Université de Montréal

# Caractérisation du cycle et des sources d'azote dans les lacs tempérés par l'utilisation d'isotopes stables

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# Caractérisation du cycle et des sources d'azote dans les lacs tempérés par l'utilisation d'isotopes stables

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a été évalué par un jury composé des personnes suivantes :

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# Résumé

Nous avons étudié l'application de plusieurs mesures d'isotopes stables afin de caractériser les processus du cycle de l'azote et les sources d'azote dans les lacs tempérés à diverses échelles spatiales et temporelles. Les résultats d'une étude à travers 65 lacs sur un gradient trophique ont démontré que le ratio d'isotopes stables d'azote ($\delta^{15}N$) des sédiments de surface est un indicateur de l'importance relative des sources d'azote anthropique, mais que ce ratio peut être altéré par la diagenèse. La mesure du $\delta^{15}N$ des sédiments demeure néanmoins un outil permettant de déterminer à long terme le changement des charges en azote anthropique aux écosystèmes lacustres et les causes de l'eutrophisation de ces systèmes. Nos résultats d'une étude sur la variation saisonnière de plusieurs isotopes stables dans trois lacs peu profonds situés sur un gradient trophique et ayant différents régimes de stratification ont démontré que cette approche est prometteuse dans les lacs mésotrophes et stratifiés. Dans ces systèmes, le $\delta^{15}N$ de la matière organique particulaire (MOP) aurait le potentiel de déterminer les sources d'azote assimilées par le phytoplancton. Cependant les mesures d'isotopes stables du carbone ($\delta^{13}C$) et du ratio C:N indiquent que les apports de matières organiques du bassin versant peuvent altérer les relations observées. Nous avons également constaté une déviation de la relation 1:1 entre les isotopes stables d'azote et d'oxygène ($\delta^{18}O$) du nitrate ($NO_3^-$) indiquant son assimilation et sa nitrification simultanée. Cette application est particulièrement prometteuse puisque la nitrification est méconnue dans les lacs et peut exacerber les effets de l'eutrophisation. **Mots-clés** : Isotopes stables, azote, lacs, sédiments, pollution, diagenèse, assimilation, nitrification, eutrophisation.

# Abstract

We studied the application of multiple stable isotopes measures with the overall objective of improving our understanding of nitrogen cycling and sources in temperate lakes over different spatial and temporal scales. Results from our study across 65 lakes on a trophic gradient demonstrated that surface sediment nitrogen stable isotope ratio ($\delta^{15}N$) is an indicator of the relative importance of anthropogenic N loads, but that diagenesis can alter this ratio. Nevertheless, sediment core $\delta^{15}N$ is a powerful proxy for the determination of long-term changing anthropogenic N loads to lake ecosystems and the causes of lake eutrophication. Results from our second study on multiple stable isotopes seasonal variation in three shallow lakes along a trophic gradient and with different stratification regimes have demonstrated that such an approach is particularly promising in mesotrophic and stratified lakes. In these systems, our results showed that the suspended particulate organic matter (SPOM) $\delta^{15}N$ could be used to assess the nitrogen sources assimilated by phytoplankton. However, measurement of carbon stable isotopes ($\delta^{13}C$) and C:N ratios from the SPOM showed that the observed relationships can be altered by watershed derived organic matter. We have also found a deviation from the 1:1 relationship between nitrogen and oxygen stable isotopes ($\delta^{18}O$) of nitrate ($NO_3^-$) indicating a simultaneous $NO_3^-$ assimilation and nitrification in our stratified system. The application of dual nitrate isotopes is promising in the study of nitrification since this process is not well understood in lakes and can increase the severity of eutrophication symptoms. **Keywords** : Stable isotopes, nitrogen, lake, sediments, pollution, diagenesis, assimilation, nitrification, eutrophication.

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# Liste des sigles et des abréviations

‰ : parts per thousand (*partie par mille*)
ANCOVA : analysis of covariance (*analyse de covariance*)
$\alpha$ : «alpha», fractionation rate (*taux de fractionnement*)
Chl*a* : chlorophyll-*a* (*chlorophylle-a)*
C : carbon (*carbone*)
$\delta$ : «delta» notation
$\delta^{15}N$ : nitrogen stable isotopes (*isotopes stables d'azote*)
$\delta^{13}C$ : carbon stable isotopes (*isotopes stables de carbone*)
$\delta^{18}O$ : oxygen stable isotopes (*isotopes stables d'oxygène*)
$\varepsilon$ : «epsilon», fractionation rate in ‰ (*taux de fractionnement en ‰*)
DIN (*NID*) : dissolved inorganic nitrogen (*azote organique dissous*)
DON (*NOD*) : dissolved organic nitrogen (*azote organique dissous*)
MANOVA : multivariate analysis of variance (*analyse de variance multivariée*)
N : nitrogen (*azote*)
$NH_3$ : ammoniac
$NH_4^+$ : ammonium
$NO_2^-$ : nitrite
$NO_3^-$ : nitrate
P : phosphorus (*phosphore*)
PCA (*ACP*) : principal component analysis (*analyse en composantes principales*)
POM (*MOP*) : particulate organic matter (*matière organique particulaire*)
$r$ : correlation coefficient (*coefficient de corrélation*)
$R^2_{\text{adj.}}$ : coefficient of determination adjusted (*coefficient de détermination ajusté*)
RDA (*ACR*) : redundancy analysis (*analyse canonique de redondance*)
TN (*NT*) : total nitrogen (*azote total*)
TP (*PT*) : total phosphorus (*phosphore total*)

SPOC (*COPS*) : suspended particulate organic carbon (*carbone organique particulaire en suspension*)

SPON (*NOPS*) : suspended particulate organic nitrogen (*azote organique particulaire en suspension*)

SPOM (MOPS) : suspended particulate organic matter (*matière organique particulaire en suspension*)

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# Chapitre 1 : Introduction générale

La production d'énergie et l'intensification de l'agriculture depuis la révolution industrielle ont grandement augmenté les quantités d'azote (N) fixé et mis en circulation dans les écosystèmes. Les principales sources de cet azote sont la synthèse chimique d'azote par le procédé Haber-Bosch, le développement des cultures fixatrices d'azote (p. ex. les légumineuses, le riz) et la combustion de carburant fossile. La production d'azote réactif (Nr), qui se distingue du $N_2$ gazeux assimilable que par des bactéries fixatrices spécialisées dites diazotrophes, est estimée être au moins le double de la production naturelle et est en augmentation continuelle (Galloway and Cowling 2002, Galloway et al. 2004). Plusieurs problématiques environnementales sont reliées à cette augmentation du Nr. En effet, l'azote est naturellement un élément limitant la production primaire et l'augmentation des charges en azote aux écosystèmes aquatiques stimule la production et l'accumulation de la biomasse algale, entrainant l'eutrophisation de ces systèmes. Parmi les symptômes de l'eutrophisation, citons l'augmentation de la croissance algale, la dominance des cyanobactéries, la diminution des concentrations d'oxygène dissous menant à une mortalité accrue des poissons et une baisse de la biodiversité des écosystèmes touchés (Vitousek et al. 1997, Carpenter et al. 1998). Bien qu'il y ait consensus sur la nécessité de réduire la charge en phosphore (P) pour endiguer l'eutrophisation des lacs et des cours d'eau (Schindler 2006), le rôle de l'azote dans la problématique de l'eutrophisation est grandement débattu (Schindler et al. 2008, Conley et al 2009). De plus en plus d'études montrent néanmoins qu'une charge accrue d'azote combinée avec un phosphore élevé aggrave cette problématique (Elser et al. 1990, Fenn et al. 2003, Elser et al. 2007). Peu de données étant disponibles à long terme, la méthode paléolimnologique montre un potentiel à valider les effets de l'azote sur l'eutrophisation sur une échelle temporelle centenaire, voire décennale (Bunting et al. 2007, Savage et al. 2010).

La présence et la concentration élevée de certaines formes d'azote réactif dans les réservoirs d'eau potable peuvent aussi être dommageables pour la santé humaine et la santé des écosystèmes. Par exemple, des concentrations élevées de nitrates ($NO_3^-$) peuvent provoquer l'acidification des eaux de surface ainsi que leur eutrophisation et peuvent être cancérigènes pour les populations humaines (Vitousek et al. 1997, Nestler et al. 2011). Une particularité du cycle de l'azote est que la disponibilité des différentes formes chimiques de l'azote soit générée en grande partie par des processus microbiens (Fig. 1.1). Ainsi, les formes d'azote disponibles pour le phytoplancton dans un lac tiennent d'une dynamique entre les apports d'azote (la fixation de $N_2$, les apports du bassin versant), la minéralisation de la matière organique (l'ammonification, la nitrification) et la perte d'azote du système (la dénitrification). Cette disponibilité dans les différentes formes azotées stimulant la production primaire (p. ex. les formes inorganiques) peut aussi affecter la composition de la communauté phytoplanctonique. Par exemple, il est généralement admis que les cyanobactéries non diazotrophes sont de bonnes compétitrices pour les formes réduites d'azote et l'ajout d'ammonium ($NH_4^+$) ou d'urée ($(NH_2)_2CO$) favorise leur présence et la production de cyanotoxines (Blomqvist et al. 1994, Finlay et al. 2010). Il a également été démontré que l'augmentation des concentrations en azote totale (NT) est une meilleure variable explicative que le phosphore total (PT) de la hausse de la biomasse d'algues toxigènes dans les lacs du Québec méridional (Giani et al. 2005). Malgré l'importance des formes d'azote disponibles sur les effets de l'eutrophisation, les changements du cycle de l'azote à divers niveaux trophiques et leur rôle dans cette problématique sont méconnus.

Une approche prometteuse pour comprendre à la fois l'effet d'un apport accru en azote aux systèmes aquatiques et les mécanismes du cycle de l'azote est l'utilisation des isotopes stables. Dans cette étude, nous évaluerons l'application de mesure isotopes stables d'azote ($\delta^{15}N$) des sédiments lacustres pour la reconstruction des changements dans la charge en azote aux lacs afin de mieux comprendre l'eutrophisation à grande échelle temporelle. Nous explorerons également l'utilisation croisée de plusieurs isotopes stables de la matière organique particulaire et des nutriments de la colonne d'eau pour la caractérisation et la compréhension des processus dominants du cycle de l'azote dans les lacs peu profonds.

## *1.1 Théorie sur les isotopes stables*

Les isotopes stables sont des atomes d'un même élément ayant un nombre différent de neutrons ce qui engendre des masses atomiques différentes. Les isotopes stables se différencient des isotopes radioactifs qui se dégradent dans le temps. Plusieurs isotopes stables sont présents naturellement. Ceux utilisés en écologie et en biogéochimie ont de faibles masses atomiques, ont une large différence d'abondance naturelle entre l'isotope lourd et l'isotope léger, existent dans plusieurs composés et sont assez abondants pour assurer la précision des données (Scharp 2007b). Les isotopes les plus utilisés sont donc ceux de l'azote, du carbone (C), du soufre (S), de l'oxygène (O) et de l'hydrogène (H). Le développement des technologies de spectrométrie de masse a permis de mesurer les infimes variations de l'abondance naturelle des isotopes stables. Dans le cas de l'azote, l'isotope lourd $^{15}N$ est mesuré par rapport à l'isotope léger $^{14}N$ plus abondant (99,634 % des atomes)

(Sulzman 2007). Dans le spectromètre de masse, les masses isotopiques (p. ex. $^{15}$N, $^{14}$N) sont mesurées par une charge (en volt) proportionnelle aux nombres d'atomes de chacune des masses isotopiques d'intérêt dans l'échantillon. Étant donné cette mesure et les infimes variations du ratio isotopique absolu, les isotopes sont plutôt exprimés par la notation relative δ (équation 1.1, exemple pour les isotopes stables d'azote). Cette notation exprime la déviation du ratio de l'isotope lourd sur le léger (p. ex. $^{15}$N/$^{14}$N) d'un échantillon par rapport à un standard (le $N_2$ atmosphérique pour l'azote) en partie par mille (‰). Un échantillon avec un ratio $^{15}$N/$^{14}$N comparativement plus élevé que le standard aura donc un $\delta^{15}$N positif, un échantillon avec un ratio plus faible aura un $\delta^{15}$N négatif alors qu'un échantillon avec des proportions en $^{15}$N et $^{14}$N identiques au standard aura un $\delta^{15}$N de 0 ‰.

$$\delta^{15}\mathrm{N} = \left[\frac{^{15}\mathrm{N}/^{14}\mathrm{N}_{\text{échantillon}}}{^{15}\mathrm{N}/^{14}\mathrm{N}_{\text{standard}}} - 1\right] \times 1000 \qquad \text{équation 1.1}$$

À cause de leurs masses distinctes, les isotopes se comportent quantitativement de manières différentes. Cet effet se nomme le fractionnement et se définit comme étant une différence isotopique entre le substrat et le produit d'une transformation chimique. On parlera de fractionnement d'équilibre lors de réactions bidirectionnelles comme lors des changements de phase où l'isotope lourd a tendance à s'accumuler où les liaisons sont les plus fortes (Scharp 2007a). Dans le cas du cycle de l'azote, c'est plutôt le fractionnement cinétique qui est important étant donné les nombreuses réactions biologiques qui caractérisent ce cycle. Lors d'une réaction chimique unidirectionnelle, l'atome lourd $^{15}$N a tendance à réagir plus lentement que l'isotope léger $^{14}$N et à se concentrer dans le substrat de la réaction (Peterson and Fry 1987). À mesure que le substrat est consommé, les ratios isotopiques du substrat résiduel, du produit instantané et du produit cumulé augmentent progressivement jusqu'à ce que le produit cumulé à la fin de la réaction ait la même composition isotopique que le substrat au début de la réaction (Fig. 1.2). En système fermé, le fractionnement est donc observable seulement lorsqu'il y a une consommation partielle du réservoir initial de substrat (Montoya 2007) alors que dans un système ouvert, le fractionnement peut être constamment observé (Evans 2001). Ce phénomène en système fermé est le fractionnement cinétique de Rayleigh et est décrit par le taux de fractionnement ($\alpha_{A\text{-}B}$ et ε). Le taux de fractionnement $\alpha_{A\text{-}B}$ décrit la différence du ratio isotopique entre le substrat (substance A) et le produit instantané (substance B, équation 1.2) alors que la notation ε exprime le fractionnement en partie par mille (équation 1.3).

$\alpha_{A-B} = R^A/R^B$ où $R = N^{15}/N^{14}$ équation 1.2

$\varepsilon = (\alpha_{A-B} - 1) \times 1000$ équation 1.3

Les isotopes stables peuvent aussi permettre de déterminer les sources qui dominent un mélange. En effet, la répartition des isotopes dans l'environnement est non aléatoire et le fractionnement produit des réservoirs de molécules organiques et inorganiques qui ont des signatures isotopiques similaires (Peterson and Fry 1987). Lorsque plusieurs éléments forment un mélange, les isotopes permettent d'en calculer leur contribution à l'aide de modèles de mélange. L'équation 1.4 décrit un modèle de mélange simple. L'utilisation de ces modèles requiert des informations de base telles les signatures isotopiques des composés formant le mélange (Fry 2006).

$\delta_{échantillon} = (\delta_{Source\ 1}) \times f_1 + (\delta_{Source\ 2}) \times f_2\ \ tel\ que\ f_1 + f_2 = 1$ équation 1.4

### *1.3 Le cycle de l'azote dans les lacs et les isotopes stables : sources*

L'utilisation des isotopes stables dans les milieux lacustres peut permettre tout d'abord d'identifier les sources d'azote provenant du bassin versant. La signature isotopique des composés azotés entrant dans un lacs est fonction de l'utilisation du territoire et de la déposition atmosphérique. Les signatures isotopiques des principales sources d'azote potentielles aux écosystèmes aquatiques sont identifiées dans la figure 1.3 et contextualisées par la figure 1.4.

Dans les écosystèmes vierges de l'activité humaine, puisque la première source d'azote est la fixation, les apports dissous ou particulaires qui y sont associés ont un $\delta^{15}$N faible (Fig. 1.3) (Kendall 1998). En comparaison des sols naturels, les sols agricoles ont des signatures beaucoup plus positives. Bien que les fertilisants inorganiques (produits par le procédé Haber-Bosch) aient des signatures proches de 0 ‰, la nitrification et la dénitrification suivant leur application sur les terres agricoles peuvent augmenter de 15 à 30 ‰ le $\delta^{15}$N du $NO_3^-$ qui est acheminé au milieu lacustre (Finlay and Kendall 2007). À cause de leurs origines diversifiées (composte, fumier, etc.), les fertilisants naturels ont des signatures isotopiques plus variées mais aussi généralement plus élevées. L'urée présente dans ces composés est hydrolysée en ammoniac ($NH_3$), rapidement volatilisée ($\varepsilon$ = 40-60 ‰) et entraine l'enrichissement en $^{15}$N de l'ammonium résultant (Heaton 1986, Kendall 1998). La nitrification et la dénitrification peuvent encore augmenter le $\delta^{15}$N du $NH_4^+$ et du $NO_3^-$ produits. De la même façon, les eaux usées et les déchets humains ont des signatures isotopiques élevées et les déversements de $NO_3^-$ de fosses septiques ou d'égouts sont difficilement différentiables de déchets d'animaux puisque leurs $\delta^{15}$N se chevauchent. En comparaison, le $\delta^{15}N$ de la déposition atmosphérique a généralement une signature basse à négative (Kendall 1998, Elliott et al. 2007, Kendall et al. 2007). Les effets des apports atmosphériques sur la productivité des lacs et sur la signature isotopique sont principalement observés dans des lacs oligotrophes de haute altitude (p. ex. Wolfe et al. 2001, Jones et al. 2004, Holtgrieve et al. 2011).

### *1.2 Le cycle de l'azote dans les lacs et les isotopes stables : processus*

L'azote provenant du bassin versant et qui est acheminé aux lacs peut ensuite être transformé par les processus du cycle de l'azote. Or, les isotopes stables peuvent rendre compte de ces transformations. Les cinq réactions biologiques principales qui contrôlent la dynamique des isotopes stables d'azote dans les lacs sont la fixation, l'assimilation, l'ammonification, la nitrification et la dénitrification (Finlay and Kendall 2007). Ces processus sont interreliés et cycliques, un processus (et les composés azotés produits) étant précurseur pour un autre. La figure 1.4 schématise ces processus dans un lac non stratifié. Les taux de fractionnement mesurés sur les isotopes stables d'azote pour chaque processus varient grandement et sont résumés dans le tableau I.I.

