contamination of the digestion blank (unreasonably high). This is the case for all samples digested on:

- August 25, where the 0.019047 mg $P·L^{-1}$ value was used (rep3 2 août FD)
- Sept 13, where the 0.02182 mg P $·L^{-1}$ value was used (rep3 13 sept FD)
- Sept 21, where the 0.0258 mg P $·L^{-1}$ value was used (rep2 20 sept FD)
- Sept 30, where the 0.027673 mg P $·L^{-1}$ value was used (rep3 27 sept FD)
- Oct 4, where the 0.021022 mg P $·L^{-1}$ value was used (rep2 4 oct FD)
- Oct 21, where the 0.018716 mg P $·L^{-1}$ value was used (rep1 11 oct FD)

Similarly, the digestion blank's N value for the 5 first weeks (19 juillet, 26 juillet, 2 août, 9 août, 16 août) had to be estimated from the lowest reading : 0.100 $mg·L^{-1}$ (GST3 19 juillet 2010), because of obvious contamination of the digestion blank (unreasonably high).

# Appendix V. Processing of experimental data

## Detection limits

### Method detection limit

The Method Detection Limit (MDL) represents the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero (Huston and Juarez-Colunga, 2009). The MDL takes into account the variance brought about by the observer as well as the whole set of lab procedures, including the chemicals and the solutes (Ripp, 1996). Values under the MDL are called "non-detects", and most probably are inaccurate, considering the disproportionally large standard deviation, compared to the signal itself. However, values greater than the MDL are not necessarily accurate (see Limit of quantitation below). The USEPA (1982) recognises four methods in determining the MDL. The purpose of a MDL is to discriminate against false positives. Values below the MDL have a high uncertainty but still can provide insight into the lower concentration distribution (e.g., are most values closer to the MDL, or are they closer to zero?). However, warn should be kept that on top of potentially being inaccurate, this value might be not different from zero, although not necessarily; the analyte can be present, but in trace amount, below the currently available MDL.

The best way to report non-detects is as a censored proxy, i.e. as a range bounded by zero and the MDL ([0, MDL]), usually reported as < MDL.

### Limit of quantitation

The Limit of Quantitation (LOQ), also called the Practical Quantification Limit (PQL), is the threshold from which the value can be considered as true within reasonable doubt, and thereof reported as a single value of right accuracy (Antweiler and Taylor, 2008). Values below the LOQ can lose accuracy, the standard deviation being rather large compared to the signal itself. Data below the LOQ can also be reported in its uncensored or censored version. Values between the MDL and the LOQ are 99% sure to be non-zeros, but still are possibly inaccurate. Again, a few different methods can be used to determine the LOQ (USEPA, 1982).

## Parametric vs. non-parametric statistics

Non-parametric tests definitely are more robust (higher protection against type I error) and are more powerful (higher protection against type II error) if not almost as powerful, depending if the normality assumption is violated or not, respectively (Berryman et al., 1988; Conover, 1971; Glass et al., 1972). When analyzing water quality data, many authors recommend non-parametric tests over parametric ones (Berryman et al., 1988; Hirsch et al., 1982; Lettenmaier, 1976).

## Dealing with non-detects

### Classical methods

Although reprehensible, some authors outright exclude non-detects, i.e. eliminate, ignore or delete them, like is done for an outlier or a fluke. In no case can a value below the MDL be excluded, as these data are representative of the lower ambient concentration range. If they were excluded, it would result in a bias towards higher values (especially in summary statistics) and would reduce the size of the sample, which may lead to incorrect conclusions (Helsel, 2005b; Huston and Juarez-Colunga, 2009; USEPA, 1982; 2006). As a matter of fact, the meaning of the quartiles (25th percentile, median and 75th percentile) is completely destroyed if non-detects are excluded, for instance when building a boxplot.

