# Soluble and particulate nitrogen losses from tile drained agricultural fields in southern Quebec, Canada

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**This thesis is dedicated to my supportive parents and my husband, with love**

## Abstract

Eutrophication and cyanobacteria blooms are a growing problem in Missisquoi Bay of Lake Champlain in southern Quebec, and these are largely attributed to non-point source phosphorus and nitrogen (N) pollution from agricultural land in the surrounding watersheds. Residual soil N left after crop harvest contains soluble and particulate forms of N that are at risk of being transported from tile drained agricultural fields to waterways. This study aimed to find the sources of soluble N (mainly nitrate; $NO_3$-N) and particulate organic N (PON) that are susceptible to loss, and the transport pathways by which they move to surface water through tile drained agricultural fields. Water samples were collected at the tile drainage outlet of fields with a clayey and a sandy soil during fall 2010, spring and fall 2011 and spring 2012. There was 1.3 times greater $NO_3$-N concentration and 1.1 fold higher PON concentration in tile drainage water from sandy soil than clayey soil and electrical conductivity measurements indicated that preferential flow was the main pathway for PON loss from clayey soil. Using a dual stable isotopes of $\delta^{15}N$ and $\delta^{18}O$ of $NO_3$ -N coupled with a mixing model, inorganic $NH_4$ fertilizer was found to be the most important contributor to the $NO_3$-N pool in tile drainage water within two weeks of fertilizer application; however, microbially-processed $NO_3$-N was the main source (40 to 49% of $NO_3$-N in tile drainage water) when crops were not growing in the field. Sources of PON in tile drainage water were manure N (47%) and plant residue N (20%) from topsoil layer of the clayey soil, while soil organic N (SON) contributed 94% of PON lost from the topsoil of the

sandy soil. More specifically, the PON pool contained N-rich soil organo-mineral complexes from the top soil layer that reached the tile drains by preferential flow pathways. Decreasing $NH_4$ inputs from fertilizer and allocating sufficient N credits to manure and legume residue inputs could reduce the buildup of $NO_3$-N and organic N, thereby reducing $NO_3$-N and PON losses from these sources. I conclude that source fingerprinting techniques using stable isotope tracers are an effective way of assembling information on the susceptibility of N inputs to loss and transport pathways, which need to be considered when choosing best management practices to reduce non-point source N pollution from the agricultural sector.

## Resume

L'eutrophisation et les proliférations de cyanobactérie sont un problème croissant dans la Baie Missisquoi du Lac Champlain dans le sud du Québec. Celles-ci peuvent être largement imputées a une pollution en phosphore et azote (N) d'origine diffuse, provenant de terres agricoles dans les basins versants s'y déversant. L'azote résiduel du sol, qui demeure après la récolte, comprend des formes soluble et particulaires qui risquent d'être transportées des champs équipés d'une système de drainage souterrain vers les cours d'eau. Cette étude tenta d'identifier les sources d'azote soluble (principalement les nitrates; $NO_3$-N) et d'azote organique particulaire (AOP) qui sont vulnérables aux pertes, et les voies de transport par lesquelles elles se rendent des champs agricoles équipés de systèmes de drainage souterrains aux eaux de surface. Des échantillons d'eau furent prélevés à l'exutoire du système de drainage souterrain de champs aux sols argileux ou sablonneux, à l'automne 2010, au printemps et à l'automne 2011, et au printemps 2012. Les concentrations en $NO_3$-N et en AOP furent 1.3 et 1.1 plus élevées, respectivement, dans l'eau de drainage provenant du sol sablonneux que du sol argileux, Un suivi de l'électroconductivité du sol indiqua que l'écoulement préférentiel fut la principale voie des pertes en AOP dans le sol argileux. Le suivi d'isotopes stables ($\delta^{15}$N et $\delta^{18}$O) du $NO_3$-N du sol et des eaux de drainage, en combinaison avec un modèle de combinaison, démontra que, dans les deux semaines après son épandage, l'engrais inorganique à base de $NH_4$ contribua le plus au stock de $NO_3$-N des eaux de drainage souterraines. Cependant, le $NO_3$-N transformé par les microbes fut la principale source (40 à 49%) du

$NO_3$-N dans les eaux de drainage, lorsque les cultures étaient absentes. Or, 47% et 20% de l'AOP dans les eaux de drainage provint, respectivement, d'azote de fumier et d'azote des résidus de cultures ayant leur origine dans la couche arable du sol argileux, tandis que l'azote organique de la couche arable du sol sablonneux contribua 94% de l'AOP perdu. Plus particulièrement, le stock d'AOP de la couche arable contenait des complexes organominéraux riches en azote, qui se sont rendus au drains par des voies préférentielles d'écoulement. Une diminution des apports en $NH_4$ provenant d'engrais, et une prise en compte des crédits d'azote associés au fumier et aux résidus de plantes légumineuses, pourrait réduire l'accumulation de $NO_3$-N et d'azote organique, réduisant ainsi les pertes en $NO_3$-N et AOP provenant de ces sources. Les techniques d'empreinte isotopique on donc permis de faire un suivi efficace des intrants azotées tout en générant de nouvelles connaissances sur la vulnérabilité des intrants azotées aux voies de perte et de transport. Celles-ci devront être considérées lors du choix et de la mise en œuvre de pratiques de gestion optimales dans le secteur agricole visant à réduire la pollution azotée diffuse

## Preface and contribution of authors

This thesis is composed of four chapters, preceded by a general introduction explaining the context of this research. Chapter 1 is a literature review that summarizes the body of knowledge surrounding this thesis. Chapters 2, 3 and 4 are written in manuscript format according to the guidelines of the McGill University Graduate and Postdoctoral Studies Office. Connecting paragraphs between these chapters show the progression from one manuscript to the next. Finally, the general conclusion, that summarizes the author's findings and contributions to knowledge, highlights the original research findings arising from this study, and suggests areas for further research.

The candidate was fully responsible for designing and conducting the experiments, collecting samples from the field, performing laboratory analyses, statistical analysis and data interpretation, and writing the manuscripts. Dr. Joann K. Whalen provided scientific guidance and editorial assistance with all manuscripts, Dr. Aubert R. Michaud provided feedback and general comments on Chapter 3. Aubert R. Michaud and the IRDA research team also provided logistical support in the field. Dr. Chandra A. Madramootoo and the Brace Center for Water Resource Management, McGill University provided logistical and financial support in the field and general guidance and advice on the experimental design. Dr. Mohamed Chikhaoui trained the candidate on the use of hydrology models. Dr. Pierre Dutilleul provided advice on the statistical analysis presented in Chapter 4.

The manuscripts that compose the body of this thesis appear in the following order:

Chapter 1: Rasouli, S., Whalen, J. K., Madramootoo, C. A. Will reducing residual soil nitrogen control soluble and particulate nitrogen losses from agroecosystems in Quebec and Ontario? Best management practices, policies and perspective. Canadian Journal of Soil Science (to be revised and resubmitted).

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Chapter 3: Rasouli, S., Whalen, J. K., Michaud A. R., Madramootoo, C. A. 2012. Stable isotopes of nitrogen and oxygen to pinpoint the sources of nitrogen loss through tile drains in Pike River watershed, southern Quebec. Journal of Environmental Quality (in preparation for submission).

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# Table of Content

**Abstract** .......... i

**Resume** .......... iii

**Preface and contribution of authors** .......... v

**Acknowledgements** .......... vii

**Table of Content** .......... ix

**List of Tables** .......... xiv

**List of Figures** .......... xvi

**List of Appendices** .......... xix

**General Introduction** .......... 1

**Forward to chapter 1** .......... 4

**Chapter 1: Will reducing residual soil nitrogen control soluble and particulate nitrogen losses from agroecosystems in Quebec and Ontario? Best management practices, policies and perspective** .......... 5

**1.1 Abstract** .......... 6

**1.2 Introduction** .......... 7

**1.3 Nitrogen dynamics in agroecosystems: relevance to residual soil nitrogen** .......... 11

**1.4 Climatic, hydrology and agricultural management controls on residual soil nitrogen loss from agroecosystems** .......... 12

**1.4.1 Climate effect on residual soil nitrogen losses from agroecosystems** .......... 12

**1.4.2 Hydrologic processes controlling residual soil nitrogen loss from agroecosystems ........ 14**

*1.4.2.1 Surface runoff as a pathway for RSN loss from agroecosystems ........ 15*

*1.4.2.2 Subsurface flow as a pathway for RSN loss from agroecosystems ........ 17*

**1.4.3 Agricultural practices ........ 19**

*1.4.3.1 Tillage practices ........ 20*

*1.4.3.2 Crop rotations ........ 22*

*1.4.3.3 Fertilization ........ 24*

*1.4.3.4 Water management structures to control residual soil nitrogen loss via surface runoff ........ 25*

*1.4.3.5 Water management structures to control residual soil nitrogen loss via subsurface flow ........ 27*

**1.5 Regulations, interventions and policies, to reduce nitrogen losses from agroecosystems in Quebec and Ontario ........ 30**

**1.5.1 Agricultural regulations for controlling non-point sources of nitrogen pollution from farms ........ 30**

**1.5.2 Best management practices (BMPs) for reducing residual soil nitrogen loss from agroecosystems ........ 31**

*1.5.2.1 Tillage ........ 32*

*1.5.2.2 Vegetation ........ 33*

*1.5.2.3 Fertilization ........ 34*

*1.5.2.4 Livestock manure storage ........ 35*

*1.5.2.5 Surface runoff ........ 36*

*1.5.2.6 Drainage* ... *36*

**1.5.3 Single BMP vs. multiple BMPs ... 37**

**1.5.4 Putting it all together: environmental farm plans (EFPs) ... 39**

**1.5.5 Incentives and policies for reducing residual soil nitrogen losses from agroecosystems ... 40**

**1.6 Conclusion and perspectives ... 42**

**Forward to chapter 2 ... 47**

**Chapter 2: Forms and pathways of nitrogen loss from agricultural fields into the tile drains in southern Quebec, Canada ... 48**

**2.1 Abstract ... 49**

**2.2 Introduction ... 50**

**2.3 Methods and materials: ... 53**

**2.3.1 The study sites ... 53**

**2.3.2 Tile drainage water sampling and analysis ... 54**

**2.3.3 Electrical conductivity and hydrologic flow data ... 54**

**2.3.4 Statistical analysis ... 55**

**2.4 Results ... 56**

**2.4.1 Nitrate ($NO_3$-N) and Particulate organic nitrogen (PON) concentrations in tile drainage water ... 56**

**2.4.2 Relationship between continuous EC measurement, hydrologic flow and N forms ... 57**

**2.5 Discussion ... 57**

**2.6 Conclusion ... 59**

**Forward to chapter 3** ........ **67**

**Chapter 3: Stable isotopes of nitrogen and oxygen to pinpoint the sources of nitrogen loss through tile drains in Pike River watershed, southern Quebec** ........ **68**

**3.1 Abstract** ........ **69**

**3.2 Introduction** ........ **70**

**3.3 Methods and materials** ........ **74**

**3.3.1 Site Description** ........ **74**

**3.3.2 Water sampling and analyses** ........ **75**

**3.3.3 Soil sampling and analyses** ........ **76**

**3.3.4 Stable Isotope Analysis in R mixing model to partition the agricultural nitrogen sources in tile drainage water** ........ **77**

**3.3.5 Statistical analysis** ........ **78**

**3.4 Results** ........ **78**

**3.4.1 Nitrate pool in tile drainage water** ........ **78**

**3.4.2 Particulate organic nitrogen pool in tile drainage water** ........ **79**

**3.4.3 Source partitioning of nitrate and particulate organic nitrogen pools with SIAR mixing model** ........ **80**

**3.5 Discussion** ........ **81**

**3.5.1 Sources of nitrate in tile drainage water from sandy soil** ........ **81**

**3.5.2 Sources of particulate organic nitrogen pool in tile drainage water from clayey and sandy soil** ........ **83**

**3.6 Conclusion** ........ **84**

**Forward to chapter 4** ........ **96**

**Chapter 4: Determining the source of erodible particulate organic nitrogen in agricultural tile drainage water with $^{15}N$ stable isotopes** ....... 97

**4.1 Abstract** ....... 98

**4.2 Introduction** ....... 100

**4.3 Methods and materials** ....... 103

**4.3.1 Site Description** ....... 103

**4.3.2 Water sample collection and analysis** ....... 104

**4.3.3 Soil sample collection and sequential density fractionation** ....... 104

**4.3.4 Nitrogen, carbon and Stable isotope analysis** ....... 106

**4.3.5 Statistical analysis** ....... 107

**4.4 Results** ....... 107

**4.4.1 Characteristics of PON and $\delta^{15}N$ in tile drainage water from clayey and sandy soils** ....... 107

**4.4.2 Characteristics of soil density fractions from clayey and sandy soils** ....... 108

**4.4.3 Relationship between PON and soil density fractions** ....... 109

**4.5 Discussion** ....... 110

**4.6 Conclusion** ....... 112

**General conclusion** ....... 120

**Contribution to knowledge** ....... 123

**References** ....... 125

## List of Tables

### Chapter 1

Table 1: Regulations to reduce nitrogen (N) non-point source pollution in agroecosystems in Quebec and Ontario, Canada. .................................. 44

### Chapter 3

Table 1: Agricultural practices at two experimental fields in the Pike River watershed, on clayey and sandy soils, during 2010 and 2011. ................ 86

Table 2: Mean values of $\delta^{15}N$ and $\delta^{18}O$ in agricultural nitrogen sources, obtained from the literature and used in the Stable Isotope Analysis in R (SIAR) mixing model. The standard deviation (SD) of the mean is given and the range is reported in brackets. ............................................................ 87

Table 3: Mean $\delta^{15}N$ of soil organic nitrogen, at two depths, and in particulate organic nitrogen (PON) from tile drainage water from two experimental fields in Pike River watershed, on clayey and sandy soils. Values (mean ± SD) within a row followed by differentletters are significantly different (P < 0.05, Student t test). .................................................................. 88

### Chapter 4

Table 1: Natural abundance of $\delta^{15}N$ and $\delta^{13}C$ of soil density fractions from a clayey agricultural soil in Pike River watershed, Quebec. Means (± standard error) within a column followed by the small same letters are not statistically different at $P$<0.05 ...................................................... 113

Table 2: Contrast analysis of $\delta^{15}N$, $\delta^{13}C$, carbon and nitrogen concentrations of

whole soil (WS) versus different soil organic matter fractions in clayey soil. ........................................................................................... **114**

Table 3: Natural abundance of $\delta^{15}N$ and $\delta^{13}C$ of soil density fractions from a sandy agricultural soil in Pike River watershed, Quebec. Means (± standard error) within a column followed by the same letters are not statistically different at $P<0.05$. ........................................................................ **115**

Table 4: Contrast analysis of δ15N, δ13C, carbon and nitrogen concentrations of whole soil (WS) versus different soil organic matter fractions in sandy soil. ........................................................................................... **116**

## List of Figures

### Chapter1


Figure 1: Nitrogen (N) cycle in an agroecosystem (modified from National Research Council, 1993) .......... **45**

Figure 2: Conceptual model of control points for nitrogen (N) loss through agroecosystems. .......... **46**


### Chapter 2


Figure 1: Daily precipitation during fall 2010, spring and fall 2011 and spring 2012. Data were collected from Philipsburg station, Quebec. Arrows shows the sampling points. .......... **61**

Figure 2: Nitrate ($NO_3$-N) and particulate organic nitrogen (PON) concentrations in tile drainage water of (a) clayey soils and (b) sandy soil collected at discrete rainfall events from October 2010 to May 2012. .......... **62**

Figure 3: Relationship between rainfall, nitrate ($NO_3$-N) and particulate organic nitrogen (PON) obtained from pooled data (fall 2010 to spring 2012) from clayey soil (a and c) and sandy soil (b and d). .......... **63**

Figure 4: Relationship between tile drainage flow and electrical conductivity (EC) in clayey and sandy soils. EC were obtained from daily monitoring of EC probes during fall 2011. .......... **64**

Figure 5: Relationship between electrical conductivity (EC), nitrate ($NO_3$-N) and particulate organic nitrogen (PON) in tile drainage water of (a) clayey soil and (b) sandy soil. .......... **65**

Figure 6: Electrical conductivity (EC), nitrate ($NO_3$-N) and particulate organic

nitrogen (PON) concentrations in tile drainage water of (a) clayey soil and (b) sandy soil during fall 2011. EC were obtained from daily monitoring of EC probes during fall 2011. Water flow data were collected from Ewing outlet during fall 2011. **66**

**Chapter 3**

Figure 1: Location of agricultural fields with clayey soil (site A) and sandy soil (site B) in the Pike River watershed, a tributary of Missisquoi Bay, which spans the Canada-United State border between Quebec and Vermont. **89**

Figure 2: Typical values of $\delta^{15}N$ and $\delta^{18}O$ of nitrate ($NO_3$-N) derived or nitrified from various nitrogen (N) sources (adopted from literature) are shown as numbered boxes. Measured $\delta^{15}N$ and $\delta^{18}O$ of $NO_3$-N in tile drainage water samples from sandy soil between March and November 2011 are represented as (pre-fertilization period, n=4), (early post-fertilization period, n=2), (late post-fertilization period, n=4) and post-harvest period (n=2). **90**

Figure 3: Seasonal nitrate ($NO_3$-N), $\delta^{15}N$ and $\delta^{18}O$ of $NO_3$-N in tile drainage water samples from a sandy soil between March and November 2011. **91**

Figure 4: Linear relationships between $\delta^{15}N$ and $\delta^{18}O$ of nitrate ($NO_3$-N) in tile drainage water samples from a sandy soil between March and November 2011. Sample periods were pre-fertilization period (n=4), early post-fertilization period (n=2), late post-fertilization period (n=4) and post-harvest period (n=2). **92**

Figure 5: Proportion of nitrate ($NO_3$-N) in tile drainage water collected from a sandy soil that was derived from various nitrogen (N) sources, based on the

Stable Isotope Analysis in R (SIAR) mixing model. Tile drainage water was collected from March to November 2011 **........................................ 94**

Figure 6: Proportion of particulate organic N (PON) in tile drainage water collected from (A) clayey soil (n=8) and (B) sandy (n=8) from March to May 2011, based on the Stable Isotope Analysis in R (SIAR) mixing model. Dark, medium, and light-grey boxes indicate 50%, 75% and 99% percentiles **........................................................................................ 95**

**Chapter 4**

Figure 1: Particulate organic N (PON) and $\delta^{15}N$ concentrations in tile drainage water samples from (A) clayey soil and (B) sandy soil from March 2011 to May 2011. **........................................................................................ 117**

Figure 2: Relationship between rainfall input (mm) and particulate organic nitrogen (PON) concentration in tile drainage water of (A) clayey soil and (B) sandy soil from March 2011 to May 2011. **....................................... 118**

Figure 3: Total nitrogen (N) and total carbon (C) concentrations of particulate organic matter (POM) in tile drainage water samples from (A) clayey soil and (B) sandy soil between March and May 2011. **................................ 119**

## List of Appendices

**Appendix 1**

Total nitrogen (N) and total carbon (C) content of soil density fractions from a clayey agricultural soil in Pike River watershed, Quebec. Means (± standard error) within a column followed by the same letters are not statistically different at $P < 0.05$……………………………………………………………………..**159**

**Appendix 2**

Total nitrogen (N) and total carbon (C) content of soil density fractions from a sandy agricultural soil in Pike River watershed, Quebec. Means (± standard error) within a column followed by the same letters are not statistically different at $P < 0.05$. ………………………………………………………………………**160**

**Appendix 3**

Stable isotopes of $\delta^{15}N$ form three soil layers of uncultivated clayey and sandy soils located adjacent of study sites, southern Quebec. Samples were taken in May 2011…………………………………………………………………………**161**

# General Introduction

World population is projected to increase from about 6 billion inhabitants currently to 8.2 billion people by 2030 (FAO, 2006). An increase in food production is required to meet the demands of the growing world population. This will inevitably lead to more nitrogen (N) fertilizer use in arable lands, animal manure production in livestock operations, and $N_2$ fixation by legumes to increase crop production. On a global scale, the N in the harvested portion of crops represents 59% of applied fertilizer N (Liu et al., 2010). This means that nearly half of the N inputs to agroecosystems either remain in the soil or are lost to the environment in gaseous or aqueous forms. Not only is low N use efficiency an economic loss for farmers, but aqueous N forms, along with phosphorus, enter streams and rivers and contribute to anoxic (no oxygen) or hypoxic (low oxygen) conditions in water courses, thereby altering biodiversity, changing food-web structure, and increasing harmful algal blooms (Howarth, 2008).

Nitrogen enrichment in Canadian surface waters is largely attributed to the agricultural sector, which is responsible for 80% of N loading, mostly through runoff and leaching from fertilized soils and livestock operations and wet and dry deposition (Chambers et al., 2001). Missisquoi Bay of Lake Champlain, located in southern Quebec, is an example of a fresh water body that receives nutrient-rich runoff from agricultural lands in the surrounding watersheds. Non-point source pollution from agriculture is responsible for episodic blooms of harmful algae and impairment of water quality in the

Missisquoi Bay (CBVBM, 2003).

Controlling N movement from agricultural systems is complicated by the spatio-temporal nature of N inputs to watercourses. Some general rules have been established. For instance, cropped soils with high residual soil N due to fertilizer N (including manure N) inputs and leguminous crop residues should be more susceptible to N loss. Spring snowmelt and rainfall events are peak times for N losses. Soil texture also affects the N loss, with more losses occurring from coarse-textured soils than fine-texture soils, due to the porous nature of the latter (i.e., sandy soils).

Nitrogen leaves agricultural fields by surface runoff or subsurface flow. Surface flow may erode significant amounts of N in association with soil particles (e.g. up to 65%, of total N; Sharpley et al., 1987). In Quebec with two million hectares of croplands being equipped with subsurface tile drains (Helwig et al., 2002), about 35 to 49% of annual rainfall is discharged as tile drainage water (Simard, 2005), which carries 70-90 % of the N (in form of nitrate; $NO_3$-N) out of the field. Up to 27% of the total N can also be also transported in tile drain outflow as N associated with suspended solids (i.e. particulate organic N; PON) (Carter et al., 2003).

However, the sources and the mechanism by which these N forms are transported to tile drains have not been studied extensively; thus, much work must be done to understand more precisely their source and transport pathway. The objective of this research is to examine the forms, pathways and sources of N loss from tile drained agricultural fields with clayey and sandy soils during the frost-free period in southern Quebec, Canada. The specific objectives are:

1. To review the factors that influence the residual soil N pool in relation

to $NO_3$-N and PON losses from Quebec and Ontario agroecosystems and to assess the effectiveness of best management practices (BMPs) and other policies to reduce $NO_3$-N and PON loading into surface waters.

2. To assess the N forms and their transport pathways from two agricultural fields with contrasting soil textures (clayey and sandy soils) after rainfall events and to understand the pathways of $NO_3$-N and PON losses from agricultural fields using electrical conductivity (EC) as a tracer of the water flow pathway.

3. To identify the agricultural N sources of $NO_3$-N and PON in tile drainage water from agricultural fields by comparing the $\delta^{15}N$ and $\delta^{18}O$ isotopic signatures of $NO_3$-N, and the $\delta^{15}N$ isotopic signature of PON to known source materials using the SIAR model.

4. To find the sources of PON in tile drainage water from annually-cropped agricultural fields with clayey and sandy textures using $\delta^{15}N$ isotopic signatures of soil organic N fractions and PON.

# Forward to chapter 1

Chapter one is a literature review discussing the factors that influence the residual soil nitrogen (RSN) pool in relation to soluble and particulate N loss through the soil profile. The review examines the nature and transformations of $NO_3$-N and PON compounds of RSN and suggests approaches to improve BMPs to reduce $NO_3$-N and PON losses into surface waters.

This chapter was submitted to the Canadian Journal of Soil Science and is under revision.

# Chapter 1: Will reducing residual soil nitrogen control soluble and particulate nitrogen losses from agroecosystems in Quebec and Ontario? Best management practices, policies and perspective

## 1.1 Abstract

Eutrophication and cyanobacterial blooms, a growing problem in many of Quebec and Ontario's lakes and rivers, is largely attributed to the phosphorus (P) and nitrogen (N) emanating from intensively cropped agricultural fields. In fact, 49% of N loading in surface waters comes from runoff and leaching from fertilized soils and livestock operations. The residual soil nitrogen (RSN), which is the unused portion of annual N inputs to cropland, contains soluble and particulate forms of N that are prone to being transported from agricultural fields to waterways. Policies and best management practices (BMPs) to regulate manure storage and restrict fertilizer and manure spreading, can help in reducing RSN loss from agroecosystems. However, reduction of RSN also requires an understanding of the complex interactions between climate, soil type, topography, hydrology and cropping systems. Reducing N loss from agroecosystems can be achieved through careful accounting in nutrient management plans for all N inputs (e.g., N credits for legumes and manure inputs), including those applied in previous years, as well as the strategic implementation of multiple BMPs and calibrated soil N testing for crops with high N requirements. We conclude that increasing farmer awareness and motivation to implement BMPs will be achieved through incentives and better communication with crop advisors and provincial ministries of agriculture and the environment.

## 1.2 Introduction

Many lakes and rivers of Quebec and Ontario have become increasingly eutrophic, experiencing episodic blooms of algae and impaired water quality. For example, cyanobacterial outbreaks were reported nearly every summer since 1999 in Missisquoi Bay of Lake Champlain in southern Quebec (CBVBM, 2003), since 1988 in the Yamaska River Basin in southwestern Quebec, and since the 1970s in Lake Ontario, Lake Superior and Lake Simcoe in southern Ontario (Chambers et al., 2001; LSEMS, 2003). Phosphorus (P) and nitrogen (N) are the key limiting nutrients in most freshwater systems that trigger eutrophication and cyanobacterial growth (Schindler, 1974; Howarth and Marino, 2006). According to Chambers et al. (2012), levels of total N exceeding 1.1 mg $L^{-1}$ in Quebec and Ontario streams, contribute to eutrophication and impairment of water quality.

Nitrogen enrichment in Canadian surface waters is largely attributed to the agricultural sector, which is responsible for 49% of N loading, mostly through runoff and leaching from fertilized soils and livestock operations (Chambers et al., 2001; Janzen et al., 2003). Gaseous N components, such as ammonia and nitrous oxides originating from agricultural activities, also enter surface waters through wet and dry deposition. As a result, 80% of the total N load in surface water is attributable to agriculture (Chambers et al., 2001). Based on 2006 census data, the average N inputs from atmospheric deposition, synthetic fertilizers, manure, biological $N_2$ fixation and crop residue, totaled 133.2 kg N $ha^{-1}$ in Quebec farmlands and 137 kg N $ha^{-1}$ for Ontario (De Jong et al., 2009). On average, only 59% of N inputs are recovered in crop biomass (Liu et al., 2010), therefore more than 40% of N inputs may remain as residual soil N (RSN). The RSN, or the unused portion of annual N inputs to cropland, ranged from 20 to 30 kg N $ha^{-1}$ in Quebec farmlands and 30 to 50 kg N $ha^{-1}$ in Ontario farmlands over the period 1981 to 2006 (De Jong et al., 2009). If soils receive surplus water (e.g. from rainfall, snowmelt), part of RSN may be transmitted to surface waters through leaching and/or runoff. It is estimated that 10% of the annual N input from fertilizers, atmospheric deposition and manure, as well as 10% of mineralized N from soil organic matter (SOM), are lost from Canadian agroecosystems every year (Janzen et al., 2003).