La fixation du diazote ($N_2$) constitue une entrée dans le cycle de l'azote où l'azote est incorporé à la matière organique. La différence entre les deux grandes formes d'azote organique, soit particulaire (NOP) et dissous (NOD), est purement une définition technique dérivée des méthodes de prélèvement (NOD < 0,45 µm) bien que le NOD soit plus typiquement produit lors de la sénescence des organismes présents dans le lac (Kalff 2002). La source d'azote assimilée lors de la fixation étant le $N_2$ atmosphérique (le standard isotopique pour l'azote, équation 1.1) et le fractionnement étant faible (Tableau I.I), l'azote provenant de ce processus a une signature très proche de 0 ‰ (Hoering and Ford 1960, Kendall 1998). La fixation est un processus qui est très couteux énergétiquement et qui est restreint à des organismes spécialisés, soit dans les lacs par les cyanobactéries fixatrices de $N_2$. Les formes d'azote généralement assimilables sont plutôt les ions inorganiques $NH_4^+$ et $NO_3^-$. Le fractionnement lors de l'assimilation est très variable et dépend de l'espèce et de son taux de croissance et par le fait même des conditions environnementales dans lesquelles l'organisme se retrouve telles la température et la disponibilité des nutriments (Fogel and Cifuentes 1993, Montoya and McCarthy 1995). Par exemple, lorsque les concentrations en azote sont limitantes l'organisme aura tendance à assimiler sans distinguer entre l'isotope lourd et léger et le fractionnement ne sera pas mesuré (Evans 2001). En milieu naturel, les isotopes stables d'azote peuvent fournir un indicateur de l'assimilation des nutriments par le phytoplancton (Altabet and Francois 1994). L'assimilation peut être observée par la relation inverse entre le $\delta^{15}N$ de la matière organique particulaire et le logarithme de la concentration en nutriment qui modélise le fractionnement cinétique de Rayleigh en système fermé (Teranes and Bernasconi 2000, Lehmann et al. 2004a). La relation est altérée lorsque 1) le N est limitant, 2) plusieurs nutriments différents sont assimilés, 3) une quantité importante de matière organique provenant du bassin versant supplante le signal interne.

La matière organique produite par la fixation et l'assimilation (NOP ou NOD) est dégradée et minéralisée en $NH_4^+$ par l'action microbienne. L'ammonification a généralement un fractionnement faible (0-5 ‰), mais l'ammonium produit est légèrement appauvri en $^{15}N$ (Kendall et al. 2007). La nitrification oxyde ensuite le $NH_4^+$ en nitrite

($NO_2^-$) puis en $NO_3^-$. La réaction est conduite en présence d'oxygène par des bactéries chimiolithotrophes qui fixent le $CO_2$ avec l'énergie obtenue par l'oxydation du $NH_4^+$ (Ward 2008). Le haut taux de fractionnement global de la réaction est déterminé par l'étape limitante, généralement l'oxydation de l'ammonium. Très peu de mesures existent en milieux lacustres sur le fractionnement lors de la nitrification. Le $NO_3^-$ produit peut par la suite être réduit en $N_2$ par la dénitrification. Pour que la dénitrification ait lieu, il faut une disponibilité de $NO_3^-$, de très faibles concentrations d'oxygène et de la matière organique. Dans les lacs, la dénitrification a lieu principalement à l'interface eau/sédiment, mais également dans les eaux profondes anoxiques de lacs stratifiés (Seitzinger et al. 2006). Bien que la dénitrification ait un fractionnement très élevé (Kendall 1998, Finlay and Kendall 2007), les mesures de $\delta^{15}N$ du nitrate des eaux sus-jacentes aux sédiments montrent que ce fractionnement est faible lors de la dénitrification benthique (Brandes et Devol 1997, Sebilo et al. 2003). En effet, l'étape limitante de cette réaction serait la diffusion du nitrate dans les sédiments et puisqu'ils sont généralement entièrement consommés dans les sédiments, le fractionnement n'est pas observé (Lehmann et al. 2004b, Galbraith et al. 2008). Selon le niveau trophique d'un système et sa morphométrie, les processus dominants et leurs effets sur le $\delta^{15}N$ des différentes formes azotées devraient donc différer.

### *1.3 Les isotopes stables d'azote en paléolimnologie*

La signature en $\delta^{15}N$ des sédiments est influencée par les apports du bassin versant et de l'atmosphère et par le recyclage de l'azote dans le lac. L'azote organique des sédiments constitue donc un intégrateur des processus du bassin versant et du lac permettant de reconstituer les changements de ces écosystèmes à grandes échelles temporelles. Dans cette approche, le $\delta^{15}N$ des sédiments est souvent utilisé comme indicateur des changements dans les sources d'azote où il peut refléter une augmentation de l'azote provenant des eaux usées, des activités agricoles (fertilisant et déchets animaux) ou de la déposition atmosphérique (p. ex. Wolfe et al. 2001, Elliott and Brush 2006, Bunting et al. 2007). D'autres études ont plutôt montré que le $\delta^{15}N$ peut être utilisé comme un indicateur du niveau de productivité passé des lacs (Brenner et al. 1999, Wu et al. 2006). Cette utilisation est basée sur une augmentation progressive du $\delta^{15}N$ avec une augmentation du niveau trophique des lacs et une diminution du $\delta^{15}N$ dans les lacs hypereutrophes à cause de la fixation d'azote par les cyanobactéries. Plusieurs études ont de plus regardé l'effet de la dégradation sur le $\delta^{15}N$ des sédiments, mais les résultats sont contradictoires avec parfois une augmentation (Ostrom et al. 1998, Freudenthal et al. 2001) ou parfois une diminution du $\delta^{15}N$ lors de la décomposition (Galman et al. 2009, Kohzu et al. 2011). Quelques études ont examiné les contrôles sur la signature isotopique des sédiments dans les lacs de haute élévation (Bunting et al. 2010), les lacs subtropicaux (Gu et al. 1996) et les lacs nourriciers du saumon (Selbie et al. 2009). Cependant, dans les lacs tempérés où l'activité humaine est présente, aucune étude à notre connaissance ne s'est penchée sur la régulation de la signature en isotopes stables d'azote des sédiments. De telles connaissances sont prérequises à une interprétation juste et adéquate des carottes de sédiments lacustres, une étape vers l'amélioration de la compréhension de l'augmentation de la charge en azote sur l'eutrophisation des lacs.

### *1.4 Utilisation croisée des isotopes stables*

L'utilisation croisée de plusieurs isotopes stables sur différentes formes azotées a le potentiel de fournir des indications sur les processus dominants du cycle de l'azote dans les lacs. Par exemple, Hadas et al. (2009) en mesurant le $\delta^{15}N$ du $NO_3^-$, du $NH_4^+$ et de l'azote organique dissous ont identifié les variations saisonnières de la nitrification et les changements dans les formes d'azote assimilées par le phytoplancton. Les mesures additionnelles des isotopes stables de l'oxygène ($\delta^{18}O$) peuvent également permettre de déterminer l'effet conjugué de l'assimilation (ou de la dénitrification) et de la nitrification sur le $NO_3^-$. En effet, lors de l'assimilation et de la dénitrification, le fractionnement sur les isotopes stables d'oxygène et d'azote du $NO_3^-$ est similaire. Ce fractionnement est dit couplé et a un ratio $\varepsilon^{18}:\varepsilon^{15}$ de ~1 (Granger et al. 2004, Granger et al. 2008). Le fractionnement est similaire puisque la cause dominante du fractionnement pour ces deux processus est la réduction du $NO_3^-$. Au contraire pour le $\delta^{18}O$, le fractionnement est découplé puisque l'atome d'azote provient du $NH_4^+$ recyclé dans le système (Sigman et al. 2005) alors que pour l'oxygène deux atomes proviennent de l'eau ($H_2O$) et un atome de l'oxygène dissous ($O_2$; Fig. 1.4) (Casciotti et al. 2011). L'incorporation d'atomes d'oxygène de l'eau peut être plus importante lors de l'oxydation de l'ammonium étant donné les échanges entre l'oxygène du $NO_2^-$ et l'eau (Casciotti et al. 2010). En zone euphotique les études océanographiques ont montré que la déviation de la relation 1:1 entre le $\delta^{15}N$ et le $\delta^{18}O$ assumée pour l'assimilation permet de déterminer la proportion de $NO_3^-$ produit par la nitrification (Wankel et al. 2007, DiFiore et al. 2009). Dans les zones de minimum d'oxygène, la relation 1:1 est plutôt signe d'une dénitrification et une déviation de cette relation s'explique par un apport de $NO_3^-$ ayant un $\delta^{15}N$ faible provenant de la reminéralisation d'azote nouvellement fixé (Sigman et al. 2005). En milieu d'eau douce, les isotopes du $NO_3^-$ sont utilisés principalement pour déterminer la source du $NO_3^-$ provenant de la nitrification du bassin versant, de la déposition atmosphérique, d'eaux usées ou de fertilisants (p. ex. Pardo et al. 2004, Anisfeld et al. 2007, Barnes and Raymond 2010). En effet, lorsque les sources d'azote ont des signatures isotopiques qui se chevauchent, les sources potentielles peuvent être restreintes par l'utilisation croisée des isotopes. Par exemple, l'identification du $NO_3^-$ atmosphérique et de fertilisants de $NO_3^-$ est possible avec l'utilisation du $\delta^{18}O$ puisque ces sources ont des valeurs de $\delta^{18}O$ très élevées et distinctes (respectivement 63 à 94 ‰ et 17 à 25 ‰) comparativement à leurs valeurs de $\delta^{15}N$ indistinctes (respectivement -15 à 15 ‰ to -4 à 4 ‰) (Kendall et al. 2007). De la même façon, dans les milieux où les apports terrestres sont importants, l'utilisation des isotopes stables du carbone ($\delta^{13}C$) permet de déterminer la source de la matière organique (Finlay and Kendall 2007). Bien que dans les systèmes d'eaux douces les isotopes stables croisés soient plutôt utilisés pour déterminer les sources, ils peuvent aussi indiquer des processus qui ont lieu dans le bassin versant (Finlay and Kendall 2007). Dans ces études, une pente de 0,5 sur un graphique du $\delta^{18}O$ vs le $\delta^{15}N$ du $NO_3^-$ est donc interprétée comme un signe de dénitrification (Kendall et al. 2007). En effet, dans les eaux souterraines, les zones ripariennes et l'hypolimnion anoxique des lacs, la relation entre le fractionnement de l'oxygène et de l'azote du $NO_3^-$ ($\varepsilon^{18} : \varepsilon^{15}$) est de ~ 0,5-0,6 (Bottcher et al. 1990, Mengis et al. 1999, Lehmann et al. 2003). Cependant il n'y a aucune indication qu'une telle relation serait observée dans la zone euphotique des lacs où très peu d'études utilisant les isotopes des $NO_3^-$ ont été conduites. À notre connaissance, aucune étude à ce jour n'a utilisé ces techniques d'isotopes stables croisés dans les lacs peu profonds où elles ont un grand potentiel à déterminer les processus dominants du cycle de l'azote.

## *1.4 Objectifs de l'étude*

L'objectif global de cette étude est de caractériser et d'améliorer la compréhension des sources d'azote et des processus du cycle de l'azote dans les lacs tempérés par l'utilisation de mesures d'isotopes stables. Cette étude se sépare en deux volets afin d'évaluer les sources et processus dominants du cycle de l'azote à diverses échelles temporelles (échelle centenaire vs annuelle) pouvant être identifiés par les mesures d'isotopes stables.

Le premier objectif est de déterminer quels sont les facteurs qui contrôlent la signature en $\delta^{15}N$ des sédiments des lacs tempérés (chapitre 2). Nous explorerons dans 65 lacs sur un gradient trophique les relations entre le $\delta^{15}N$ des sédiments, la composition élémentaire des sédiments, les sources d'azote des lacs, la topographie du bassin versant, l'occupation du territoire du bassin versant, la physico-chimie des lacs et leur morphométrie. Il s'agit d'une approche corrélationnelle consistant à déterminer quelles sont les (ou la) meilleures variables explicatives de la composition en isotope stable d'azote des sédiments. La détermination de variables explicatives permettra une meilleure interprétation du $\delta^{15}N$ des carottes de sédiments lacustres.

Le deuxième objectif est d'appliquer une approche isotopique croisée dans trois lacs tempérés peu profonds se situant sur un gradient trophique et ayant différents régimes de stratification (chapitre 3). Puisque cette approche est novatrice dans les lacs peu profonds, nous voulons d'abord déterminer si l'utilisation du $\delta^{15}N$ de plusieurs composés azotés (nutriments et azote organique) permet de connaître les formes d'azote assimilées par le phytoplancton. Nous explorerons également l'utilisation croisée des isotopes du $NO_3^-$ pour déterminer s'ils peuvent être utilisés pour comprendre l'assimilation et la nitrification dans la colonne d'eau ou s'ils sont plutôt indicateurs des sources d'azote. Cette approche multiisotopique vise à circonscrire les processus *in situ* dominants du cycle de l'azote.

## *1.5 Tableaux et figures*

Tableau I.I : Les taux de fractionnement mesurés sur les isotopes stables d'azote ($\varepsilon^{15}$) pour les processus majeurs du cycle de l'azote. Les symboles font référence à la source des données : * Fogel and Cifuentes 1993, $^{\Delta}$ Robinson 2001, $^{+}$ Kendall 1998, ■ Finlay and Kendall 2007.

| Processus | Réaction | $\varepsilon^{15}$ (‰) |
|---|---|---|
| Fixation | $N_2 \rightarrow$ N organique | 3 à -1* |
| Assimilation | $NO_3^- \rightarrow$ N organique (cultures) | 0 à 24* |
| | $NO_3^- \rightarrow$ N organique (observations de terrain) | 4 à 5* |
| | $NH_4^+ \rightarrow$ N organique (cultures) | 0 à 27* |
| | $NH_4^+ \rightarrow$ N organique (observations de terrain) | 10* |
| (plantes) | $NO_3^- \rightarrow$ N organique | 0 à 19$^{\Delta}$ |
| | $NH_4^+ \rightarrow$ N organique | 9 à 18$^{\Delta}$ |
| (microbes) | $NO_3^- \rightarrow$ N organique | 13$^{\Delta}$ |
| | $NH_4^+ \rightarrow$ N organique | 14 à 20$^{\Delta}$ |
| (animaux) | N organique (déamination et transamination) | 1 à 6$^{\Delta}$ |
| Ammonification | production de $NH_4^+$ par la décomposition de la matière organique | 0 à 5$^{\Delta}$ |
| Nitrification | oxydation $NH_4^+ \rightarrow N_2O$ et NO | 35 à 60$^{\Delta}$ |
| | $NH_4^+ \rightarrow NO_3^-$ | 15 à 35$^{\Delta}$ |
| Dénitrification | réduction $NO_3^- \rightarrow N_2O$ et $N_2$ | 28 à 33$^{\Delta}$ |
| | $NO_3^- \rightarrow N_2$ | 5 à 40$^{+}$ |
| (sédiments) | $NO_3^- \rightarrow N_2$ | 1,5 à 3,6■ |
| Physique | volatilisation du $NH_3$ | 40 à 60$^{\Delta}$ |

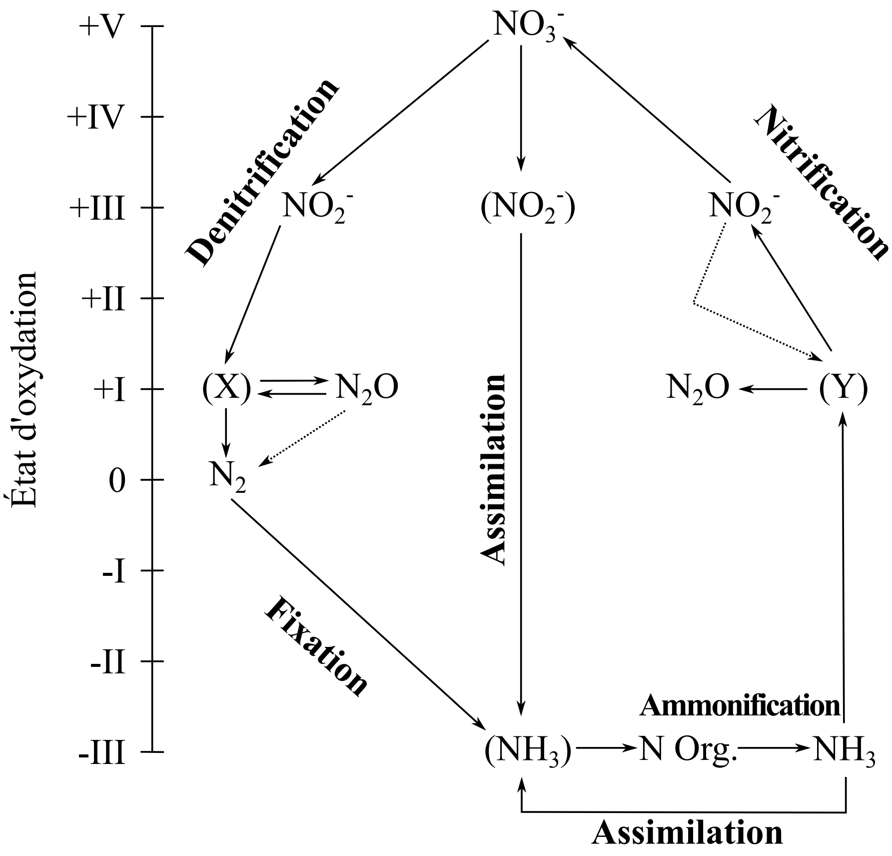

Figure 1.1 : Cycle de l'azote modifié selon la figure de Altabet (2006). L'état d'oxydation (axe vertical) est un facteur déterminant les conditions environnementales sous lesquelles les processus représentés en lettre gras sont favorisés. En milieu d'eau douce et à pH faible (< 9) l'ammoniac ($NH_3$) est plutôt présent sous forme d'ammonium ($NH_4^+$). Les lettres X, Y et Z représentent les molécules qui précèdent les flèches les pointant, ces lettres sont employées afin de respecter l'axe vertical d'état d'oxydation.

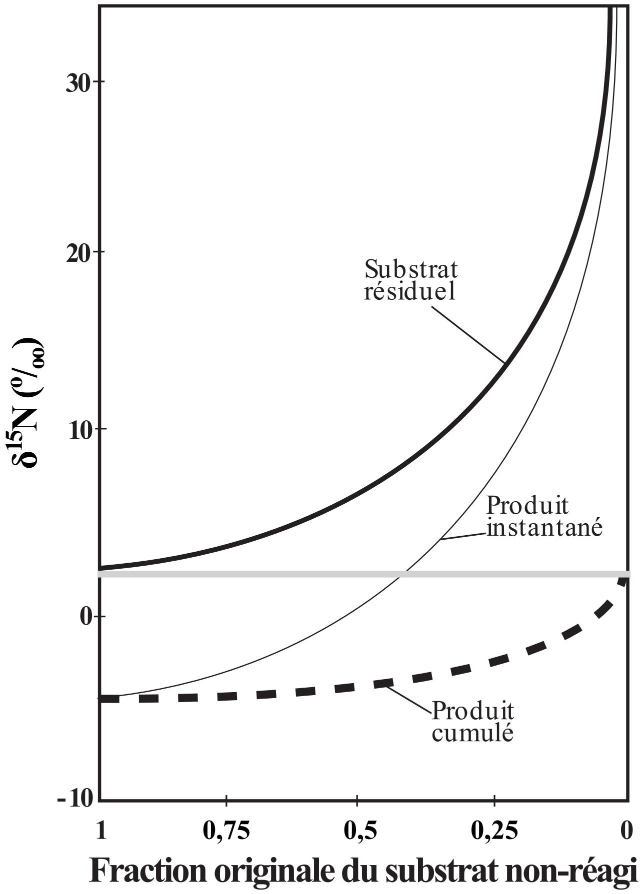

Figure 1.2 : Courbes de fractionnement de Rayleigh en système fermé modifiées à partir de la figure originale de Montoya (2007). À mesure que la réaction se déroule, le $\delta^{15}$N du substrat résiduel, du produit instantané et du produit cumulé augmentent. Le $\delta^{15}$N du produit cumulé à la fin de la réaction est égal au $\delta^{15}$N du substrat au début de la réaction.