Other authors report non-detects as a fabricated proxy, substituting the observation for a multiple of the MDL (e.g., 0.5 × MDL). This still often is the case in the water quality assessment realm, even though there is no theoretical basis to support this and in spite of the fact that the resulting statistics can be biased (Helsel and Hirsch, 1992; Lee and Helsel, 2005; 2007; She, 1997). Substitution clearly down-casts the variability, for it is extremely unlikely that all samples recorded as beneath the MDL would actually have bored the very same concentration (Huston and Juarez-Colunga, 2009). The choice for one substitute or another (typically 0 × MDL, 0.1 × MDL. 0.5 × MDL, 1 × MDL or others) is completely arbitrary (Huston and Juarez-Colunga, 2009). One is just as good as the other: nothing can support one against the other, nor defend any. It often is assumed that overall, the data lying beneath the MDL level would be normally distributed; following this logic, their average would equal 0.5 × MDL. Therefore, the 0.5 × MDL is often used as a substitute for censored data (e.g., Ward et al., 1988). However, this assumption of normal distribution of the data comprised between 0 and the MDL limit is very far-fetched. Especially with environmental data, which are, more often than not, right-skewed. Plus, absolutely no factual proof backs the 0.5 × MDL substitution method (Helsel, 2005a). Thereof, many authors advocate that it never is appropriate, nor scientifically defensible to use substitution when dealing with non-detects in scientific reporting (e.g., Helsel, 2005b).

In the last few decades, this situation has been decried by many authors, with proven cases of wrong conclusions drawn by the substitution short-cut (e.g., the Challenger explosion), and with suggestion of alternative statistics that would give more accurate results (e.g., Annan et al., 2009; Antweiler and Taylor, 2008; Clarke, 1998; Singh and Nocerino, 2002). Fact is that any alternative to substitution methods are more tedious, keeping them “whoefully underutilized” (Helsel and Lee, 2007). Use of proper methods for statistical analysis is paramount when the analyte has an effect at very low concentration, such as arsenic, dioxins, pesticides or pharmaceuticals (Helsel, 2005b). Phosphorus can arguably be put in that category, depending on what is heard as “low concentration”, which is tributary of the lab method involved in the analysis.

### Alternative statistics for the computation of summary statistics: Robust methods

When a data set comports non-detects, three robust methods are recognized for the determination of summary statistics (Table AV-1). These methods *address* uncertainty, rather than increasing it, leading to reliable conclusions and thereof facilitating decision making (Huston and Juarez-Colunga, 2009). However, the USEPA is currently developing more definitive guidelines (Warren and Nussbaum, 2009). Note that at a high degree of censoring (>70% censored data), no technique will produce reliable estimates of summary statistics (USEPA, 1982; 2006). The only case where substitution may be acceptable is when an estimate of the central tendency needs be rapidly calculated for exploratory purpose (USEPA, 2006). If indulging in substitution, it is generally recommended to try out more than one substitute, and see how it changes the results – comparable results increase confidence; if the results do not agree, a more sophisticated, but robust method might be necessary (Helsel and Lee, 2006).

Table AV-1: Options for treating censored data, according to the destination of the information, the size of the sample and proportion of data that is censored (USEPA, 2006).

| Size of sample | Small | Large | Very large |
|---|---|---|---|
| Substitution (for exploratory usage only) | - If only a few observations are censored.<br>- Use 0.5xMDL. | - If <15% observations are censored.<br>- Use 0.5xMDL. | - Not suitable. |
| Maximum Likelihood Estimate (MLE) (publication usage) | - Not suitable. | - If distribution is approximately normal.<br>-For publication purpose. | - If distribution is normal. |
| Regression on order statistics (ROS) (publication usage) | - Not suitable. | - If >30% observations are censored.<br>- If distribution of censored data can be assumed to be normal (Annan et al., 2009). | |
| Kaplan-Meier (K-M) (publication or regulatory purpose) | - Suitable. | - Suitable. | - If distribution is not normal. |

The Kaplan-Meier (K-M) method is to be used when the sample size is small or when the distribution assumption is questionable. K-M is a non-parametric method, making no assumption about the statistical distribution of the data, and making use only of the ranks of data; it also is insensitive to outliers. K-M renders a step-function (cumulative distribution function, or survival function), estimating the “chance of survival”, or chance of passing from one level to another. Summary statistics can be extracted therefrom. The percentiles can be estimated up to a concurrence of the censored proportion (Huston and Juarez-Colunga, 2009). That is, if the censored proportion attains 50%, only the median and percentiles above can be computed (i.e. in this case, the first quartile cannot be estimated) (Annan et al., 2009).

For groups containing non-detects, non-parametric tests can be used for the computation of comparative statistics (e.g., group comparisons, correlations or regressions). K-M estimator is used to generate the step functions that will be contrasted. Here, the null hypothesis that is tested is that the risk of event (passing from one step to another) is the same among the groups. When comparing two groups (two step functions), a (generalized) Wilcoxon test can suffice (Mann-Whitney modification in the case of unpaired observations).