Soluble N compounds in the RSN pool, particularly nitrate ($NO_3$-N), are readily leached from agricultural fields. The amount of $NO_3$-N lost from fields in drainage water ranged from 7.2 to 11.7 kg N $ha^{-1}$ in Quebec's farmlands and 8.4 to 9.4 kg N $ha^{-1}$ in Ontario farmlands from 1981 to 2006 (De Jong et al., 2009). In a 3-year study in southwestern Ontario involving corn-oat-alfalfa-alfalfa rotations and conventional tillage practices, the average $NO_3$-N concentration in drainage water was 16.5 mg $L^{-1}$ (Tan et al., 2002b), which was above the water quality limit for eutrophication and harmful algal blooms. Other soluble N forms such as dissolved organic N (DON) are found in leachate and runoff from intensive livestock operations (Anderson and Cabana, 2005). Van Kessel et al. (2009) reported that DON concentrations ranged from 0.2 to 3.5 mg N $L^{-1}$ in leachate from agricultural soils, with higher DON concentrations coming from manure-amended soils. Therefore, agricultural soils with a history of manure application could also be a source of DON entering waterways in Quebec and Ontario (Schindler, 2006). Moreover, there is evidence that microbial breakdown of organic compounds such as proteins releases amino acids that are components of the DON pool, so soils with N-rich organic residues are expected to have higher DON concentrations than those receiving inorganic N fertilizer only (Neff et al., 2000; Shand et al., 2000; Kalbitz and Geyer, 2002). Both $NO_3$-N and DON contribute to the soluble N lost from agricultural soils.

Particulate N, including exchangeable $NH_4$ and organic N bound to clay particles and erodible organo-mineral fractions, is another component of the RSN pool. Concentrated in the topsoil (plough layer), particulate N is susceptible to loss through surface runoff or may be transported through preferential flow and leave the fields through tile drains (Simard, 2005). Cade-Menun et al. (2013) reported that 9 to 20% of total N concentration is transported in surface runoff in the form of PON and Tiessen et al. (2010) reported that the contribution of PON to annual TN losses in surface runoff from a clay loam soil under conventional tillage was 12% and under conservation tillage was 26%. According to Carter et al. (2003), the PON fraction accounted for up to 27% of the total N loss in tile drain outflow. Van der Salm (2012) observed that PON contributed to 48 to 57% of the N losses from the tile drains of a dairy farm with clayey soil. Globally, organic N associated with sediments (particulate organic N; PON) exported from agricultural catchments to rivers is between 0.02 and 29.7 kg N $ha^{-1}$ $yr^{-1}$ (Alvarez-Cobelas et al., 2008). However, there is little information on the quantities of PON lost from agricultural soils in Quebec and Ontario.

Given that the RSN pool contains soluble and particulate forms of N that are at risk of being transported from agricultural fields and contributing to the N load in surface waters, can we use information about the RSN as an indicator of N enrichment in surface waters in Quebec and Ontario? Many best management practices (BMPs) aim to control N pollution in waterways by maximizing N use-efficiency (or yield) and reducing RSN. There is a sense that policies regulating manure storage and restricting fertilizer and manure spreading periods will also limit the RSN. However, despite the promotion of these BMPs and policies, agricultural soils in Quebec and Ontario still have high RSN (De Jong et al., 2009). This is attributed to the complex interactions between climate, soil type, topography, hydrology and cropping systems, all of which affect the RSN pool and consequently N losses from agricultural lands in the region.

Our objective is to review the factors that influence the RSN pool in relation to soluble and particulate N losses from Quebec and Ontario agroecosystems. This information will be used to assess the effectiveness of BMPs and other policies, including regulations, to reduce soluble and particulate N loading into surface waters. This paper is composed of three sections. The first section offers a brief review of N dynamics relevant to understanding RSN transformations in agroecosystems. The second section presents a comprehensive review of the physical and agricultural management controls on the amount and forms of RSN accumulated in agroecosystems, and relate this to soluble and particulate N exported from agroecosystems. The third section focuses on BMPs and policies in Quebec and Ontario that attempt to minimize RSN, and consequently N loss from agroecosystems. We will conclude with perspectives on the potential of various interventions to reduce N loss from agroecosystems.

## 1.3 Nitrogen dynamics in agroecosystems: relevance to residual soil nitrogen

Plant-available N ($NH_4$-N and $NO_3$-N, also referred to as mineral N) is added to agroecosystems by fertilizer and manure applications, atmospheric deposition, and also comes from mineralization of soil organic N and crop residues. Fertilizer and manure are typically applied at agronomic rates to meet crop N requirements, which can be up to 200 kg N $ha^{-1}$ for N-demanding crops such as corn, cabbage and tomatoes. Wet and dry N depositions add mineral N; in eastern Canada, annual wet N deposition is less than 5 kg NO3 $ha^{-1}$, while southern Ontario receives the highest levels of atmospheric N deposition in Canada, up to 15 kg $NO_3$ $ha^{-1}$ $year^{-1}$ (Vet and Shaw, 2004). The soil organic N pool contains 2000 to 6000 kg N $ha^{-1}$ depending on organic matter inputs, soil depth, and soil physical characteristics, and from about 1 to 2.5% of the soil organic N may be mineralized each year (CRAAQ, 2010).

Higher mineralization rates are expected in sandy soils than clayey soils, and in warmer regions than cooler regions. Decomposition of crop residues and organic N compounds in manure releases $NH_4$-N, with greater mineral N release expected from young green manure, leguminous crop residues, liquid and semi-solid manure (CRAAQ, 2010).

Mineral N is available to plants, but not all the mineral N added or generated from microbially-mediated mineralization in soil is used by plants. Mineral N remaining in soil at the end of growing season is defined as RSN (Drury et al., 2007). The RSN may remain for a time as mineral N, subject to chemical and biological transformations that lead to gaseous N losses ($NH_3$,

$N_2O$, $N_2$) or be assimilated by microorganisms. Following immobilization in microbial biomass, the N can be remineralized as DON, $NH_4$-N and $NO_3$-N or it may persist as organic N associated with soil minerals. In some soils of eastern Canada, up to 34% of recently added $NH_4$-N is fixed by soil clay minerals (Chantigny et al., 2004). Dissolved N compounds (DON, $NH_4$-N and $NO_3$-N) are components of soluble N that is measured in leachates and runoff water, while N in organo-mineral complexes and fixed $NH_4$-N are included in the pool of particulate N detected in drainage water and runoff from agricultural fields.

Accumulation of RSN in agricultural soils and its transmission from soil to water bodies is influenced by factors such as precipitation, soil texture, hydrological pathways, N inputs, crop type and rotation, tillage and land drainage. The next section describes how these factors control RSN accumulation and movement from the soil profile towards surface waters.

## 1.4 Climatic, hydrology and agricultural management controls on residual soil nitrogen loss from agroecosystems

### 1.4.1 Climate effect on residual soil nitrogen losses from agroecosystems

Transportation of soluble forms of RSN into surface waters occurs as a function of the volume of water flowing over the soil surface or passing through the rooting zone. The amount of water leaving the soil profile depends on precipitation and soil properties (e.g. texture, infiltration rate, etc.). Annual precipitation of 900 to 1200 mm in Quebec and 750 to 1200 mm in Ontario creates an average annual drainage water depth of 202 mm in Quebec and 186 mm in Ontario and an average annual surface runoff of 200 to 600 mm in both provinces (De Jong et al., 2009). Therefore, a large portion of N (up to 95%) moves with drainage water from agroecosystems (Cambardella et al., 1999) to surface waters. Intensity of rainfall also influences the erosion of N-rich particles that leave agricultural fields either by preferential flow or in surface runoff. More erosion occurs when soil moisture is near field capacity and evapotranspiration is low (Randall and Mulla, 2001), which corresponds to field conditions in Quebec and Ontario during the frost-free period when crops are not growing (e.g., early spring, late fall).

Most of the RSN remaining from the previous growing season is lost through percolation and gravitational flow from the crop root zone during the fall and winter (non-growing season), due to high soil moisture (Zebarth et al., 2005; 2009). For example, up to 22.9 kg N $ha^{-1}$ in Quebec and 14.7 kg N $ha^{-1}$ in Ontario can be lost from November to May (De Jong et al., 2009). In Ontario and Quebec, because of the geothermal gradient in the winter, the deeper soil horizons are warmer than the topsoil, allowing nitrification to continue in the soil profile over winter. The $NO_3$-N produced from this process is expected to percolate through the soil profile and may be lost in tile drain outflows during snowmelt and heavy rainfall events in early spring.

Build-up of RSN might occur during a dry summer, due to the mineralization of SOM, low drainage and reduced N uptake by plants (Stanhope et al., 2009). Upon soil rewetting, $NO_3$-N leaching could be expected due to high concentrations of soil mineral N and high drainage water flow (Randall and Mulla, 2001). Jaynes et al. (1999) reported N loss in association with summer tile drain discharges, specifically when fertilizer (chemical or manure) was applied in the early summer. Wetting and drying cycles also cause soil macroaggregates to break apart, exposing physically-protected organic matter to erosion, degradation and mineralization (Lundquist et al., 1999).

Air temperature, which directly affects potential evapotranspiration (PET) and consequently all components of the soil-water balance, is expected to have little effect on N leaching, especially in the non-growing season. De Jong et al. (2007) projected that RSN losses would only decrease by 1.4% if daily maximum and minimum air temperatures were increased by 15%. This was due to the fact that drainage volume was high in the non-growing season, regardless of temperature. Soluble N loading in surface waters is less in summer than other times of the year due to an increase in N uptake by vegetation, as well as denitrification in soil, streams and near-stream zones (e.g. Geyer et al., 1992; Cirmo and McDonnell, 1997). However, as temperature affects the biological processes that control mineralization, nitrification and immobilization, warmer temperatures are expected to increase the amount of $NO_3$-N in soil solution that is susceptible to leaching as water drains through the soil profile.

### 1.4.2 Hydrologic processes controlling residual soil nitrogen loss from agroecosystems

Both surface and subsurface hydrological pathways are important for transporting soluble and particulate N that are part of the RSN (Iqbal and

Krothe, 1995; Peterson et al., 2002; Petry et al., 2002; Silva et al., 2005). Incoming rainfall, melting snow and irrigation water either percolate through the soil profile, carrying soluble and particulate N with it through matrix and preferential flow, or exceed the soil infiltration capacity and run off the soil surface, along with soluble and particulate N. Soil texture and topography exert a major control on the hydrologic pathway responsible for transporting N from agricultural soils, although these factors can be modified by installations such as tile drains, surface inlets and buffer strips which alter hydrologic patterns. We outline the basic hydrological processes controlling RSN transport from agroecosystems in this section, and will discuss how agricultural management can alter partitioning of water amongst flow pathways in the next section.

### *1.4.2.1 Surface runoff as a pathway for RSN loss from agroecosystems*

Surface runoff can be a significant pathway for N loss on slightly undulating agricultural land and on poorly drained clayey soils (Oenema and Roeset, 1998). Silt loams, very fine sandy loams and loams are also at the risk of generating surface runoff when they become waterlogged and experience ponding at the soil surface. Surface runoff can be generated by rainfall, snowmelt or irrigation. Topography determines both the convergence and velocity of water flow, a steeper slope implies a larger risk of soluble and particulate N erosion (Hairsine and Rose, 1992). D'Arcy and Carignan (1997) explained that nearly half of the variability in soluble N concentration was related to catchment slope in the Canadian Shield of southern Quebec with higher N concentrations in surface runoff from rolling regions. When the regional surface gradient is relatively flat, the routing of runoff is mainly determined by microtopography, which influences the retention of water that does not flow, but is stored in depressions to await infiltration or evaporation (Antoine et al., 2009).

Runoff is generated from four dominant processes: (i) Hortonian overland flow due to infiltration excess, (ii) saturation overland flow due to saturation excess, (iii) lateral subsurface flow in the soil (Naef et al., 2002). Given the distribution of precipitation and weather patterns in Quebec and Ontario, saturation excess runoff is the most common type of runoff occurring in this region. Overland flow is the result of cumulative rainfall and snowmelt events rather than isolated, intense rainfall events (Lapp, 1996). Under these climatic conditions, saturation excess runoff from a particular field is largely a function of landscape position, water table position, stream levels, impermeable subsoils, slope breaks and convergent subsurface flows.

High intensity rainfalls increase both surface runoff and the loss of particulate N with eroded topsoil (Smith et al., 2001). In spring and fall, when the soil profile is saturated with water from repeated rainfall events and there is little evapotranspiration from bare soil, the risk of N loss by surface runoff in soluble and particulate forms is higher. Surface runoff can cause significant PON loss (e.g. up to 65% of total N; Sharpley et al., 1987). Drury et al. (2009) found that flow weighed $NO_3$ concentrations in surface runoff from a fertilized clay loam soil varied from 0.43 to 3.87 mg N $L^{-1}$. Although it is a challenge to determine what proportion of RSN may be lost through surface runoff due to the extreme non-linearity and watershed dependence of this transport pathway

(Sarle, 1994), more RSN loss is expected during spring and fall rainfall events and from imperfectly drained soils.

*1.4.2.2 Subsurface flow as a pathway for RSN loss from agroecosystems*

Much of the land in Quebec (95%) and Ontario (70%) lies on the Canadian Shield, which is composed of glacial deposits of boulders, gravel and sand. Postglacial seawater and lakes have left thick clay deposits on some parts of the Shield (Card, 1990). Consequently, soil located on rolling hills has a predominantly coarse texture (e.g. loamy with coarse fragments or sandy/loamy) overlying a clayey/loamy subsoil layer. Agricultural activities in Quebec occur mostly in the St. Lawrence lowlands, a relatively flat region with clayey soils or coarse-textures soils overlying clay deposits left behind by the Champlain Sea. Agricultural land in southern Ontario is located in the Great Lakes-St.Lawrence lowlands, which is dominated by clayey soils.

The generation of subsurface flow depends on rainfall or irrigation events, and soil conditions such as hydraulic conductivity and texture (Naef et al., 2002; Chae et al., 2004; Silva et al., 2005). The subsurface flow pathway is important in drained sandy soils, imperfectly drained loamy and clayey soils and in soils with shallow groundwater level and/or with tile drain systems (Oenema and Roeset, 1998). Subsurface water movement occurs through the soil matrix and preferential flow (by-pass flow). Matrix flow is the slow percolation of water through the soil matrix, whereas preferential flow is the direct transfer of surface water through preferred pathways like macropores (Jia et al., 2007). Soil macropores include root channels, earthworm burrows, large pores, cracks or others semi-continuous voids within the soil, which act as a rapid bypass from upper to lower soil horizons.

Soil texture influences hydrological parameters (water retention, infiltration, porosity) that govern the flow pathway (matrix vs. preferential) for water and nutrients, including RSN, through the soil profile. In clayey soils, preferential flow pathways are responsible for transporting up to 90% of water and N through the soil profile and into the tile drains (Li and Ghodrati, 1997; Simard et al., 2000). Preferential flow can also occur in sandy soils (Kung, 1990), although N is leached easily through the porous matrix of coarse-textured soils (Dosskey and Bertsch, 1994; McClain et al., 1997; Campbell et al., 2000). In agricultural soils of Quebec and Ontario, this could result in subsurface outflow from the coarse-textured soil layer, or water could continue to move down through the marine clay subsoil, probably by preferential flow, before exiting the field. Another feature of agricultural soils in southern Quebec and southwestern Ontario is that swell-shrink clay minerals in the soil profile tend to form cracks during the summer months that can act as preferential flow pathways for transporting RSN during rainfall events. When fields are tile drained and macropores are connected to the drain lines, preferential flow becomes an important conduit for nutrient transport from soil to surface water (Grant et al., 1996). Many researchers have demonstrated that the subsurface flow pathway is the preferential pathway for $NO_3$-N transport (e.g. Baker, 1980; Gilliam et al., 1986; Skaggs et al., 1994). Pionke et al. (1999) showed significantly greater $NO_3$-N (70-90% of total N) in subsurface flow than in surface runoff in an agricultural watershed with silt loam soil located in the Chesapeake Bay Basin. Although suspended soil particles are often transported by overland flow (Heathwaite, 1997), they can be intercepted by macropores and transported through the soil profile to tile drains (Simard et al., 2000). Consequently, eroded soil particles that are typically enriched with organic matter and absorbed or occluded nutrients, can be transported to tile drains by preferential flow. Carter et al. (2003) reported that particulate-associated N represented up to 27% of the total N transported in tile drain outflow. Therefore, preferential flow pathways increase RSN loss by facilitating water movement through the soil profile.

### 1.4.3 Agricultural practices

Agricultural practices affect the accumulation of RSN in the field. The source and amount of N fertilizer inputs, the timing of fertilizer application, the choice of crops grown and tillage practices all influence biological processes in the soil N cycle that increase or decrease the size and chemical composition of the RSN pool. Soil hydrology is influenced to some degree by crop type and rooting system (e.g., root channels act as macropores) and tillage (e.g., surface cover by residues, type of tillage), but even more by the installation of structures that deliberately control water movement and outflows from the field (e.g., tile drainage, surface inlets, grassed waterways, vegetated buffer strips along the edge of fields). Thus, agricultural management exerts an important control on the hydrologic processes responsible for transporting soluble and particulate components of the RSN. These processes are described in the next sections. Since field crops in Quebec and Ontario are not generally irrigated, we do not consider the effect of irrigation on RSN loss from agroecosystems, although it could be important for vegetable crops.

### *1.4.3.1 Tillage practices*

Tillage practices influence soil physical and biological properties that are important for hydrological processes and soil N transformations. These can alter the size and chemical composition of the RSN. Conservation tillage encompasses the many types of tillage methods that leave crop residues on the soil surface. Crop residues cushion the erosive impact of rain drops on the soil surface and slow surface flow, thus enhancing infiltration and reducing sediment transport with surface runoff. Conservation tillage practices tend to minimally disturb soil structure and macroporosity, which facilitates N and water movement through the soil profile (Follett and Delgado, 2002). In contrast, tillage reduces water infiltration through the soil profile by disturbing the connectivity of macropores and rearranging the soil matrix. Consequently, tillage increases the susceptibility of surface soil to erosion and the generation of erodible sediments (Fawcett et al., 1994).

Some studies have reported greater RSN leaching in no-till systems compared to tilled systems (Patni et al., 1998; Tan et al., 2002b) due to formation of continuous soil macropores that increase $NO_3$-N movement through preferential flow. Conversely, others have reported greater $NO_3$-N leaching in tilled soils partly due to higher rates of denitrification in no-till soils (Mkhabela et al., 2008), greater infiltration in tilled soils, or enhanced N mineralization in tilled soils (Constantin et al., 2010). Other authors have reported no effect of tillage on soluble N loss from soils (Stoddard et al., 2005; Fuller et al., 2010). Therefore, the effect of tillage on $NO_3$-N leaching will differ from year to year and between spatial units (St. Luce et al., 2011).

No-tillage leaves residue cover on the soil surface, which increases water infiltration into the soil and reduces surface runoff and soil surface erosion (Kenimer et al., 1987). Thus, the loss of PON is expected to be lower from runoff in no-tilled soil than moldboard-ploughed soils. However, more sediment and thus sediment-associated N could be lost in conservation tillage than in moldboard plowed soils due to the connectivity between macropores and tile drains, and therefore more preferential flow pathways. For example, Zhao et al. (2001) found 4-fold greater sediment loss in tile drains under ridge tillage than moldboard-ploughed soils.

No-tillage also enhances SOM mineralization as crop residues that remain on the soil surface have a priming effect, which stimulates N mineralization (Bruulsema and Christie, 1987) and contributes to the RSN pool. In some cases, decay rates of residues left on the soil surface are slow compared to residues that are incorporated in moldboard plowed soils (Beare et al., 1994; Parton et al., 1994). However, surface residues appear to decay rapidly when moisture and nutrient status are not limiting (Scott et al., 1996; Alvarez et al., 1998).

In Quebec and Ontario, the common tillage practice in corn fields is primary tillage (moldboard plowing) in fall and secondary tillage (harrowing) in spring. Although moldboard plowing in fall enhances soil drying and warming the following spring (Zhao et al., 2001), its most pronounced effect is the reduction of residues and organic matter on the soil surface. Therefore, it is expected that more RSN will be lost via surface runoff in moldboard-ploughed soils in this region, whereas conservation tillage systems, including no-till, will result in RSN loss through subsurface processes.

*1.4.3.2 Crop rotations*

Production of high-yielding crops in Quebec and Ontario requires selection of crop species and cultivars that are well adapted for the local soil and climate conditions. Judicious use of fertilizers and agrochemicals is necessary to maximize yields, but may contribute to pollution in surface waters. The risk of $NO_3$-N leaching is generally higher in shallow-rooted crops that have a low fertilizer N use efficiency, particularly when they grow on coarse-textured soils and receive large inputs of N fertilizer. For example, $NO_3$-N leaching is common in potato production systems due to the fact that potatoes are grown on sandy soils and can receive in excess of 200 kg N $ha^{-1}$ (Zebarth and Rosen, 2007). Soil $NO_3$-N concentration measured at a 0.30 m depth in spring from 228 commercial potato fields in New Brunswick ranged from 3% to 100% of soil $NO_3$-N at harvest in the preceding fall, indicating that significant leaching occurred between fall and spring (Zebarth et al., 2003). Since the RSN leaching in conventionally-managed potato production systems can be substantial (e.g. 116 kg $NO_3$-N $ha^{-1}$ of the fertilizer N input (177 to 303 kg N $ha^{-1}$; Gasser et al., 2002), farmers should be aware of options to reduce the RSN, which are discussed in section 1.5.2.

Crop rotations have a role in controlling RSN loss from agroecosystems. Corn production, which covers 1.4 million ha in Canada and occurs mainly in southern Ontario and Quebec (Statistics Canada, 2007), is an example of a crop with high N demand that is met partly from the soil N supply and partly from N fertilizer inputs (Cassman et al., 2002; Ladha et al., 2005). The RSN in soils under corn production may be less than 25 kg N $ha^{-1}$ to approximately 40 kg N $ha^{-1}$ and is susceptible to loss from the agroecosystem through the various pathways described earlier (De Jong et al., 2007). Nitrogen loss in a tile drained field in Ontario was highest with continuous corn, intermediate with a corn-oat-alfalfa-alfalfa rotation, and lowest with continuous bluegrass (Bolton et al., 1970). This was attributed to the fact that continuous corn received N fertilizer inputs of 160 kg N $ha^{-1}$ each year and led to a build-up of RSN, whereas growing corn in rotation depleted soil mineral N reserves because oat received less N fertilizer and alfalfa received none at all, relying on $N_2$ fixation and the soil N supply to meet the plant N requirements. Cumulative $NO_3$-N loss through tile drainage from a clay–loam soil in Southwestern Ontario after three years was 82 kg N $ha^{-1}$ for fertilized continuous corn, 100 kg N $ha^{-1}$ for fertilized rotation corn (corn–oat–alfalfa–alfalfa), and 70 kg N $ha^{-1}$ for second year fertilized alfalfa (Tan et al., 2002b). It should be noted that the N fertilizer input was the same for continuous corn and corn planted after plow-down of the alfalfa crop; if an appropriate N credit was given for alfalfa residues, this would likely reduce $NO_3$-N loss from the agroecosystem. In conclusion, incorporating crops that use RSN in the rotation and accounting for the N released from decomposing crop residues (particularly leguminous crops) is expected to reduce soluble N leaching between growing seasons.

*1.4.3.3 Fertilization*

Non-leguminous crops grown in Quebec and Ontario require N fertilizer inputs to achieve economic yields because the humid climate and N mineralization from soil organic N is insufficient to meet their N requirements. Among mineral fertilizers, ammonium based fertilizers are the most widely sold in North America because of accessibility and cost (Canadian Fertilizer Institute, 2007; USDA, 2008). Hong et al. (2007) reported that half of applied fertilizer N was consumed by corn, immobilized in SON or leached from the soil during the growing season, and the other half of fertilizer N was recovered as RSN. Zhang et al. (2004) found high RSN leaching during spring rainfall events and increased potential risk of surface water pollution from corn farms in Quebec due to high levels of RSN from the previous cropping year.

Therefore, applying appropriate amounts of fertilizer N can reduce RSN and its subsequent loss from cropping systems to surface water (Mitsch et al., 2001). According to Vinten et al. (1994), the leaching of $NO_3$-N is a fairly weak function of fertilizer application rate, until crop demand for N is satisfied. The RSN left after harvest can be lost through surface runoff or denitrified. Therefore, altering the rate of N fertilizer to match crop N demand is a necessary step in improving on-farm economic benefits and preserving water quality in the environment.

Manure is also available on many farms in Quebec and Ontario and can be applied as a sole source of N fertilizer or in conjunction with mineral fertilizer. Manure contains 50 to 80% of N originally present in the animal feed depending on the type of livestock and feed (Chamber et al., 2001). Hence, most of the N in manure is not immediately available to crops, but becomes available gradually as decomposition occurs. Jayasundara et al. (2007), working on an agricultural field in Ontario, reported that 45-69% of applied manure N remained in soil after harvest and N mineralization continued until soil freezing. This implies that over-winter N losses are more likely from a manured field than one receiving inorganic N fertilizer, given equal application rates of total N.

The time of fertilizer application, relative to plant growth, affects N losses. Bjorneberg et al. (1996) reported that much of the pre-plant N fertilizer and mineralized N in the soil may be leached before plant uptake is possible. The timing and form of N loss can be controlled by implementing appropriate N application methods (Bakhsh et al., 2002). For instance, split application of N fertilizer based on a late-spring $NO_3$-N test can reduce N leaching time and at the same time increase N uptake by plants (Bakhsh et al., 2002). Other studies confirm that the timing of N application, particularly manure, coupled with the use of controlled-release N fertilizers can significantly reduce $NO_3$-N leaching in agroecosystems (Fuller et al., 2010; Wilson et al., 2010; Ziadi et al., 2011).

#### *1.4.3.4 Water management structures to control residual soil nitrogen loss via surface runoff*

Grassed waterways reduce surface runoff volume and velocity, by increasing roughness of the soil surface and improving the infiltration (Borin et al., 2005; Deletic and Fletcher, 2006). Therefore, decreasing flow volume and velocity and increasing water infiltration from the soil surface would result in a reduction of surface runoff and consequently soluble and particulate N transporting with runoff water. Another water management structure to reduce surface runoff is terracing in combination with grassed waterways (Daigle, 1983). In rolling landscapes with 5 to 9% slope, terraces break long slopes into shorter segments and safely dispose of runoff through grassed waterways (Chow et al., 1999).

Riparian buffer strips are also beneficial in reducing N and sediment transport in surface runoff. Riparian buffers can remove N from overland flow by uptake and storage in vegetation, microbial immobilization and storage in the soil as organic nitrogen and microbial conversion to gaseous forms of nitrogen (denitrification; Weller et al., 1994). Mander et al. (1997) reported the N removal capacity in riparian buffers as high as 964 kg $ha^{-1}$ $year^{-1}$. They attributed the very high estimated N removal to high denitrification in the buffer area. The influence of riparian buffers on reducing soluble and particulate N depends upon its width, species composition and vegetation management (Broadmeadow and Misbet, 2004). The recommended widths are between 10 and 30 m. Narrow buffer strips are likely to provide inadequate protection of aquatic systems and too wide buffers may reduce the area of cropping (Broadmeadow and Misbet, 2004). Schmitt et al. (1999) compared the performance of several vegetative strip designs (different types of plant cover and different strip widths) in reducing contaminant losses to runoff and drainage water. These authors found that 7.5 m wide grass strips and 15 m wide grass strips reduced sediment losses by 76% and 93%, respectively, whereas for these strips $NO_3$-N movement was decreased by 24% and 48%.

Mander et al. (1997) and Snyder et al. (1998) investigated the filtering efficacy of riparian forest buffer strips and found that young treed strips have a greater capacity to retain N. Grazing of riparian area vegetation can contribute to lower soil infiltration rates and increased runoff, erosion, and sedimentation (McGinty et al., 1979, Self-Davis et al., 2003). The effectiveness of filter strip systems is often low in the first year after establishment because of the limited vegetation cover. In conclusion, the effectiveness of these systems in reducing RSN in surface runoff is field-specific and may vary based on the widths of filters and type of filter vegetation.