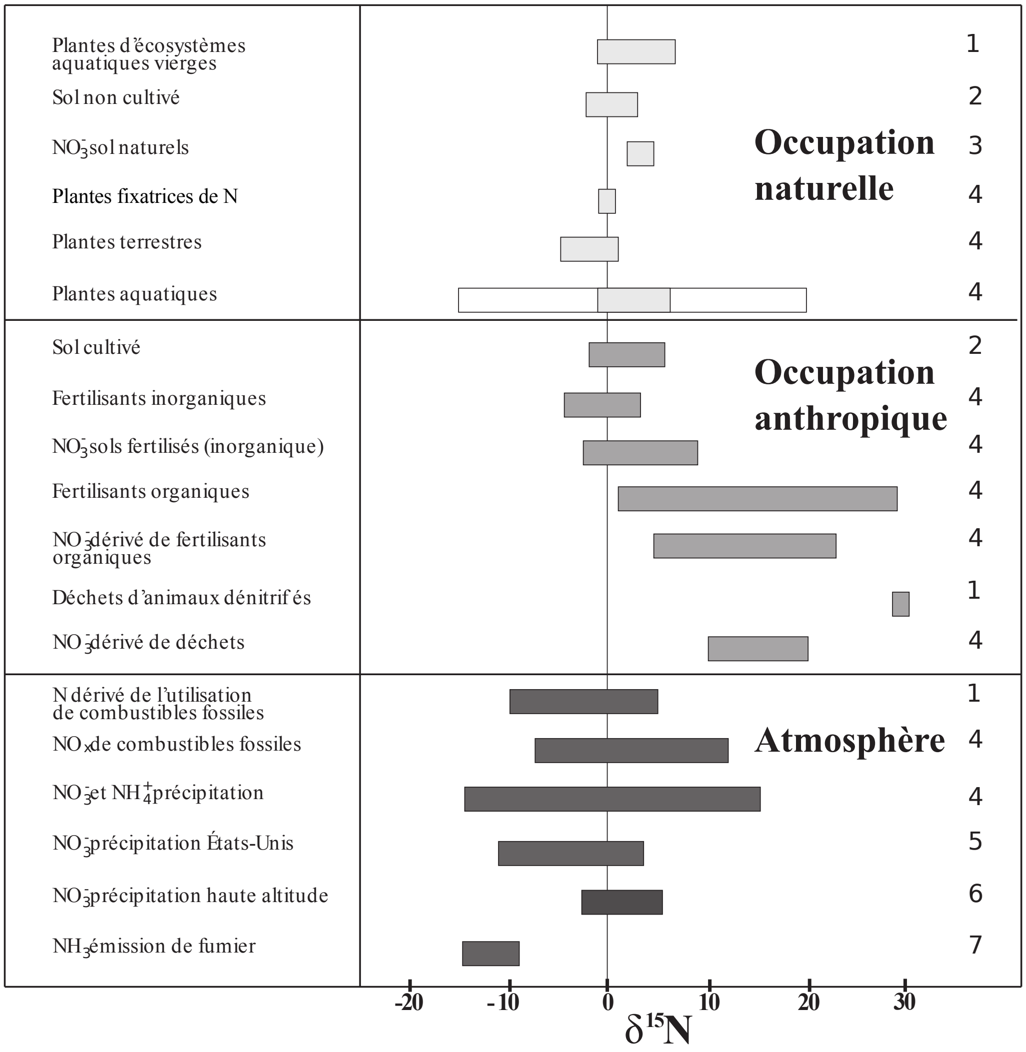

Figure 1.3 : Signatures isotopiques mesurées pour les principales sources d'azote aux écosystèmes lacustres pour des occupations du territoire naturelles ou anthropiques et des composés de nature atmosphérique. Les rectangles pleins représentent l'étendue et les rectangles blancs sont des signatures non-typiques. **1** Finlay and Kendall 2007; **2** Broadbent et al. 1980; **3** Kendall 1998; **4** Kendall et al. 2007; **5** Heaton 1986; **6** Kendall et al. 1995; **7** Macko and Ostrom 1994.

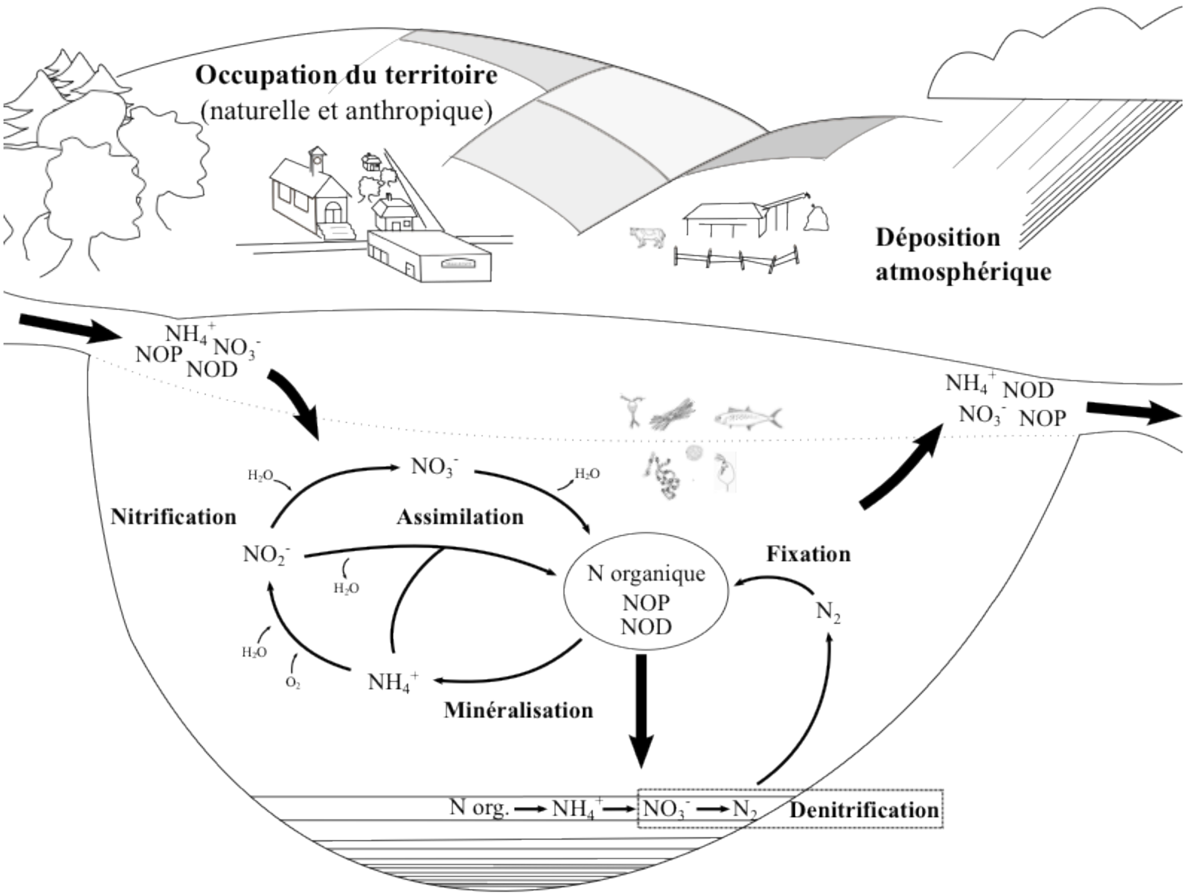

Figure 1.4 : Schéma conceptuel du cycle de l’azote dans un lac non-stratifié. Les mesures des isotopes stables de la matière particulaire, des nutriments et des sédiments peuvent informer sur l’azote provenant du bassin versant selon l’utilisation du territoire (naturelle et anthropique, de type agricole ou urbaine) et l’importance de la déposition atmosphérique. Cet azote est assimilé par les organismes (N organique) du lac et recyclé par les processus du cycle d’azote (en gras dans la figure); les isotopes stables peuvent refléter ces transformations. L’incorporation et la sortie d’atomes d’oxygène lors du cycle sont également représentées. Dans un lac stratifié, la dénitrification peut aussi avoir lieu dans l’hypolimnion anoxique. L’azote organique qui s’accumule dans les sédiments lacustres enregistre les changements temporels de ces sources et processus. NOD : azote organique dissous; NOP : azote organique particulaire.

# Chapitre 2 : Empirical analysis of factors regulating nitrogen stable isotopes ($\delta^{15}N$) variation of surface sediments from temperate lakes

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## ABSTRACT

We investigated the controls of nitrogen stable isotope ($\delta^{15}N$) variation from surface sediments of 40 lakes from Quebec and 25 lakes from Alberta, Canada. The effect of water-quality and morphometric variables, as well as anthropogenic N load, were considered as possible predictors of sediment $\delta^{15}N$ (ranging from -3.0 to 8.6‰) across and between the two regions. We found that across regions water column total nitrogen (TN), %N in the sediments and lake morphometric variables were the best predictors of sedimentary $\delta^{15}N$, explaining 66 % of its variation. Significant relationships were also found between sediment $\delta^{15}N$ and anthropogenic N load ($R^2_{adj.} = 0.23$, $p < 0.001$), the latter being a strong predictor of TN ($R^2_{adj.} = 0.68$, $p < 0.001$). There was also an inverse relationship between %N in the sediments and sedimentary $\delta^{15}N$ consistent for both regions suggesting that early diagenesis is an important factor altering the isotopic signature. The two regions exhibited distinct regional $\delta^{15}N$ controls whereby Alberta lake sedimentary $\delta^{15}N$ signature was dominated by anthropogenic N load. In contrast, Quebec sediment $\delta^{15}N$ was best explained by diagenesis and lake volume. Our findings indicate that the use of $\delta^{15}N$ in paleolimnological investigations can effectively reconstruct changing N sources to lake systems but early diagenesis in oxygenated waters may alter the surface sediment $\delta^{15}N$ signature. As such, interpretations of sediment $\delta^{15}N$ are likely to be strongest when multiple lines of evidence are employed.

## INTRODUCTION

Eutrophication is one of the greatest threats to freshwater ecosystems and ultimately results in the dominance of noxious algal blooms, decreases in oxygen concentrations and losses in biodiversity. Despite the widespread consensus that phosphorus (P) loads need to be controlled to mitigate eutrophication in lakes (Schindler 2006), there is growing evidence that enhanced N loads can also result in water quality degradation and promote algal blooms, especially toxic species (Giani et al. 2005, Conley et al. 2009, Lewis et al. 2011). A more complete understanding of N pollution and its impact on eutrophication is possible through the historical perspective afforded by a paleolimnological approach. Sedimentary nitrogen stable isotopes ratio ($\delta^{15}N$) of organic matter is a proxy that can be used to track N pollution to lakes (e.g. Elliott and Brush 2006, Leavitt et al. 2006). However, very few studies to date have tried to determine empirically the drivers of lake sedimentary $\delta^{15}N$ across the landscape. Existing studies have focused on high altitude lakes (Jones et al. 2004, Bunting et al. 2010), sub-tropical lakes (Gu et al. 1996) and salmon nursery lakes (Selbie et al. 2009), but no study to our knowledge has addressed how human activities have shaped sedimentary $\delta^{15}N$ in temperate lakes within and between regions.

A commonly-held assumption with the use of bulk sediment organic matter to reconstruct past environmental conditions is that sediments reflect the organic matter produced in the lake. Thus, stratigraphic variations in $\delta^{15}N$ can record changes in N sources available to primary producers over time. For example, synthetic fertilizers have $\delta^{15}N$ ~0‰ whereas human and animal waste typically have $\delta^{15}N$ ~5‰, which can be further enriched in $^{15}$N because of the high degree of fractionation related to ammonia volatilization (Heaton 1986, Kendall 1998). N processing on the landscape of any of these N sources by nitrification and denitrification will further increase their $\delta^{15}$N signature (Kendall et al. 2007). Several previously published paleolimnological studies have attempted to track different N sources from wasterwater N (Leavitt et al. 2006), agricultural N from organic and inorganic fertilizers (Bunting et al. 2007), atmospheric N deposition (Jones et al. 2004, Holtgrieve et al. 2011) and N-fixation (Riedinger-Whitmore et al. 2005, Schindler et al. 2008) using sediment $\delta^{15}$N. Conceptually, the expected $\delta^{15}$N signature will first depend on the dominant N source, with N derived from agriculture or human waste increasing the $\delta^{15}$N with increasing load as compared to increasing atmospheric inputs resulting in its decrease (Fig. 2.1A,B).

The $\delta^{15}$N signature of these externally derived N sources may also be altered by lake internal microbial transformations. Nitrification and denitrification are two processes that have a particularly high fractionation effect (Robinson 2001). Changing planktonic and dissolved inorganic nitrogen (DIN) $\delta^{15}$N originating from nitrification and denitrification in lakes has been reported (Hodell and Schelske 1998, Syvaranta et al. 2008, Hadas et al. 2009), but there are very few studies where this signal is reflected in the sediment isotopic signature. In lake systems, the direct microbial processing of organic matter may be more important in altering the sediment isotopic signature as compared to the indirect role of bacterial transformations of water column nutrient $\delta^{15}$N. However, there is conflicting evidence on the effect of diagenesis on sedimentary $\delta^{15}$N where some studies have found it resulted in an increase in the isotopic signature (Ostrom et al. 1998, Freudenthal et al. 2001), whereas others have found that it resulted in a decrease (Galman et al. 2009, Kohzu et al. 2011).

Contrary to the source effect, other studies have used sedimentary $\delta^{15}N$ as a paleoproductivity indicator (e.g. Brenner et al. 1999, Wu et al. 2006). From this perspective, fractionation during N assimilation would explain changes in $\delta^{15}N$ as a function of changing trophic state and productivity (Fig 2.1C) (Gu 2009, Gu and Schelske 2010). In particular, as N becomes more limiting with increased trophy, there would be a decrease in the $^{15}N$ fractionation with continued phytoplankton growth, resulting in a $^{15}N$ enrichment of phytoplankton (Wada and Hattori 1978, Fogel and Cifuentes 1993). Moreover in hypereutrophic lakes, low N:P ratios could lead to N fixation (-1 to -2‰) resulting in a marked decrease in planktonic $\delta^{15}N$ (Gu et al. 1996, Brenner et al. 1999) (Fig. 2.1C). However, studies using $\delta^{15}N$ as a paleoproductivity indicator are mostly located in subtropical lakes and often do not report information on watershed characteristics and the N sources that could also drive observed patterns.

Although multiple factors have been identified as drivers of $\delta^{15}N$ sediment variation, few studies have looked at broad scale patterns of sedimentary $\delta^{15}N$. Since the interpretation of sediment records is dependent on such knowledge, our aim is to determine what are the best variables explaining sediment $\delta^{15}N$. In this study we compare the relative importance of several processes that could influence the sediment $\delta^{15}N$ signature in temperate lakes from two geographically distinct regions. We hypothesize that across systems, sediment $\delta^{15}N$ is largely a function of the dominant N source. However, given that some studies have identified productivity as an important driver of the sedimentary $\delta^{15}N$ (Gu et al. 2009, Gu and Schelske 2010), we evaluate whether N source is a stronger predictor of sedimentary $\delta^{15}N$ than productivity metrics. Finally, we also test if lake morphometric features are significant predictors of sediment $\delta^{15}N$ because internal processing of N has been strongly linked to lake morphometry (Harrison et al. 2009) and could regulate sediment diagenesis across systems.

## METHODS

### *Study sites*

Surface sediment samples were collected from lakes in two contrasting regions of Canada, southern Quebec and Alberta (Fig. 2.2). Lakes from southern Quebec are located in the Appalachian Orogen in a region dominated by mixed forest but where agriculture is present at different intensities. Quebec lakes have circumneutral pH, span large phosphorus and nitrogen gradients and are predominantly shallow. The majority of Alberta lakes are located in the aspen parkland, a transition zone between the prairies and boreal forest biomes. The exceptions to this are Elkwater and Reesor lakes and Spruce Coulee reservoir, which are located on a plateau rising 200 m above the Canadian prairies and fall within the Cypress Hill Provincial Park. Alberta sites are generally low elevation lakes, with large watersheds and are naturally productive as their watersheds are rich in phosphorus (Prepas and Trew 1983). However, agriculture is well developed in the parkland region thus contributing to the cultural eutrophication of lakes (Taranu and Gregory-Eaves 2008).

### *Sediment geochemical analyses*

Surface sediments (top 0-1 cm) were retrieved from the deep-water depositional zone of 25 lakes across Alberta and 40 lakes in Southern Quebec using a gravity corer (Glew et al. 2001). Cores were collected in duplicate at the deepest sites of the lakes, which is the more accurate representation of the sediment depositional zone. Sediments from Alberta were collected in summer 2006 and sediments from Southern Quebec in summers 2007 and 2008. Details on sampling are provided in Taranu et al. (2010) and Vermaire et al. (2011). Based on $^{210}$Pb age models, the upper 1cm of Alberta lakes represents between ~ 2 yrs to a maximum of 5 yrs (Taranu et al. 2010, Köster et al. 2008: http://www.lica.ca) and for Quebec lakes, ~ 2 yrs of sedimentation (Vermaire 2011). The elemental proportion of sedimentary nitrogen (N) and carbon (C) was measured on freeze dried, homogenized bulk sediment with a Fisons EA1108 Elemental Analyzer according to standard techniques (Meyers and Ishiwatari 1993). All %C measurements reported represent organic carbon content since carbonates were removed prior to analyses by fumigation with 1M HCl. Samples were weighed in silver capsules and placed in a closed glass container to ensure that air was saturated with acid (Hélie 2009). This method was suitable for our samples as none of the sites were located in regions dominated by dolomite which resist the fumigation treatment (J.-F Helie pers. comm.). Analytical precision for organic C and for N was ± 0.02 % and ± 0.05 % respectively. Nitrogen isotopic composition was measured using a continuous flow Micromass Isoprime™ IRMS coupled to a Carlo Erba NC 1500 elemental analyzer located at the GEOTOP Research Center (Université du Québec à Montréal).

Analytical precision was ± 0.2 ‰ and for samples below 1 % N the analytical precision was ± 0.4 ‰. Isotopic values are reported as the δ notation ($\delta = ([R_{sample}\text{-}R_{standard}]/R_{standard}) \times 1000$, where $R={}^{15}N/{}^{14}N$). Values for $\delta^{15}N$ are referenced against atmospheric $N_2$ gas. For all the analyses of %N, %C and $\delta^{15}N$ duplicates were run on 10 % of samples; coefficient of variation for %N, %C and $\delta^{15}N$ were less than 10 %.

### *Chemical analyses*

All of the data on lake water-quality was acquired from publicly available monitoring programs for Alberta (Lake Water Quality Data: http://environment.alberta.ca/; Provincial Parks Lake Monitoring Program: http://www.environnement.gov.ab.ca/info/; Alberta Lake Management Society: http://www.alms.ca). Average growing season values from these data were used in our analyses. For Quebec lakes, physicochemical variables were primarily measured at a single time point in August for all lakes when the sediment samples were originally collected (see Vermaire et al. 2011). For some of these lakes, growing season means were also available through a monitoring program (Y. T. Prairie and A. Parkes unpubl.). In order to remain consistent among regions, we ran simple least square regression models ($R^2_{adj.} > 0.60$, Tableau A.I) between single point measures from August and the growing season averages to correct for the potential differences. In a few instances, a regression model approach was also applied, ($R^2_{adj.} > 0.77$, Tableau A.I, A.II) to account for missing data in the Quebec and Alberta datasets.

### *Morphometry and land use data acquisition*

To characterise lake morphometry, landscape physiography and land use, geographic information system (GIS) techniques were applied. For Quebec lakes, lake volume was computed from bathymetric maps digitized in ESRI ArcGIS version 9.3.1. When bathymetric maps were not available, lake volume was taken from Prairie and Parks (unpubl.). For Alberta lakes, shapefiles were obtained from the Alberta Geological Survey (AGS; www.ags.gov.ab.ca) or lakes were digitized from Alberta Lake Management Society maps (ALMS; http://www.alms.ca). The digitized maps were rasterized using the nearest neighbour algorithm and lake volume was calculated following the formula provided in Kalff (2002). Area and shoreline length were directly computed in ArcGIS and all other morphometric indices were derived from these measurement. Mean depth was calculated as the ratio of volume to lake area ($V/A_0$), the index of basin permanence (IBP; Kerekes 1977) was computed as the ratio of volume in $10^6$ $m^3$ to shore line length in km ($V/L$).

Lakes watersheds were delineated using a digital elevation model (DEM). The watershed in this study is defined as the total land and water surface area draining upstream of the lake outlet minus the area of the lake itself. When the digitized bathymetric maps of the lakes were not available, the lakes' outlines from the Canadian National Topographic Database (NTDB; www.geogratis.ca) were superimposed over DEM data from the Canadian Digital Elevation Data Level 1 at a scale of 1:50 000 (CDED1; www.geobase.ca). Maximum and mean slope statistics were calculated using the computed watershed overlays on DEM data. For Alberta lakes, land coverage of different land use types was extracted as in Taranu et al. (2010) and number of buildings quantified from CanVec (CanVec; www.geogratis.ca). For Quebec lakes, the proportion of vegetation cover and number of buildings were calculated using the watershed overlay on CanVec data and the proportion of agriculture data were taken from the *Base de donnée sur les cultures généralisées* (BDCG: www.fadq.qc.ca/). To minimize distortion, all area estimates were done using the Canadian Albers equal-area conic projection. The drainage ratio was calculated as the watershed area divided by the lake area (WA:LA) and V:WA refers to the ratio of volume to watershed area.

### *Computation of anthropogenic N loading to watersheds*

The anthropogenic N load to a watershed is defined herein as the sum of N applied as fertilizer, N from human and livestock waste and N from atmospheric deposition on the watershed (referred to in the following text as anthropogenic N load). County level fertilizer expenditure and farm animal numbers were acquired from the 2006 Canadian census of agriculture (Statistics Canada 2006a,b) and the number of inhabitants from the 2006 census of population (Statistics Canada: http://www12.statcan.ca/). Spatial data describing fertilizer sales were scaled to the watershed by weighting each county by the agricultural land area included within the watershed boundaries to the total area of agricultural land of each county. For this calculation we assumed that the fertilizer sold in one county is applied within that same county. Similarly, animal and population data were scaled by weighing with fraction of land area and number of buildings, respectively. Fertilizers in dollars were converted to kg of N using provincial total amount of fertilizer and nutrient sold (Canadian Fertilizer Institute: http://www.cfi.ca/elibrary/). Livestock N excretion reported in Culley and Barnett (1984) were used to estimate the total N from manure since they best represent agricultural practices in Canada. N loaded by the human population was estimated to be 5.6 kg per individual per year (Castro et al. 2003), representative of a typical North American diet and the use of septic tanks. Atmospheric N deposition was estimated by multiplying lake and watershed area by an average N deposition rate of 8 kg N $ha^{-1}$ $yr^{-1}$ for Quebec and 4 kg N $ha^{-1}$ $yr^{-1}$ for Alberta (Schindler et al. 2006, Krzyzanowski 2010 : http://www.ccme.ca/). The atmospheric, fertilizer, livestock and population estimated N loads are all reported as kg N $yr^{-1}$.

### *Statistical analyses*

All variables were transformed (square-root or natural logarithm) prior to analysis to satisfy the assumption of normality and a multivariate Levene's test was conducted to satisfy homoscedasticity. All analyses were performed in R statistical software. Principle component analysis (PCA) was used to visualize the correlations between the different variables. Simple linear regressions were computed between $\delta^{15}N$ and each explanatory variable. Since one of our working hypotheses included a non-linear response model, polynomial regressions were also computed between $\delta^{15}N$ and each variable. Only significant polynomial terms were included as new variables into our models (volume$^2$ and IBP$^2$). A least square multiple linear regression (MLR) approach was used to explain the maximum variation in $\delta^{15}N$ ("ape" package in R). Because of high colinearity in the dataset, variables (including polynomial terms) were first screened to remove those that were highly correlated with each other. Variables with the highest adjusted $R^2$ ($R^2_{\text{adj}}$) were first selected and the variable related to the selection with an $r > 0.6$ were considered collinear and eliminated. We then ran forward selection on the pre-selected variables ("packfor" package in R) to maximize parsimony. To assess the overall difference between the two regions, a MANOVA with RDA was conducted on the isotopes and environmental data (the explanatory variables) and a binary factor coding for the regions (the response variable) using the "vegan" package in R (Legendre and Anderson 1999). To determine if variables were significantly different between regions, multiple T-tests with a Holm correction for multiple comparisons were done. Analysis of covariance (ANCOVA) was used to compare relationships (slopes and intercepts) between the two regions. Finally, variation partitioning was computed on the final predictor variables of $\delta^{15}$N to determine their relative contribution when parsing out the effect of each variable on the other (Borcard et al. 1992).

## RESULTS

### *Relationships between limnologic and morphometric variables*

Simple regression analyses across the two regions demonstrated that nutrient concentrations are the strongest predictors of $\delta^{15}$N. Dissolved phosphorus (DP) and total nitrogen (TN) were the strongest predictors of $\delta^{15}$N (respectively $R^2_{\text{adj.}} = 0.29$, $p < 0.01$, n= 65; $R^2_{\text{adj.}} = 0.32$, $p < 0.01$; Fig. 2.3A,B). Morphometric variables also explained a significant fraction of the variation whereby volume and IBP were related in a unimodal fashion to $\delta^{15}$N (respectively $R^2_{\text{adj.}} = 0.28$, $p < 0.01$; $R^2_{\text{adj.}} = 0.25$, $p < 0.01$; Fig. 2.3C,D).

Other significant relationships were found between sedimentary $\delta^{15}$N and % agricultural area ($R^2_{\text{adj.}} = 0.22$, $p < 0.01$), lake area ($R^2_{\text{adj.}} = 0.20$, $p < 0.01$) and watershed area ($R^2_{\text{adj.}} = 0.19$, $p < 0.01$) and a weaker albeit significant relationship was found with watershed slope ($R^2_{\text{adj.}} = 0.10$, $p < 0.01$; Fig. 2.3E). Although some watershed variables were significant predictors of $\delta^{15}$N, we failed to detect a significant relationship with drainage ratio and V:WA (Fig. 2.3F). Across all of our analyses, five lakes (Qc: Monts, Français, Rat-Musqué, Whitton; Ab: Wolf) were consistently below the general trends (Fig. 2.3). These lakes had the lowest $\delta^{15}$N and the highest %N in their sediments, and were amongst the shallower Quebec lakes. However, one of these lakes (Wolf lake) was among the larger and deeper lakes of the dataset but had a high %N sediment.

PCA showed the strong correlation structure among the water-quality variables. The first two PCA axes accounted for 50 % of the variance and thus variables were well represented in the reduced ordination space (Fig. 2.4A). The PCA illustrated that lakes were located on a trophic gradient with Alberta lakes being more nutrient rich compared to Quebec lakes (Fig. 2.4B). Specifically, we found that the water-quality variables (TN, DP, TP, DOC, chl*a*, pH, secchi depth) were highly correlated with each other ($r > 0.6$, $p < 0.01$). Furthermore, the water-quality variables were significantly correlated with the morphometric (e.g. watershed slope and areas as well as lake volume) and N loading variables. Because of high colinearity, only TN, lake volume and IBP$^2$ were kept for further analysis. For the sedimentary variables, only %N was kept for the MLR because of high correlation between %N and %C ($r = 0.90$, $p < 0.01$) and %N and C:N ($r = -0.61$, $p < 0.01$).

### *Total anthropogenic N load as a predictive variable*

Statistical analyses showed that sedimentary $\delta^{15}N$ varied with changes in the source of N to lakes. We quantified the total and the differential sources of anthropogenic N load to watersheds between regions. These analyses showed that N derived from livestock waste, followed by fertilizer and then atmospheric deposition were the largest N sources for Alberta lakes (Fig. 2.5A). In comparison, Quebec had lower anthropogenic N loads to its lakes (Fig. 2.5B). Across both regions, however, the sum of anthropogenic N load was found to be a significant predictor of $\delta^{15}N$ ($R^2_{\text{adj.}} = 0.23$, $p < 0.01$; Fig. 2.5C). Weaker relationships with $\delta^{15}N$ were found when each anthropogenic source was considered independently. Of particular note, we detected a negative relationship between $\delta^{15}N$ and the proportion of N from atmospheric deposition as a fraction of total anthropogenic N load (Fig. 2.5D). The negative relationship was significant but weak ($R^2_{\text{adj.}} = 0.09$, $p = 0.009$), suggesting that atmospheric N is not a dominant source affecting sedimentary $\delta^{15}N$ of all lakes.

We found that TN was significantly correlated with total anthropogenic N and was a stronger predictor of sedimentary $\delta^{15}N$ than total anthropogenic N. Specifically, we found that across all lakes 44 % of the variation in TN could be explained by total anthropogenic N ($R^2_{\text{adj.}} = 0.44$, $p < 0.01$). There was an increase in the amount of variance explained in TN by total anthropogenic N when regions were considered (ANCOVA: $R^2_{\text{adj.}} = 0.68$, $p < 0.01$; Fig. 2.5E). Using an ANCOVA of the relationship between total anthropogenic N load and TN revealed similar slopes ($F_{1,63} = 2.6$, $p = 0.11$) but significantly different intercepts ($F_{1,63}$

= 89.7, $p < 0.01$) between regions, where Alberta lakes had 2.5 mg $L^{-1}$ higher TN concentrations on average (Fig. 2.5E). Given that anthropogenic N load was strongly related to TN (as well as many other limnological and morphometric variables) and that TN was a stronger predictor of $\delta^{15}N$ compared to anthropogenic N load, we have used TN in all subsequent analyses. Interestingly, the five lowest $\delta^{15}N$ values followed the general trend between TN and anthropogenic N load (Fig. 2.5E). However, they did not follow the trend in the relationship between $\delta^{15}N$ and anthropogenic N load and removing these five sites improved the relationship ($R^2_{\text{adj.}} = 0.38$, $p < 0.01$). This result suggests that although lake TN seemed to be controlled by anthropogenic N from the watershed, the variability in the relationship between $\delta^{15}N$ and anthropogenic N load may be influenced by other processes or atmospheric N inputs leading to a $^{15}N$ depletion of the sediment.

### *Sedimentary $\delta^{15}N$ variation*

Our MLR model showed that a significant fraction of the sedimentary $\delta^{15}N$ variation could be explained by TN, %N in the sediment and morphometry. Of the 30 variables originally calculated (including polynomial terms, Tableau A.III), only 13 were included in the forward selection because of high colinearity. TN, %N from the sediments, volume and $IBP^2$ were chosen by the forward selection and our final MLR model explained 66 % of the total variation in the sedimentary $\delta^{15}N$ (Tableau II.I). The majority of the variation was explained by TN and %N in the sediment.

### *Interregional difference in response and explanatory variables*

We detected significant regional differences in the matrix of environmental data and sedimentary $\delta^{15}N$ signature (MANOVA $p < 0.05$). Strong differences were evident in the sedimentary variables with Alberta having higher %N and higher $\delta^{15}N$ than Quebec lakes (Fig. 2.6A,B). All the water-quality variables (TN, TP, pH, DP, chl*a*, secchi) reflective of lake trophic state were also higher for Alberta (Fig. 2.6C,D,E). Several lake and watershed morphometric variables also differed significantly. Specifically, Quebec lakes were smaller and shallower, although some systems had deeper basins (Fig. 2.6F,G). Likewise, the topography was different and Quebec lakes were located in smaller watersheds with steeper mean watershed slopes (Fig. 2.6H,I). Despite the differences in basin and watershed morphometries, the drainage ratio and V:WA were similar between the two regions. They were also similar in terms of population and agricultural area (Tableau A.III), however, Alberta exhibited greater agriculture intensity (Fig. 2.5A).

### *Relationships with proportion of N in the sediment*

The significant differences in the environmental data between regions resulted in stronger relationships with sedimentary $\delta^{15}N$ when regional models were compared to the cross-regional models. For example, only 15 % of the $\delta^{15}N$ variation was explained by the %N in the sediment considering all lakes ($p < 0.01$; Fig. 2.7A) but the coefficient of determination improved significantly ($R^2$adj = 0.47, $p < 0.01$; Fig. 2.7A) using the ANCOVA. Indeed, ANCOVA indicates that the intercept was significantly different between regions, where the signature was ~2.6 ‰ higher in Alberta lakes ($F_{1,63} = 40.8$, $p <$

0.01). However, the slopes were comparable for the two regions ($F_{1,63} = 0.6$, $p = 0.43$). The %N of sediments was a particularly good predictor of sediment $\delta^{15}N$ composition for Quebec lakes; when doing a simple regression across Quebec lakes alone, almost 60 % of the $\delta^{15}N$ variation was explained by %N ($R^2_{adj.} = 0.57$, $p < 0.01$). The five lakes with the lowest $\delta^{15}N$ values were located at the higher end of the inverse relationship between $\delta^{15}N$ and %N, indicating that %N is a strong determinant of their isotopic composition. Although significant relationships were found between $\delta^{15}N$ and %N and %C of sediments, there was no significant relationship with the sediment C:N ratio (Fig. 2.7B).

### *Variation partitioning*

Variation partitioning was computed independently on the two regions given the differences in average $\delta^{15}N$ observed (Fig. 2.7A). Lake volume, TN and %N in the sediments were included as possible predictors in the variation partitioning as these variables were identified to be significant and moderately independent predictors of $\delta^{15}N$ variation within each region. %N in the sediments was the single most important predictor of $\delta^{15}N$ for Quebec lakes explaining 34 % ($p = 0.05$) of the variation, with an additional 20 % of variation shared with lake volume ($p = 0.05$, Fig. 2.8A). A modest fraction of the variation in $\delta^{15}N$ was explained by TN, but this variation overlapped completely with lake volume and %N in the sediments. However, by considering total anthropogenic N load instead of TN, we found that more variation could be explained (i.e. a total of 16 %, which overlapped strongly with both volume and %N).

Conversely for Alberta lakes, TN was the single most important predictor explaining 47 % (*p* = 0.01) of the $\delta^{15}N$ variation (Fig. 2.7B). Given that the general trend between sediment $\delta^{15}N$ and lake volume was positive when the consistent outlier site was removed (Wolf Lake; Fig. 2.3C), this site was excluded in further analyses. As predictors of $\delta^{15}N$, TN and lake volume shared 12 % of the variation (*p* = 0.01). Shared variation (14 %) is also evident if we consider lake volume and total anthropogenic N load instead of TN. These results suggest that the relationship between $\delta^{15}N$ and morphometry may be driven more by an increase in N load with increasing lake size in Alberta. %N in the sediments was also important in Alberta, where the proportion of $\delta^{15}N$ variance explained was 19 % (*p* = 0.05).

## DISCUSSION

Defining the controls of sedimentary $\delta^{15}N$ variation is of primary importance for its application to paleolimnological records and identifying causes of eutrophication. Our analysis of surface sediments from 65 temperate lakes demonstrated that over a large spatial scale, N sources and concentrations are strong predictors of sedimentary $\delta^{15}N$. These findings are in agreement with spatial (Selbie et al. 2009, Bunting et al. 2010) and temporal studies (Elliott and Brush 2006, Bunting et al. 2007) of sedimentary $\delta^{15}N$ control. The anthropogenic N sources to lakes originating from agriculture activities and human waste had the same additive effect of increasing the $\delta^{15}N$ signature of lake sediments whereas atmospheric N tended to lower $\delta^{15}N$, also consistent with previous reports (Baron et al.

2000, Anderson and Cabana 2006, Bunting et al. 2007). However, in contrast to studies suggesting that changes in $\delta^{15}N$ serve as an indicator of increasing productivity and fixation by cyanobacteria (Gu et al. 1996, Gu 2009, Gu and Schelske 2010), the $\delta^{15}N$ relationship with trophic state variables was one which showed a monotonic increase. No evidence supported that fractionation during phytoplankton uptake or fixation was the causal mechanism of the observed $\delta^{15}N$ sediment signal in the lakes of these two regions. Our analysis also revealed that one of the strongest predictors of sedimentary $\delta^{15}N$ for both regions was sediment %N. Lakes with low sediment N tend to have higher $\delta^{15}N$ signatures, suggesting that fractionation during early degradation of organic matter is a factor altering the sedimentary N isotopic signature. This effect is consistent with studies on early diagenesis in oxygenated water (Saino and Hattori 1980, Altabet 1988) but other trends are found in post-burial diagenesis (Galman et al. 2009, Kohzu et al. 2011). Our analysis also showed that sedimentary $\delta^{15}N$ must be considered in a regional context.

### *The role of sources of N on sedimentary $\delta^{15}N$*

Studies on $\delta^{15}N$ distribution in ecosystems have long recognized the use of $\delta^{15}N$ natural abundance as a tracer of anthropogenic N sources (Heaton 1986, Peterson and Fry 1987). Indeed paleolimnological reconstructions often report increasing trends in $\delta^{15}N$ coincident with post-industrialisation human population growth or more intense agricultural practice (e.g. O'Reilly et al. 2005, Engstrom et al. 2006, Wu et al. 2008). To date, however, a rigorous analysis of the controls of $\delta^{15}N$ across temperate lakes has been lacking. Our analysis confirmed that there was a relationship between the anthropogenic N load and sediment $\delta^{15}N$. The total anthropogenic N load to watersheds was a good predictor of $\delta^{15}N$ although TN and DP concentrations were the best predictors (Fig. 2.3A,B, 4B). TN was itself highly correlated to N anthropogenic load suggesting it was controlled by this N source (Fig. 2.5E).

Our work complements earlier time series analyses that have linked changes in N source to variation in $\delta^{15}N$, but provides a more generalized framework because we have looked at trends across many lakes. A strong example of a temporal analysis is provided by Elliott and Brush (2006) who reported that 86 % of the sedimentary $\delta^{15}N$ variation was explained by wastewater N load. Such temporal studies typically have higher predictive power than our spatial model but require long-term time series data on N-loading. Furthermore, it is only once many temporal studies are completed that one can start to parse out general patterns. Our analysis of anthropogenic N load could be refined as we did not take N loss on the watershed into account. A full mass balance of N loading requires detailed information of all N inputs to the watershed (fertilizer N, net import of N in agricultural product, biological N fixation, atmospheric deposition) as well as N outputs (riverine export or estimation of the loss of N by denitrification) (Boyer et al. 2002); unfortunately these data were not available. Certain models accounting for N loss terms have achieved high predictive power when applied to $\delta^{15}N$ sediment time series; Savage et al. (2010) and Bunting et al. (2007) reported an $R^2$ of 0.57 and 0.92 respectively. In our analysis of N load, we did not account for N losses and biological N fixation and yet we are still able to account for 23 % of $\delta^{15}N$ sediment variation over space. When we removed the five outlier sites affected either by atmospheric N or some other mechanism, the proportion explained increased to 38 %.