#### *1.4.3.5 Water management structures to control residual soil nitrogen loss via subsurface flow*

Tile drainage, which is widespread in humid regions (Madramootoo et al., 2007; Goswami et al., 2008) is a subsurface conduit, made of fired clay, concrete or perforated corrugated plastic that removes excess water from the soil profile. In Quebec and Ontario, approximately two million hectares of cropland has tile drainage (Helwig et al., 2002). In the Pike River watershed, which drains into the Missisquoi Bay of Quebec, 44% of the cultivated area has tile drains (CBVBM, 2003). In Ontario, tile drains are installed on about 60 to 70% of agricultural lands under corn and soybean cultivation (McKague et al., 2006).

Tile drainage can be effective in reducing sediment associated N and soluble N loss via surface runoff because it improves infiltration and prevents soil saturation (Gaynor et al., 1995), reduces anoxia and associated denitrification in soils and reduces the contact between water and oxic soils or riparian areas (McIsaac and Hu, 2004; Royer et al., 2006; David et al., 2010). Other studies have clearly illustrated that tile drainage facilitates transport of soil pore water (Beauchemin et al., 1998), which results in N loss in tile drainage water. Controlled water table management structures may reduce N loss from tile drains, but the extent of their use is not known in Quebec and Ontario.

Water table management is an agricultural practice that was reported to improve water quality while maintaining and increasing crop yield (Kalita and Kanwar, 1993; Drury et al., 1996; Cooper et al., 1999). Water table management includes controlled drainage (CD) and subirrigation (SI). Under CD, water is prevented from leaving the drain outlet by raising the water table above the outlet. No supplemental water, other than rainfall, is added to the system. Studies showed that CD is an effective method for retaining crop-available water and dissolved nutrients in the root zone (Wesstrom and Messing, 2007). Gilliam et al. (1979) observed that CD reduced annual $NO_3$-N in drainage water by 50% from a poorly drained soil in eastern North Carolina.

Subirrigation involves pumping supplemental water into the system to maintain the water table at a designed level during drought periods. This system is used during dry summer months when there is insufficient rainfall to maintain soil moisture at an adequate level (40-60 mm of water every 10-14 days) for field crop production on clayey soils (Tan et al., 1999). Subirrigation is only possible on relatively flat lands, where soil type and conditions permit the easy movement of water from the water table to the root zone via upward flux or capillary rise. It is practiced in some parts of Quebec and Ontario.

Controlled drainage-subirrigation (CD-SI) serves a dual function of controlling drainage outflow during periods of excess water and injecting water back into tile drains (Tan et al., 1999). This method of water table management reduces $NO_3$-N pollution either by restricting the volume of drain discharge (Gilliam and Skaggs, 1986; Kliewer and Gilliam, 1995; Wright et al., 1992) and/or by creating anaerobic conditions that enhance denitrification (Elmi et al., 2000; Jacinthe et al., 2000). More $NO_3$-N reduction can be observed if CD also operates during the early spring when the soil is more susceptible to N loss (Patni et al., 1998) and there is no crop present in the field. However, high water tables in the spring would make many fields untrafficable and is undesirable for farms in Quebec and Ontario where cold wet soil conditions are already an impediment for timely planting of annual crops.

Installation of tile drains at shallower depths (e.g. 0.75 m to 1.0 m) can reduce the height of the drainage outlet (Skaggs and Chescheir, 2003). Such an installation behaves similar to CD, therefore it can reduce drainage outflows and increase deep seepage (Bruchell et al., 2003). The result is a saturated soil zone below the tile drains that promotes denitrification and reduces $NO_3$-N losses in drainage outflows. Using such a system, Gordon et al. (1998) found a reduction of 34% in $NO_3$-N losses in tile drainage water. Contrary to these findings, Burchell et al. (2003) reported no difference between $NO_3$-N export in shallow tile drainage (0.7-1 m) and deep tile drainage (1-1.5 m) on a clayey soil. Similar to CD, high water tables due to the spring snowmelt and rainfall would limit the use of this system in Quebec and Ontario.

## 1.5 Regulations, interventions and policies, to reduce nitrogen losses from agroecosystems in Quebec and Ontario

There is no question that the climate and hydrologic conditions in Quebec and Ontario make agricultural soils vulnerable to N loss. Recognizing the link between high RSN and high N loading in water bodies, the Quebec and Ontario governments have developed guidelines and regulations that aim to reduce RSN accumulation in agroecosystems. In addition to legislation, a number of interventions and policies are being employed to protect water quality in these provinces. Best management practices (BMPs), environmental farm plans (EFP) and agricultural subsidies for modernizing farm operations are examples of government- and producer-led initiatives to control N pollution from farms, and are discussed in the next sections.

### 1.5.1 Agricultural regulations for controlling non-point sources of nitrogen pollution from farms

In Quebec and Ontario, the provincial ministries of agriculture and environment collaborate to devise regulations that support crop production, maintain environmental health and protect surface water quality. In Quebec, the Agricultural Operations Regulations (AOR) is the set of regulations used for soil and water protection in agricultural environments. These regulations came into force on June 14, 2002 and were an update of 1997 regulations aiming to reduce pollution from agricultural sources. The regulations are based on P requirements for plant growth, and the P saturation capacity of soils.

Although the regulations are based on P-based manure management, producers following the regulation will probably keep the N inputs at a reasonable level so that concentrations to surface water do not exceed the limit of 1.1 mg total N $L^{-1}$ proposed by Chambers et al. (2012), since the N:P ratio of manure is fairly constant at 1:3 to 1:4 (Kellogg et al., 2000). Using a mass balance approach, producers are able to calculate the annual P inputs to farm fields from livestock manure, fertilizer and other sources, and cannot exceed P application limits set for particular crops and soils.

Ontario initially laid out legal requirements for the storage and handling of manure and other nutrients under the Nutrient Management Act (NMA). This regulation was developed by the Ministry of the Environment and the Ministry of Agriculture and Food (2002) as part of the government's Clean Water program. The regulations control the storage, handling and application of nutrients to cropland. According to these regulations, if more than one type of nutrient source is stored on site, the nutrients must be managed in accordance with the most restrictive requirements applicable to the nutrient sources. Key points of the nutrient management regulations for Quebec and Ontario are described in Table 1.

### 1.5.2 Best management practices (BMPs) for reducing residual soil nitrogen loss from agroecosystems

Best management practices are guidelines intended to minimize the impact of agricultural activities in soil and water resources while maintaining productivity (OFA, 2006). Results from the 2006 Farm Environmental

Management Survey (FEMS) showed that producers across Canada employed a number of BMPs to manage manure, fertilizers and pesticides, and protect land and water resources (Environment Canada, 2007). This section will focus on the BMPs designed to prevent RSN buildup in the soil and thereby reduce N pollution from agricultural lands. BMPs that are effective in reducing soluble and particulate pools of RSN losses from agroecosystems are described in Fig. 2.

*1.5.2.1 Tillage*

Conservation tillage limits soil disturbance by keeping at least 30% of crop residue on the soil surface. This BMP can increase infiltration and reduce soil erosion and runoff, which in turn can reduce the loss of RSN through surface transport processes (Sprague and Gronberg, 2012). Under certain conditions, conservation tillage may not be effective in reducing RSN loss. For example, surface application of fertilizer or manure in no-tilled fields may result in N loss in runoff, particularly if RSN is high at the time that spring snowmelt occurs in Quebec and Ontario. No-till may reduce particulate N but not soluble N losses (Gassman et al., 2006). Often $NO_3$-N concentrations in tile drainage water are less under no till than conventional till, but flows are greater and net loads are similar (Dinnes et al., 2002). In a 5-yr study, no-tilled soils increased tile drainage volume by 48% and soluble N loss by 29% (82.3 kg N $ha^{-1}$) compared with tilled soils, which lost 63.7 kg N ha-1 in soluble N (Tan et al., 2002a).

*1.5.2.2 Vegetation*

Planting catch crops in August-September, after the higher value main crop (grown April-August) has been harvested, is a BMP that can reduce the RSN pool (Thorup-Kristensen et al., 2003; Strock, 2004). The catch crop will take up mineral N that was not used by the main crop or that is mineralized during the fall. Also, having vegetative cover on the field can reduce soil surface erosion and consequently decrease the particulate-associated N (e.g. PON) concentration in runoff during the fall and the next spring. Winter cover crops have been shown to reduce late fall $NO_3$-N concentrations in tile drainage from a variety of systems (Guillard et al., 1995; Philips and Stopes, 1995), but the plow-down of these residues may either increase or decrease spring $NO_3$-N levels, depending on the extent of N immobilization from the crop residue (Wegger and Mengal, 1988). Staver and Brinsfield (1998) reported a reduction of 54% in TN load from tile drainage when rye winter cover crop was planted after corn. Intercropping or using rotations in which crops add N to the system to reduce fertilizer N input is effective in reducing $NO_3$-N loss from agroecosystems (Ofori and Stern, 1987; Hesterman et al., 1992). For example in a corn-soybean rotation, Soybean does not receive fertilizer N and accumulates N through soil uptake and atmospheric N fixation. Soybean uptake of residual N remaining from the previous maize crop may increase fertilizer recovery and decrease potential N leaching losses (Gentry et al., 1998). In an experiment in Ontario, cumulative $NO_3$ leaching loss was reduced by 51% from 133 kg N $ha^{-1}$ in conventional practices to 68 kg N $ha^{-1}$ when considering 30 kg N $ha^{-1}$ N credit from soybean from the previous year as well as using cover crops such as red clover where possible (Jayasundara et al., 2007).

Agroforestry systems in which trees extract water and nutrients from greater depths than most agricultural crops is also effective in reducing $NO_3$-N loss via leaching (Van Noordwijk et al., 1996). Thevathasan (1998) have shown that $NO_3$-N leaving crop-tree (barley-poplar) intercropping sites in Ontario can be potentially reduced by 50% compared with a conventional monocropped field.

*1.5.2.3 Fertilization*

BMPs to improve N fertilizer use efficiency are among the least costly practices and are helpful in reducing RSN, thereby mitigating N losses from agroecosystems. Improving N management by properly accounting for all major sources of N, including N added in animal manure and crop residues, and mineralization of soil organic matter, to reduce N fertilizer inputs is a simple and effective BMP that can reduce fertilizer costs on farms (OFA, 2006). For example, no more than 75% of the crop N requirement should come from manure since organic N in manure will contribute to RSN (OFA, 2006).

Careful timing of N fertilization in synchrony with key growth stages is important to maximize N use efficiency. Whenever possible, N fertilization must be avoided during periods when major leaching is predicted. Placement of N fertilizers in proximity to the crop root zone is also expected to reduce N pollution. Smiciklas and Moore (2004) reported that the fall application of N (anhydrous ammonia) results in about 50% greater $NO_3$-N loading in subsurface drainage water than when the same rate of N was applied in the spring. Jaynes et al. (2004) indicated that late spring application of N fertilizer could significantly reduce net N applications compared with standard (pre-plant N application) practices followed by farmers. Adoption of late spring application could also reduce the $NO_3$-N concentration in surface water by 30% compared to pre-plant application (Jaynes et al., 2004).

Further improvements in fertilizer use are expected with the development and standardization of soil N tests for humid regions. The pre-sidedress soil $NO_3$-N test for corn is calibrated to adjust N fertilizer inputs in Ontario, but there is no comparable test for other crops grown in Ontario, nor is there a standard soil N test available for use in Quebec. A soil N test that considers the amount of plant-available N at seeding and predicts the soil N supply during the growing season is needed to achieve better N fertilizer recommendations in this region. Eventually, the soil N test could be automated with on-the-go sensor technology to achieve variable rate N fertilizer applications in site-specific agriculture (Erhart et al., 2005; Grigatti et al., 2007).

*1.5.2.4 Livestock manure storage*

The BMPs for livestock manure storage emphasize structures and practices that prevent runoff, protect groundwater and surface water, minimize odour and air pollution, provide sufficient manure storage until it can be safely applied to the land, and minimize nutrient losses during storage. Each type of manure storage system - whether liquid, semi-solid or solid - has specific BMPs that attempt to reduce the risks posed by non-point source N pollution.

For example, to prevent surface water pollution, diversion ditches should be constructed to direct surface water runoff away from the manure storage site. Grass filter strips are also useful to prevent runoff of manure and capture eroded sediments from livestock housing and fields where manure is applied (Ag Can and OMAF, 1994).

#### *1.5.2.5 Surface runoff*

Buffer strips are vegetated areas at the edge of fields that are used to intercept runoff before it enters local water ways. These structures provide a naturalized barrier to hinder runoff allowing it to slowly percolate through the buffer, infiltrate into the ground, and therefore also provide sediment and N removal (Hubbard et al., 1998; Snyder et al., 1998). Peterjohn and Correll (1984) reported reduction of 89.7% of suspended particles and 60.4% of $NO_3$-N concentrations in runoff water after it passed through a 19 m vegetated buffer. Xu et al. (1992) found that concentrations reduced from 764 mg N $kg^{-1}$ soil to 0.5 mg N $kg^{-1}$ soil within the first 10 m of the buffer area.

Grassed waterways act as buffers to trap sediment and nutrients moving into the waterway from surrounding agricultural lands. The vegetation also stabilizes the banks and shores from the erosive action of the streamflows. An experimental study in southern Quebec showed that grassed waterways reduced runoff water volumes by 40%, total suspended solids by 87%, and NO3-N by 33% (Duchemin and Hogue, 2009).

#### *1.5.2.6 Drainage*

Skaggs et al. (1982) proposed tile drainage as a BMP for reducing erosion on flat lands. Another BMP that is effective in reducing N loads in surface water is a CD system, by reducing $NO_3$-N leaching by 40 to 90% in tile drained land (Meek et al., 1970; Doty et al., 1986; Belcher and Fogiel, 1991; Madramootoo et al., 1992; Madramootoo, 1994; Drury et al., 1996; Tan et al., 1998; Tan et al., 1999). Drury et al. (1996) found a reduction of 43% in annual $NO_3$-N losses from CD compared to conventional drainage. Nitrate losses were better controlled with a CD system in conjunction with conservation tillage. However, as water limitations are reduced by CD and CD-SI, this may result in N limitations for crop growth and so crops may need additional N fertilizer to maximize yield. Tile drainage reduces surface runoff by increasing water infiltration, thereby increasing soluble N movement through the soil profile (Drury et al., 2001). Consequently BMPs such as a balanced N fertilization program and installing biofilters to the tile drain outlet to intercept and treat $NO_3$-N lost from fields may be needed to mitigate N loss to waterways.

**1.5.3 Single BMP vs. multiple BMPs**

The reduction of RSN loss from agricultural fields is unlikely to be solved with a single BMP. While a single BMP might be effective in reducing the loading of a specific form of N into the surface water, it could have no effect or even increase the transport of other N forms in runoff. For example, cover crops can reduce sediment loads but can increase water movement through the soil profile and therefore contribute to dissolved N losses through drainage (Martel et al., 2007). Also, physical characteristics of the agricultural systems (texture and hydrologic characteristics) influence the BMPs' impact on the biological and physical parameters than control the size and chemical composition of the RSN, as well as the transport pathway that causes RNS loss from the agroecosystem. Moreover, in an agricultural watershed with multiple farms, it is challenging to choose the right combination of BMPs that provide maximum reduction of RSN loss at the watershed scale with a reasonable cost of implementation. The selection of multiple BMPs should be optimized to achieve maximum N reduction at minimum cost to the producer (Maringanti et al., 2011).

A study in the Walbridge basin of the Missisquoi Bay watershed examined the effect of multiple BMPs on the sediment and N export to surface water (Michaud et al., 2008). More than 60% of the land in the Walbridge river basin is dominated by annual crops such as grain corn. The upstream portion of the basin has proportionately more swine and poultry operations than the downstream area. Michaud et al. (2008) tested scenarios that combined BMPs to reduce N, P and suspended solid loadings into surface water, and compared them with a single baseline scenario. Overall, multiple BMPs were more advantageous than a single BMP, although the multiple BMPs did not necessarily interact in a synergistic manner (positive interaction) or even a cumulative manner (neutral interaction) in relation to a given water quality parameter (i.e. sediment, N and P). In practice, the effect of multiple BMPs varied according to the water quality parameter considered, but a few BMPs emerged as highly promising for reducing non-point source nutrient pollution and sediment loading in the Wallbridge basin. For example, the introduction of no-till farming in a grain corn field generated substantial reductions in sediment, N and P exports. Another positive outcome was the estimated 54% reduction in N export when N fertilizer incorporated immediately (within 24 hours) and cover crop BMPs were adopted, compared to the baseline scenario (conventional tillage practices with fall plowing and spring (pre-plant) manuring).

### 1.5.4 Putting it all together: environmental farm plans (EFPs)

As discussed in the previous sections, the size of the RSN pool and amount of N loss are regulated by a number of factors including soil characteristics (Fig. 2). Since soils and other site-specific characteristics (e.g. cropping systems, tillage practices, fertilizer sources and application methods, water management structures) are different on individual farms, the nutrient management program and BMPs should be considered in the context of those site-specific conditions to ensure that the practices function together to achieve the overall management goals. To help producers identify and address site-specific risks to the environment, Ontario and Quebec created voluntary, confidential educational programs that help producers develop environmental action plans for their farms. Ontario's program is the Environmental Farm Plan (EFP) program, started in the 1990's. Quebec's program is the agri-environmental support program (PAA) that was initiated in 2004 to support the adoption of improved agricultural practices on farms.

An EFP/PAA starts with an agroenvironmental profile of a farm, including an assessment of practices related to regulations and BMPs. Then the EFP/PAA will be completed by identifying BMPs that can solve particular problems, determine which ones to implement and setting a schedule for action. In the next step, the farmer will implement the EFP/PPA plan. The actions on farms will be evaluated by the farmer and eco-advisors, who are government-certified consultants trained to help producers to complete EFPs/PAAs. Outcomes resulting from the implementation of BMPs are summarized in annual activity reports. The EFP/PAA helps the farmers identify the strengths and weaknesses of their operation in protecting the environment, and is an effective tool for selecting and implementing appropriate BMPs to reduce RSN and control N loss from their farms.

### 1.5.5 Incentives and policies for reducing residual soil nitrogen losses from agroecosystems

Although farmers are becoming aware of the importance of soil management, water quality and storage of manure, the number of farmers who participate in EFPs indicate that 38.4% of farmers in Ontario (23,000 applicants) participated in workshops by 2003, but around 38% of participants took no further part in the scheme (Robinson, 2006). From 2004 to 2008, the number of Agri-Environmental Advisory Clubs (AEAC) member farms in Quebec that adopted AOR actions like spreading liquid livestock with a boom sprayer increased from 29 to 60%, while those that installed barriers to prohibit livestock access to streams increased from 63 to 76% (Agri-environmental Advisory Clubs, 2009).

This situation clearly illustrates a need to increase farmer’s motivation to prepare and implement EFPs in Quebec and Ontario. Lobley and Potter (1998) and Wilson (1997) identified the lack of EFP compatibility with ongoing farm management plans, financial reasons and lack of information about the Guideline as determinants of the decision to participate in EFP. Other determinants are presence and absence of a successor for the farm (Brotherton, 1990), the quality of the information provided on the Guideline (Cundliffe, 2000) and peer pressure (Wynn et al., 2001). Between 1993 and 2009, 35,400 farm businesses participated in EFP workshops at least once, and about 28,500 projects were completed by over 17,000 farmers. Factors that supported BMP adoption were education, proven practices, regulation and peer pressure (Agri-environmental Advisory Clubs, 2009).

Many farmers avoid BMPs because they feel that using less N fertilizer or manure, reducing tillage intensity, or making other changes in their practices will cause a decrease in farm income. Therefore a guarantee against any potential loss of income as a result of BMP adoption can be a helpful incentive. This can be achieved by compensating farmers if yield and income were reduced while participating in EFPs. A number of municipalities, conservation authorities and other organizations across Ontario offer financial incentives to farmers to support on-farm environmental improvements. For example, the Christian Farmers Coalition (CFC) has established an Ontario Environmental Initiative Loan Fund Program such that farmers are eligible to receive loans when they prepare an EFP Action Plan (Robinson, 2006).

An example of non-financial incentives is the Ontario Stewardship program. Initiated by Ontario‘s Ministry of Natural Resources (OMNR) in 1995, this program encourages farmers to care responsibly for their lands. The program provides encouragement via education, collaborative arrangements and peer networking by 39 Community Stewardship Councils, which receive financial support from the OMNR (Robinson, 2006). The benefits of this program for the farmers were identified as transfer of knowledge, broadening and strengthening of their chain of contacts, and greater access to key agencies and associations.

Increasing the environmental awareness among Quebec producers and supporting them in their agri-environmental efforts can be achieved via ”accompanying measures”. These include: knowledge enhancement initiatives (soil degradation inventories, environmental monitoring, agri-environmental portraits), education, training, and technology transfer activities (State of the St. Lawrence Monitoring Committee, 2008), as well as financial assistance programs to help them achieve regulatory compliance, especially for liquid manure storage structures.

## 1.6 Conclusion and perspectives

Considerable progress has been made in the past years to improve nutrient management practices and reduce N losses from agroecosystems. Despite such advances, N loss to the aquatic ecosystems is still above the acceptable limits for water quality protection. Research is still needed to identify the source of N in waterways, and to determine whether RSN losses can be controlled with BMPs. To improve the efficiency of N fertilizer use, accurate estimates of N mineralization rates from organic N in manure, crop residues and SOM are needed. Careful accounting for N from all inputs, including soil-based N credits and N credits for legumes and manure inputs in the previous year will be helpful in this regard. Soil testing for N is also recommended, although test methods remain to be standardized and calibrated in relation to N fertilizer requirements for crops grown in Quebec and Ontario. More research on the effect of multiple BMPs on RSN accumulation and loss from agricultural fields is necessary. Encouraging farmers to participate in an agro-environmental clubs and publicizing “success stories” will have a positive impact on the adoption of BMPs. Financial intensives and better communication between farmers, agro-environmental advisors, provincial and federal organizations are also expected to be beneficial for the implementation of BMPs that are effective at reducing RSN, thereby mitigating soluble and particulate N losses from agroecosystems in Quebec and Ontario.

Table 1: Regulations to reduce nitrogen (N) non-point source pollution in agroecosystems in Quebec and Ontario, Canada.

| | Regulation in Quebec [1] | Regulation in Ontario[2] |
|---|---|---|
| N inputs on the farm | • Agrienvironmental fertilization plan (PAEF) is required for a farm (cumulative area ≥15 ha, excluding pasture areas and grassland) having annual P ($P_2O_5$) production greater than 1,600 kg and operators of spreading sites. | • Nutrient management plan (NMP) is required for a farm if manure is stored or used on the farmland<br>• Nutrient management strategy (NMS) is required if generated manure is for removal by the deadline date (manure storage facilities have a capacity for at least 240 days storage |
| Time of N fertilizer application | • Between April 1 to October 1<br>• After October 1 if not frozen or covered with snow | • Between April 1 to October 1<br>• After October 1 if not frozen or covered with snow |
| Manure storage | • The pile must be at least 150 m from streams, rivers, lakes, ponds, wetlands, or natural swamps<br>• Total run-off areas are greater than 2 $m^2$, and more than 15 m from irrigation ditches;<br>• The ground surface must be covered with vegetation; the ground must have a slope of less than 5%;<br>• Surface runoff must not be able to reach the pile;<br>• The pile must not remain in the same location for two years in a row.<br>• Raising facilities with solid manure management, whose annual production of P ($P_2O_5$) exceeds 1600 kg must have access to watertight storage facilities for all livestock waste produced in them, or to any other equipment or building.<br>• Raising facilities with liquid manure management must have immediate access to watertight storage facilities for all livestock waste produced in them. The drain must not be connected to the storage facility, and its outflow is connected to an observation well of a minimum interior diameter of 40 cm, accessible for taking samples.<br>• The drain must remain functional at all times and make use of gravity or a pump to take water samples. | • Minimum of 15 m from all field drainage tiles or piped municipal drains.<br>• When building a permanent nutrient storage facility, locate and remove all existing field drains within the area bounded by the perimeter of the facility, plus 15 m. Redesign the existing drainage system to direct the flow away from or around the storage facility. If a drainage system is required within 15 m of a permanent nutrient storage facility, any water collected by these drains must be discharged to a treatment system, or the drains must be equipped with an observation catch basin and shut-off valve.<br>• Permanently vegetated flow path as a runoff management system at least 0.5 m-deep soil and not located within 3 m of a field tile drain, 100 m of a municipal well, 15 m of a drilled well or 30 m of any other well<br>• The minimum length of vegetated flow path to surface water and all tile inlets must be increased to 150 m for a solid manure storage handling manure with a lower dry matter content of between 30 percent to 50 percent.<br>• For manure with a dry matter content of 50 percent or more the vegetated flow path only needs to be 50 m from the surface water. |

[1] Adopted from The Ministère du Développement durable, de l’Environnement.
[2] Adopted from Ontario Ministry of Agriculture and Food