The negative albeit weak relationship observed between the proportion of %N atmospheric deposition and $\delta^{15}N$ also indicates that there is a possible mixing effect between multiple N sources to the study systems. Indeed, atmospheric N typically has low to negative $\delta^{15}N$ values. For example, Kendall et al. (2007) have reported atmospheric $NO_3^-$ $\delta^{15}N$ values across United States to be between -11‰ to +3.5‰. Thus increasing the relative importance of atmospheric inputs may increase TN load but wouldn't necessarily result in an increase in sedimentary $\delta^{15}N$ signature due to mixing.

### *Limitations of the use of $\delta^{15}N$ as an indicator of productivity*

Our analysis failed to support the hypothesis that sediment $\delta^{15}N$ was driven by changes in phytoplankton N assimilation and fixation along a trophic gradient as outlined in Fig. 2.1C. In addition to the lack of consistency between this response model and our isotopic data, our analyses of water chemistry and other studies support this conclusion. For example, we detected significant negative relationships between N:P in TP in both regions, indicative of a declining contribution of N to the total nutrient pool when fertilizer, sewage and animal manure, as well as internal loading are the predominant nutrient sources (Downing and McCauley 1992). These data suggest that N limitation is possible (Pick and Lean 1987), and yet we failed to detect a significant relationship between sediment $\delta^{15}N$ and the N:P ratio, which would be expected if N-fixation were the dominant process operating in lakes with low N:P. In terms of N fractionation by phytoplankton, other studies have only observed this effect in oligotrophic lakes, where negative relationships were apparent between sediment $\delta^{15}N$ and water column $NO_3^-$ concentration (Owen et al. 1999, Teranes and Bernasconi 2000). These observations were possible because of incomplete assimilation of the $NO_3^-$ pool by phytoplankton and according fractionation following Rayleigh kinetics. Lehmann et al. (2004) made the same observation for Lake Lugano in years of low $NO_3^-$ concentrations but suggested that in eutrophic lakes $\delta^{15}N$ mainly reflects N loading from the watershed. Furthermore, Teranes and Bernasconi (2000) found good relationships between $NO_3^-$ concentration and sediment $\delta^{15}N$ only from summer and fall sediment strata. In lakes without lamination, the mixing of summer and winter sediment deposition, more strongly influenced by allochtonous N and heterotrophic production (Hodell and Schelske 1998), would likely dilute this effect. Since sediments are an integrator of functional, spatial and temporal variation of lake organic matter, paleolimnological reconstruction looking at the effect of nutrient utilization by phytoplankton should also consider alternate hypotheses and thus include information on the N loading histories of the study systems.

### *Potential effect of diagenesis on sedimentary $\delta^{15}N$*

Our study revealed that there is an effect of the proportion of N in sediments on the sedimentary $\delta^{15}N$ signature across both regions where we observed that lake sediments with low %N tended to have higher $\delta^{15}N$. Bunting et al. (2010) found the same relationship in surface sediments of 75 lakes from the Rocky Mountains in Alberta ($R^2 = 0.45$). The consistency of this relationship in diverse lake systems across Canada suggests that it is a common feature of temperate lakes, although very few studies report it either because %N was not measured or included as a predictive variable of sediment $\delta^{15}N$.

The spatially consistent relationship between %N and sediment $\delta^{15}N$ strongly supports that nitrogen consumption by bacterial degradation during sedimentation can significantly alter sedimentary $\delta^{15}N$. During early diagenesis, primary organic matter is consumed by bacteria and a low proportion of this organic matter reaches the sediment surface (Meyers 1997). Many marine sediment studies associated the bacterial degradation of phytoplankton to increased $\delta^{15}N$ of the residual organic matter (Saino and Hattori 1980, Altabet 1988, Altabet and Francois 1994, Freudenthal et al. 2001). The causal mechanism was assumed to be the preferential release of $^{15}N$-depleted dissolved N from bacterial metabolism. In an incubation experiment, Lehmann et al (2002) showed that the increased in $\delta^{15}N$ of the particulate organic matter (POM) during the first 30 days was related to oxidative degradation. Similarly, the observed negative relationship between morphometry and %N in Quebec lakes suggest that oxygenation is an important factor of $\delta^{15}N$ shift during early diagenesis. Larger and deeper lakes will have particles residing longer in the water column and more prone to oxidative degradation compared to shallow lakes with a more rapid sediment burial and shorter exposure to oxidation in the water column (Meyers and Ishiwatari 1993). Furthermore, oscillation between oxic and anoxic conditions in the water column of large and deep lakes can increase the average $\delta^{15}N$ signature of the POM as observed in Lake Kinneret (Hadas et al. 2009). By contrast, shallow lakes are typically more productive systems with anoxic sediments, which are both factors that could lead to better preservation of the organic matter (Sachs and Repeta 1999). Studies have shown that anoxic degradation can produce a $^{15}$N-depletion of the sediment organic matter $\delta^{15}N$ (Libes and Deuser 1988, Lehmann et al. 2002). Such effects in the anoxic sediment of shallow lakes would reinforce the negative relationship between $\delta^{15}N$ and %N.

Although our spatially explicit analysis suggested that early diagenesis is an important determinant of $\delta^{15}N$ from surface sediment, we cannot claim that this trend would be transposed through time based on our study alone. Studies comparing multiple cores taken at different years showed that diagenesis tended to lower sediment $\delta^{15}N$ with aging (Galman et al. 2009, Kohzu et al. 2011). Kohzu et al. (2011) also showed that there was a $^{15}$N-enrichment of surface sediment but that the decreasing $\delta^{15}N$ trend occurred below 3cm, probably at the oxidation-reduction boundary. Our increasing sedimentary $\delta^{15}N$ with low sediment %N would thus reflect early diagenesis in oxygenated waters.

### *Regional effect on sedimentary $\delta^{15}N$*

A combined analysis using TN, %N in the sediments and morphometry showed that these variables were excellent predictors of sediment $\delta^{15}N$ across the entire dataset, but the variation partitioning showed strong differences in sedimentary $\delta^{15}N$ between Quebec and Alberta (Fig. 2.8A,B). Quebec $\delta^{15}N$ was strongly explained by consumption of N during early diagenesis whereas Alberta sediments were more controlled by N load. The lack of a significant relationship between $\delta^{15}N$ and TN could be explained by the relatively low N loading to Quebec lakes (Fig. 2.5B) and/or the mixing of $^{15}$N depleted N from atmospheric deposition in this region where deposition rates are amongst the highest in Canada (Schindler et al. 2006). Furthermore, agriculture in Southern Quebec is dominated by growth of feed for livestock and these crops often include alfalfa, a known N fixer that could also lower the $\delta^{15}N$ of incoming N to lakes. Unfortunately detailed spatial data on crop type were not available (BDCG: www.fadq.qc.ca/). Differences between regions suggest that sedimentary $\delta^{15}N$ variation is dependent on local processes and nutrient sources to lakes.

### *Recommendations for paleolimnological reconstruction*

Paleolimnological reconstructions are powerful tools to understand eutrophication histories in lake systems. Increasing $\delta^{15}N$ shifts in recent times have occasionally been explained by fractionation during phytoplankton assimilation. Our study highlights that $\delta^{15}N$ is also a source indicator and knowledge of N sources are prerequisites to the interpretation of sediment record in lakes. Furthermore, our work shows that sedimentary $\delta^{15}N$ should be considered in a regional context, where knowledge of the isotopic signature of the major N sources is critical. Our study also points out that there should be careful interpretation of upper sediment signatures that can be subjected to early diagenesis in oxygenated waters. We recommend the examination of the %N profile to determine the depth at which %N is more constant, indicative of reduced bacterial consumption. Furthermore, a negative relationship between %N and $\delta^{15}N$ in the first centimeters of a sediment core could also be used to assess this diagenesis effect. Given the multiple factors that influence it, sedimentary $\delta^{15}N$ should thus be used as part of a multiproxy approach, in conjunction with proxies of algal community composition such as fossil pigments and of the organic matter sources such as sediment C:N ratio to assess changes in N sources and productivity over time.

## TABLES AND FIGURES

Tableau II.I: Least squares multiple linear regression (MLR) results with forward selection using permutation test to model sediment $\delta^{15}$N

| Significant explanatory variables | Standardized coefficient | Collinear variables ($r \geq 0.6$) | Collinear variables ($0.4 \leq r < 0.6$) | $p$ value (two-tail) | $R^2$ adj. |
|---|---|---|---|---|---|
| TN (ln) | 0.52 | TP (ln)<br>DP (ln)<br>DOC (ln)<br>Chla (ln)<br>secchi depth (√)<br>pH (ln)<br>fertilizer N (ln)<br>anthropogenic N load (ln)<br>max slope (ln)<br>mean slope (ln)<br>shore length (ln)<br>lake area (ln) | % agriculture area (ln(x+1))<br>watershed area (ln)<br>lake volume (ln)<br>livestock N (ln)<br>IBP(ln)<br>atmospheric N (ln) | 0.001 | 0.66 |
| %N sediment (√) | -0.59 | %C sediment (√)<br>C:N (√) | | 0.001 | |
| Volume (ln) | 0.27 | pH (ln)<br>anthropogenic N load (ln)<br>watershed area (ln)<br>mean slope (ln)<br>max depth (ln)<br>mean depth (ln)<br>shore length (ln)<br>lake area (ln)<br>IBP (ln)<br>atmospheric N (ln) | TN (ln)<br>TP (ln)<br>DP (ln)<br>DOC (ln)<br>anthropogenic N load (ln)<br>fertilizer N (ln)<br>population N (ln)<br>livestock N (ln)<br>V:WA (ln) | 0.008 | |
| IBP^2 (ln) | -0.20 | volume^2 (ln) | | 0.011 | |

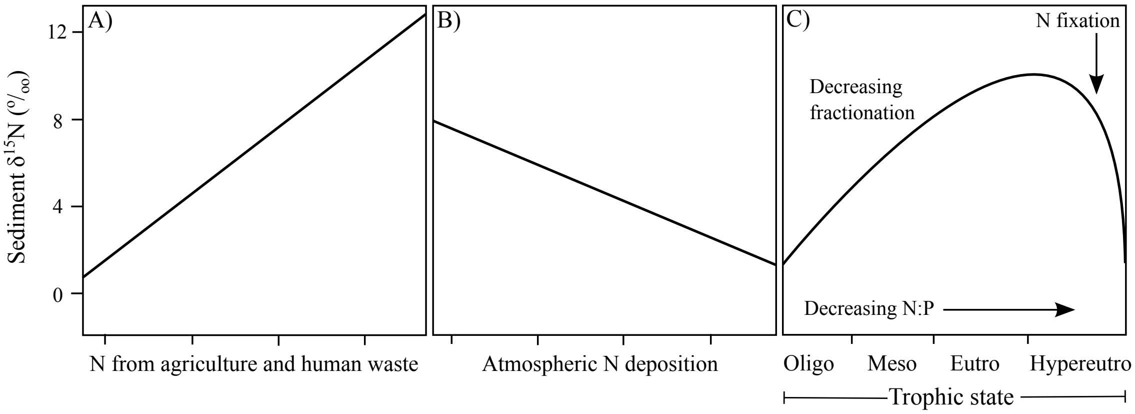

Figure 2.1: Conceptual diagram showing different processes and their hypothetical effect on sediment $\delta^{15}N$. A) The dominant N sources from agriculture (fertilizer and manure) and human wastes would act to increase the $\delta^{15}N$ sedimentary signature. B) The dominant source from atmospheric N deposition would tend to lower the sediment $\delta^{15}N$. C) Effect of phytoplankton fractionation during assimilation on sediment $\delta^{15}N$ at different trophic state. Expected sediment $\delta^{15}N$ range in ‰ are approximated from Leavitt et al. (2006), Bunting et al. (2007), Elliott and Brush (2006), Jones et al. (2004) and Gu et al. (1996).

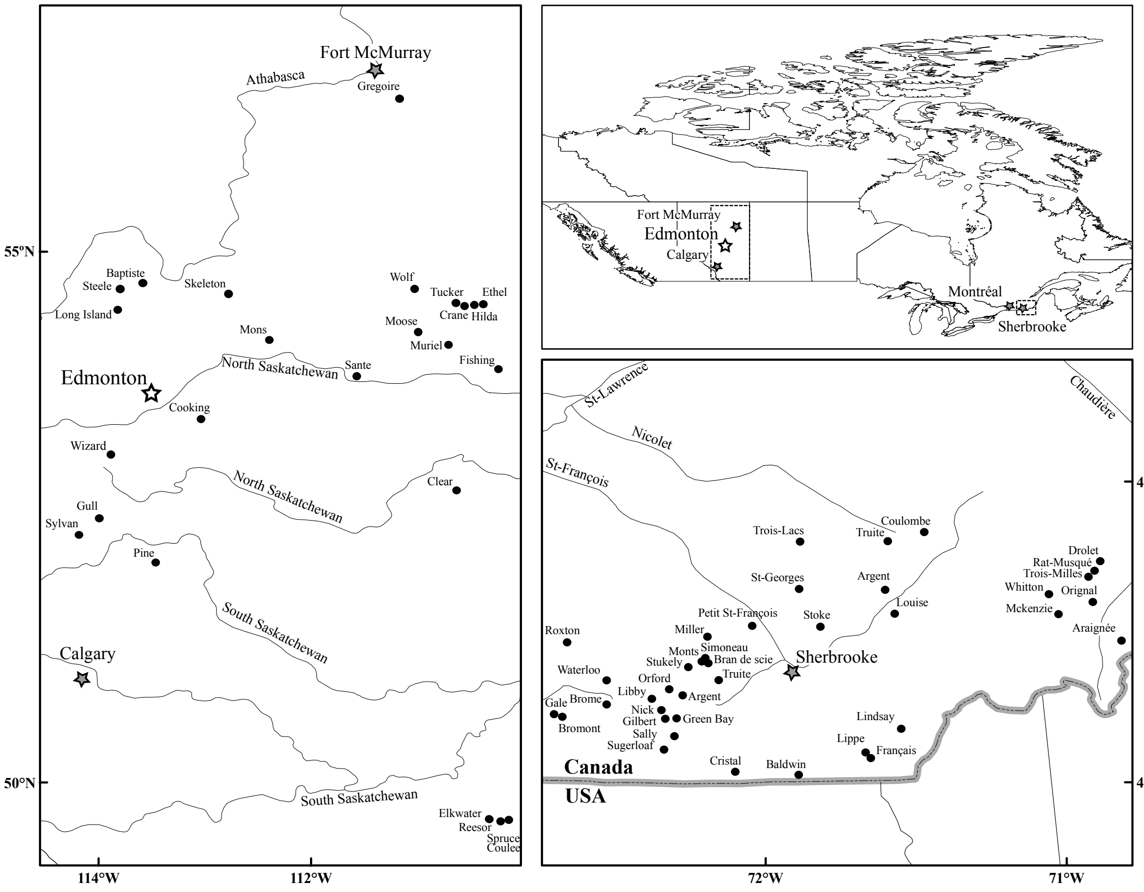

Figure 2.2: Map of the study sites and the major river systems from Southern Quebec and Alberta provinces of Canada. Region location presented in inset.

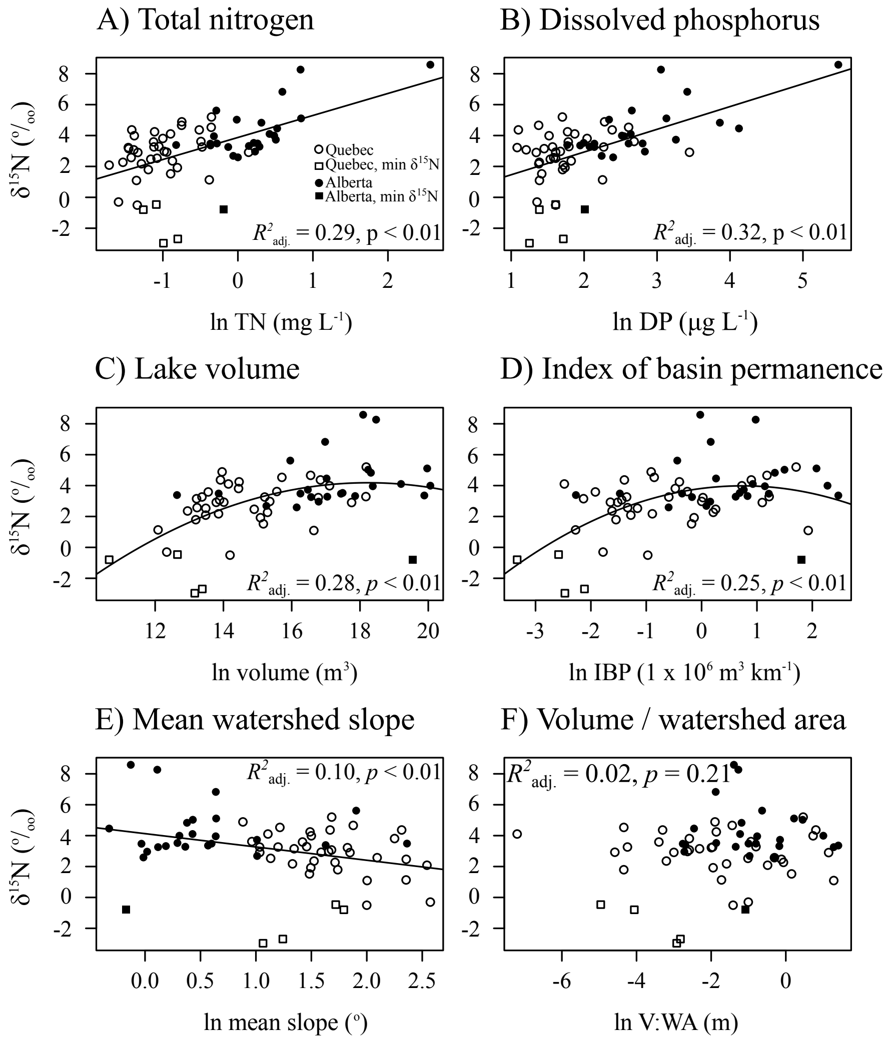

Figure 2.3: Relationships between $\delta^{15}N$ and A) total nitrogen (mg $L^{-1}$), B) dissolve phosphorus (µg $L^{-1}$), C) lake volume ($m^3$), D) index of basin permanence (IBP; 1 x $10^6$ $m^3$ $km^{-1}$), E) mean watershed slope (°), F) volume / watershed area (m). Open circles (squares) are Quebec sites and full circles (squares) are Alberta sites. Sites in squares are extreme values of $\delta^{15}N$ and systems with highest %N in their sediments. Simple regression analysis of our data yielded the following equations A) $\delta^{15}N = 1.43 \ln TN + 3.87$; B) $\delta^{15}N = 1.47 \ln DP - 0.01$; C) $\delta^{15}N = 3.41 \ln volume - 0.09 \ln volume^2 - 26.92$; D) $\delta^{15}N = 0.45 \ln IBP - 0.30 \ln IBP^2 + 3.82$; E) $\delta^{15}N = -0.86 \ln mean\ watershed\ slope + 4.13$.