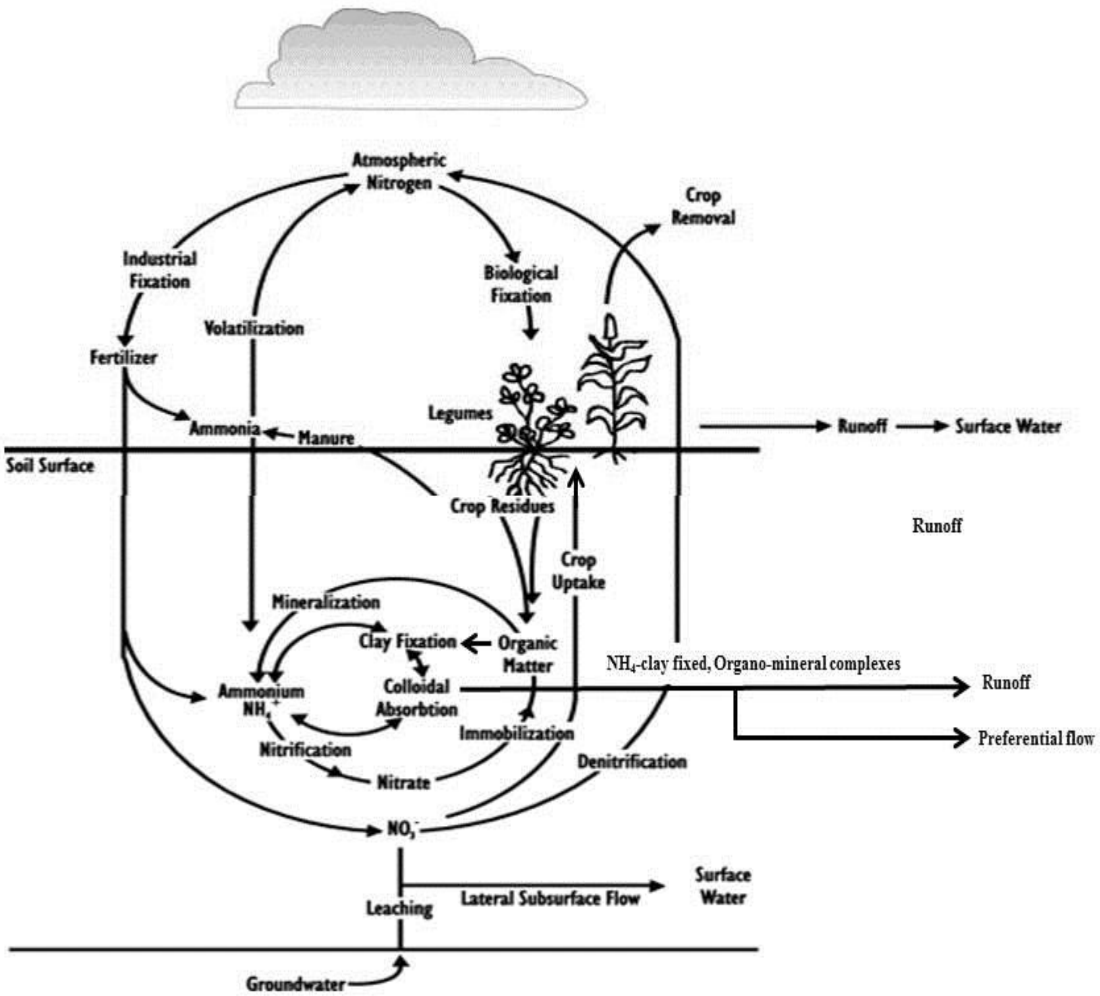



**Figure 1:** Nitrogen (N) cycle in an agroecosystem (modified from National Research Council, 1993)

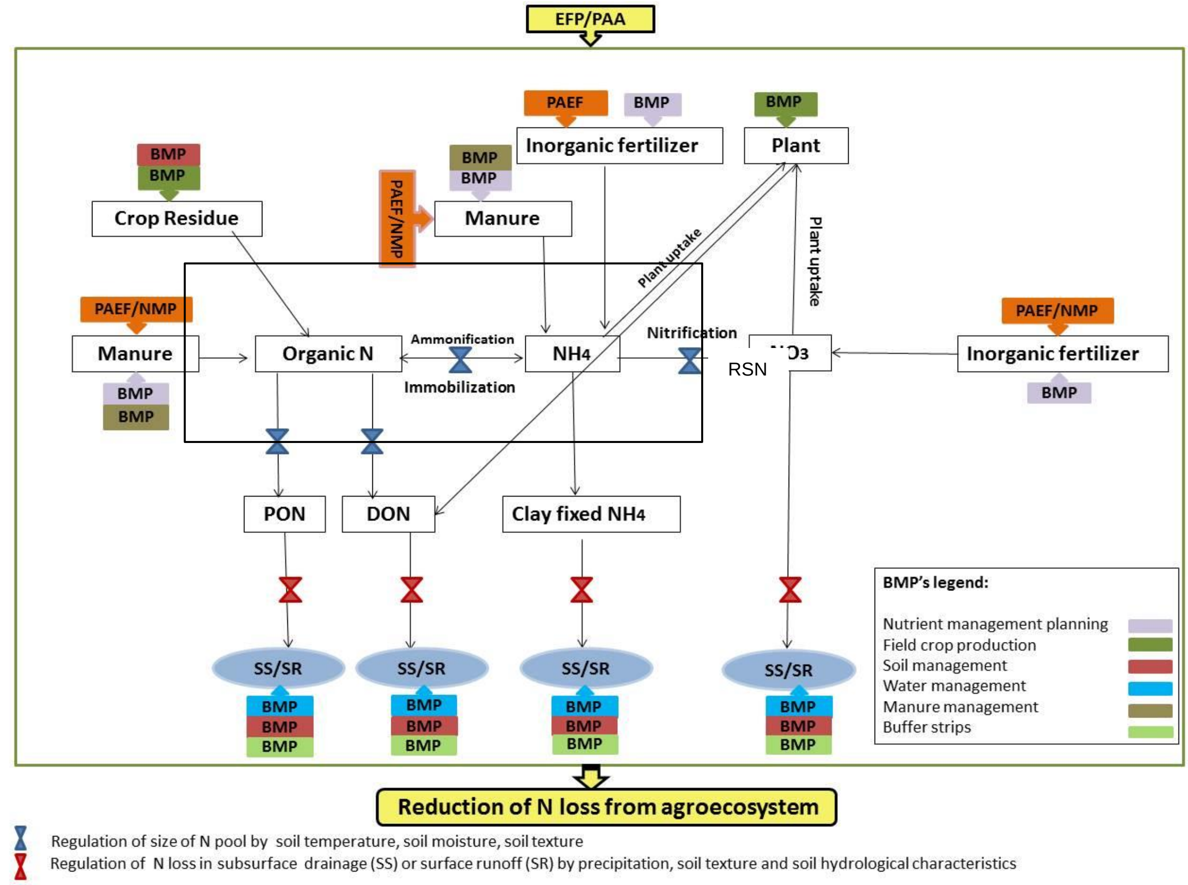



Figure 2: Conceptual model of control points for nitrogen (N) loss through agroecosystems.

## Forward to chapter 2

The literature review revealed that $NO_3$-N and PON compounds of RSN are lost through tile drained agricultural fields and preferential flow as a transport pathway increases the $NO_3$-N and PON leaching from the soil profile to tile drain outlet. However, this hypothesis needed to be tested under field conditions. The objective of this first experiment was to evaluate the N forms that were transported from two agricultural fields with contrasting soil texture (clayey and sandy soils) and to understand the pathways of $NO_3$-N and PON losses from agricultural fields.

This chapter is in preparation for submission to the Canadian Journal of Soil Science.

# Chapter 2: Forms and pathways of nitrogen loss from agricultural fields into the tile drains in southern Quebec, Canada

## 2.1 Abstract

Agricultural nitrogen (N) inputs in excess of crop needs can accumulate in the soil profile as residual soil N (RSN). Transportation of soluble and particulate forms of RSN into surface waters occurs through surface runoff or subsurface flow in tile drained agricultural fields. About 70 to 90% of total N in tile drainage water is in the form of nitrte ($NO_3$-N) and up to 30% of total N is in the form of particulate organic N (PON). These N forms are transported to tile drains by preferential flow or matrix flow. The aim of this study was to describe the transport pathways of $NO_3$-N and PON from two tile drained agricultural fields with contrasting soil texture (clayey and sandy soils) after rainfall events in (fall 2010, spring and fall 2011 and spring 2012). Water samples were collected from tile drain outlets and analyzed for $NO_3$-N and PON concentrations as well as electrical conductivity (EC). There was 1.3 times greater $NO_3$-N concentration and 1.1 fold higher PON concentration in tile drainage water from the sandy soil than clayey soil during the sampling period. Matrix flow was responsible for $NO_3$-N loss from both soils while preferential flow was responsible for transporting PON to tile drains in the clayey soil, based on electrical conductivity signal. I conclude that EC can be a rapid indicator of the transport pathway and concentration of N lost from agricultural fields through tile drains.

## 2.2 Introduction

A gricultural fields typically receive nitrogen (N) fertilizer to meet yield goals, but 50-70 % of applied N fertilizer leaves the fields in harvested plants (Ladha et al., 2005; Chien et al., 2009; Gagnon and Ziadi, 2010, Liu et al., 2010). The high rates of N uptake are largely attributable to the extensive area of leguminous crops (Liu et al., 2010). Therefore up to 50% of N is left behind as residual soil N, which accumulates as soil organic N or is lost to the environment (Umuhire, 2007). To minimize N loss and increase agricultural productivity, it is essential to account for the N forms that are exported from cropping systems, and to understand the pathways of N transport from soil to water ways.

Nitrogen can move from soil to water in soluble forms, or in particulate forms, bound to suspended sediments. Soluble N is lost from agricultural fields primarily as nitrate ($NO_3$-N), with minor contributions of dissolved organic N (DON) and ammonium ($NH_4$-N). Sediment associated N (i.e. particulate organic N (PON) and $NH_4$ fixed on the clay particles) is also susceptible to transport and can result in enhanced mobility of N. De Jong et al. (2009) reported that the amount of $NO_3$-N export from annually cropped agricultural fields receiving fertilizer, and/or manure to surface water ranged from 7.2 to 11.7 kg N $ha^{-1}$ in Quebec's farmlands from 1981 to 2006. Alvarez-Cobelas et al. (2008) also reported that global PON export from agricultural fields to rivers ranged from 0.02 to 29.7 kg N $ha^{-1}$ $y^{-1}$.

The variability in N export is due to the differences between fine and coarse-textured soils, since hydrological parameters (water retention, infiltration, porosity) are strongly influenced by texture, leading to more $NO_3$-N leaching below the root zone in coarse-textured than fine-textured soils (Dosskey and Bertsch, 1994). Carter et al. (2003) reported an increase of PON loss as the clay and silt content increased, which may be related to more preferential flow paths in fine textured soils. Seasonal changes in biotic (plant and soil microbe activity) and abiotic (hydrological transport) factors influence the $NO_3$-N and PON losses from agricultural tile drains. From 70 to 95% of annual $NO_3$-N loss was observed from November to May when vegetation growth was minimal (De Jong et al., 2009; Drury et al., 1996; Patni et al., 1998). Summer discharges associated with high rainfall or irrigation events might also cause $NO_3$-N and PON loss (Jaynes et al., 1999), particularly if they occur soon after fertilizer (chemical or manure) is applied (Schilling, 2002).

Surface runoff and subsurface flow are considered the two main transport pathways for $NO_3$-N and PON. In fields where tile drainage is installed, subsurface flow is expected to be a major conduit for N transport. In Quebec, approximately two million hectares of croplands have subsurface drainage (Helwig et al., 2002) and about 35 to 49% of annual rainfall discharges as tile drainage water (Simard, 2005). Between 70 to 90% of the total N load in tile drainage water of agricultural fields was reported to be in the form of $NO_3$-N (e.g. Paasonen-Kivekäs et al., 1999; Tang et al., 2011). Van der Salm (2012) observed that PON contributed to 48 to 57% of the N losses from the tile drains of a dairy farm with clayey soil.

Water infiltrating the soil surface is displaced to deeper layers by matrix flow or it can rapidly bypass the soil matrix and moves through macropores and cracks, wormholes and root channels through preferential flow; in some cases, water reaches the tile drains by passing through both preferential and matrix flow pathways (e.g. Bevenand Germann, 1982; Bouma, 1986; Jarvis and Leeds-Harrison, 1987). Although $NO_3$-N is highly soluble and could move readily through matrix flow, Kung et al. (2000) and Gentry et al. (2000) reported that macropores were the main carrier of $NO_3$-N to tile drains. Moreover, sediment associated N can also be intercepted by macropores and transported rapidly through preferential flow to tile drains (Simard et al., 2000).

Since water infiltration is 2 to 3 times more rapid through preferential than matrix flow (Meek et al., 1989), this suggests that large amount of $NO_3$-N and PON reaching tile drains can be transported via preferential flow. There are no direct methods to evaluate the proportion of N lost through preferential flow, but Steenhuis et al. (1994) found that calcium (Ca) can indicate the contact time and ion exchange with the soil matrix, and consequently, of the flow pathway. As water percolates deeper in the soil profile, it picks up different kinds of ions and its EC would reflect the ionic composition of soil solution, rather than that of rainfall or irrigation water. Chikhaoui et al. (2008) showed that electrical conductivity (EC), an indicator of solute cations, was strongly correlated to the Ca, Mg, Na and K concentrations in tile drain water from alkaline clay subsoils of the St. Lawrence Lowlands, Quebec. Using the Ca concentration in tile-drains as semi-conservative indicator of the origin of subsurface water, they developed a two-component model that relied on an electrolyte mass balance approach to differentiate between water transported through soil macropores to the tile drains and water that percolated through the soil profile (matrix flow). High Ca concentration indicated that water had moved slowly through the soil profile, preliminary through the matrix flow, whereas low Ca concentration was indicative of water that was transported rapidly from the soil surface to tile drains via preferential flow. Electrical conductivity is related to $NO_3$-N and PON in tile drainage because cations are subject to being leached from the soil profile together with $NO_3$-N and PON to maintain electrical neutrality in soil solution and in tile drainage water. It is hypothesized that the EC of tile drainage water is an indicator of macroporepathway and related to $NO_3$-N and PON concentrations.

The objectives of this study were to 1) to assess the N forms transported from two agricultural fields with contrasting soil texture (clayey and sandy soils) after rainfall events during periods with little crop growth (spring and fall), 2) to understand the pathways of $NO_3$-N and PON losses from agricultural fields with contrasting soil texture using EC as a tracer of the water flow pathway.

## 2.3 Methods and materials:

### 2.3.1 The study sites

Study sites were on two working farms, one field with clayey soil and one field with sandy soil, located in the Pike River watershed, which spans the Quebec - Vermont border and drains into the Missisquoi Bay. The study area has an annual temperature of 6.8°C and a frost-free period of 155 d. The 30 year climatic normal for precipitation collected from Philipsburg Station (45° 7' 0 N, 72° 58' 60 W), located about 9 km from the research sites, is 1095 mm $yr^{-1}$ (203 mm $yr^{-1}$ as snowfall), with annual evapotranspiration of 602 mm $yr^{-1}$. A description of the study sites and management practices was presented in chapter 3.

### 2.3.2 Tile drainage water sampling and analysis

Tile drainage water samples were collected at 7 rainfall events during fall 2010 (October to December), 16 rainfall events during spring 2011 (March to May), 10 rainfall events during fall 2011 (September to November) and 9 rainfall events in spring 2012 (March to May) to capture the seasonal variation in N forms during the frost-free period when no crop was growing in the fields. Rainfall events selected for this study were discrete events with ≥ 5 mm falling in a 24 h period, as presented in Fig. 1. Tile drainage water was collected in high density polyethylene plastic bottles and stored at 4$^{o}$C until analysis. Water samples were filtered (< 0.45 μm) prior to analysis following APHA (2005) standard methods for soluble N forms: $NH_4$-N, $NO_3$-N and total dissolved N (TDN) as well as calcium (Ca), potassium (K), sodium (Na) and magnesium (Mg). Unfiltered samples were analyzed for total N (TN) and EC (APHA, 2005), and the PON concentration was the difference between TN and TDN.

### 2.3.3 Electrical conductivity and hydrologic flow data

A HOBO conductivity logger (U24-001) (Hoskin Scientifique LIMTEE, Montreal, QC, Canada) was placed in the tile drain in May 2011 inside the same manhole that had the DMU-93 meter. This probe recorded EC and temperature data of tile drainage water in 15-min intervals during fall 2011. The U24 readings were calibrated periodically with a field conductivity meter. Data accuracy (in calibrated range) was ±3% of readings or ±5μs/cm. It is well known that EC of water depends on temperature, therefore the EC values were normalized to conductivity at 25°C. Hydrologic flow data were obtained from Ewing subwatershed outlet, about 10 km downstream from the study sites, for the period of September, 2011 to November, 2011. We used water flow data from Ewing subwatershed outlet because it is located about 10 km from working sites.

### 2.3.4 Statistical analysis

All $NO_3$-N concentration data were logarithmically transformed to normalize their distribution before statistical analysis. The effects of season (fall *vs*. spring) on $NO_3$-N concentration in each soil type (clayey, sandy) were tested with analysis of variance (ANOVA) with JMP 8.0 software (SAS Institute, 2008), considering $NO_3$-N form as a dependent variable. Particulate organic N in tile drainage water obtained in spring and fall for each soil type (clayey, sandy) were statistically tested using non-parametric Wilcoxon signed-ranked test due to non-normally distributed data to test the effects of season (fall *vs*. spring) on PON concentration in each soil type (clayey, sandy).

Linear equations were used to describe the relationship between EC and N forms ($NO_3$-N and PON) in tile drainage water of spring and fall samples as well as the relationship between N forms ($NO_3$-N and PON) and rainfall amount and between EC and Ewing tile drainage flow of fall 2011 for each soil type (clayey, sandy). The strength of the relationship between EC and Ewing tile drainage flow and EC and N forms were described with Pearson correlation coefficients.

## 2.4 Results

### 2.4.1 Nitrate ($NO_3$-N) and Particulate organic nitrogen (PON) concentrations in tile drainage water

In both clayey and sandy soils, $NO_3$-N and PON concentrations in tile drainage water fluctuated during the sampling periods (Fig. 2a, 2b). Higher $NO_3$-N concentrations were noted one week after fertilization (the second and third week of May 2011) in sandy soil. No clear trend was observed in $NO_3$-N concentration of tile drainage water in clayey soil during the spring 2011, perhaps because the fields was under soybean cultivation in the previous year, but greater $NO_3$-N concentration in tile drainage water in clayey soil occurred in the first week of May 2012 shortly after N fertilizer application.

There was 1.3 times greater $NO_3$-N concentration and 1.1 fold higher PON concentration in tile drainage water from sandy soil than clayey soil during the whole sampling period. However, no significant difference was observed in $NO_3$-N concentration in tile drainage water of clayey vs. sandy soils and in spring vs. fall. There was no difference in PON concentration in tile drainage water of clayey vs. sandy soils. The PON concentration in tile drainage water was significantly higher in spring than fall samples in clayey soil (DF=1, Z= -3.27, $P$<0.05), but no seasonal difference was observed in sandy soil (data not shown). The pattern of the positive relationship between rainfall and $NO_3$-N concentration in tile drainage was the same in both clayey and sandy soil (Fig.

3a, 3b). There was a positive relationship between rainfall amount and PON concentration in tile drainage water of clayey soil (Fig. 3c), but not for sandy soil (Fig. 3d).

### 2.4.2 Relationship between continuous EC measurement, hydrologic flow and N forms

There was a significant negative correlation between EC in the tile drainage water of clayey soil and hydrologic flow at the Ewing outlet, but no relationship was observed between EC and hydrologic flow for the sandy soil (Fig. 4).

Due to the similarity in $NO_3$-N and PON concentrations in spring and fall rainfall events, data were pooled for each soil type (clayey and sandy), and correlated to EC measurements. The positive relationship between EC and $NO_3$-N in tile drainage water was significant for clayey soil and sandy soil (Fig. 5a, 5b). The relationship between EC and PON was significant in clayey soil, but not in sandy soil (Fig. 5a, 5b). In clayey soil, 3 out of 8 rainfall events during fall 2011, there was a flush of PON that corresponded to greater hydrologic flow at the Ewing outlet and a decrease in EC of tile drainage water in the field (Fig. 6a). In the sandy soil, no clear pattern between these variables was observed (Fig. 6b).

## 2.5 Discussion

I found higher $NO_3$-N concentration in tile drainage water of sandy soil than clayey soil during sampling period, but the pattern was almost the same in both soils, although the agricultural practices were different. According to Ritter and Bergstrom (2001), two conditions are necessary for $NO_3$-N leaching through the soil profile. First, $NO_3$-N levels in soils must be high and secondly, there must be downward movement of water to transport the nutrients. These two factors caused $NO_3$-N to be easily washed from the soil profile. I didn't find a clear pattern between rainfall amount and $NO_3$-N concentration in tile drainage water. Tang et al. (2011) also did not find any relationship with rainfall and $NO_3$-N loss in agricultural catchments. In contrast, Liang et al. (2011) observed the heavier rainfall could bring the higher N and higher leachate volume in a clayey soil. However, Anderson and Burt (1982) and Hornberger et al. (1994) determined that dynamics of labile nutrient concentration is commonly contributed to "flushing" hypothesis. On the other hand, increasing in the rainfall amount increased PON concentration in tile drainage water in clayey soil. This was consistent with Tang et al. (2011) who found greater PON concentration with increasing rainfall intensity. A dilution effect was observed for $NO_3$-N and PON concentrations in both soils due to the fact that very high volume of water moving through the soil profile dilutes $NO_3$-N and PON concentrations.

We hypothesized that EC would be an indicator of $NO_3$-N and PON concentration, which was supported by positive significant correlation between EC and $NO_3$-N in both soils and significant negative correlation between EC and PON in clayey soil. Increasing $NO_3$-N leaching from the soil profile with increasing EC was interpreted to mean that water percolating slowly thorough the soil matrix would become enriched with cations and anions from the profile. Therefore I concluded that slow matrix flow was responsible for $NO_3$-N transport from the soil profile. The negative correlation between PON leaching and EC in clayey soil illustrated that water moved rapidly through the soil profile and had less contact time with the soil matrix, therefore preferential flow were likely responsible for transporting PON from the clayey soil. This result was supported by inverse relationship between EC and outlet drainage water that shows there was a rapid movement of water through preferred pathways in 40% of the sampling events. The sandy soil showed a negative tendency, but the correlation between EC and PON was not significant. This may be due to the relatively low proportion of preferential flow pathways in sandy soil. Chikhaoui et al. (2008) showed that water was mostly transported through matrix flow in sandy soil (70% of total water flow), whereas preferential flow was responsible for about 80% of water flow in clayey soil. However, since the sandy soil is a very porous media and also there was not any significant correlation between PON and EC, there may be a flush of water at this point that has moved the PON from the soil profile. More research is needed to fully understand the transport mechanism of $NO_3$-N and PON in tile drained soils. A chemical mixing model based on EC values and hydrograph separation can be helpful to estimate the preferential and matrix flow and the contribution of $NO_3$-N and PON loss from each of these pathways.

## 2.6 Conclusion

Nitrate and PON are susceptible to loss through tile drainage water from clayey and sandy soil. Nitrate was susceptible to loss from the soil profile of clayey and sandy soils via matrix flow and PON was susceptible to be transported from the clayey soil through preferential flow according to EC measurements.

Abatement of $NO_3$-N and PON loss via tile drainage could be achieved by reducing drainage outflow through drainage control structures (e.g. contorted drainage) or through the reduction of N concentrations in the soil (e.g. properly accounting for N credits to keep RSN low). The significant positive correlation between EC and $NO_3$-N in both clayey and sandy soils implies that EC could be used as quick in-field indicator of $NO_3$-N concentration in drainage outflow. However this should be confirmed by coupling EC measurements with chemical and hydrological models.

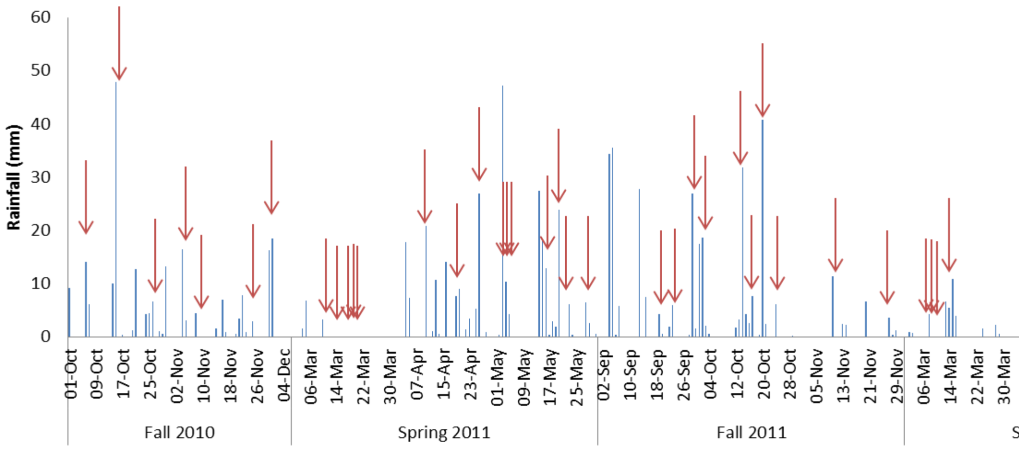



Figure 1: Daily precipitation during fall 2010, spring and fall 2011 and spring 2012. Data were collected from Philipsburg station, Quebec. Arrows shows the sampling points.

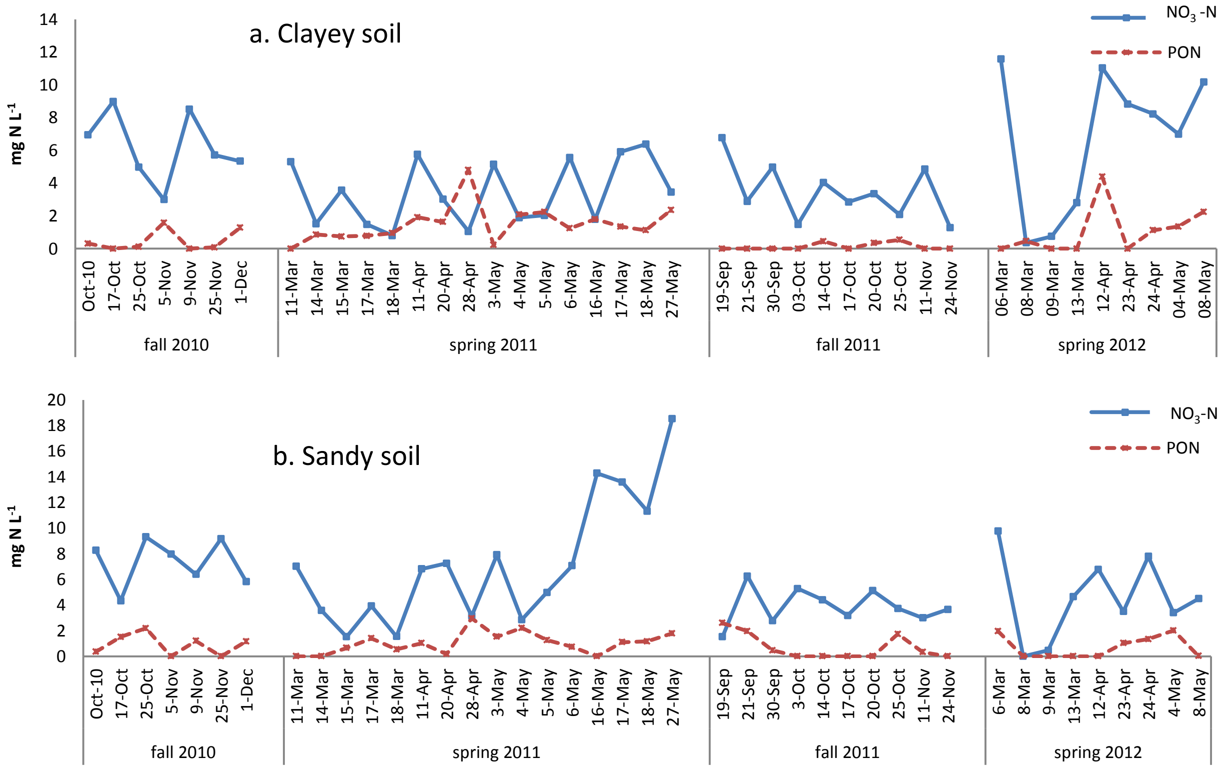



Figure 2: Nitrate ($NO_3$-N) and particulate organic nitrogen (PON) concentrations in tile drainage water of (a) clayey soils and (b) sandy soil collected at discrete rainfall events from October 2010 to May 2012.

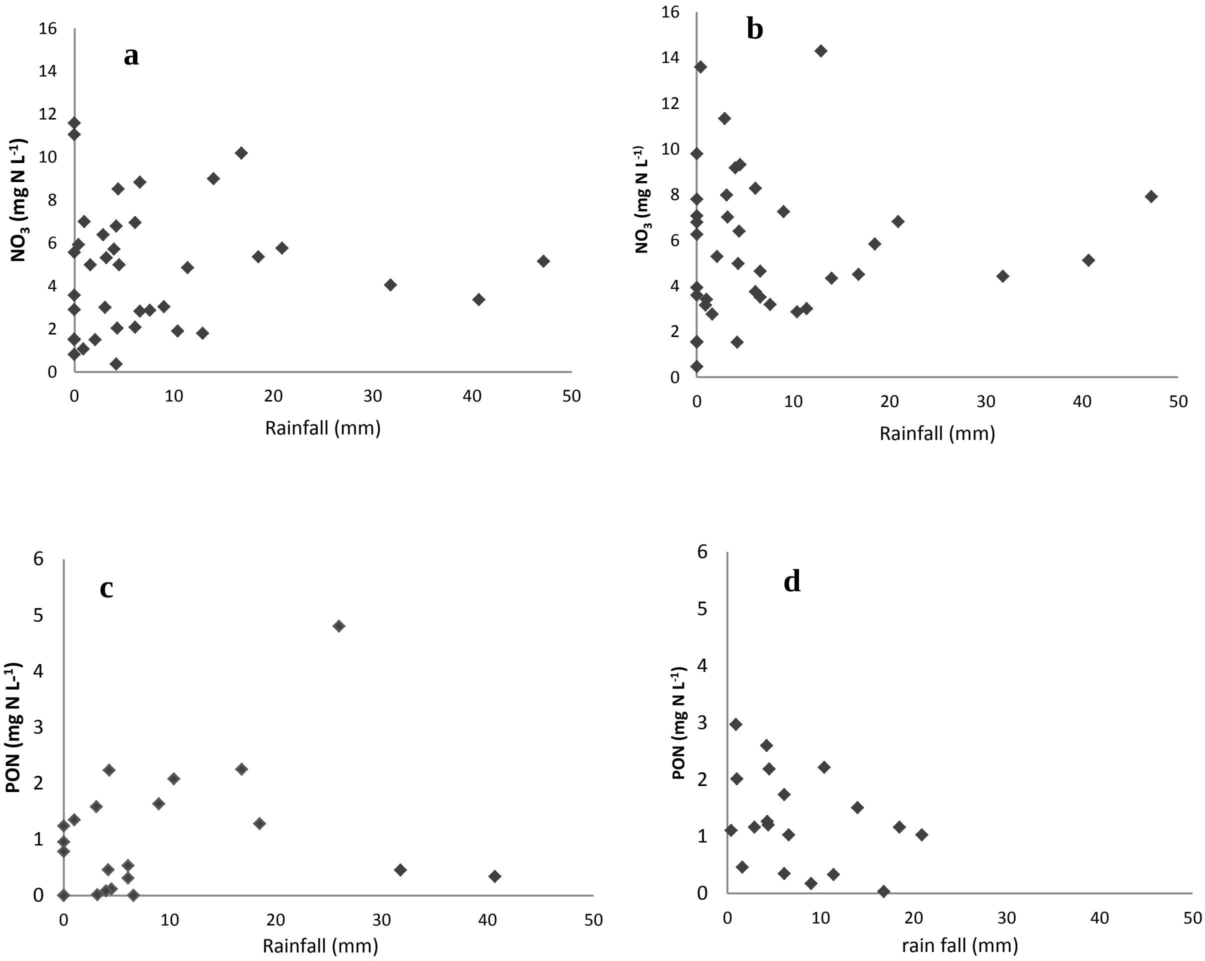



Figure 3: Relationship between rainfall, nitrate ($NO_3$-N) and particulate organic nitrogen (PON) obtained from pooled data (fall 2010 to spring 2012) from clayey soil (a and c) and sandy soil (b and d).

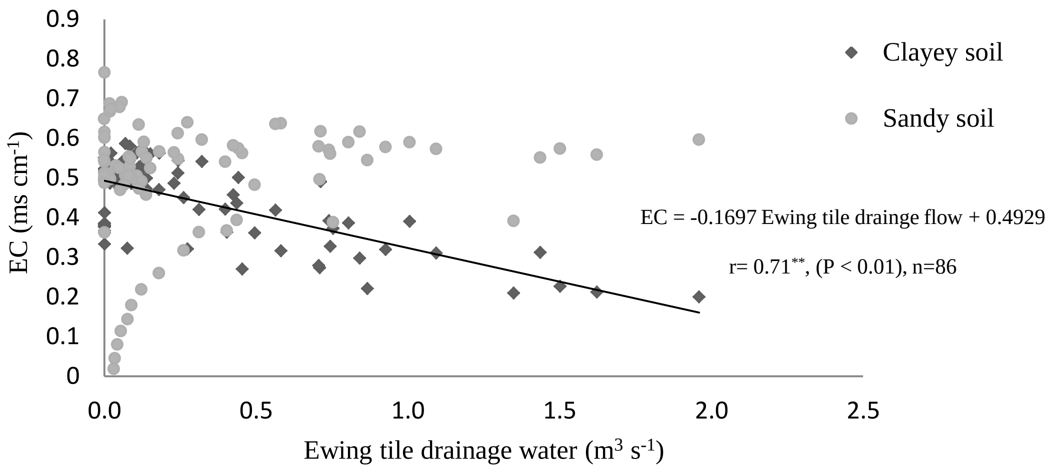



Figure 4: Relationship between tile drainage flow and electrical conductivity (EC) in clayey and sandy soils. EC were obtained from daily monitoring of EC probes during fall 2011.

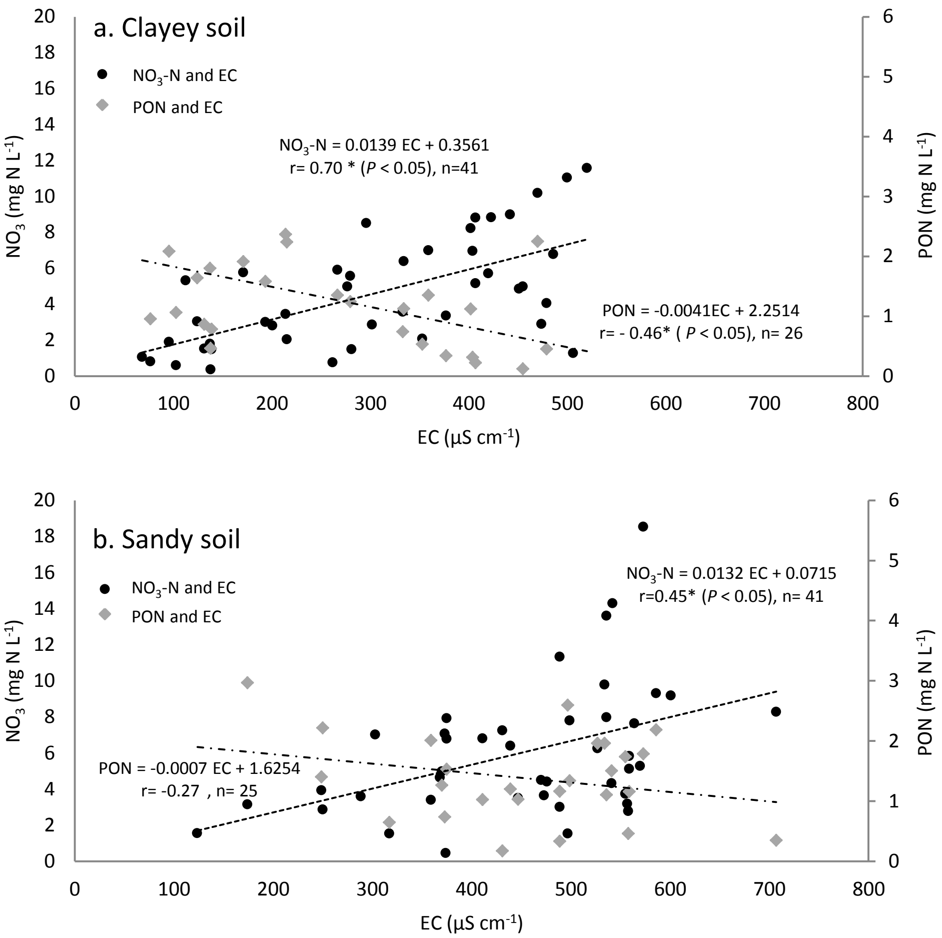



Figure 5: Relationship between electrical conductivity (EC), nitrate ($NO_3$-N) and particulate organic nitrogen (PON) in tile drainage water of (a) clayey soil and (b) sandy soil.

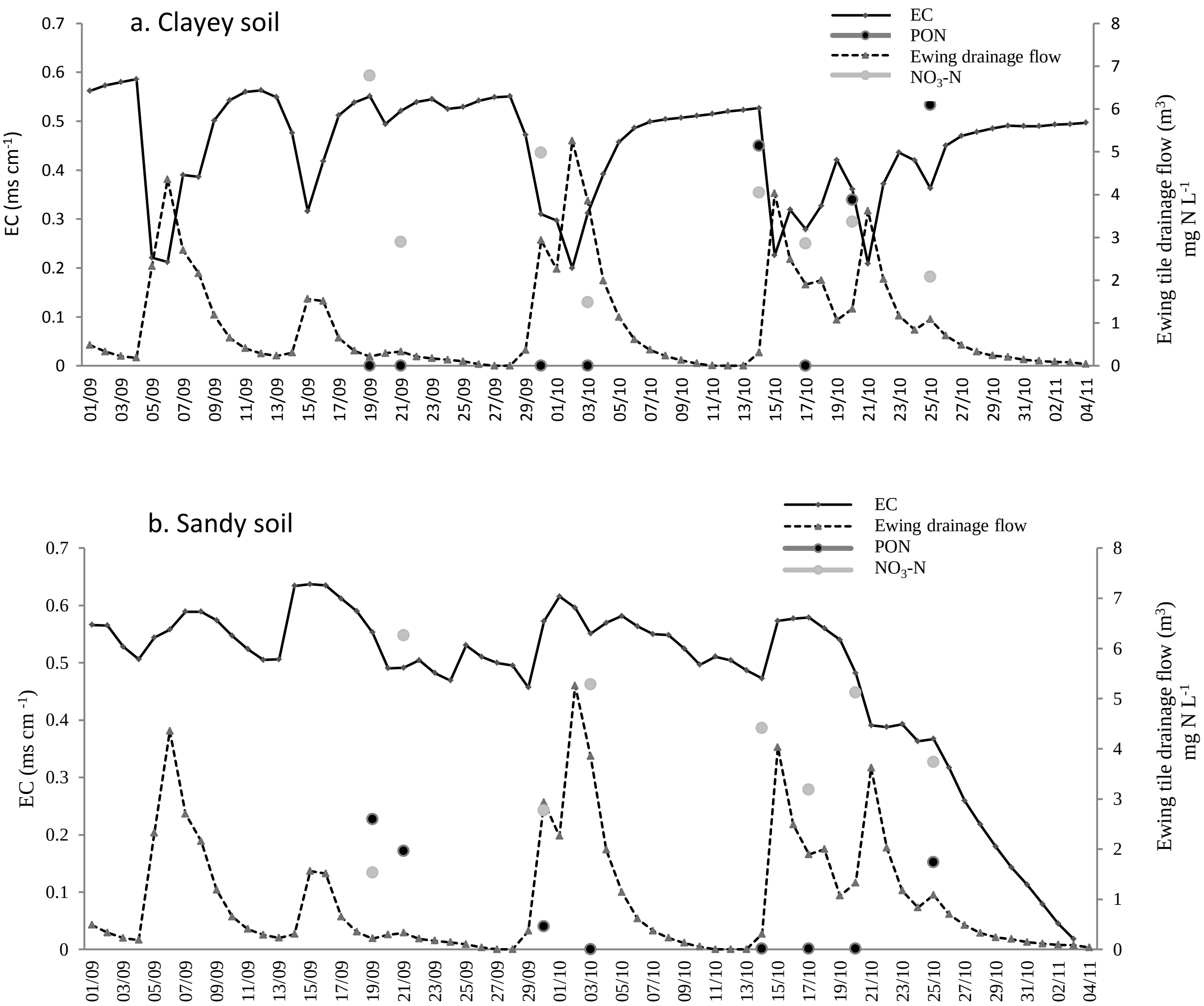



Figure 6: Electrical conductivity (EC), nitrate ($NO_3$-N) and particulate organic nitrogen (PON) concentrations in tile drainage water of (a) clayey soil and (b) sandy soil during fall 2011. EC were obtained from daily monitoring of EC probes during fall 2011. Water flow data were collected from Ewing outlet during fall 2011.

## Forward to chapter 3

Results from Chapter 2 indicate that $NO_3$-N and PON are the major forms of N lost through tile drainage water from agricultural fields in the study region. However, the source of $NO_3$-N and PON remains unclear – are these N forms originating from microbially-processed soil N, fertilizer N, manure N, atmospheric N deposition, or plant residue? To answer this question, I used the natural abundance of stable isotopes $\delta^{15}N$ and $\delta^{18}O$ to detect the sources of $NO_3$-N lost from agricultural soils, and the stable isotope of $\delta^{15}N$ to discern the origin of PON from agricultural soils.

This chapter in preparation for submission to the Journal of Environmental Quality.

# Chapter 3: Stable isotopes of nitrogen and oxygen to pinpoint the sources of nitrogen loss through tile drains in Pike River watershed, southern Quebec

## 3.1 Abstract

The Missisquoi Bay of Lake Champlain in southern Quebec has become progressively eutrophic since 1999, partially due to nitrogen (N) loading from agricultural activities in the Pike River watershed. Nitrate ($NO_3$-N) and particulate organic N (PON) are the dominant N forms entering surface waters from tile drained agricultural fields. Determining the contribution of agricultural N inputs to the $NO_3$-N and PON loads could lead to better N management in the Pike River watershed. This study aimed to identify the sources of $NO_3$-N and PON in tile drainage water from agricultural fields under annual crop production. Water samples were collected from tile drains under sandy and clayey soils in spring 2011 and analyzed for $\delta^{15}$N and $\delta^{18}$O of $NO_3$-N, and the $\delta^{15}$N in PON. The Stable Isotope Analysis in R (SIAR) mixing model was used to estimate the proportional contribution of N sources to $NO_3$-N and PON. Except for a period of two weeks after fertilization when $NH_4$ fertilizer was the primary source of $NO_3$-N, microbially-processed $NO_3$-N accounted for 40 to 49% of $NO_3$-N in tile drainage water. Sources of PON in tile drainage water were manure N (47%) and plant residue N (20%) in a clayey soil, while soil organic N (SON) contributed to 94% of PON lost from a sandy soil. In all cases, PON originated from topsoil. Decreasing $NH_4$ inputs from fertilizer and allocating sufficient N credits to manure and legume residue inputs could reduce the buildup of $NO_3$-N and organic N, thereby reducing $NO_3$-N and PON losses from these sources.

## 3.2 Introduction

Proliferation of cyanobacteria in freshwater lakes is a major water quality issue. In some lakes, nitrogen (N) loading triggers cyanobacteria blooms and the production of cyanotoxins (e.g. Klemer et al., 1982; Stevens et al., 1981; Elser et al., 2009; Paerl, 2008). The Missisquoi Bay of Lake Champlain, spanning the border of Quebec (Canada) and Vermont (United States), had cyanobacteria blooms reported nearly every summer since 1999 (Smeltzer et al., 2012), in part due to the N loading from the Pike River, its major tributary. The annual N load from the Pike River watershed was more than 800 kg N $km^{-2}$ $y^{-1}$ from 1990 to 2009 (Medalie et al., 2012), and much of the N loading is attributed to agricultural activities occurring in southern Quebec, close to the watershed outlet.

Agricultural land is a major source of N loading in the Pike River watershed due to the widespread use of N fertilizer to achieve crop yield objectives. Fields that receive higher N inputs, such as for corn production (120 to 170 kg N $ha^{-1}$; CRAAQ, 2010), either from inorganic fertilizer or manure applications, are susceptible to N losses. Biological $N_2$ fixation is another N input in agricultural systems, particularly where leguminous crops are grown, that leaves N-rich residues to decompose in the field after harvest and contributes to N loading in watersheds (Chambers et al., 2001). Atmospheric N deposition is on average 10 kg N $ha^{-1}$ $y^{-1}$, with values up to 15 kg N $ha^{-1}$ $y^{-1}$ or higher reported in agricultural areas where livestock operations are concentrated (Vet and Shaw, 2004). Excess N in fields is transferred to waterways in soluble forms mostly nitrate ($NO_3$-N), with minor amounts of ammonium ($NH_4$-N), nitrite ($NO_2$-N) and dissolved organic N (DON) - and with eroded sediments, mostly particulate organic N (PON). Surface runoff and subsurface drainage (natural and artificial tile drainage) are responsible for transporting soluble and particulate N forms to waterways. Tile drainage is probably the most important pathway for N loss in the Pike River watershed, since 50% of the annual precipitation (Enright et al., 2003) and 65% of the $NO_3$-N lost (Umuhire et al., 2007) from agricultural fields to the Pike River was transmitted through tile drains. The PON fraction accounted for up to 27% of the total N in tile drain outflow according to Carter et al. (2003). The amount of water, soluble and particulate N transported through tile drains is partly controlled by texture, with more PON loss expected from clayey than sandy soils for instance. Yet, we still do not know how different N sources contribute to the N load in tile drains, which is essential to manage agricultural N inputs in the Pike River watershed. Determining the contribution of different N sources to the N load could lead to better management of agricultural N inputs in Pike River watershed.

The dominant forms of N lost through tile drains, $NO_3$-N and PON, could originate from many sources (e.g., inorganic fertilizer, animal manure, biological $N_2$ fixation, atmospheric deposition and soil organic N (SON)). Isotope tracing with $\delta^{15}N$ has the potential to distinguish N sources because each anthropogenic N input has a distinctive isotopic range. On average, $\delta^{15}N$ values for inorganic fertilizer range from -3 to +2‰, and animal wastes are from +10 to +20‰ (Gautam and Iqbal, 2009). The $\delta^{15}N$ values for $NO_3$-N in precipitation were between -15 and +15‰ in many studies (e.g. Moore, 1977;

Freyer, 1978) and for $NH_4$-N were -3.4 ±2.1‰ (Garten, 1992). Plants that fix $N_2$ from the atmosphere have $\delta^{15}N$ values of about -3 to +1 ‰. The $\delta^{15}N$ value of SON ranged from +2‰ to +8‰ in agricultural soils (Kendall, 1998). If a fraction of the N is transferred directly through tile drains to waterways, $\delta^{15}N$ and $\delta^{18}O$ signatures reflect the initial source values. However, most of the N from different inputs is transformed biologically and chemically in the soil profile (Kendall et al., 2007) and these processes alter the $\delta^{15}N$ and $\delta^{18}O$ signatures of N forms in tile drainage. Therefore, it is hypothesized that microbially transformed $NO_3$-N would be the major source of $NO_3$-N in tile drainage water during most of the growing season, but inorganic fertilizer would be the important source of $NO_3$-N shortly after fertilizer application (since the N fertilizer could be leached directly to the tile drain). Enriched microbial byproducts of residue and manure decomposition accumulate on soil mineral surfaces as SON, which is the precursor to PON recovered in eroded soil particles. We hypothesize that SON associated with soil minerals is the dominant source of PON in tile drainage water.

How can the $\delta^{15}N$ values of $NO_3$-N and PON in tile drainage water be attributed to agricultural N sources, given the fact that several N sources, subject to a variable degree of transformation (e.g. mineralization, immobilization, ammonia volatilization, nitrification and dentrification) in the soil profile, may be transported through tile drains at the same time? For example, $NO_3$-N in tile drainage water may consist of microbially-processed $NO_3$-N as well as $NO_3$-N from precipitation. Since the $\delta^{15}N$ signature of these N sources overlap, additional information needs to distinguish between the two N sources. In $NO_3$-N analysis, a dual isotope approach using $\delta^{15}N$ in combination with $\delta^{18}O$ (Wassenaar, 1995; Kendall, 1998; Spoelstra et al., 2001) eliminates difficulties associated with relying on $\delta^{15}N$ alone. The $\delta^{18}O$ value of $NO_3$-N coming directly from inorganic fertilizer is near +23‰ (Amberger and Schmidt, 1987), while $NO_3$-N produced from mineralization has $\delta^{18}O$ values from +2 to +14‰ (Mayer et al., 2001). Dual isotope analysis also accounts for N losses through denitrification, as isotope fractionation results in a correlation between $\delta^{15}N$ and $\delta^{18}O$ with a slope of 1:2 (Aravena and Robertson, 1998; Deutsch et al., 2006).

Stable isotope mixing models may hold promise for partitioning the $\delta^{15}N$ of different N sources, while considering the $\delta^{18}O$ signature, thereby allowing us to distinguish the concentration of the N from inorganic fertilizer, manure, biological $N_2$ fixation and SON to the $NO_3$-N and PON pools. Mixing models such as Stable Isotope Analysis in R (SIAR) are able to quantitatively predict the proportional contribution of several sources to a mixture in dual isotope systems (Parnell et al., 2010) and have been successfully applied to estimate the proportional contribution of multiple $NO_3$-N sources in surface waters (e.g. Xue et. al., 2012). The SIAR model provides advantages over standard, mass balance multi source mixing models (e.g. IsoSource; Phillips and Gregg, 2003) by integrating the sources of variability associated with multiple sources, fractionation and isotopic signatures. Model output is presented as true probability density functions, rather than a range of feasible solutions (Parnell et al., 2010).

The goal of this study was to identify the agricultural N sources of $NO_3$-N and PON in tile drainage water from agricultural fields. This was accomplished by comparing the $\delta^{15}N$ and $\delta^{18}O$ isotopic signatures of $NO_3$-N, and the $\delta^{15}N$ isotopic signature of PON to known source materials using the SIAR model. Sources of $NO_3$-N were evaluated during four study periods - pre-fertilization, early post-fertilization, late post-fertilization and post-harvest - to account for seasonal variation in N inputs, soil N transformations and fluctuations in precipitation that would affect the $\delta^{15}N$ and $\delta^{18}O$ signatures of $NO_3$-N in tile drainage water. Sources of PON were evaluated in tile drainage water from fields with different agricultural N inputs (inorganic fertilizer, manure, SON, biological $N_2$ fixation and precipitation) and contrasting soil texture (clayey *vs*. sandy).

## 3.3 Methods and materials

### 3.3.1 Site Description

Two agricultural fields selected for this study (Fig. 1) are located near the town of Bedford, Quebec, Canada (45° 7' 0 N, 72° 58' 60 W) in the Pike River watershed. Bedford has an average annual temperature of 6.8°C and a frost-free period of 155 d. Mean annual evapotranspiration is 602 mm $yr^{-1}$ and mean annual precipitation is 1095 mm $yr^{-1}$, with 203 mm coming from snowfall. The Pike River is about 58 km long and drains a 629 $km^2$ watershed (530 $km^2$ within the province of Quebec), with an average annual water yield of 476 mm (Deslandes et al., 2007).

The agricultural fields are located on privately owned farms and were selected for this study because tile drainage outlets were readily accessible.

Tile drains were installed at 1.1 to 1.3 m depth in the C horizon on both farms about 30 years prior to this study. Site A (hereafter referred to as clayey soil), located 3 km west of Bedford, had a surface drainage area of 10.2 ha, a tile drainage area of 7.8 ha and an average slope of 0.8%. The clayey soil was classified as a Haplic Gleysol with three soil series in the field: Suffield clay loam (9.4%), Ste. Rosalie clay loam (69.9%) and Bedford sandy clay loam (20.7%). Site B (hereafter referred to as sandy soil) is situated 1 km west of Bedford, with surface and tile drainage areas of 6 ha and average slope of 2%. The sandy soil was a Podzol classified as a Rubicon sandy loam soil series. Details of the fertilizer sources, application rates and the agricultural practices at both sites are presented in Table 1.

### 3.3.2 Water sampling and analyses

Tile drainage water was collected from clayey and sandy soils at discrete events (samples taken over intervals ranging from one hour to one day) during spring 2011 (March to May) and fall 2011 (September to November) to capture the variation in N forms and concentrations during the frost-free period. Tile drainage water samples were taken from clayey and sandy soils by collecting them in high density polyethylene (HDPE) plastic bottles and stored at $4^{o}C$ until analysis. Water samples were filtered (< 0.45 µm) prior to analysis following APHA (2005) standard methods for soluble N forms: $NH_4$-N, $NO_3$-N and total dissolved N (TDN). Unfiltered samples were analyzed for total N (TN) (APHA, 2005), and the PON concentration was the difference between TN and TDN.

Since the sandy soil was fertilized for corn production in two subsequent years, we selected a subset of water samples from the sandy soil for $\delta^{15}N$ and $\delta^{18}O$ analysis of the $NO_3$-N pool. The discrete events with ≥ 10 mm rainfall in a 24 h period occurred in spring 2011 (March to May, 6 events) and in fall 2011 (September to November, 6 events), and these were divided into 4 groups: pre-fertilization (n=4), early post-fertilization (n=2), late post-fertilization (n=4) and post-harvest (n=2). Filtered water samples were transferred to 30 mL Nalgene-type bottles and frozen (-20$^{o}$C) until analysis for $\delta^{15}N$ and $\delta^{18}O$ with a Thermo Finnigan GasBench + PreCon trace gas concentration system interfaced to a Thermo Scientific Delta V Plus isotope-ratio mass spectrometer (UC Davis Stable Isotope Facility). The $\delta^{15}N$ of PON was associated with sediments (at least 70 mg TSS retained on 0.45 µm filters, oven-dried for 1 h at 60$^{o}$C and packaged in tin capsules) in tile drainage water samples collected at 8 discrete events (≥ 10 mm rainfall in a 24 h period) in spring 2011 (March to May) from clayey and sandy soils. Such events mobilize large quantities of soil particles containing PON as a result of raindrop impact on the soil surface (Kwaad, 1991).

### 3.3.3 Soil sampling and analyses

The native $\delta^{15}N$ value of soil was assessed by taking 6 to 7 individual soil cores from the agricultural fields in early May 2011 from two depths: top-soil

(0-20 cm) and sub-soil (20-60 cm). Soil cores were combined to make a composite sample for each depth, which was air-dried immediately after collection and stored at $4^{o}C$ until analysis. A subsample from each composite sample was oven-dried (1 h at $60^{o}C$), packaged and sent for analysis for $\delta^{15}N$ with a PDZ Europa ANCA-GSL elemental analyzer interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (UC Davis Stable Isotope Facility).

### 3.3.4 Stable Isotope Analysis in R mixing model to partition the agricultural nitrogen sources in tile drainage water

To estimate the contribution of $NO_3$ sources in four sampling periods (pre-fertilization, early post-fertilization, late post-fertilization and post-harvest), two isotopes ($\delta^{18}O$ and $\delta^{15}N$ of $NO_3$-N) and four potential $NO_3$-N sources ($NO_3$ in precipitation, microbial $NO_3$, $NH_4$ in fertilizer, N deposition) were considered in the SIAR model, based on literature values of $\delta^{18}O$ and $\delta^{15}N$ of N sources (Table 2). We assumed a negligible contribution of biological $N_2$ fixation to the $NO_3$ and PON pools in tile drainage water of sandy soil, which was under corn production in 2010-2011. To estimate the contribution of the N sources to PON pool in tile drainage water, the $\delta^{15}N$ of PON and five potential sources of N (SON, $NH_4$ in fertilizer, manure, $NH_4$ from deposition and biological $N_2$ fixation) were considered in clayey and sandy soils (Table 2).

### 3.3.5 Statistical analysis

Descriptive statistics (mean, standard deviation) of the N forms and stable isotopes in tile drainage water and field soils at two depths were calculated and the differences between the $\delta^{15}$N of PON in tile drainage water and $\delta^{15}$N in soil at two depths were determined for each soil type (clayey, sandy) using a Student *t* test ($P < 0.05$). Differences in $NO_3$-N and isotope ($\delta^{15}$N, $\delta^{18}$O) concentrations between four sampling periods (pre-fertilization, early post-fertilization, late post-fertilization and post-harvest) were determined using non-parametric Wilcoxon signed-ranked test due to uneven sample sizes and non-normal distributed data. Linear regressions were fit between $\delta^{15}$N-$NO_3$ and $\delta^{18}$O-$NO_3$ to determine whether denitrification caused a significant N loss, where slopes of 1:2 are indicative of denitrification (Aravena and Robertson, 1998; Deutsch et al., 2006).

## 3.4 Results

### 3.4.1 Nitrate pool in tile drainage water

Nitrate was the major source of N lost in tile drainage water of sandy soil, contributing 90% of the total N concentration in water samples collected for the study. Measured $\delta^{15}$N and $\delta^{18}$O of $NO_3$-N in tile drainage water were in the same range as the literature values of $\delta^{15}$N and $\delta^{18}$O of $NO_3$-N derived from nitrification (Fig. 2). No difference in $NO_3$-N concentration of tile drainage water was detected between pre-fertilization, early post-fertilization, late post-fertilization and post-harvest periods according to a Wilcoxon signed-rank test (data not shown). The highest $NO_3$-N concentration in tile drainage water occurred in the early post-fertilization period, which coincided with $NH_4$ fertilizer application, and the lowest concentration was measured in the pre-fertilization period (Fig. 3).