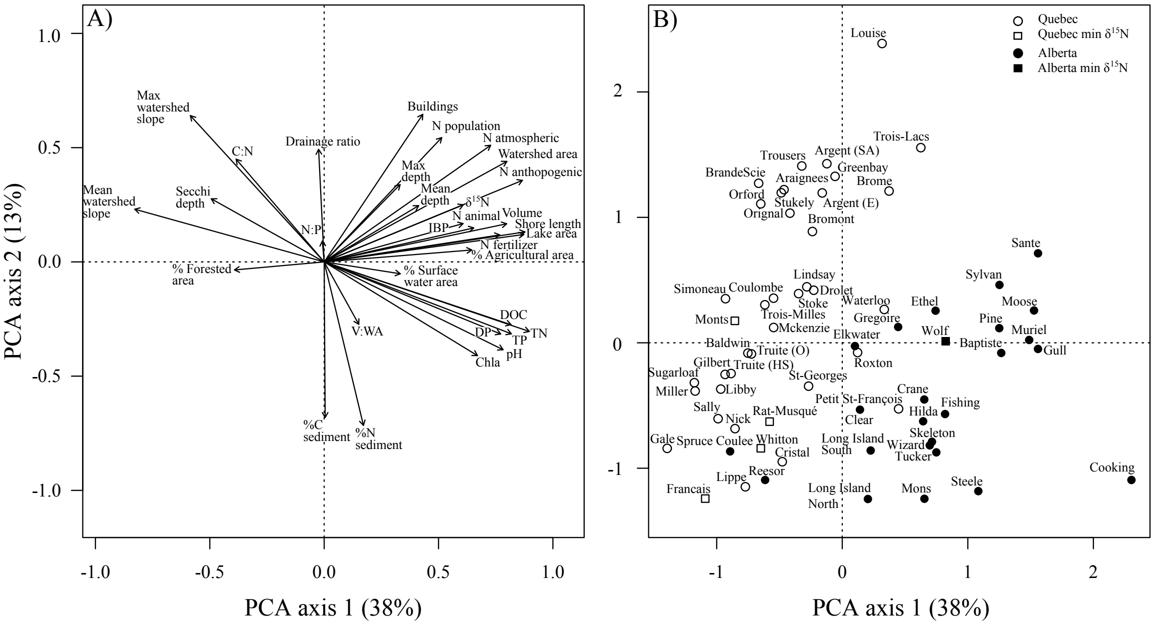

Figure 2.4: Principal component analysis (PCA) of the environmental data including nitrogen stable isotopes, scaling type 2. First axis explains 38 % of the variation and second axis 13 %. A) Environmental variables: angles between arrows are proportional to the correlations between variables. Shorter arrows are variables that contribute less to the formation of the reduce space; angles in that case are less representative of correlations. B) Sites scores: sites in squares are extreme values of $\delta^{15}$N and systems with highest %N in their sediments.

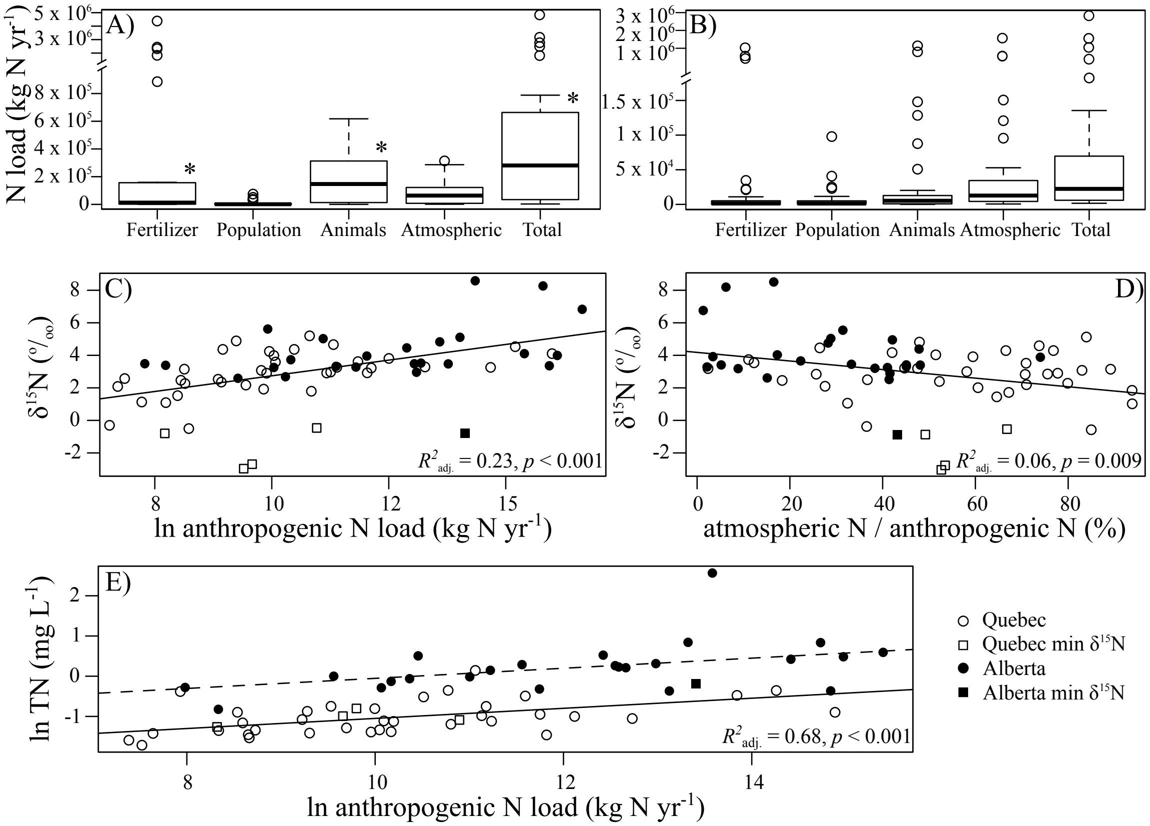

Figure 2.5: Relationships between $\delta^{15}$N, anthropogenic N watershed load and total nitrogen concentrations in lakes. A) Box and whisker diagrams representing the difference between the type and amount of N applied in the watersheds for Alberta and B) for Quebec. Solid horizontal line within each box indicate regional mean. Box boundaries represent 25th and 75th and whisker extent represent 10th and 90th percentiles. Dots represent values outside of the 10th and 90th percentiles, * indicates that the variable is significantly higher for Alberta than Quebec ($p < 0.001$). Notice the truncated axis and the different y axis scale for the two regions. C) Relationship between $\delta^{15}$N and anthropogenic N load to watershed (kg N yr$^{-1}$). D) Relationship between $\delta^{15}$N and atmospheric N divided by the total anthropogenic N load (%). E) ANCOVA between total nitrogen (mg L$^{-1}$) and total anthropogenic N load to watershed for the two regions (kg N yr$^{-1}$). For C), D) and E) sites in squares are extreme values of $\delta^{15}$N and systems with highest %N in their sediments.

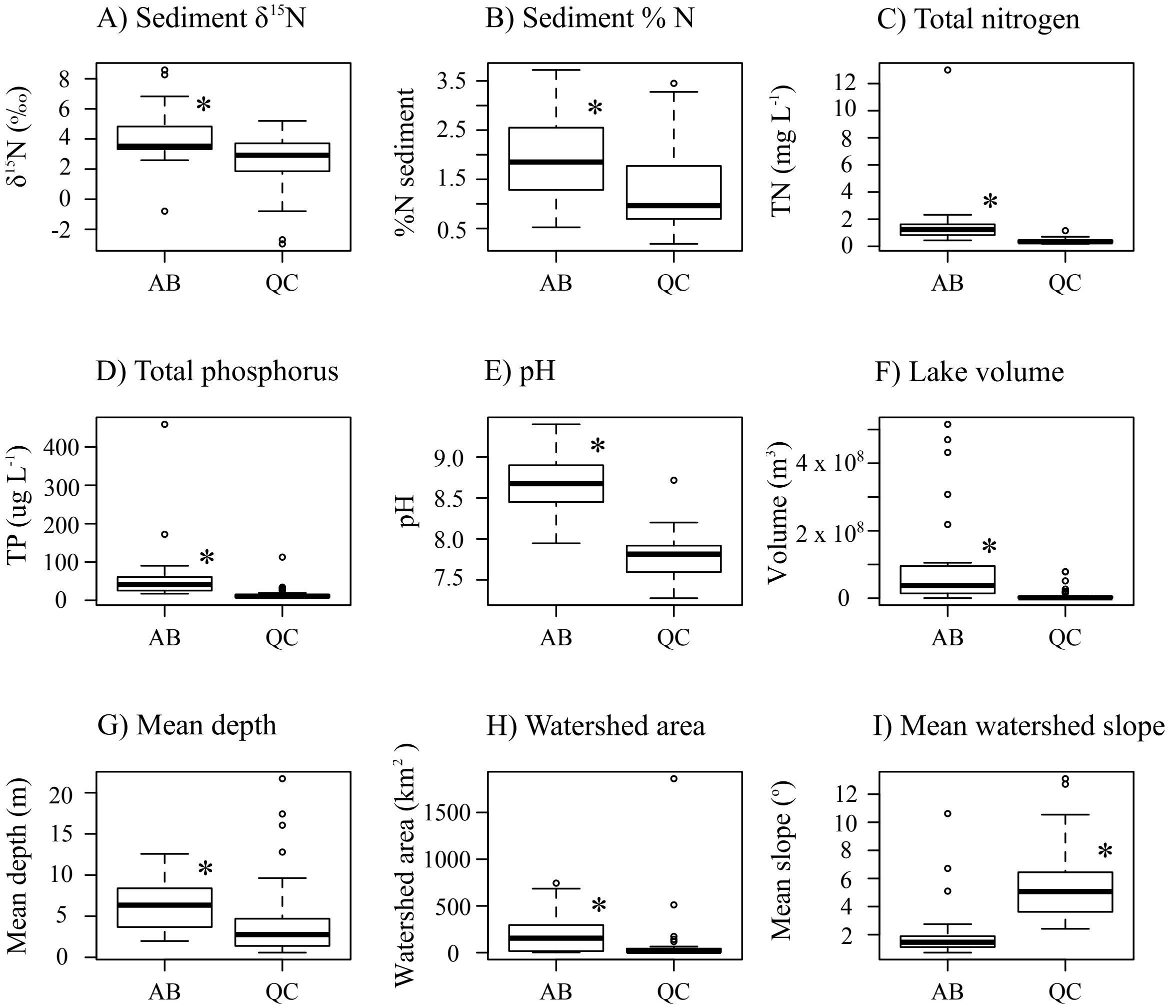

Figure 2.6: Box and whisker diagrams of selected variables representing differences between the two study regions, Alberta (AB) and Quebec (QC). Solid horizontal line within each box indicate regional mean. Box boundaries represent 25th and 75th and whisker extent represent 10th and 90th percentiles. Dots indicate sites exhibiting values outside of the 10th and 90th percentiles. Significance between regional means was assessed using t-test with Holm correction for multiple tests; * denotes variables significantly higher at level $p < 0.001$.

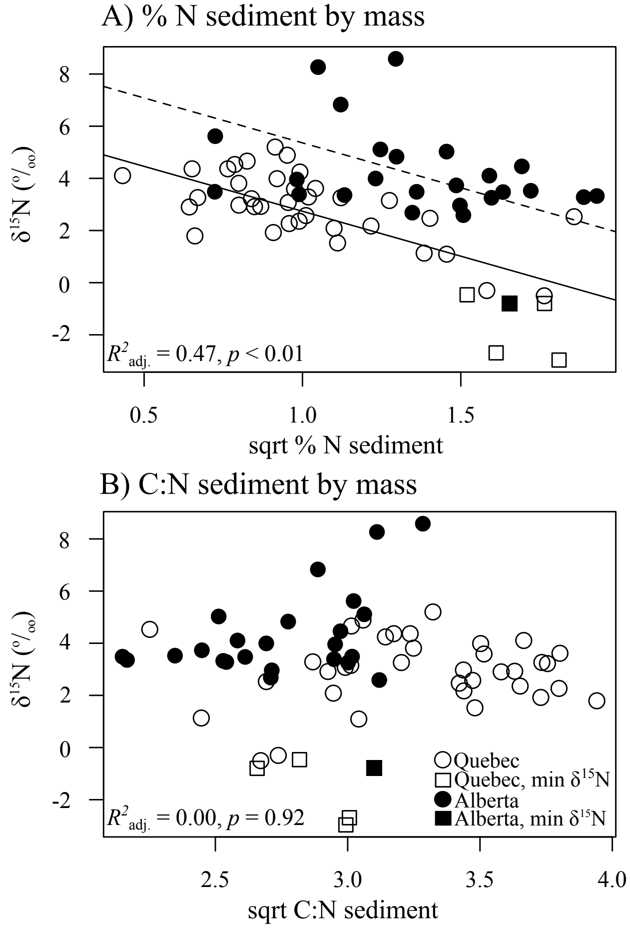

Figure 2.7: Relationships between $\delta^{15}$N and A) %N from sediment by mass and B) C:N from sediment by mass. ANCOVA showed that the slopes of %N vs $\delta^{15}$N between the two regions are not different but that the intercepts are significantly different. The overall relationships were the following: Quebec $\delta^{15}N = -3.44 \ln \%Nsed + 6.18$; Aberta: $\delta^{15}N = -3.44 \ln \%Nsed + 8.81$. Open circles (squares) are Quebec sites and full circles (squares) are Alberta sites. Sites in squares are extreme values of $\delta^{15}$N and systems with highest %N in their sediments.

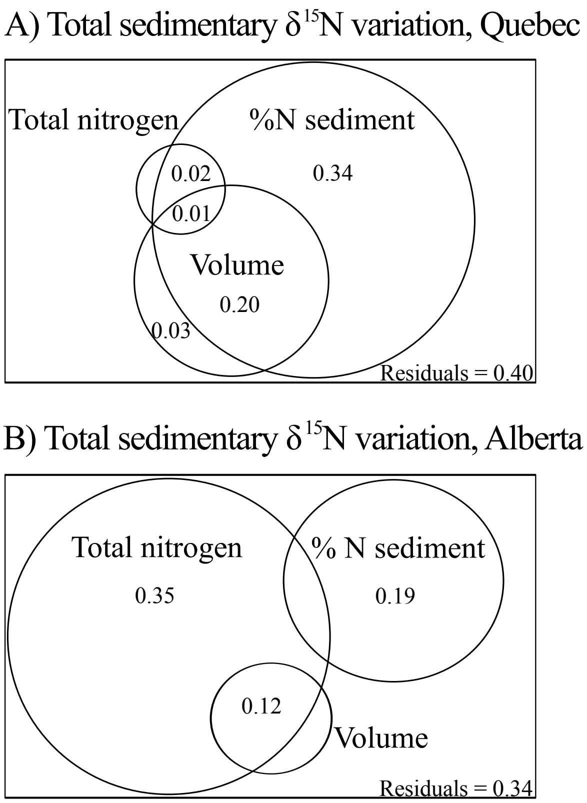

Figure 2.8: Variation partitioning of the variables selected by forward selection. A) Total sedimentary $\delta^{15}N$ variation for Quebec, B) Total sedimentary $\delta^{15}N$ variation for Alberta. Wolf lake was removed for the Alberta variation partitioning.

## ACKNOWLEDGMENTS

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# Chapitre 3 : Isotopic evidence for nitrogen cycling in three shallow lakes

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## ABSTRACT

Nitrogen (N) inputs to freshwater ecosystems have dramatically increased in recent decades altering the biogeochemical cycling of N. The use of multiple natural abundance stable isotopes on dissolved N species in water and suspended particulate organic matter (SPOM) may permit a better understanding of dominant N sources and biogeochemical processes transforming N in these systems. Here, we apply this technique to three small and shallow temperate lakes on a trophic gradient and with different mixing regimes. We measured the variation in the seasonal nutrient concentrations ($NO_3^-$, $NO_2^-$, $NH_4^+$, DON, TN) and stable isotopes ($\delta^{15}N$, $\delta^{13}C$, $\delta^{18}O$) from the SPOM, nitrate ($NO_3^-$) and dissolved organic N (DON). Inlets were also sampled to determine the average isotopic signature entering the system using a mixing model. Seasonally the stable isotopic signatures of the SPOM and the DON were relatively invariable compared to the $\delta^{18}O$ and $\delta^{15}N$ of $NO_3^-$ that increased during summer. The analysis of the SPOM indicates that the nitrogen stable isotope signature ($\delta^{15}N$) track phytoplankton nutrient assimilation in our dimictic lake whereas the polymictic lakes appear to be more influenced by external inputs of organic matter or sediment resuspension. In the dimictic lake, our analysis of dual nitrate stable isotopes ($\delta^{18}O$, $\delta^{15}N$) revealed a deviation from the 1:1 relationship suggesting that nitrification is an important process regulating nitrate concentrations in this system during the growing season. Although a challenge to interpret given dynamic external and internal inputs to small and shallow lakes, the use of natural abundance stable isotopes of different N forms is a promising technique in the interpretation of N cycling dynamics.

## INTRODUCTION

In recent decades, human activities such as fertilizer use and fossil fuel combustion have greatly increased the amount of bioavailable N circulating in the biosphere resulting in widespread ecosystem degradation (Galloway et al. 2008). As such, high concentrations of nitrate ($NO_3^-$) are considered toxic and can promote eutrophication and acidification of surface waters (Nestler et al. 2011). Increasing concentrations of reduced N forms ($NH_4^+$-ammonium, $(NH_2)_2CO$ -urea) are also known to stimulate non-$N_2$-fixing cyanobacteria biomass and toxin production (Blomqvist et al. 1994, Finlay et al. 2010). In freshwater systems, there is growing evidence that elevated N concentrations are a better predictor of cyanobacteria toxicity than phosphorus (P) (Giani et al. 2005). However, there is a poor understanding of the underlying N processes that can control the availability of these nutrients. Indeed, the N cycle is characterised by removal and regeneration of the various chemical N forms by bacterially mediated processes.

The identification of dominant processes and N sources can be provided by the application of a multiple natural abundance stable isotopic approach. Compared to rate incubation experiments, the measurement of natural abundance stable isotopes has the advantage of avoiding sample manipulation or addition of exogenous nutrient tracers that can bias measured rates. Furthermore it provides a more ecosystem scale understanding of the dominant sources and internal processing (e.g. Hadas et al. 2009). The nitrogen stable isotope signature ($\delta^{15}N$) of seston and different nutrients has been widely used in ecological studies (Heaton 1986, Robinson 2001), however overlapping $\delta^{15}N$ signatures of different sources can limit the interpretation of N fluxes and pathways involved (Bedard-Haughn et al. 2003). The simultaneous measurement of $\delta^{15}N$ and carbon stable isotopes ($\delta^{13}C$) from the organic matter or of the $\delta^{15}N$ and the oxygen stable isotopes ($\delta^{18}O$) of nitrate ($NO_3^-$) can help elucidate and constrain the main primary producers, organic matter and nutrients sources and microbial cycling pathways (Finlay and Kendall 2007, Casciotti et al. 2011). Such an approach has been mostly developed in oceans (Casciotti et al. 2008, DiFiore et al. 2009), internal seas (Finlay et al. 2007, Kumar et al. 2011), deep lakes (Hadas et al. 2009) and rivers (Kendall et al. 2007, Deutsch et al. 2009, Kendall et al. 2010). The application of a multiple stable isotopes approach is of particular interest in small lakes systems (~1 km$^2$ surface area) since they are among the most common freshwater systems (Downing et al. 2006), are heavily impacted by N pollution (Carpenter et al. 1998) and serve as important water supply and recreational sites. To our knowledge, studies using such an approach in small and typically shallow lakes are to date lacking.

The use of $\delta^{15}N$ from the suspended particulate organic matter (SPOM) has been used in the past as an index of nutrient availability and utilization by phytoplankton (Altabet and Francois 1994, Kumar et al. 2011). Mass dependent fractionation typically causes a $^{15}N$-enrichment of the substrate (e.g. nutrients) and a $^{15}N$-depletion of the instantaneous product (e.g. phytoplankton). There is eventually a progressive $^{15}N$-enrichment of both N pools, which occurs when nutrient concentrations are decreasing. This effect can be modelled by Rayleigh fractionation kinetics and the inverse relationship between $\delta^{15}N$ of SPOM and nutrient concentrations (Teranes and Bernasconi 2000, Lehmann et al. 2004a). A low $\delta^{15}N$ of SPOM can also be interpreted by increasing importance of $N_2$ fixation ($N_2$ = ~0 ‰)

(Patoine et al. 2006). However, when phytoplankton is not an important fraction of the seston, the use of $\delta^{13}C$ and C:N ratio can help identify the dominant organic matter sources (Finlay and Kendall 2007).

Recent developments of $NO_3^-$ dual isotopes measurements have allowed the precise and rapid quantification of $\delta^{15}N$ and $\delta^{18}O$ at low $NO_3^-$ concentration (~ 0.5 µM) (Sigman et al. 2001, McIlvin and Altabet 2005). This powerful tool permits the assessment of the differential fractionation effects on both isotopes, which varies as a function of the dominant *in situ* N cycling processes in the system. The magnitude of the fractionation is expressed by ε, which represents the difference in the isotopic composition of the substrate and the instantaneous products. Culture studies have shown that there is a coupled fractionation effect of both isotopes during $NO_3^-$ assimilation and denitrification whereby the water column $NO_3^-$ $\delta^{15}N$ and $\delta^{18}O$ are simultaneously enriched with a $^{18}\varepsilon$:$^{15}\varepsilon$ ratio of 1 (Granger et al. 2004, Granger et al. 2008). Other processes such as nitrification can be interpreted as decoupled given the different N and O sources and resulting fractionations observed during this microbial process. The N atom of nitrified $NO_3^-$ comes from remineralized $NH_4^+$ and is likely $^{15}N$-depleted because of the high fractionation effect during nitrification ($\varepsilon$ = 15-35 ‰) (Robinson 2001). The oxygen (O) atoms however come mostly from the oxygen of the water and are affected by fractionation during ammonia oxidation and nitrite reduction, the two steps involved in nitrification (Buchwald and Casciotti 2010, Casciotti et al. 2010). Thus the deviation of $\delta^{15}N$ and $\delta^{18}O$ from the 1:1 fractionation relationship expected from assimilation or denitrification can be use to assess the relative importance of consumption (assimilation or denitrification) vs. production (nitrification) of $NO_3^-$ (Sigman et al. 2005, Wankel et al. 2007). In turn, given that assimilation and denitrification are processes conducted at different oxygen levels and that benthic denitrification does not have an effect on water column $NO_3^-$ isotopic signature (Sebilo et al. 2003, Brandes and Devol 1997), the occurrence of one of these processes in lake can be determined based on the sample location in the water column (e.g. epilimnion vs hypolimnion).

In riverine systems, the dual isotopes of $NO_3^-$ are typically used to determine the dominant sources of $NO_3^-$ (e.g. Pardo et al. 2004, Anisfeld et al. 2007, Barnes and Raymond 2010). The oxygen isotopes of $NO_3^-$ are particularly useful in constraining such sources. For example, $NO_3^-$ from the atmosphere, fertilizer and nitrification have a distinct $\delta^{18}O$ signature (63 to 94‰, 17 to 25‰ and -15 to 15‰ respectively) compared to their overlapping $\delta^{15}N$ signatures (-15 to 15‰, -4 à 4‰ and -10 to 25‰ respectively) (Finlay and Kendall 2007, Nestler et al. 2011).

Due to their typically short water residence time, small shallow lakes can be viewed as intermediate sites between rivers and lakes systems. Given their highly dynamic nature, a first step in the application of natural stable isotopes to N cycling in shallow lakes is the evaluation of the isotopic seasonal variation. As such, our objectives are to compare the temporal stable isotopic variation of SPOM and nutrients from three shallow lakes of different trophic status and with different morphometric features. We first want to test if the use of the stable isotopes from the SPOM can be use to understand its source and infer the dominant primary producer assimilation pathways. We also want to explore the use of the stable isotopes from the nutrients to assess their source and cycling. In particular, we used the dual isotopes of $NO_3^-$ ($\delta^{15}N$ and $\delta^{18}O$) to understand the relative importance of production vs. consumption of $NO_3^-$. We also report here the first measurements to our knowledge of $\delta^{15}N$ from the dissolved organic nitrogen (DON) in shallow lakes.

## METHODS

### *Study sites*

To compare the importance of N sources vs. processes on the isotopic signature of SPOM and $NO_3^-$ at different nutrient levels, three lakes of different status were chosen (Table III.I). Since the sites were part of a broader study looking at factors influencing cyanobacteria in lakes, they were also chosen for their phytoplankton communities dominated by cyanobacteria. The three lakes are located in the province of Quebec, Canada north of the Vermont border, USA (Fig. 3.1A) in the Appalachian Orogen region characterised by metamorphic and sedimentary rock remodelled by glacial erosion (Occhietti 1989). Common to all lakes is the presence of dams that artificially control the discharge of the outlets. Likewise, all of our study lakes are quite similar in terms of lake and catchment surface area, but differ in terms of basin shape and watershed land use (Table III.I).

Lake Bromont is a mesotrophic lake (average epilimnetic summer TP: 28.9 $\mu g\ L^{-1}$) located in a small and mountainous watershed. It is our deepest lake (max depth: 7.5m), but due to its relative shallowness, only epilimnion and metalimnion strata are present throughout the summer, with a thin hypolimnion present from early august until fall turn over. Bromont watershed is mainly forested (72%), but there is a ski hill and a concentration of residential properties around the lake and in the nearby Bromont town (Fig. 3.1B). Most of the residences are connected to a sewage system (Ville de Bromont 2011). Agricultural lands cover 7% of the watershed and are primarily dedicated to the production of feed for livestock or livestock production.

Lake Waterloo is a eutrophic (average summer TP: 39.3 μg $L^{-1}$) and polymictic lake (max depth: 4.8m). It has the highest water residence time (116 d) compared to the faster flushing of lake Bromont and Petit St-François (respectively 39.4 d and 21.9 d). Waterloo watershed contains the highest human population densities amongst our three lakes (reaching 157 people per $km^2$) and contains substantial commercial and industrial developments. Similar to Bromont, much of the agricultural lands in the watershed (10%) are dedicated to livestock production and growth of feed for the animals (Fig 3.1D). Efforts have been made to reduce external nutrient loads to the lake through the establishment of a wastewater treatment plant in the city of Waterloo in the 1980's, however, nutrients released from septic fields are a source in some regions. The presence of a golf course has also been pointed out as an important source of nutrients to the lake (DESSAU 2008).

Lake Petit St-François (PSF, also named Tomcod) is a hypereutrophic (average summer TP: 210.8 μg $L^{-1}$), polymictic and our shallowest lake (max depth: 1.8m). There are numerous signs that human activities have heavily modified nutrient cycles in this watershed. For example, the PSF watershed has the largest agricultural area (22% of the watershed, Fig. 3.1C) and the form of agriculture is nutrient intensive with the cultivation of cereals (corn, oat, soya and fodder) (BDGC: http://www.fadq.qc.ca/). Furthermore, the nearby town of St-François-Xavier de Brompton is an important population centre (population: 2079). Most of the residences within the town and in the surrounding area are probably connected to the sewage network established in the 1990s (Gouvernement du Québec: http://www.mamrot.gouv.qc.ca/).

### *Lake sampling and water collection*

To cover seasonal variation, lakes were sampled eight times between April 2010 and October 2010. To capture winter conditions, lakes were also sampled under ice in February 2011. For most sampling dates, we collected integrated water column samples for nutrient and isotopes analyses in duplicate from the deepest point of the lake and transferred these water samples into acid-cleaned, tripled-rinsed 4L polyethylene bottles. When Lake Bromont was stratified, discrete metalimnion and hypolimnion samples were collected using a horizontal 4L Van Dorn bottle. During the winter sampling, water was collected using a polyethylene bottle attached to a stick and plunged underneath lake ice to obtain a sample of mid-lake depth.

The major lake inlets and the outlets were sampled in April, May, June, July, August and October. Water was collected at each site for nutrient and isotope analysis ($\delta^{15}$N of TDN, DON, $NH_4^+$, $NO_3^-$ and $\delta^{18}$O of $NO_3^-$) with care to prevent any sediment perturbation. The flow velocity was measured at each 0.5m of the streams cross section using a Pygmy current meter as described in Harrelson et al. (1994). In periods of minimum flow, the velocity was estimated by measuring the average time a float took to travel down 2m and corrected by applying a friction factor for rocky bottoms of 0.85 (Harrelson et al. 1994). The discharge was calculated with the equation $Q = \sum(Va)$ where a is the area of the cross section and $V$ is the average flow velocity.

Ancillary limnological data were obtained at each sampling event to characterise the seasonal variation in physical and biological parameters. Oxygen and temperature profiles of the water column were measured using a YSI™ 556MPS. In lake Bromont and Petit St-François, we also collected continuous measurements of oxygen and temperature by placing a D-opto optical logger 1m below the water surface. During the ice-free season, light extinction coefficient was measured using a Li-Cor™ LI-1000. The ratio of irradiance at depth *z* to irradiance at the surface of the lake ($I_z / I_0$) was measured at each 0.5m until no light was detectable. The light extinction coefficient was computed as the slope of the relationship between $\ln(I_z / I_0)$ and depth *z* and the euphotic zone as the depth receiving more than 1 % incident light (Kalff 2002). The secchi depth was also used to monitor water transparency and integrated water samples were collected for analyses of chlorophyll-*a* (chl*a*) and phytoplankton community composition.

Upon return to laboratory, SPOM samples for elemental and stable isotope analyses of nitrogen and carbon were prepared by filtration at low pressure (~10 psi) of lake water on pre-combusted (450°C, 4 h) and pre-weighed 47mm GF/F glass-fiber filters until the filters were saturated. The filters were immediately dried at 50°C overnight and weighted after zooplankton had been removed with forceps. The samples for chl*a* were similarly filtered in the dark but immediately frozen until extraction. Samples for measurement of dissolved nutrients concentration ($NH_4^+$, $NO_3^-$, $NO_2^-$, TDN, TP) and nitrogen stable isotopes ($\delta^{15}N$ of $NO_3^-$, $NH_4^+$ and TDN) were filtered through a sterile 0.45 µm membrane filter. The samples were kept frozen at -22°C in acid washed 125ml Nalgene bottles until nutrient and isotopic analysis.

### *Elemental and isotopic analyses of particulate N and C*

For elemental and stable isotope analysis of the SPOM, subsamples of know area and mass of the GF/F filter were loaded into tin capsules. For both elemental and isotopic C analysis, samples were not pre-treated for carbonate removal since previous analysis had shown that particulate organic matter from these three lakes have negligible carbonate content. The %C and %N content were analysed on a Fisons EA1108 CHN Elemental Analyzer. Samples were oxidized at 1020°C and reduced to $N_2$ and $CO_2$ through a copper column. Resulting peaks were compared to known mass of acetylanilide standard to determine the atomic %C and %N. The suspended particulate organic N and C (SPON, SPOC) in $\mu$mol $L^{-1}$ were calculated by multiplying the atomic %N (or %C) by the filter mass and dividing by the volume filtered. Analyses were run in duplicate for 10 % of the samples and reproducibility was better than ± 0.002 % for N and ± 0.02 % for C.

N and C isotopic composition was measured using a continuous flow Micromass Isoprime™ IRMS coupled to an elemental analyzer Carlo Erba NC 1500 at GEOTOP Research Center (Université du Québec à Montréal). The resulting N and C ratios were calibrated against their respective international standards $N_2$ atmospheric gas and Pee Dee Belemnite. All isotopic values are reported as the δ notation ($\delta = ([R_{sample}-R_{standard}]/R_{standard}) \times 1000$, where $R={}^{15}N/{}^{14}N$ or ${}^{13}C/{}^{12}C$). Samples were run in duplicate on at least 20 % of the sample total and reproducibility was better than 0.4 ‰ for $\delta^{15}N$ and 0.2 ‰ for $\delta^{13}C$.

*Nutrient and chla analyses*

Dissolved inorganic N concentrations ($NO_3^-$, $NO_2^-$, $NH_4^+$) were measured spectrophotometrically according to standard techniques (American Public Health Association 2005). Briefly, $NO_2^-$ concentration was measured using the Griess reaction in which sulfanilamide is added to a sample followed by N-naphthyl-ethylenediamine to form a purple stable azo compound that can be compared to a standard calibration curve equally treated. $NO_3^- + NO_2^-$ was similarly measured but was first reduced to $NO_2^-$ by passing the sample through a cadmium coil. $NO_3^-$ final concentration was obtained by using the equation $[NO_3^-] = [NO_3^- + NO_2^-] - (100 / \%\ \text{Cd column efficiency}) \times [NO_2^-]$ (Wetzel and Likens 2000). $NH_4^+$ was measured using the indophenol method where $NH_4^+$ reacts with hypochlorite and phenol to produce the indophenol blue compound. Total dissolve N (TDN) was measured following the method described by Valderrama (1981) where filtered water is digested with recrystallize persulfate to produce $NO_3^-$ subsequently measured as described earlier. Dissolved organic N (DON) concentrations were computed by subtracting $NO_3^- + NO_2^-$ and $NH_4^+$ to TDN. Standard deviation (STD) for DON was calculated following the error propagation formula $STD_{DON} = (S^2_{TDN} + S^2_{NH4} + S^2_{NO3+NO2})^{1/2}$ where $S^2$ is the variance (Bronk et al. 2000). Total N (TN) was calculated as the sum of TDN and SPON, standard deviation was calculated in similar manner as $STD_{DON}$. All nutrients were run with 10 % samples duplicate and the reproducibly for $NO_2^-$, $NO_3^-$, $NH_4^+$, TDN, DON and TN is respectively (in µmol $L^{-1}$) ± 0.01, ± 0.6, ± 0.5, ± 0.7, ± 1.0 and ± 0.7. Nitrogen loads for $NO_3^-$, $NH_4^+$ and DON were computed by multiplying the concentration by the discharge. Nitrogen budgets were calculated by subtracting the outlet

N load from the sum of inlets N loads for each N species. Our budgets are calculated by sampling date and should provide good estimates given the short residence time of our lakes. Measurement of total phosphorus (TP) and chl*a* followed standard protocols detailed in Wetzel and Likens (2000).

### *Isotopic analysis of dissolved N*

The determination of nitrogen ($\delta^{15}N$) and oxygen ($\delta^{18}O$) stable isotope ratios of $NO_3^-$ followed the method of McIlvin and Altabet (2005) with the modification of Ryabenko et al. (2009). When $NO_2^-$ concentrations were above 0.2 μmol $L^{-1}$, pre-existing $NO_2^-$ was removed by addition of sulfanilic acid to 110% of the expected $NO_2^-$ concentration. The sample $NO_3^-$ was then reduced to $NO_2^-$ using activated Cd followed by $NO_2^-$ reduction to $N_2O$ using azide buffered at pH 4-5 with acetic acid. For the analysis of $\delta^{15}N$ of TDN, the procedure was similar but first the persulfate oxidation method was used to convert TDN into $NO_3^-$ (Knapp et al. 2005). $NO_3^-$ and $NO_2^-$ were measured after the persulfate oxidation and the Cd reduction steps; the reactions yields were all above 95%. The produced $N_2O$ was introduced into a continuous flow mass spectrometer Micromass Isoprime™ at UMass Dartmouth and mass 44, 45 and 46 were integrated for measurement of $\delta^{15}N$ and $\delta^{18}O$. In-house organic (Zhang and Altabet 2008) and $NO_2^-$ working standards were inserted in every sample batch to ensure the accuracy of the TDN oxidation and the azide step. Internationally accepted $NO_3^-$ standards (IEAEA N3, USGS34, USGS35) were used to calibrate N and O isotopic ratios against air and VSMOW. These standards were chosen to represent natural N and O isotopic variation. Dual $NO_3^-$ isotopes were measured on samples with $NO_3^-$ concentrations above 0.45 μmol $L^{-1}$ and was therefore not measured for 3 samples from both the meta- and hypolimnion of Bromont and for respectively 4 and 5 samples from Lake Waterloo and Petit St-François. The N isotopic signature of $NH_4^+$ was also measured using the hypobromite oxidation converting $NH_4^+$ into $NO_2^+$ (Zhang et al. 2007) followed by azide reduction. The hypobromite oxidation appeared to be inhibited in the majority of our samples, and measurements were only possible for Bromont meta- and hypolimnion samples with high $NH_4^+$ concentration (> 90 μmol $L^{-1}$) and are reported on samples with the highest yields (> 75%). Reproducibility was nominally 0.3‰ for all the dissolved nutrient isotopic analysis.

The $\delta^{15}N$ of DON was calculated using the following mixing model (equation 3.1) (Knapp et al. 2010). In the high $NH_4^+$ concentration samples, $NH_4^+$ was substituted to $NO_3^-$ in the mixing model.

$$\delta^{15}\mathrm{N}_{\mathrm{DON}} = \frac{([\mathrm{TDN}] * \delta^{15}\mathrm{N}_{\mathrm{TDN}} - [\mathrm{NO}_3^-] * \delta^{15}\mathrm{N}_{\mathrm{NO3}})}{([\mathrm{TDN}] - [\mathrm{NO}_3^-])} \qquad \text{(equation 3.1)}$$

To compare the measured lake stable isotope composition with the isotopic baseline of the water coming from the watershed, we also computed a mean inlet isotopic signature for $\delta^{15}N$ of DON and $NO_3^-$ and $\delta^{18}O$ of $NO_3^-$. This mean isotopic signature was computed using a mixing model (equation 3.2).

$$\delta^{15}\mathrm{N} = \textstyle\sum_{i=1}^{n}(\delta^{15}\,\mathrm{N}_{\,i} * \,(\mathrm{load}_i/\mathrm{total\ load})) \qquad \text{(equation 3.2)}$$

The equation was summed according to the *i* number of inlets for each lake. To obtain the summer mean inlet $NO_3^-$ isotopic signature, we calculated the mean over the six sampling date. Using this mean summer inlet $NO_3^-$ N and O isotopes, we calculated the isotopic discrepancy Δ(15,18) from the 1:1 fractionation relationship expected from assimilation. The discrepancy can be graphically viewed as the horizontal distance in $\delta^{18}O$ against $\delta^{15}N$ space between a line with a slope ($^{18}\varepsilon$:$^{15}\varepsilon$) of 1 assumed for $NO_3^-$ consumption running through the summer mean inlet $\delta^{15}N$ and $\delta^{18}O$ signatures (Sigman et al. 2005). Such deviation is observed when $NO_3^-$ production (nitrification) is coupled to its consumption (assimilation or denitrification). The deviation was calculated using the following equation:

$$\Delta(15,18) = (\delta^{15}N - \delta^{15}N_m) - (^{15}\varepsilon:^{18}\varepsilon) \text{ x } (\delta^{18}O - \delta^{18}Om) \qquad \text{(equation 3.3)}$$

where $\delta^{15}N_m$ and $\delta^{18}O_m$ are the $\delta^{15}N$ and $\delta^{18}O$ of the mean summer inlet $NO_3^-$.