Values of $\delta^{15}N$ and $\delta^{18}O$ in $NO_3$-N from tile drainage water samples generally increased from pre-fertilization to the post-harvest period (Fig. 3). Although there was no difference in $\delta^{15}N$ of $NO_3$-N between pre-fertilization, early post-fertilization, late post-fertilization and post-harvest periods, a Wilcoxon signed-rank test showed a significant difference in $\delta^{18}O$-$NO_3$ between pre-fertilization and late post-fertilization periods (DF= 1, Z = -2.17, $P < 0.05$). The slope of linear equation fitted between $\delta^{15}N$-$NO_3$ and $\delta^{18}O$-$NO_3$ showed a 1:2 ratio in the early post-fertilization period, implying denitrification caused significant N losses from soil solution, but the slopes of linear equations were less than 1:2 in pre-fertilization, late post-fertilization and post-harvest periods (Fig. 4).

### 3.4.2 Particulate organic nitrogen pool in tile drainage water

Particulate organic N accounted for 55% of total N in tile drainage water from clayey soil and 33% of total N in tile drainage water of sandy soil at peak events in spring 2011, with $\delta^{15}N$ values of 5 to 5.5 ‰ in PON. Although

$\delta^{15}N$-PON in tile drainage water was similar to $\delta^{15}N$-SON in topsoil, it was greater than the $\delta^{15}N$-SON in subsoil ($P < 0.05$, $t$ test= 2.26) (Table 3).

### 3.4.3 Source partitioning of nitrate and particulate organic nitrogen pools with SIAR mixing model

Microbially-processed $NO_3$-N was the dominant source of $NO_3$-N in tile drainage water according to the SIAR model, constituting 49% of the $\delta^{15}N$ signature in $NO_3$-N from tile drainage water in the pre-fertilization period and 40% of the $\delta^{15}N$ signature in late post-fertilization period (Fig. 5A, 5C). However, in the early post-fertilization and post-harvest periods, microbially-processed $NO_3$-N and $NH_4$ fertilizers contributed almost equally to the $NO_3$-N in tile drainage water, according to the SIAR model (Fig. 5B, 5C).

Manure-N was predicted to be the dominant source of PON in tile drainage water of clayey soil by the SIAR model, constituting 47% of the $\delta^{15}N$ signature in PON from tile drainage water (Fig. 6A). N-rich plant residue that derived $N_2$ from biological $N_2$ fixation contributed 20% of the PON pool as well. In contrast, SON was the dominant source of $\delta^{15}N$-PON (94% of the $\delta^{15}N$ signature) in tile drainage water from the sandy soil (Fig. 6B).

## 3.5 Discussion

### 3.5.1 Sources of nitrate in tile drainage water from sandy soil

We hypothesized that inorganic fertilizer would be the main source of $NO_3$-N shortly after fertilizer application, but microbially-processed $NO_3$-N would be the major source of $NO_3$-N in tile drainage water during the rest of the growing season. Plotting the dual isotope data against expected ranges of $\delta^{15}N$ and $\delta^{18}O$ of $NO_3$ partially supported our hypotheses, but the SIAR model predicted that fertilizer N, microbially-processed $NO_3$-N and $NH_4$ from precipitation contributed almost equally to the $NO_3$-N in tile drainage water at most periods during the growing season. Although the nitrification rate is expected to be lower during the pre-fertilization period, still we observed a portion of microbially-processed $NO_3$-N leached through the soil profile, which may be due to the lower rate of biological assimilation and more intense rain events during that period (201 mm; Environment Canada), as suggested by Foster et al. (1989). In early post-fertilization period, fractionation associated with nitrification occurs because $NH_4$ is available and abundant in soil following the application of $NH_4$ based fertilizers (Feigin et al., 1974). Therefore, microbially-processed $NO_3$-N and fertilizer N contributions to the $NO_3$-N pool were expected, and we also noted greater $NO_3$-N concentration (14-18 mg $NO_3$-N $L^{-1}$) in tile drainage water collected during the early post-fertilization period.

In the late post-fertilization and post-harvest periods, we noted progressive enrichment of $\delta^{15}N$ and $\delta^{18}O$ in tile drainage water, compared to the early post-fertilization period. This suggests that microbial fractionation of $\delta^{15}N$ and $\delta^{18}O$ was occurring in these periods, so microbially-processed $NO_3$-N (from nitrification) was the source of $NO_3$-N in tile drainage water, as indicated by simple plot of the dual isotope against expected $\delta^{15}N$ and $\delta^{18}O$ ranges for various N sources in Fig. 2. However, the SIAR model predicted almost equal contributions of microbial $NO_3$-N, $NH_4$ based fertilizers and $NH_4$ from precipitation to the $NO_3$-N pool in these periods. These findings are consistent with Savard et al. (2007) and Smith and Kellman (2011), who suggest that nitrification occurs throughout the frost-free period and therefore multiple N sources can be transformed to $NO_3$-N and subsequently leached to tile drains. Since microbial activity generates $NO_3$-N constantly, apparently from multiple N sources, accurate quantification of the nitrification rate, which controls the microbial derived $NO_3$-N pool size in the field, merits further investigation.

The SIAR model, described by Parnell et al. (2010), uses a Bayesian framework to determine the probability distribution of the relative contribution of each N source to a mixture. Moreover, SIAR accounts for the uncertainties arises from temporal and spatial variability in $\delta^{18}O$ and $\delta^{15}N$ of $NO_3$-N, isotope fractionation during denitrification and situations where the number of N sources is greater than the number of isotopes +1 that contribute to the mixture (Moore and Semmens, 2008; Xue et al., 2009). However, we noted that the SIAR model underestimated the microbial $NO_3$-N contribution to the $NO_3$-N pool during the growing season so the result should be interpreted with caution. Main sources of error in predicting the $NO_3$-N source contribution by the SIAR model arise from the wide range of $\delta^{15}N$ values from various sources. There was overlap in the ranges for $NH_4$ in fertilizer and precipitation and $NO_3$-N derived from nitrification, due to the standard deviation associated with mean values of $\delta^{18}O$ and $\delta^{15}N$ in these sources. The SIAR output would be improved by analyzing the original source material at the field sites, which should have a narrower isotopic composition ($\delta^{15}N$, $\delta^{18}O$) than reported in the literature.

### 3.5.2 Sources of particulate organic nitrogen pool in tile drainage water from clayey and sandy soil

We hypothesized that microbially-processed SON would be the major source of PON in tile drainage water, which was correct for the sandy soil that received inorganic N fertilizer only, but not for the manured clayey soil. Manure and plant residue that derived $N_2$ from biological $N_2$ fixation were the two most important sources of PON in tile drainage water from the clayey soil. These findings imply that incompletely decomposed organic materials, rich in N, are absorbed to the soil mineral surface and susceptible to loss as PON. As only 45 and 20% of organic N in manure is mineralized during the year of application and the following year (Drury et al., 2012), the remaining organic N could be associated with clay minerals and form organo-mineral complexes that are susceptible to transport through the soil profile to the tile drains when significant rainfall occurs ($\geq$ 10 mm in a 24 h period). Particle size analysis of TSS may provide information about the size of soil fractions that contribute to the organo-mineral complexes (and PON) losses from agricultural fields.

There is little doubt that PON originated from topsoil, not subsoil, based on the similarity in $\delta^{15}N$ signature of $\delta^{15}N$-SON in topsoil and $\delta^{15}N$-PON in tile drainage water. This was in consistent with Foster et al. (2003), who used $^{137}Cs$ and $^{210}Pb$ tracers to show that sediments from top soil accounted for 73% of the TSS exported through tile drains. The transfer of N-rich sediments from topsoil suggests that preferential flow pathways are responsible for PON losses to tile drainage water in both clayey and sandy soils, but this should be confirmed with ancillary measurements such as $^{137}Cs$ analysis.

## 3.6 Conclusion

Stable isotopes of N and O were powerful tools for detecting inorganic $NH_4$ fertilizer as an important contributor to the $NO_3$-N pool in tile drainage water within two weeks of application, and the dominance of microbially-processed $NO_3$-N in tile drainage water at other sampling events. The SIAR output would be improved by determining the site-specific values of $\delta^{15}N$ and $\delta^{18}O$ in potential $NO_3$-N sources. In manured soil, the PON was derived from manure and N-rich plant residue transmitted from topsoil, whereas inorganically-fertilized soils have an enriched topsoil SON pool that is lost as PON, probably through preferential flow. Since fertilizer and organic N inputs to agricultural fields contribute an abundance of $NH_4$-N that is rapidly transformed by microorganisms to $NO_3$-N, as well as increasing particle-associated organic N, this suggests several strategies to reduce $NO_3$-N and PON losses through tile drains. Proper accounting for N credits from inorganic N inputs, legumes and manure in crop rotations could reduce the contribution of these sources to the $NO_3$-N and PON pools. Agricultural practices that merit further investigation include side-dressing fertilizers, no-tillage and nitrification inhibitors to slow nitrification rates and diminish the $NO_3$-N pool susceptible to leaching. No-tillage could stabilize topsoils and thereby reduce PON loss to tile drains.

Table 1: Agricultural practices at two experimental fields in the Pike River watershed, on clayey and sandy soils, during 2010 and 2011.

| Year | Fertilizer source | Fertilizer rate | Timing of the fertilizer application | Fertilizer application method | Crop | Tillage practices |
|---|---|---|---|---|---|---|
| | | | **Clayey soil** | | | |
| **2010** | Poultry manure<br>Liquid N (32-0-0) | 45 kg N $ha^{-1}$<br>90 kg N $ha^{-1}$ | First week of May | Broadcast and incorporated | Corn | Disc+ spring cultivator |
| **2011** | No fertilizer | 0 kg N $ha^{-1}$ | No fertilizer | No fertilizer | Soybean | Disc+ spring cultivator |
| | | | **Sandy soil** | | | |
| **2010** | Urea (46-0-0) | 155 kg N $ha^{-1}$ | First week of May | Broadcast and incorporated | Corn | Conventional and spring harrow |
| | Sulfammo (26-0-0) | 33 kg N $ha^{-1}$ | First week of May | Band | | |
| **2011** | Urea (46-0-0) | 155 kg N $ha^{-1}$ | First week of May | Broadcast and incorporated | Corn | Conventional and spring harrow |
| | Sulfammo (26-0-0) | 33 kg N $ha^{-1}$ | First week of May | Band | | |

Table 2: Mean values of $\delta^{15}N$ and $\delta^{18}O$ in agricultural nitrogen sources, obtained from the literature and used in the Stable Isotope Analysis in R (SIAR) mixing model. The standard deviation (SD) of the mean is given and the range is reported in brackets.

| **Potential sources** | **Mean $\delta^{15}N$ ‰** | **Mean $\delta^{18}O$ ‰** | **Reference** |
|---|---|---|---|
| $NH_4$ fertilizers | -0.98 ± 1.88 (-7.4 – 3.6 ) | - | Gautam and Iqbal, 2009 |
| Manure | 10.98 ± 4.44 (10 – 20) | - | Curt et al., 2004, Kendall and McDonnell 1998 |
| Microbial $NO_3$ | 4.70 ± 5.40 (0 – 10) | 0.0 ± 2 (-5 – 15) | Mayer et al., 2001; Voerkelius (1990) |
| Soil organic N | 0.65 ± 2.6 (2 – 8) | - | Kendall, 1998 |
| $NO_3$-precipitation | 4.34 ± 1.10 (-10 – 15) | 64.5 ± 4.8 (25 – 80) | Moore, 1977; Freyer, 1978 |
| $NH_4$-precipitation | -3.4 ± 2.1 (-10 – 10) | - | Garten, 1992 ; Hubner, 1996 |
| Biological-$N_2$ fixation | 1.5 ± 0.6 (-3 – 1.0 ) | 5.1 ± 0.9 NA | Kendall, 1998; Oelmann et al., 2007 |

Table 3: Mean $\delta^{15}N$ of soil organic nitrogen, at two depths, and in particulate organic nitrogen (PON) from tile drainage water from two experimental fields in Pike River watershed, on clayey and sandy soils. Values (mean ± SD) within a row followed by differentletters are significantly different ($P < 0.05$, Student t test).

| Soil type | Soil organic N ($\delta^{15}N$ ‰ ) | | PON ($\delta^{15}N$ ‰) in tile drain water |
|---|---|---|---|
| | Topsoil (0-20 cm) | Subsoil (20-60 cm) | |
| Clayey | 5.33 ± 0.59 ab | 3.8 ± 1.07 b | 5.46 ± 0.74 a |
| Sandy | 4.66 ± 0.14 AB | 2.40 ± 0.11 B | 5.02 ± 1.58 A |

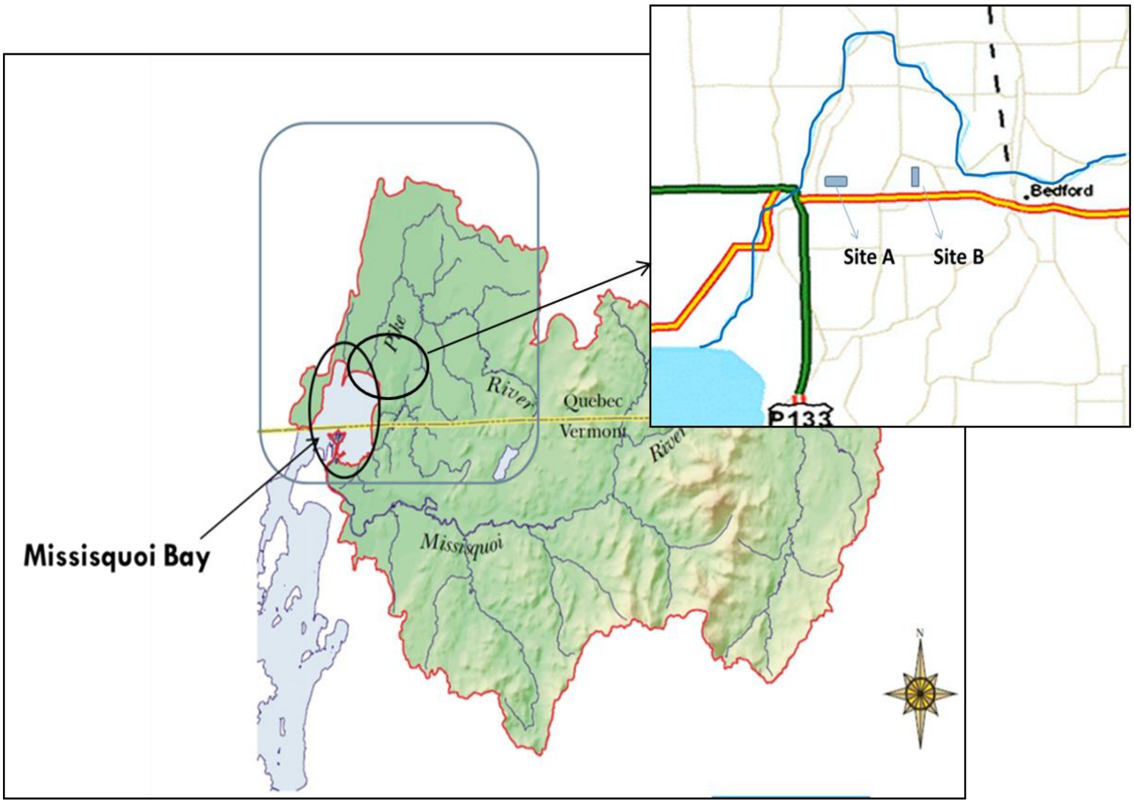



Figure 1: Location of agricultural fields with clayey soil (site A) and sandy soil (site B) in the Pike River watershed, a tributary of Missisquoi Bay, which spans the Canada-United State border between Quebec and Vermont.

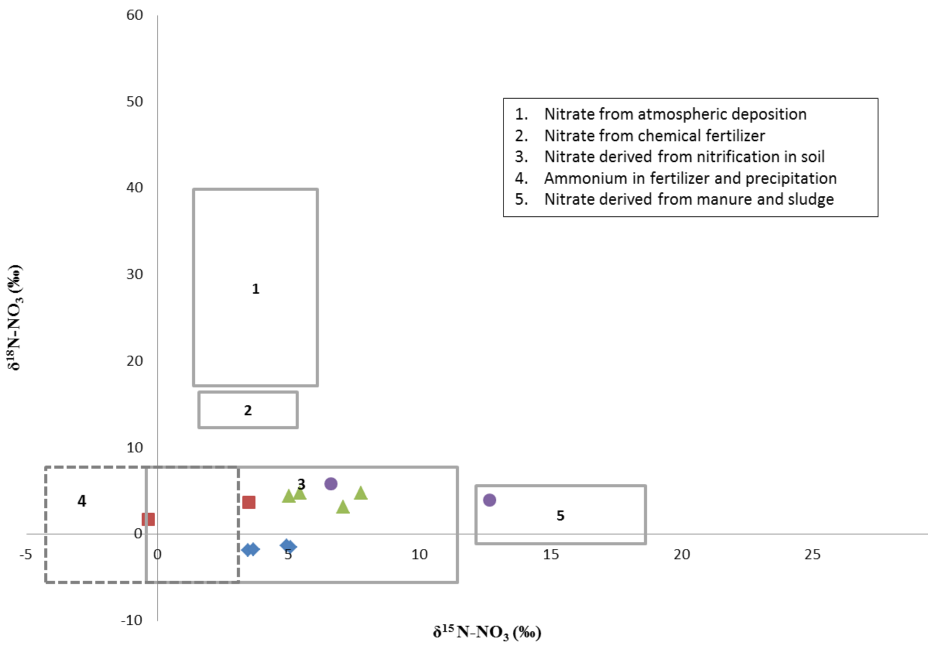



Figure 2: Typical values of $\delta^{15}N$ and $\delta^{18}O$ of nitrate ($NO_3$-N) derived or nitrified from various nitrogen (N) sources (adopted from literature) are shown as numbered boxes. Measured $\delta^{15}N$ and $\delta^{18}O$ of $NO_3$-N in tile drainage water samples from sandy soil between March and November 2011 are represented as ◆ (pre-fertilization period, n=4), ■ (early post-fertilization period, n=2), ▲ (late post-fertilization period, n=4) and ● post-harvest period (n=2).

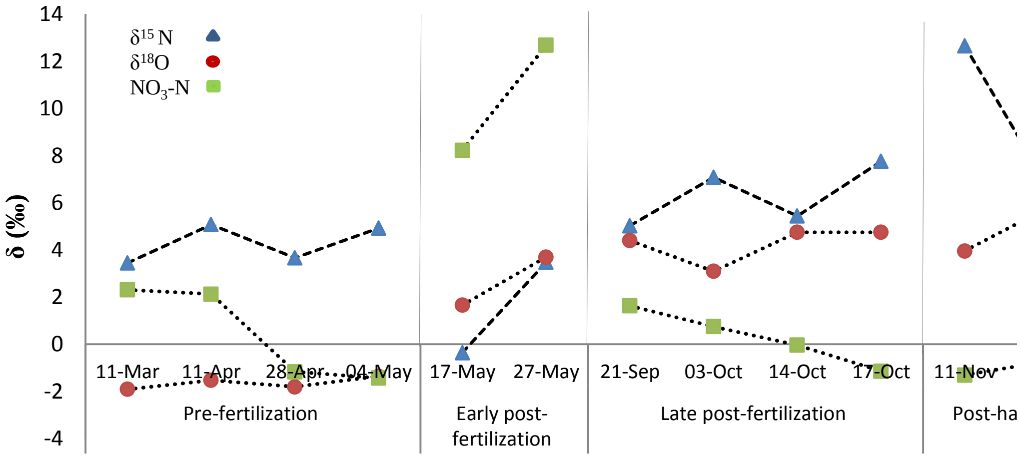



Figure 3: Seasonal nitrate ($NO_3$-N), $\delta^{15}N$ and $\delta^{18}O$ of $NO_3$-N in tile drainage water samples from a sandy soil between March and November 2011.

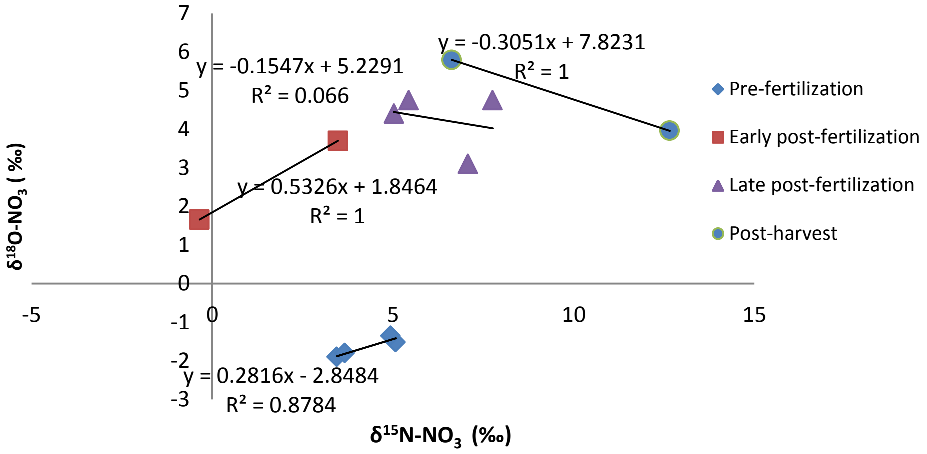
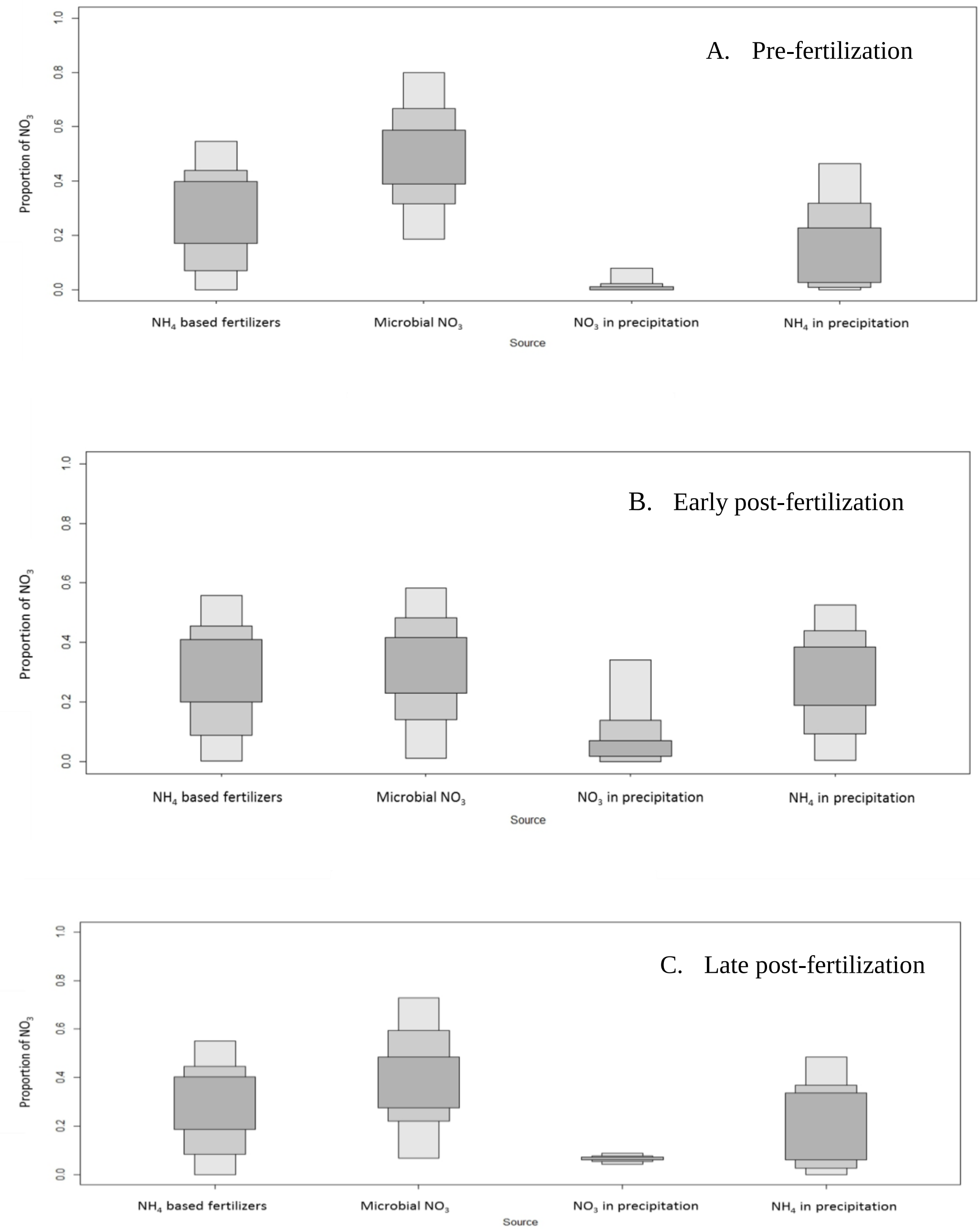



Figure 4: Linear relationships between $\delta^{15}N$ and $\delta^{18}O$ of nitrate ($NO_3$-N) in tile drainage water samples from a sandy soil between March and November 2011. Sample periods were pre-fertilization period (n=4), early post-fertilization period (n=2), late post-fertilization period (n=4) and post-harvest period (n=2).


A. Pre-fertilization
B. Early post-fertilization
C. Late post-fertilization
Proportion of NO3
NH4 based fertilizers
Microbial NO3
NO3 in precipitation
NH4 in precipitation
Source
0.0
0.2
0.4
0.6
0.8
1.0

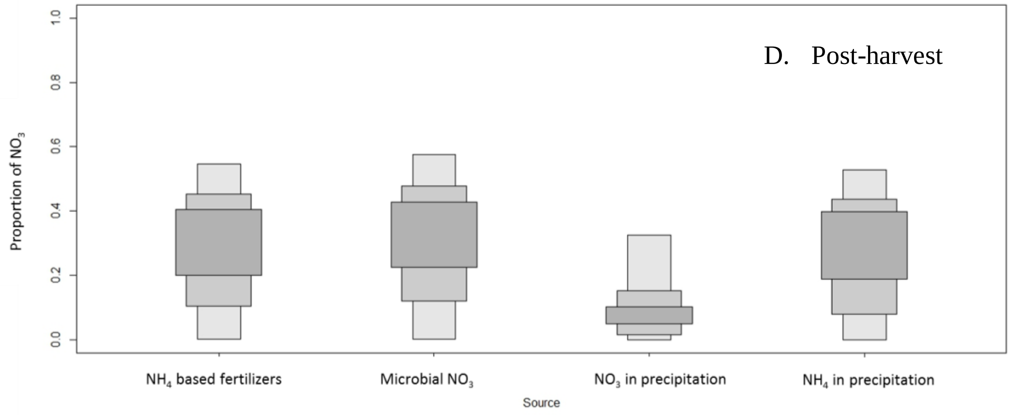



Figure 3: Proportion of nitrate ($NO_3$-N) in tile drainage water collected from a sandy soil that was derived from various nitrogen (N) sources, based on the Stable Isotope Analysis in R (SIAR) mixing model. Tile drainage water was collected from March to November 2011.

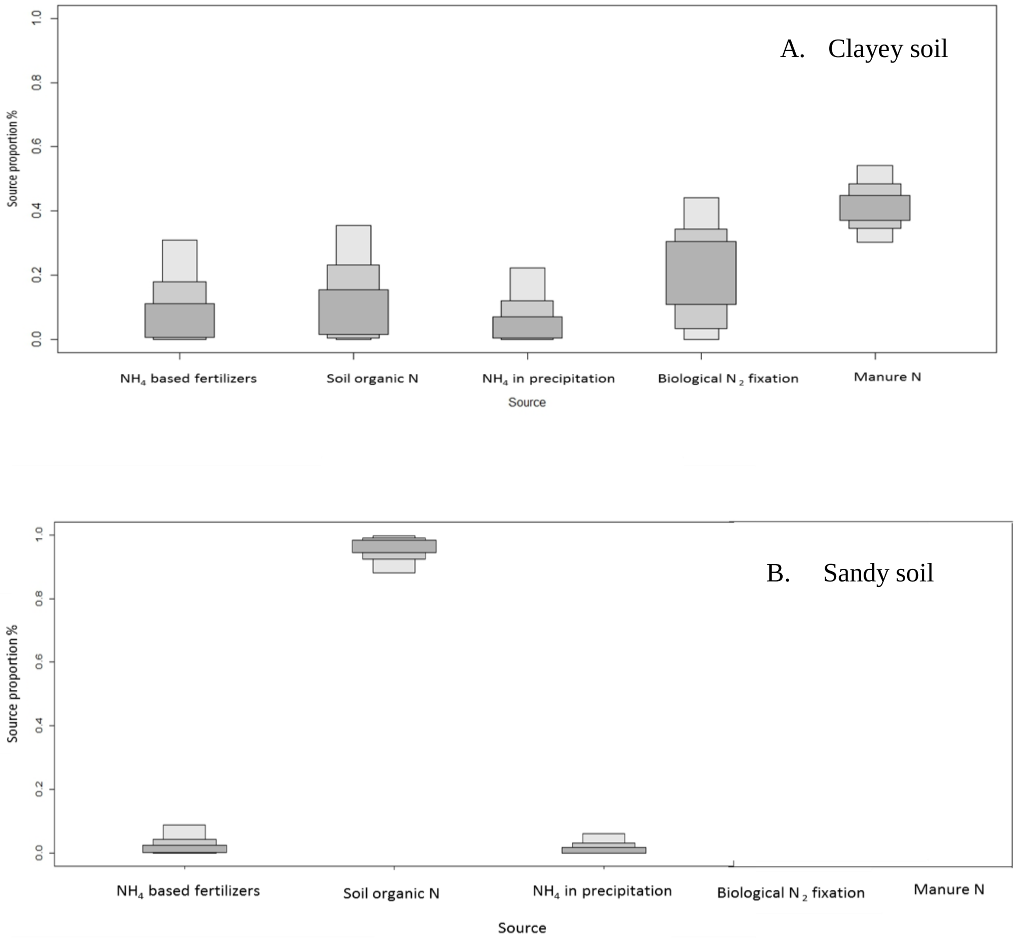



Figure 6: Proportion of particulate organic N (PON) in tile drainage water collected from (A) clayey soil (n=8) and (B) sandy (n=8) from March to May 2011, based on the Stable Isotope Analysis in R (SIAR) mixing model. Dark, medium, and light-grey boxes indicate 50%, 75% and 99% percentiles.

## Forward to chapter 4

In chapter 3, I found that N-rich organic matter in topsoil originating either from recently incorporated inputs (manure, plant residue) or stable SON is susceptible to loss via preferential flow pathways and contributes to the PON in tile drainage water. Considering partially decomposed and well decomposed organic N to be part of the SON pool, it remains unclear which SON fraction is most erodible through the preferential flow pathways. To answer this question, I used a soil OM density fractionation procedure to separate different SON fractions based on density. Then the natural abundance of stable isotopes of N in those fractions was compared to that of PON in tile drainage water.

This chapter is in preparation for submission to the Journal of Environmental Quality.

# Chapter 4: Determining the source of erodible particulate organic nitrogen in agricultural tile drainage water with $^{15}N$ stable isotopes

## 4.1 Abstract

Particulate organic nitrogen (PON) loss from agricultural fields to the surface waters can impair the quality of receiving waters and reduce soil reservoir storage. More than 65% of total N in surface runoff is transported from the soil surface to the water bodies in form of PON. Subsurface tile drains also can contribute to PON loss from the soil profile, particularly at times when a large amount of water moves through the soil profile and carries PON to the drain outlet. Consequently, PON represents more than 27% of total N is lost through tile drains. This study aimed to identify the fractions of soil organic nitrogen (SON) that contribute to the PON pool in the tile drainage water from annually-cropped agricultural fields with clayey and sandy textured soils, since since knowing the source of SON may suggest management practices to minimize its loss. Tile drainage water samples were collected at 8 discrete rainfall events from March to May 2011 and were analyzed for $\delta^{15}N$ in PON. Soil samples, taken from three depths in the soil profile (0-20 cm, 20-40 cm and 40-60 cm) in spring 2011 underwent density fractionation as following: non-occluded light fraction contains organic matter that is not occluded or protected by soil minerals (NOLF, $\rho<1.9$ g cm$^{-3}$), occluded light fraction containing organic matter protected within soil aggregates but not associated with soil minerals (OLF, $\rho<1.9$ g cm$^{-3}$), and three fraction of increasing densities ($\rho$=1.9-2.1, 2.1-2.3 and 2.3-2.5 g cm$^{-3}$). Density fractions were analyzed for $\delta^{15}N$ and $\delta^{13}C$. Result showed that the seasonal variation in PON loss from clayey and sandy soils was similar, and related to the amount of rainfall. There was more $\delta^{15}N$ and $\delta^{13}C$ enrichment of light fraction and

organo-mineral complexes in the topsoil compared to the subsoil of clayey and sandy soils, indicating more microbial processing in the topsoil than the subsoil. Based on the $\delta^{15}N$ signature, the 1.9-2.1 g $cm^{-3}$ fraction from the clayey topsoil and 2.1-2.3 g $cm^{-3}$ fraction from the sandy topsoil were most likely the sources of PON lost from clayey and sandy soil.

## 4.2 Introduction

Particulate organic nitrogen (PON) transported from agricultural fields to water bodies can impair water quality and reduce reservoir storage capacity (Walling, 2009; Larsen et al., 2010; Kemp et al., 2011). As well, erosion of N-rich organic matter (OM) associated with clay particles decreases soil nutrient reserves and soil quality. To date, most of the attention on sedimentation and sediment-associated nutrients loading in lakes and rivers has focused on suspended solids and particulate phosphorus; however PON loads may be substantial in some areas where residues and fertilizers are applied. Alvarez-Cobelas et al. (2008) reported that PON export from agricultural fields to rivers ranges from 0.02 to 29.7 kg N $ha^{-1}$ $y^{-1}$. The high variability in PON export is attributed to differences in PON lost from soils with contrasting texture, where clayey soils emit more PON than sandy soils, the history of N-rich residues and fertilizer application at a particular field site, and hydrological process (Jardine et al., 1989; Hagedorn et al., 2000). There is also seasonal variability in PON loss, with highest levels occurring in spring when lack of surface residue cover levels soil vulnerable to erosion (Zhao et al., 2001).

A substantial amount of PON leaves the agricultural fields in association with erodible suspended solids through surface runoff (e.g. up to 65%, of total N; Sharpley et al., 1987). Moreover, studies have clearly illustrated that tile drainage facilitates transport of soil pore water to surface water (Beauchemin et al., 1998) and is effective in reducing sediment associated N loss via surface runoff by improving infiltration and preventing soil saturation (Gaynor et al., 1995; Gulley et al., 1983). When fields are tile drained and macropores are connected to the drain lines, preferential flow becomes an important conduit for water and soil particle transport through the soil profile (Grant et al., 1996). For example, approximately 18% of annual suspended solids load in a plot-scale study in southern Ontario (Culley et al., 1983) were transported through subsurface drainage. Suspended solids contain organo-minerals as well as primary particles, so they are a source of organic N and carbon (C) and other absorbed or occluded elements when transport to waterways. According to Carter et al. (2003), the PON fraction accounted for up to 27% of the total N in tile drain outflow.

To reduce PON loss at the tile drain outlet, we need to identify the soil organic N (SON) fraction that is transported from the soil profile. To the best of our knowledge, no studies have determined which SON fraction is potentially erodible and contributing to PON loss. The SON fraction might be composed of recently added inputs to the soil (e.g. crop residue or manure) or from microbial processed OM. Surface soil contains more light fraction (free and occluded OM with ρ<1.9 g cm-3), mostly from recent inputs. Denser organo-mineral complexes (ρ>2.0-2.6 g $cm^{-3}$) are composed of microbially-processed OM (Sollins et al., 2006) and its formation is more pronounced in deeper soil horizons (Rumpel and Kogel-Knabner, 2011).Water flowing through the soil profile sorts particles by size and weight, therefore the smallest and lightest particles are moved furthest down the soil profile (Batjes, 1999). We hypothesized that light fraction of OM is prone to loss from topsoil layer, whereas organo-mineral complexes that contain microbially-processed N are absorbed to the soil matrix and are less prone to leaching.

Nitrogen in each soil density fraction has distinct isotopic signature ($\delta^{15}N$) that allow us to differentiate between recently incorporated N (e.g. plant fragments) or microbial processed N sources. For example, free OM consists mainly of partly decomposed residues, whereas occluded OM has undergone more extensive decomposition and become physically protected within aggregates (Golchin et al., 1995). Organo-mineral complexes in the occluded OM fractions show a "microbial fingerprint", indicating a lower C to N ratio than the original residue (Knicker, 2004) and enrichment in $\delta^{15}N$ and $\delta^{13}C$ (Gleixner et al., 2001) because microorganism preferentially use the lighter isotopes of C and N in metabolic processes (Kendall, 1998). Some studies pointed out the existence of at least two different C and N pools in heavy SOM fractions ($\rho$ >2.0-2.6 g $cm^{-3}$): an older, more stable pool of C and N, and a younger, labile pool of C and N (Trumbore et al., 1989; Strickland et al., 1992; Swanston et al., 2005). This implies that free OM and organo-mineral complexes have distinct $\delta^{15}N$ and $\delta^{13}C$ isotope signatures. Therefore, the natural abundance of N ($\delta^{15}N$) in soil OM density fractions can be compared to the $\delta^{15}N$ of PON to distinguish the source of PON in tile drainage water. We are not aware of studies that have used natural isotopes of N in soil density fractions to trace the source of PON in tile drainage water from agricultural fields.

The objective of this study was to find the sources of PON in the tile drainage water from annually-cropped agricultural fields with clayey and sandy textured soils. We compared the $\delta^{15}N$ values of soil OM density fractions with those in PON collected from tile drainage water at selected rainfall events from March to May, 2011.

## 4.3 Methods and materials

### 4.3.1 Site Description

Two agricultural fields selected for this study are located on privately owned farms (site A and site B) in the Pike River watershed, the second major tributary of Missiquoi Bay. Both sites are near the town of Bedford, Quebec, Canada (45° 7' 0 N, 72° 58' 60 W). This area has average annual temperature of 6.8°C and a frost-free period of 155 d, from April to October. Mean annual evapotranspiration is 602 mm $yr^{-1}$ and mean annual precipitation is 1095 mm $yr^{-1}$, with 203 mm coming from snowfall.

The sites were selected for this study due to accessibility to the tile drainage outlets. Tile drains were installed at 1.1 to 1.3 m in the C horizon on both farms about 30 years prior to this study. Site A (hereafter referred to as clayey soil), located 3 km west of Bedford, had a surface drainage area of 10.2 ha, a tile drainage area of 7.8 ha and an average slope of 0.8%. The clayey soil was classified as a Haplic Gleysol with three soil series in the field: Suffield clay loam (9.4%), Ste. Rosalie clay loam (69.9%) and Bedford sandy clay loam (20.7%). Site B (hereafter referred to as sandy soil) is situated 1 km west of Bedford, with surface and tile drainage areas of 6 ha and average slope of 2%. The sandy soil was a Podzol classified as a Rubicon sandy loam soil series. A detailed description of the site locations and history of management practices was presented by Rasouli et al. (2013).

### 4.3.2 Water sample collection and analysis

Tile drainage water was collected at 8 discrete rainfall events from March 11, 2011 to May 6, 2011. Each event was characterized as a high rainfall event, receiving >10 mm rainfall in 24 h, during which drain samples were collected from the tile drains. Such events mobilize large quantities of soil particles containing PON from the topsoil as the result of raindrop impact (Kwaad, 1991). Water samples were collected in high density polyethylene (HDPE) bottles and stored at $4^oC$ until analysis within one week of collection. Water samples were filtered (< 0.45 μm) prior to analysis following APAH (2005) standard methods for soluble N forms: $NH_4$-N, $NO_3$-N and total dissolved N (TDN). Unfiltered samples were analyzed for pH, electrical conductivity (EC), total N (TN) and total suspended solids (TSS). The PON concentration was calculated as the difference between TN and TDN.

### 4.3.3 Soil sample collection and sequential density fractionation

Individual 6-7 soil cores samples (250 $cm^3$) were taken from three depths in the soil profile (0-20 cm, 20-40 cm and 40-60 cm) from the two agricultural fields in spring 2011 and were combined to make a composite soil sample for each depth. Soil samples were air-dried immediately after collection and stored at 4 $^oC$. Sequential density fractionation involved separation into two light and three dense fractions based on Poirier (2011), who worked on soils with similar mineralogy in the Saint Lawrence lowlands. Density separation solutions were made with LSTFastfloat, a high density liquid with ρ=2.8 g $cm^{-3}$ (Pangea, Chippenham, UK), diluted with deionized water. The separated fractions were as following: (1) non-occluded light fraction contains soil organic material that is not occluded or protected by soil minerals (NOLF, ρ< 1.9 g $cm^{-3}$), (2) occluded light fraction containing organic matter protected within soil aggregates but not associated with soil minerals (OLF, ρ< 1.9 g $cm^{-3}$), and four fraction of increasing densities (ρ=1.9-2.1, 2.1-2.3 and 2.3-2.5 g $cm^{-3}$), based on Basile-Doelsch et al. (2007).

Briefly, the fractionation involved weighing 7.5 g of air dried soil into a 50 ml polycarbonate centrifuge tube. Then 20 ml of 1.9 g $cm^{-3}$ LST solution was added and mixed by inverting the tube six times, and it was centrifuged for 26 minutes at 12 500 x *g*. The supernatant containing NOLF was recovered through siphoning and rinsed three times with 25 ml. For isolation of OLF material, 18 ml of 1.9 g $cm^{-3}$ LST was added to the remained soil and solution was pulse sonicated to disrupt soil aggregates (first with 5.5 sec on and 9.9 sec off for 30 sec at 60% energy input, followed by 9.9 sec on and 2.5 sec off for 4 min at 35% energy input) with an ultrasonic dispersion treatment in an ice bath using Vibra Cell 75041 sonicator (Fisher Bioblock Scientific Inc., Aalst, Belgium). After sonification, the soil and solution mixture was centrifuged for 128 min and OLF was recovered by siphoning the supernatant. This step was repeated twice to ensure the complete recovery of OLF material, using pulse sonication (5.5 sec on, 9.9 sec off) for 30 sec at 60% energy input to recover the remaining OLF. Supernatants containing OLF were combined and rinsed by washing with deionized water and centrifuging (three times). Three dense soil fractions (1.9-2.1, 2.1-2.3, 2.3-2.5 g $cm^{-3}$) were then isolated sequentially.

Remaining soil from previous step was suspended with 15-25 ml of the LST density solution, depending on the available headspace in the centrifuge tube, and pulse sonicated (5.5 sec on and 9.9 sec off) for 30 sec at 60% energy input, centrifuged and supernatant was recovered by siphoning. Each sonication processes were repeated twice. Centrifugation times were 134 min for the 1.9-2.1 g $cm^{-3}$ fraction, 150 min for the 2.1-2.3 g $cm^{-3}$ and 210 min for the 2.3-2.5 g $cm^{-3}$ fraction. The material recovered from both extraction steps were combined and then washed three times with deionized water and centrifuged. All recovered density fractions were dried at 60 $^{o}$C for 1 h before analysis.

### 4.3.4 Nitrogen, carbon and Stable isotope analysis

The PON associated with sediments (at least 70 mg TSS retained on 0.45 µm filters, oven-dried for 1 h at 60$^{o}$C) from clayey and sandy soils was packaged in tin capsules. The six soil density fractions from three depths in each soil type were also oven-dried (1 h at 60$^{o}$C) and packaged. The whole soil (WS) from each depth, PON and soil density fractions were analyzed for total N and total C using a Carlo-Erba C and N analyzer (Milano, Italy). The $\delta^{15}$N concentration of PON, as well as the $\delta^{15}$N and $\delta^{13}$C concentration of the WS and soil density fractions were determined with a PDZ Europa ANCA-GSL elemental analyzer interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (UC Davis Stable Isotope Facility,Davis, CA, USA).

### 4.3.5 Statistical analysis

Descriptive statistics (mean, standard deviation) of the stable isotopes in WS and soil density fractions at three depths were calculated and differences between $\delta^{15}N$ and $\delta^{13}C$ of different depths were determined for each soil type (clayey, sandy) using a Student t-test ($P<0.05$) in JMP software (Version 8, SAS Institute Inc., Cary, NC). Contrast analysis of the means of $\delta^{15}N$, $\delta^{13}C$ , C and N concentrations for WS versus soil OM fractions was done ($P<0.01$) in JMP software (Version 8, SAS Institute Inc., Cary, NC). A forward stepwise regression analysis was applied to the $\delta^{15}N$ concentration of PON and soil density fraction data for each soil type (clayey and sandy soils) and two linear regression models were constructed using JMP software to predict the source of PON in tile drainage water. Critical probabilities of $P= 0.05$ and $P=0.1$ were used to control entry and removal of variables, respectively, in the stepwise regression. Linear correlations were run to test for the relationship between rainfall input and PON concentration for each soil.

## 4.4 Results

### 4.4.1 Characteristics of PON and $\delta^{15}N$ in tile drainage water from clayey and sandy soils

Concentration of PON in tile drainage water of clayey soil tended to increase from March to April and to decrease in May (Fig. 1A). In sandy soil, PON concentration from tile drainage water did not show a clear temporal pattern during the sampling period (Fig. 1B). The PON concentrations tended to be higher in tile drainage water of sandy soil than clayey soil, and the $\delta^{15}N$ concentrations were greater in clayey soil than sandy soil in 70% of the samples (Fig. 1A, 1B). There was a positive relationship between the amount of rainfall and PON concentration in clayey soil (Fig. 2A) and in sandy soil (Fig. 2B), showing greater PON concentrations with higher rainfall. Total N and total C concentration of PON in tile drainage water from clayey soil tended to decrease slightly during the sampling period (Fig. 3A), but total N and total C concentration in PON from the sandy soil was relatively stable (Fig. 3B). The C to N ratio of PON ranged from 5.0 to 9.9 in the clayey soil and from 5.1 to 14.6 in the sandy soil.

### 4.4.2 Characteristics of soil density fractions from clayey and sandy soils

In clayey soil, the differences in the $\delta^{15}N$ concentration of OLF, 1.9-2.1 (g $cm^{-3}$) and 2.1-2.3 (g $cm^{-3}$) fractions in 0-20 cm and 40-60 cm depths were significant ($P$<0.05) (Table 1). The $\delta^{13}C$ concentration was significantly different for 1.9-2.1 (g $cm^{-3}$), 2.1-2.3 (g $cm^{-3}$) and 2.3-2.5 (g $cm^{-3}$) fractions in 0-20 cm and 40-60 cm (Table 1). In 0-20 cm depth, the heavier fractions were more enriched in $\delta^{15}N$ and $\delta^{13}C$ than WS, but the differences were not significant. The OLF fraction was significantly enriched in $\delta^{15}N$ relative to the WS in 20-40 cm depth. In 40-60 cm depth, NOLF and OLF fractions were significantly enriched in $\delta^{15}N$ compared with WS, and 1.9-2.1 fraction was enriched in $\delta^{13}C$ compared to the WS (Table 2). Also, NOLF and OLF fractions had more N and C than WS in 0-20 cm depth. In 20-40 cm depth, NOLF, OLF and 1.9-2.3 fractions had more N than WS and 2.3-2.5 fraction had less N than WS. The NOLF, OLF and 1.9-2.1 fractions had more C than WS. In 40-60 cm depth, 2.1-2.3 and 2.3-2.5 fractions had more N than WS, while NOLF had less N than WS, but more C than WS.

In sandy soil, the differences in $\delta^{15}N$ and $\delta^{13}C$ concentration of NOLF, OLF, 2.1-2.3 (g cm$^{-3}$) and 2.3-2.5 (g cm$^{-3}$) fractions were significant between 0-20 cm and 20 to 60 cm (Table 3). In sandy soil, in 20-40 cm and 40-60 cm depths, WS was enriched in $\delta^{15}N$ and $\delta^{13}C$ relative to all fractions. The NOLF fraction had more N than WS, while 2.1-2.3 and 2.3-2.5 fractions had less N than WS and NOLF and 1.9-2.1 fractions had more C than WS in 0-20 cm depth. In 20-40 depth, the OLF fraction had more N than WS, while 1.9 to 2.5 fractions had less N than WS and Only NOLF and OLF had higher C than WS. In 40-60 cm depth, NOLF, OLF and 1.9-2.1 fractions had more N than WS, but 2.3-2.5 fraction had less N. NOLF, OLF and 1.9 to 2.3 fractions had higher C and 2.3-2.5 fraction had less C than WS (Table 4).

### 4.4.3 Relationship between PON and soil density fractions

The forward stepwise regression equation obtained for PON and soil density fractions in clayey soil was:

$PON_{\delta^{15}N} = 18.63 – 2.11 \ (1.9\text{-}2.1_{\ 0\text{-}20cm})$, $R^2$=0.96, $P$<0.05

with the heavy fraction (1.9-2.1 g $cm^{-3}$) fraction from 0-20 cm explaining the variation in PON of tile drainage water from clayey soil. In sandy soil, we obtained the regression equation:

$PON_{\delta^{15}N} = 12.57 – 1.49\ (2.1\text{-}2.3_{\ 0\text{-}20cm})$, $R^2$=0.91, $P$<0.05

with heavy fraction (2.1-2.3 g $cm^{-3}$) from 0-20 cm depth explaining the variation in PON in tile drainage water of sandy soil.

## 4.5 Discussion

We found a similar variation in PON loss from both clayey and sandy soils, which was probably due to the similar rainfall amount, intensity and duration at the two sites. Laubel et al. (1999) also explained variation in POM concentration in tile drainage water at their experimental fields as a function of water inputs. The amount of rainfall can affect PON losses regardless of the soil type. The C to N ratio of PON was in the similar range as dense SON fractions containing microbially-processed soil with enriched N and low C content.

There was more $\delta^{15}N$ and $\delta^{13}C$ enrichment of light fractions and organo-mineral complexes in topsoil than subsoil for both clayey and sandy soils, indicating more microbial processing in topsoil than subsoil. The light fraction of OM in clayey and sandy soils had higher C and N concentrations and higher C to N ratio than heavy fraction. Whalen et al. (2000) also showed that the heavy fraction had a lower C to N ratio than light fraction. Poirier

(2011) and Fließbach et al. (1999) reported that the lightest density fractions were enriched in residue-derived C and N and had a higher C to N ratio than heavy fractions, which underwent more microbial processing and decomposition of OM. In contrast to our result, Salomé et al. (2010) reported the higher $\delta^{15}N$ in soil density fractions of subsoil than of topsoil (i.e. higher microbial processing in subsoil) due to the accumulation of enriched $\delta^{15}N$ microbial products on mineral surfaces in the subsoil. In their soil, C concentration (from root exudates of wheat-corn rotation), respiration and microbial communities were greater in subsoil than in topsoil. Gregorich et al. (2009) and Poirier (2011) also explained that in temperate agroecosystems like in southern Quebec, recent input and fresh incorporated organic matter are likely to be retained in the subsoil because of lower soil organic carbon saturation level and high clay content than the topsoil.

We hypothesized that the light fraction from topsoil would be the source of PON in tile drainage water in clayey and sandy soils, but our results showed that organo-mineral complexes (1.9-2.1 g $cm^{-3}$ fraction in clayey soil and 2.1-2.3 g $cm^{-3}$ fraction in sandy soil) from topsoil layer were the most likely source of PON in tile drainage water, based on $\delta^{15}N$ signature. The fact that SON fractions from topsoil were most closely related to the PON pool, suggest that they were transport to tile drains through preferred flow. This is consistent with work using $^{137}Cs$ tracers that shows topsoil to be the source of suspended solids in tile drains (Foster et al., 2003). The rate of soil particle erosion is a function of size of the particles, the rainfall amount and intensity, concentration of particles remaining to be washed off and flow velocity. The loosely bound, poorly decomposed plant fragments in most agricultural soils have high potential for transport via preferential flow (Ghadiri and Rose, 1991), so why was the light fractions not related to PON? It is possible that the first rapid flow of water flushes the loose light particles with overland flow and that no light particles remained to be transported through preferential flow, as was observed by Laubel et al. (1999). Subsequent flushes of water would then move the next lightest organo-mineral complexes from the topsoil layer, namely the lighter heavy fractions (1.9-2.1 g $cm^{-3}$ and 2.1-2.3 g $cm^{-3}$).

## 4.6 Conclusion

In manured clayey soil and in inorganically-fertilized sandy soil, N-enriched organo-mineral complexes from the topsoil layer contributed to the PON in tile drainage water through preferential flow pathways. This suggests management practices (e.g. no-tillage) to stabilize topsoil and thereby reduce PON loss to tile drains. The results showed a mechanism of soil OM transport from topsoil to the tile drains that depend mainly on the mass of the SON fractions. Research is needed to confirm the proposed transport mechanism of SON fractions from the soil profile to tile drains. Experiments to simulate rainfall events and generate runoff simulations can be helpful to confirm that light soil OM fractions are transported via overland flow. I also suggest experiments with different crops and different fertilizer N inputs to confirm the theory that soil organo-mineral complexes are erodible particles from topsoil regardless of N input or crop.

Table 1: Natural abundance of $\delta^{15}N$ and $\delta^{13}C$ of soil density fractions from a clayey agricultural soil in Pike River watershed, Quebec. Means (± standard error) within a column followed by the small same letters are not statistically different at $P$<0.05

| | **NOLF**[1] | | **OLF**[2] | | **1.9-2.1 g cm$^{-3}$** | | **2.1-2.3 g cm$^{-3}$** | | **2.3-2.5 g cm$^{-3}$** | | **WS** | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Soil depth (cm) | **$\delta^{15}N$** | **$\delta^{13}C$** | **$\delta^{15}N$** | **$\delta^{13}C$** | **$\delta^{15}N$** | **$\delta^{13}C$** | **$\delta^{15}N$** | **$\delta^{13}C$** | **$\delta^{15}N$** | **$\delta^{13}C$** | **$\delta^{15}N$** | **$\delta^{13}C$** |
| **0-20** | 6.9±3 $^{a}$ | -21.4±2.1 $^{a}$ | 5.4±0.1 $^{a}$ | -22.7(0.7) $^{a}$ | 6.3±0.4 $^{a}$ | -21.8±0.2 $^{a}$ | 6.2±0.3 $^{a}$ | -21.8±0.2 $^{a}$ | 5.2±0.6 $^{a}$ | -21.2±1.5$^{a}$ | 5.0±0.9$^{a}$ | -22.0±0.4$^{a}$ |
| **20-40** | 6.3±0.9 $^{a}$ | -21.4±0.7 $^{a}$ | 7.3±0.4 $^{b}$ | -23.3±0.3 $^{a}$ | 4.5±2.4 $^{ab}$ | -23.7±1.7 $^{b}$ | 4.1±1.9 $^{ab}$ | -22.8±0.2 $^{b}$ | 3.9±1.4 $^{a}$ | -22.7±0.3 $^{ab}$ | 4.3±0.4$^{a}$ | -22.7±0.5$^{ab}$ |
| **40-60** | 6.0±1.1 $^{a}$ | -22.1±0.7 $^{a}$ | 5.4±0.2 $^{b}$ | -23.0±1.4 $^{a}$ | 1.8±0.0 $^{b}$ | -18.5±0.1 $^{b}$ | 3.5±0.5 $^{b}$ | -24.1±0.5 $^{c}$ | 3.5±0.3 $^{a}$ | -23.8±0.5 $^{b}$ | 3.1±0.1$^{b}$ | -22.9±0.4$^{b}$ |

[1] Non-occluded light fraction (ρ<1.9 g cm$^{-3}$)

[2] Occluded light fraction (ρ<1.9 g cm$^{-3}$)

Table 2: Contrast analysis of $\delta^{15}N$, $\delta^{13}C$, carbon and nitrogen concentrations of whole soil (WS) versus different soil organic matter fractions in clayey soil.

| | **Contrast** | **$\delta^{15}N$** | | **$\delta^{13}C$** | | **Contrast** | **Total N** | | **Total C** | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | **F** | **P** | **F** | **P** | | **F** | **P** | **F** | **P** |
| **0-20 cm** | **WS *vs*. NOLF**[1] | 2.44 | 0.14 | 0.45 | 0.5 | **WS *vs*. NOLF** | 19.87 | 0.004$^{**}$ | 847.6 | <0.0001$^{**}$ |
| | **WS *vs*. OLF**[2] | 0.01 | 0.9 | 0.52 | 0.48 | **WS *vs*. OLF** | 368.1 | <0.0001$^{**}$ | 421.5 | <0.0001$^{**}$ |
| | **WS *vs*. 1.9-2.1** | 0.91 | 0.36 | 0.03 | 0.85 | **WS *vs*. 1.9-2.1** | 0.07 | 0.79 | 1.01 | 0.35 |
| | **WS *vs*. 2.1-2.3** | 0.77 | 0.40 | 0.07 | 0.78 | **WS *vs*. 2.1-2.3** | 0.77 | 0.41 | 0.07 | 0.79 |
| | **WS *vs*. 2.3-2.5** | 0.003 | 0.95 | 0.88 | 0.36 | **WS *vs*. 2.3-2.5** | 5.73 | 0.053 | 1.73 | 0.24 |
| | | **$\delta^{15}N$** | | **$\delta^{13}C$** | | | **Total N** | | **Total C** | |
| | | **F** | **P** | **F** | **P** | | **F** | **P** | **F** | **P** |
| **20-40 cm** | **WS *vs*. NOLF** | 2.87 | 0.12 | 4.27 | 0.06 | **WS *vs*. NOLF** | 439.1 | <0.0001$^{**}$ | 270.4 | <0.0001$^{**}$ |
| | **WS *vs*. OLF** | 6.7 | 0.02$^{*}$ | 0.65 | 0.43 | **WS *vs*. OLF** | 437.7 | <0.0001$^{**}$ | 447.2 | <0.0001$^{**}$ |
| | **WS *vs*. 1.9-2.1** | 0.04 | 0.85 | 1.88 | 0.19 | **WS *vs*. 1.9-2.1** | 767.9 | 0.0001$^{**}$ | 47.7 | 0.0006$^{**}$ |
| | **WS *vs*. 2.1-2.3** | 0.09 | 0.77 | 0.00 | 0.96 | **WS *vs*. 2.1-2.3** | 11.64 | 0.014$^{*}$ | 0.18 | 0.68 |
| | **WS *vs*. 2.3-2.5** | 0.09 | 0.77 | 0.01 | 0.92 | **WS *vs*. 2.3-2.5** | 7.16 | 0.036$^{*}$ | 0.44 | 0.52 |
| | | **$\delta^{15}N$** | | **$\delta^{13}C$** | | | **Total N** | | **Total C** | |
| | | **F** | **P** | **F** | **P** | | **F** | **P** | **F** | **P** |
| **40-60 cm** | **WS *vs*. NOLF** | 48.8 | <0.0001$^{**}$ | 0.65 | 0.44 | **WS *vs*. NOLF** | 9.34 | 0.037$^{*}$ | 122.0 | 0.0003$^{**}$ |
| | **WS *vs*. OLF** | 21.5 | <0.0001$^{**}$ | 0.01 | 0.93 | **WS *vs*. OLF** | - | - | - | - |
| | **WS *vs*. 1.9-2.1** | 6.8 | 0.026$^{**}$ | 39.6 | <0.0001$^{**}$ | **WS *vs*. 1.9-2.1** | - | - | - | - |
| | **WS *vs*. 2.1-2.3** | 0.54 | 0.48 | 3.57 | 0.09 | **WS *vs*. 2.1-2.3** | 49.1 | 0.002$^{**}$ | 5.92 | 0.07 |
| | **WS *vs*. 2.3-2.5** | 0.86 | 0.37 | 1.91 | 0.19 | **WS *vs*. 2.3-2.5** | 25.7 | 0.007$^{**}$ | 0.15 | 0.71 |

* Significant at $P < 0.05$ and ** Significant at $P < 0.01$

[1] Non-occluded light fraction ($\rho$<1.9 g $cm^{-3}$), [2] Occluded light fraction ($\rho$<1.9 g $cm^{-3}$)

Table 3: Natural abundance of $\delta^{15}N$ and $\delta^{13}C$ of soil density fractions from a sandy agricultural soil in Pike River watershed, Quebec. Means (± standard error) within a column followed by the same letters are not statistically different at $P$<0.05.

| | NOLF[1] | | OLF[2] | | 1.9-2.1 g $cm^{-3}$ | | 2.1-2.3 g $cm^{-3}$ | | 2.3-2.5 g $cm^{-3}$ | | WS | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Soil depth (cm)** | $\delta^{15}N$ | $\delta^{13}C$ | $\delta^{15}N$ | $\delta^{13}C$ | $\delta^{15}N$ | $\delta^{13}C$ | $\delta^{15}N$ | $\delta^{13}C$ | $\delta^{15}N$ | $\delta^{13}C$ | $\delta^{15}N$ | $\delta^{13}C$ |
| **0-20** | 4.6±0.2 a | -22.1±0.7 a | 5.1±0.3 a | -23.0±0.6 a | 4.3±1.1 a | -21.0±3.5 a | 5.2±0.5 a | -22.5±1.4 a | 5.2±0.3 a | -23.1±0.8 a | 4.6±0.1 a | -22.5±0.3 a |
| **20-40** | 2.2±0.3 b | -26.3±0.3 b | 1.7±0.3 b | -26.2±0.4 b | 2.6±1.9 a | -25.1±1.8 a | 1.6±0.1 b | -26.5±1.4 b | 1.4±0.2 b | -25.5±1.3 b | 2.5±0.1 b | -23.1±0.4 b |
| **40-60** | 2.3±0.1 b | -26.9±1.1 b | 2.1±0.0 b | -25.9±0.4 b | 1.7±0.0 a | -25.7±0.4 a | 1.7±0.2 b | -26.1±1.3 b | 1.7±0.4 b | -25.4±0.9 b | 2.42±0.1 ab | -23.0±0.3 ab |

[1] Non-occluded light fraction (ρ<1.9 g $cm^{-3}$)

[2] Occluded light fraction (ρ<1.9 g $cm^{-3}$)

Table 4: Contrast analysis of δ15N, δ13C, carbon and nitrogen concentrations of whole soil (WS) versus different soil organic matter fractions in sandy soil.

| | Contrast | $\delta^{15}N$ | | $\delta^{13}C$ | | Contrast | Total N | | Total C | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | **F** | **P** | **F** | **P** | | **F** | **P** | **F** | **P** |
| **0-20 cm** | **WS *vs*. NOLF**[1] | 1.17 | 0.30 | 0.004 | 0.95 | **WS *vs*. NOLF** | 477.5 | <0.0001** | 331.5 | <0.0001** |
| | **WS *vs*. OLF**[2] | 0.03 | 0.87 | 0.55 | 0.47 | **WS *vs*. OLF** | - | - | - | - |
| | **WS *vs*. 1.9-2.1** | 3.04 | 0.11 | 0.57 | 0.46 | **WS *vs*. 1.9-2.1** | 5.71 | 0.06 | 42.08 | 0.0012** |
| | **WS *vs*. 2.1-2.3** | 0.001 | 0.97 | 0.15 | 0.7 | **WS *vs*. 2.1-2.3** | 43.5 | 0.001** | 2.46 | 0.18 |
| | **WS *vs*. 2.3-2.5** | NA | NA | 0.69 | 0.42 | **WS *vs*. 2.3-2.5** | 61.2 | 0.005** | 2.95 | 0.14 |
| | | $\delta^{15}N$ | | $\delta^{13}C$ | | | Total N | | Total C | |
| | | **F** | **P** | **F** | **P** | | **F** | **P** | **F** | **P** |
| **20-40 cm** | **WS *vs*. NOLF** | 5.77 | 0.009** | 15.43 | 0.002** | **WS *vs*. NOLF** | 0.02 | 0.88 | 201.38 | <0.0001** |
| | **WS *vs*. OLF** | 15.27 | 0.002** | 14.63 | 0.0024** | **WS *vs*. OLF** | 13.11 | 0.011** | 1132.54 | <0.0001** |
| | **WS *vs*. 1.9-2.1** | 6.45 | 0.026** | 6.70 | 0.02** | **WS *vs*. 1.9-2.1** | 76.4 | <0.0001** | 0.69 | 0.43 |
| | **WS *vs*. 2.1-2.3** | 15.81 | 0.001** | 17.30 | 0.001** | **WS *vs*. 2.1-2.3** | 13.71 | 0.01** | 0.53 | 0.49 |
| | **WS *vs*. 2.3-2.5** | 18.27 | 0.001** | 9.47 | 0.009** | **WS *vs*. 2.3-2.5** | 26.13 | 0.002** | 0.11 | 0.74 |
| | | $\delta^{15}N$ | | $\delta^{13}C$ | | | Total N | | Total C | |
| | | **F** | **P** | **F** | **P** | | **F** | **P** | **F** | **P** |
| **40-60 cm** | **WS *vs*. NOLF** | 27.75 | 0.0002** | 83.76 | <0.0001** | **WS *vs*. NOLF** | 80.46 | <0.0001** | X | <0.0001** |
| | **WS *vs*. OLF** | 45.17 | <0.0001** | 20.12 | 0.0007** | **WS *vs*. OLF** | 618.36 | <0.0001** | X | <0.0001** |
| | **WS *vs*. 1.9-2.1** | 98.92 | <0.0001** | 17.05 | 0.001** | **WS *vs*. 1.9-2.1** | 39.50 | 0.007** | X | <0.0001** |
| | **WS *vs*. 2.1-2.3** | 96.23 | <0.0001** | 21.84 | 0.0005** | **WS *vs*. 2.1-2.3** | 4.49 | 0.078 | 302.05 | <0.0001** |
| | **WS *vs*. 2.3-2.5** | 94.45 | <0.0001** | 13.57 | 0.003** | **WS *vs*. 2.3-2.5** | 34.0 | 0.001** | 9.67 | 0.02* |

* Significant at $P < 0.05$ and ** Significant at $P < 0.01$

[1] Non-occluded light fraction ($\rho < 1.9$ g cm$^{-3}$), [2] Occluded light fraction ($\rho < 1.9$ g cm$^{-3}$)

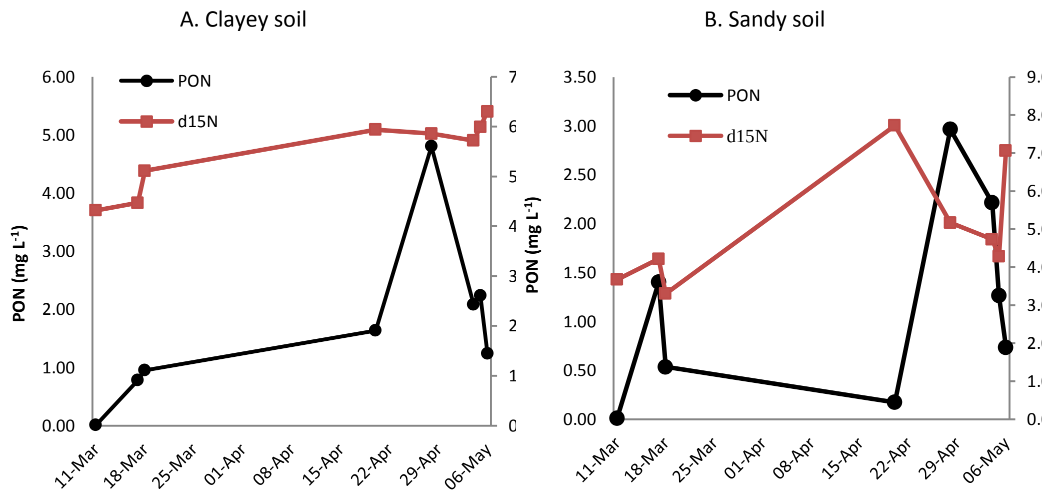



Figure 1: Particulate organic N (PON) and $\delta^{15}$N concentrations in tile drainage water samples from (A) clayey soil and (B) sandy soil from March 2011 to May 2011.

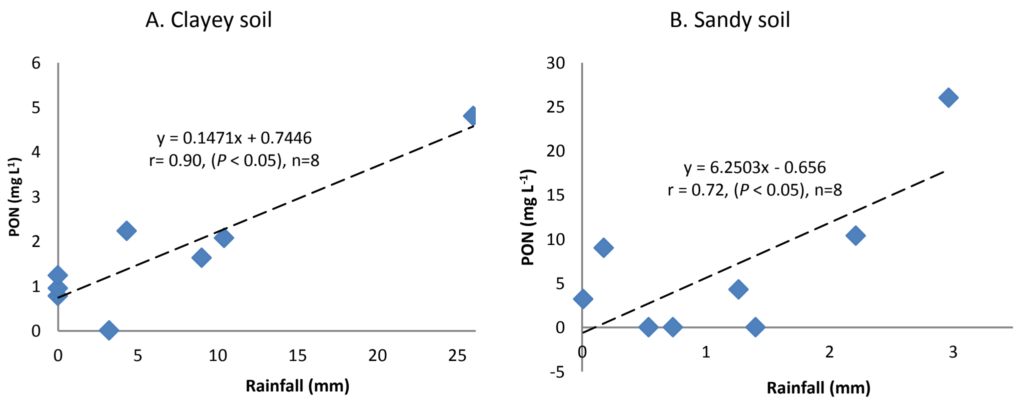



Figure 2: Relationship between rainfall input (mm) and particulate organic nitrogen (PON) concentration in tile drainage water of (A) clayey soil and (B) sandy soil from March 2011 to May 2011.

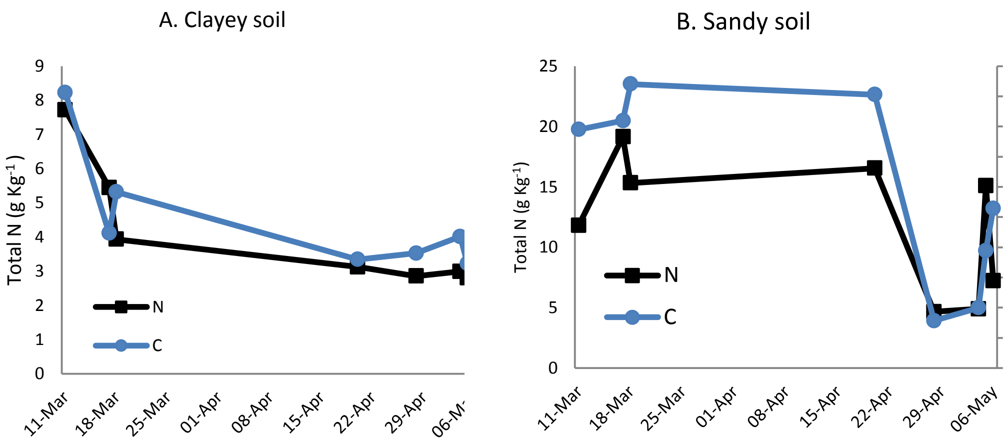



Figure 3: Total nitrogen (N) and total carbon (C) concentrations of particulate organic matter (POM) in tile drainage water samples from (A) clayey soil and (B) sandy soil between March and May 2011.

## General conclusion

From my literature review, it is clear that despite the implementation of BMPs, agricultural soils in Quebec still have high RSN that can be lost from tile drained soils through subsurface flow and contribute to enrichment of surface waters in the region. To design better BMPs, it is important to have precise knowledge of the N compounds in RSN that are susceptible to loss, their transport pathways and their sources in agricultural soils.

From the first experiment of this research, I concluded that agricultural fields equipped with tile drains are significant source of N losses to surface waters and $NO_3$-N and PON are the major forms of N that are susceptible to be transported through the soil profile during heavy rainfall events (> 5mm precipitation). Both matrix flow and preferential flow are responsible for transporting N from tile drained agricultural fields. Matrix flow is more important for $NO_3$-N movement and the preferential flow pathway is important for PON loss from agricultural soils. I also concluded that EC can serve as an indicator of $NO_3$-N and PON partitioning between matrix and preferential flow pathways. Due to limitations with instrumentation, I was not able to describe water flow characteristics and calculate the flow weighted concentrations of $NO_3$-N and PON, which would be necessary to calculate the N loads from these flows that leave the soil via preferential versus matrix flow.

My second experiment showed that the source of $NO_3$-N is primarily microbially-processed N, with direct contribution from fertilizer N shortly after it is applied, when significant rainfall (> 10mm rainfall) occurs. Particulate organic N originates from the SON pool in topsoil and may come from fresh or partially decomposed organic N sources. I concluded that the results of this experiment should be carefully interpreted because the SIAR mixing model underestimated the microbial $NO_3$-N contribution to the $NO_3$-N pool during the growing season, compared to an empirical model based on expected $\delta^{15}N$ and $\delta^{18}O$ ranges. I noted that the discrepancy between the two models was due to the range of $\delta^{15}N$ values used as input variables in the SIAR mixing model, which gave overlapping for $NH_4$ in fertilizer and precipitation and $NO_3$-N derived from nitrification. In the future, I recommend analyzing the original source material at the field sites to get a narrower site-specific isotopic composition ($\delta^{15}N$, $\delta^{18}O$) than reported in the literature. I also suggest fingerprinting the PON with other stable isotopes such as $^{137}Cs$, $^{210}Pb$, $^{13}C$ to confirm that PON leaches from the top soil layer.

From the fourth experiment, I concluded that N-enriched organo-mineral complexes from the topsoil layer contributed to the PON in tile drainage water and were transported through preferential flow pathways. I also suggested that the light and heavy fractions of OM are sorted at the soil surface, so the lighter soil OM density fractions move with overland flow and the heavier soil OM fractions are transported to tile drains with preferential flow. I suggest experiments to simulate runoff generation and to confirm that light soil OM fractions are transported via overland flow as well as direct measurements in the field. I also suggest the experiment with different crops and different fertilizer N inputs to confirm the theory that soil organo-mineral complexes are erodible particles from topsoil regardless of N input or crop.

Information on the N sources that are lost from agricultural soils and the way that they reach the drains is necessary to support BMPs. Fertilizer and organic N inputs to agricultural fields contribute an abundance of $NH_4$-N that is rapidly transformed by microorganisms to $NO_3$-N, plus they increase the concentration of particle-associated organic N in topsoil that is susceptible to loss with water. Therefore, there are several strategies that should be considered in developing BMPs. Accurate estimates of rate of organic N mineralization from manure and SOM as well as soil test N calibrated for the region are necessary steps to reduce RSN. Proper accounting for N credits from inorganic N inputs, legumes and manure in crop rotations can reduce the contribution of these sources to the RSN, which ultimately controls $NO_3$-N and PON concentrations in the tile drainage water. Agricultural practices such as side-dressing fertilizers, no-tillage and nitrification inhibitors to slow nitrification rates and water control structures (e.g. controlled drainage) can reduce the $NO_3$-N pool concentration in tile drainage outlet. Vegetated (permanently vegetated) buffer strips and no-tillage can stabilize topsoil and thereby reduce PON loss to tile drains (although no-tilllage would promote the preferential flow pathways). For efficient implemention of these BMPs, incentives and better communication between farmers and agro-environmental advisors is necessary.

## Contribution to knowledge

The research conducted in this thesis provides the following unique contributions to knowledge:

1. I have shown that EC can be used as an indicator of $NO_3$-N and PON concentrations in tile drainage water, and this is related to the flow pathways responsible for transporting these N forms to tile drains (i.e. $NO_3$-N moves mostly through matrix flow and PON moves through preferential flow particularly in clayey soil). This was the first study to look at the relationship between EC, $NO_3$-N concentration and PON concentration in the study region.

2. The work with stable isotopes coupled with SIAR model is the first time this approach has been used in Quebec. I showed that stable isotope fingerprinting of $NO_3$-N and PON samples collected from the tile drain outlet can ditinguish the relative importance of potential N sources to non-point source pollution.

3. This was the first study to trace the source of PON in tile drainage water by using density fractionation in combination of stable isotopes of N and C and also it is the first experiment of trace the source of PON back to specific SON fractions.

4. The mechanism that I proposed for transport of SON fractions from the soil profile is original, it still needs to be tested, and I have given several techniques (e.g. field-based meausurements) that could be used to validate my proposed mechanism.

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# Appendix 1

Total nitrogen (N) and total carbon (C) content of soil density fractions from a clayey agricultural soil in Pike River watershed, Quebec. Means (± standard error) within a column followed by the same letters are not statistically different at $P < 0.05$.

| | NOLF[1] | | OLF[2] | | 1.9-2.1 g cm$^{-3}$ | | 2.1-2.3 g cm$^{-3}$ | | 2.3-2.5 g cm$^{-3}$ | | WS | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Soil depth (cm) | Total N (mg N kg$^{-1}$) | Total C (mg C kg$^{-1}$) | Total N (mg N kg$^{-1}$) | Total C (mg C kg$^{-1}$) | Total N (mg N kg$^{-1}$) | Total C (mg C kg$^{-1}$) | Total N (mg N kg$^{-1}$) | Total C (mg C kg$^{-1}$) | Total N (mg N kg$^{-1}$) | Total C (mg C kg$^{-1}$) | Total N (mg N kg$^{-1}$) | Total C (mg C kg$^{-1}$) |
| 0-20 | 4.5±0.4 $^{b}$ | 232.8±18.2$^{a}$ | 10.5±0.7 $^{a}$ | 168.1±3.2 $^{a}$ | 2.5±0.1 $^{a}$ | 20.9±0.1 $^{a}$ | 2.3±0.3 $^{a}$ | 15.4±0.8 $^{a}$ | 1.7±0.3 $^{a}$ | 3.5±0.6 $^{a}$ | 2.7±0.3$^{a}$ | 13.4±0.1$^{a}$ |
| 20-40 | 7.1±0.1$^{a}$ | 85.1±5.7 $^{b}$ | 7.1±0.7 $^{b}$ | 107.9±10.4 $^{b}$ | 3.4±0.3 $^{b}$ | 36.8±1.2 $^{b}$ | 1.8±0.2$^{a}$ | $_{b}$ 7.1± 0.1 | 0±0 $^{a}$ | 1.7±0.1 $^{a}$ | 0.8±0.1$^{b}$ | 5.0±0.04$^{b}$ |
| 40-60 | 6.2±3.7 $^{c}$ | 11.9±1.3 $^{c}$ | - | - | - | - | 1.7±0.2 $^{b}$ | 4.6 ±0.6 $^{c}$ | 1.4±0.3 $^{b}$ | 2.8±0.9 $^{a}$ | 0.5±0.0$^{b}$ | 2.5±0.1$^{c}$ |

[1] Non-occluded light fraction ($\rho < 1.9$ g cm$^{-3}$)

[2] Occluded light fraction ($\rho < 1.9$ g cm$^{-3}$ )

# Appendix 2

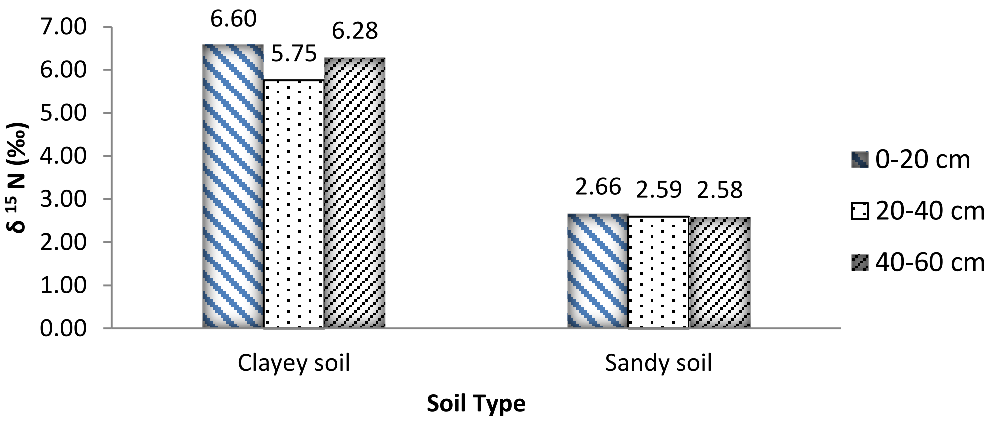
Total nitrogen (N) and total carbon (C) content of soil density fractions from a sandy agricultural soil in Pike River watershed, Quebec. Means (± standard error) within a column followed by the same letters are not statistically different at $P$ < 0.05

| | NOLF[1] | | OLF[2] | | 1.9-2.1 g cm$^{-3}$ | | 2.1-2.3 g cm$^{-3}$ | | 2.3-2.5 g cm$^{-3}$ | | WS | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Soil depth (cm) | Total N (mg N kg$^{-1}$) | Total C (mg C kg$^{-1}$) | Total N (mg N kg$^{-1}$) | Total C (mg C kg$^{-1}$) | Total N (mg N kg$^{-1}$) | Total C (mg C kg$^{-1}$) | Total N (mg N kg$^{-1}$) | Total C (mg C kg$^{-1}$) | Total N (mg N kg$^{-1}$) | Total C (mg C kg$^{-1}$) | Total N (mg N kg$^{-1}$) | Total C (mg C kg$^{-1}$) |
| 0-20 | 8.8±0.2 $^{a}$ | 129.0±12.8$^{a}$ | - | - | 4.5±0.4 $^{a}$ | 62.2±1.2 $^{a}$ | 2.3±0.2 $^{a}$ | 16.0±0.7 $^{a}$ | 2.1±0.1 $^{b}$ | 15.2±0.7 $^{b}$ | 3.9±0.1$^{a}$ | 25.0±0.9$^{a}$ |
| 20-40 | 6.9±0.1 $^{b}$ | 132.5±2.1 $^{a}$ | 8.6±0.2 $^{a}$ | 241.4±12.3 $^{a}$ | 2.5±0.5 $^{b}$ | 22.9±1.1 $^{b}$ | 5.0±0.2$^{b}$ | 57.3±2.3$^{b}$ | 4.3±03 $^{a}$ | 51.3±0.7 $^{a}$ | 6.8±0.9$^{a}$ | 53.1±5.0$^{b}$ |
| 40-60 | 5.6±0.1 $^{c}$ | 94.2±2.1 $^{b}$ | 9.7±0.5 $^{a}$ | 203.8±1.6 $^{a}$ | 5.0±0.3 $^{a}$ | 64.2±0.5 $^{a}$ | 3.9±0.1 $^{c}$ | 38.8±0.4$^{c}$ | 1.8±0.03$^{b}$ | 15.1±0.8 $^{b}$ | 3.4±0.2$^{a}$ | 18.7±0.3$^{a}$ |

[1] Non-occluded light fraction (ρ < 1.9 g cm$^{-3}$)

[2] Occluded light fraction (ρ < 1.9 g cm$^{-3}$ )

# Appendix 3




Stable isotopes of $\delta^{15}N$ form three soil layers of uncultivated clayey and sandy soils located adjacent of study sites, southern Quebec. Samples were taken in May 2011.