## RESULTS

### *Temporal variation of the suspended particulate and the nutrients*

The SPOM displayed typical seasonal variation of increasing phytoplankton biomass during the summer. The SPON was generally low in spring, increased during summer and decreased in fall and winter (Fig. 3.2A,B,C,D). The SPON was particularly high in Petit St-François where it reached a maximum of 201.9 μmol $L^{-1}$ in August (Fig. 3.2D). Summer SPON increases were consistent with the decreasing depth of the euphotic zone. For the three lakes, the depth of the euphotic zone was maximal in spring (Bromont, 6.6m; Waterloo, 3.7m; Petit St-François, 3.7m) and minimal at the end of the summer (Bromont, 2.55m; Waterloo, 1.94m; Petit St-François, 0.7m). Chl*a* displayed similar pattern as SPON and minimums were measured in the spring (Bromont, 4.3 μg $L^{-1}$; Waterloo, 5.0 μg $L^{-1}$; Petit St-François, 8.12 μg $L^{-1}$) whereas maximum concentrations were observed in July for Waterloo (26.03 μg $L^{-1}$) and in August for Bromont epilimnion and Petit-St-François (respectively 14.17 μg $L^{-1}$ and 81.79 μg $L^{-1}$). For Bromont there was also a metalimnetic phytoplankton bloom that reached a maximum chl*a* of 40.3 μg $L^{-1}$ in August.

Similarly to the SPOM, the dissolved inorganic N (DIN) displayed typical seasonal patterns (Fig. 3.2E,F,G,H). For the three lakes, $NO_3^-$ concentrations were highest during winter (Bromont, 37.8 μmol $L^{-1}$; Waterloo 29.62 μmol $L^{-1}$; Petit St-François, 23.76 μmol $L^{-1}$). For both Waterloo and Bromont, $NO_3^-$ began to decrease in spring (Bromont 18.5 μmol $L^{-1}$; Waterloo 29.62 μmol $L^{-1}$), was exhausted during summer and replenished in the fall (Fig 3.2E,F,G). The draw down was more rapid in Waterloo where the $NO_3^-$ was undetectable in early June compared to late July for Bromont. In Petit St-François, $NO_3^-$ was already low in spring (0.46 μmol $L^{-1}$) probably because it had already been drawn down by algae due to the high productivity of the lake. In this lake, $NO_3^-$ was undetectable throughout summer until late October (Fig. 3.2H). $NH_4^+$ concentrations for all lakes displayed the same seasonal variation as $NO_3^-$ although the concentrations were generally lower in spring and winter and remained low but detectable throughout the summer (< 2 μmol $L^{-1}$) for all systems. There was high accumulation of $NH_4^+$ in the anoxic hypolimnion of Bromont and concentration reached 100.6 μmol $L^{-1}$ towards the end of July, but concentrations were highest in the metalimnion (201.4 μmol $L^{-1}$) at the end of October (Fig. 3.2F). $NH_4^+$ was also high in Petit St-François during winter (48.3 μmol $L^{-1}$). $NO_2^-$ concentrations were below 0.4 μmol $L^{-1}$ for all lakes. For lake Bromont there was no trend in the temporal variation and minimum values were recorded in spring (0.005 μmol $L^{-1}$) whereas maximum values in august (0.021 μmol $L^{-1}$). For lake Waterloo and Petit St-

François, $NO_2^-$ was low throughout spring and summer (< 0.01 μmol $L^{-1}$) and increased in the fall to reach a maximum in winter (respectively, 0.40 μmol $L^{-1}$ and 0.17 μmol $L^{-1}$). Compared to DIN and SPON, the dissolved organic N (DON) remained relatively stable for all the lakes except in Petit St-François where it was undetectable in winter. DON concentrations were lower in Bromont ($\bar{x}$ = 14.94 μmol $L^{-1}$), followed by Waterloo ($\bar{x}$ = 20.50 μmol $L^{-1}$) and were the highest in Petit St-François (excluding winter; $\bar{x}$ = 34.38 μmol $L^{-1}$).

Continuous measurements of water column oxygen revealed dial variation in oxygen concentrations where water was supersaturated during the day and undersaturated at night in agreement with dial photosynthesis/respiration cycles. For both Bromont epilimnion and Petit St-François, the water column was always well oxygenating (> 80 % $O_2$ saturation) from spring to fall suggesting that water column denitrification is not a process affection the $NO_3^-$ isotopic signature. Bromont metalimnion (~ 4.5 to 6m depth) was always well oxygenated during day time sampling (between ~ 6 to 12 mg $L^{-1}$) also suggesting that water column denitrification is not a dominant process affecting the $NO_3^-$ isotopes. Bromont anoxic hypolimnion ($O_2$ ~ 0.5 mg$L^{-1}$) was formed below 6m depth from late July through September. Although no continuous data were available for Waterloo, the water column was always well oxygenated during sampling time. For both Waterloo and Petit St-François, although there was no temperature stratification, there was typically a small decrease in oxygen concentration toward the sediment. This was observed more often for Waterloo where oxygenation decreased to ~ 80 % saturation. Both Waterloo and Petit St-

François had minimum oxygen saturation in winter at the surface sediment interface (respectively ~ 53 % and ~ 10 %).

### *Variation of isotopes from the suspended particulate and the nutrients*

The variation of the isotopes during the growing season was contrasted between lakes (Fig. 3.3). In lake Bromont, the $\delta^{15}N$ of SPON was slightly higher in the epilimnion ($\bar{x}$ = 1.90 ‰) compared to the metalimnion ($\bar{x}$ = 1.45 ‰) and the hypolimnion ($\bar{x}$ = 1.73 ‰) and some extreme values tended to increase the variability in the epi- and metalimnion (Fig. 3.3A). Lake Waterloo had the lowest values of $\delta^{15}N$ of SPON ($\bar{x}$ = 1.34 ‰) and for lake Petit St-François, values were comparable to Bromont epilimnion ($\bar{x}$ = 2.03 ‰). The $\delta^{13}C$ of the SPOC had similar pattern for Bromont ($\bar{x}_{epi}$ = -33.94 ‰, $\bar{x}_{meta}$= -36.92 ‰, $\bar{x}_{hypo}$ = -37.29 ‰) then $\delta^{15}N$ of SPON, however the values were comparably higher for Petit St-François ($\bar{x}$ = -27.15 ‰) (Fig. 3.3B). The $\delta^{13}C$ values of Waterloo were an intermediate to the other lakes and remarkably stable throughout the summer ($\bar{x}$ = -30.37 ‰).

Bromont tended to have higher $\delta^{15}N$ of $NO_3^-$ in the lake ($\bar{x}$ = 9.27 ‰) as compared to its inlets ($\bar{x}$ = 7.12 ‰) and outlet ($\bar{x}$ = 6.34 ‰) (Fig. 3.3C). Both Waterloo and Petit St-François displayed greater variability of $\delta^{15}N$ of $NO_3^-$ in the lake as compared to their inlets, however the low $NO_3^-$ concentrations in these lakes restricted the number of samples for analysis. For $\delta^{18}O$ of $NO_3^-$, patterns similar to $\delta^{15}N$ were observed in Bromont ($\bar{x}_{lake}$ = 3.43 ‰, $\bar{x}_{inlet}$= -3.24 ‰, $\bar{x}_{outlet}$ = 0.38 ‰; Fig. 3.3D). For Waterloo and Petit St-François the lakes had higher $\delta^{18}O$ compared to the inlets and for Petit St-François $\delta^{18}O$ also displayed high variability. The $\delta^{15}N$ of DON was similar for all lakes and was generally stable throughout the sampling, and hovering ~ 3 ‰ (Fig. 3.3E).

The temporal variation of the isotopic signatures among the N species measured differed greatly. The $\delta^{15}N$ of SPON was surprisingly quite stable for all lakes throughout the summer (Fig. 3.4A,B,C,D) with a few exceptions. For lake Bromont epilimnion and metaliminion there was a drop in the $\delta^{15}N$ of SPON from ~ 2 ‰ to 0.31 ‰ and -0.44 ‰ in July and to 0.97 ‰ and -0.14 ‰ in October. The $\delta^{13}C$ of SPOC displayed a seasonal variation for Bromont and Petit St-François whereas it was relatively stable for Waterloo. The $\delta^{13}C$ increased during the summer reaching maximum in July for Bromont epilimnion (-30.27 ‰) and in August for Petit St-François (-23.85 ‰).

Similarly to $\delta^{15}N$ of SPON, the $\delta^{15}N$ of DON was generally stable throughout the seasons. Exceptions to this were high values in winter for Waterloo (7.5 ‰) and Petit St-François (9.9 ‰). These high values can be explained by the DON being largely constituted of $NH_4^+$ (35% of the DON for Waterloo and 100% for Petit St-François) and the fact that the calculation of the $\delta^{15}N$ of DON only took into account the $NO_3^-$ and TDN isotopic signature. Therefore, $\delta^{15}N$ of $NH_4^+$ in Waterloo and Petit St-François was probably reflected by these winter values. There was also high $\delta^{15}N$ of DON in the meta- and hypolimnion of Bromont (Fig. 3.4B). These values where measured when $\delta^{15}N$ of $NH_4^+$ was included in our mixing model. The $\delta^{15}N$ and $\delta^{18}O$ of $NO_3^-$ displayed the strongest seasonal variation among the isotopic results of the various measured species (Fig 3.4). In

Bromont, there was a general trend of increasing $\delta^{15}N$ and $\delta^{18}O$ of $NO_3^-$ during summer (Fig. 3.4A).

### *Relationships with suspended particulate isotopes and nutrients*

Regression analysis of the $\delta^{15}N$ of SPON against nutrients revealed a significant relationship in lake Bromont, but not in the other systems. Specifically, we detected a strong significant relationship between $\delta^{15}N$ of SPON and TN, (i.e. epiliminion: $R^2$adj. = 0.78, $p$ = 0.005; metalimnion: 0.86 $R^2$adj. = 0.78, $p$ = 0.005). Two extreme values potentially related to heavy storm events prior to the sampling date (June 14 and October 2), were excluded from the analysis (see appendices, Fig. C.I). A similar relationship was apparent when we used TDN as a predictor instead of TN (Fig. 3.5A,B) and to a lesser degree using DIN from the Bromont metalimnion as a predictor, although this latter relationship was not significant. These negative relationships between $\delta^{15}N$ of SPON and TDN or DIN are in agreement with Raleigh fractionation as a function of phytoplankton assimilation. However, since DIN and TDN are composed of multiple N forms, the relationship would mean that many different types of N species were assimilated by phytoplankton. Given the mixed N sources, the slope of the $\delta^{15}N$ of SPON vs TDN cannot necessarily be interpreted as an apparent assimilation fractionation rate.

The absence of relationship between $\delta^{15}N$ of SPON and DIN in the Bromont epiliminion also suggested that the SPOM was more influenced by allochthonous sources compared to the metalimnion, which was dominated by phytoplankton cells. The lack of any relationship in Waterloo and Petit St-François suggested that allochthonous organic matter was diluting the internal signal. This was further supported by the $\delta^{15}N$, $\delta^{13}C$ and C:N source plot (Fig. 3.6A,B). The isotopic and elemental composition of the particulate organic matter for the polymictic lake Waterloo and Petit St-François as well as the Bromont epilimnion sites were mostly representative of terrestrial sources (soil and leaves) or vascular plants (macrophyte) (Finlay and Kendall 2007). By comparison, values for Bromont metalimnion are more typical of phytoplankton elemental and isotopic composition.

### *N budgets*

The elevated $NO_3^-$ concentrations measured in the inlets of Petit St-François suggested that its watershed is heavily impacted by $NO_3^-$ and fertilizer pollution. Indeed, compared to our other two lakes, concentrations (up to 111 $\mu$mol $L^{-1}$) were higher (see appendices Fig. C.II). Petit St-François as well as Bromont and Waterloo seemed to retain $NO_3^-$ given generally lower concentrations at their outlets comparatively to their inlets (see appendices, Fig. C.II). However, we only successfully measured N budgets for lake Bromont, which effectively retain most N forms during summer but tend to export $NO_3^-$, $NH_4^+$ and DON in spring and fall (see appendices, Fig. C.III).

### *Dual nitrate isotopes*

The dynamics of the dual $NO_3^-$ isotopes was much different in lake Bromont as compared to the shallower systems where both a clear temporal trend (Fig. 3.7A,B) and a significant relationship between $\delta^{15}N$ and $\delta^{18}O$ was observed. Lake Bromont was also the only lake were we successfully calculated a mean summer inlet isotopic signature. This mean $NO_3^-$ isotopic signature was well constrained with values for $\delta^{15}N_m = 7.88 \pm 0.88$ ‰ and $\delta^{18}O_m = -1.94 \pm 2.75$ ‰. Bromont showed strong reprocessing of the $NO_3^-$ during the growing season with an increase in both $\delta^{15}N$ and $\delta^{18}O$ in summer (Fig. 3.7A). The $\delta^{18}O$: $\delta^{15}N$ relationship in Bromont clearly deviated from the 1:1 relationship, the latter being expected if fractionation was simply a result of assimilation (Fig. 3.7B,C). The deviation varied temporally and the discrepancy was the strongest in mid summer (lower $\Delta(15,18)$ values) and increased again in the fall (Fig. 3.7B). This deviation suggests that part of the observed $NO_3^-$ available for assimilation was internally produced via nitrification. The slope of the significant relationship between $\delta^{15}N$ and $\delta^{18}O$ was 1.72 ($R^2$adj. = 0.99, $p <$ 0.001, Fig. 3.8C). There was also significant relationships between the $\delta^{15}N$ and $\delta^{18}O$ of $NO_3^-$ and ln $[NO_3^-]$ (see appendices, Fig. C.IVA,D). The slopes approximate Rayleigh fractionation and were 2.59 for $\delta^{15}N$ and 4.49 for $\delta^{18}O$. Noticeably, the $\delta^{18}O$ values for April (1.35 ‰) and February (3.65 ‰) were higher than would be expected from their $NO_3^-$ concentrations and did not follow the trend.

The dual $NO_3^-$ isotopes from Waterloo and Petit St-François displayed a high variability (Fig. 3.8A,B). For both lakes, there was no significant relationship with the $NO_3^-$ isotopic signature and $NO_3^-$ concentrations (see appendices, Fig. C.IVB,C,E,F). Due to reduced flow we were also unable to estimate an accurate mean summer $NO_3^-$ $\delta^{15}N$ and $\delta^{18}O$ load. The absence of synthetic fertilizer use in Waterloo catchment and the low $\delta^{18}O$ values from the inlet compared to the lake signature suggests an internal process leading to a $^{18}O$ enrichment of lake $NO_3^-$. Indeed, by drawing a line between the three summer $NO_3^-$ isotope values for Waterloo, we found a similar slope (2.0) as the one observed for Lake Bromont (1.72). For Petit St-François, the fertilizer use in the catchment and the high $\delta^{18}O$ values of both inlets and lake $NO_3^-$ suggests lake $NO_3^-$ reflect the lake nutrient sources. However, the paucity of the data as a function of the very low $NO_3^-$ concentrations prevents us from drawing any strong conclusion.

## DISCUSSION

Our analyses of three temperate lakes revealed that the use of multiple isotopes from the suspended particulate matter and different dissolved N species is a promising approach to study N cycling dynamics in some shallow lakes. Surprisingly, the isotopes from the suspended particulate matter in all systems displayed a generally stable N signature compared to what has been previously reported in other lake studies (Hodell and Schelske 1998, Syvaranta et al. 2008, Hadas et al. 2009). There was no clear indication that the main nutrient source to the phytoplankton in the SPOM fraction was $NO_3^-$ given its higher isotopic variation and the distinctive pattern of increasing $\delta^{15}N$ and $\delta^{18}O$ of $NO_3^-$ observed during summer. The application of multiple stable isotopes was also different according to the nutrient status and the lake mixing regime where patterns were much clearer in our stratified, mesotrophic system. In lake Bromont, significant relationships were found between $\delta^{15}N$ of SPON and nutrient concentrations, consistent with previous lake and oceans studies using isotopes to assess nutrient utilization (Altabet and Francois 1994, Lehmann et al. 2004a, Kumar et al. 2011). In contrast to these studies, the best relationship was found with TDN concentrations suggesting that primary producers use both dissolved organic and inorganic N sources and that internal recycling processes, are extremely rapid. The deviation from the 1:1 line in Bromont enabled the use of the dual isotope of $NO_3^-$ ($\delta^{15}N$, $\delta^{18}O$) to understand the dynamics of production vs. consumption of $NO_3^-$, where our findings are in good agreement with other studies in Ocean systems and in the Great Lakes (Sigman et al. 2005, Finlay et al. 2007, Wankel et al. 2007). However, in the more nutrient rich and very shallow polymictic lakes, a multiple stable isotopic approach appears to be more useful in identifying the nutrients and organic matter sources, a more common approach used in river systems studies (Kendall et al. 2007, Barnes and Raymond 2010, Kendall et al. 2010). Furthermore, the use of the dual $NO_3^-$ isotopes in highly productive shallow lakes may be limited by the rapid primary producers $NO_3^-$ draw down or the rapid benthic denitrification given the proximity of sediment and the inability to observe significant yield over most of the growing season.

### *Stable isotope signature from the suspended particulate organic matter*

Interestingly and in contrast to other studies looking at the isotopic signature of suspended POM in lakes, we observed very little seasonal variation and this in all three systems. In temperate lakes, the typical pattern of $\delta^{15}N$ of POM is of depleted $^{15}N$ values during the summer stratified period and $^{15}N$-enriched values during the mixed water column period. Reported seasonal ranges vary from 2 to 20 ‰ (Hodell and Schelske 1998, Lehmann et al. 2004a, Syvaranta et al. 2008) and this pattern has been explained by changing sources of organic matter with the dominance of low $\delta^{15}N$ phytoplankton during summer and high $\delta^{15}N$ heterotrophic or detrital sources toward the fall/winter period.

Similarly to what we observed, Owen et al. (1999) also reported a restricted annual variation (range = ~1 ‰) of the $\delta^{15}$N from the seston in two comparatively small albeit deeper lakes from the Adirondack, USA, although they had a general trend of lower values in the summertime. The relative stability in the seston $\delta^{15}$N signal in small and shallow lakes suggests that land derived allochthonous inputs and/or sediment particles resuspended from wind mixing are dominating over the internally produced organic matter. The source plot using $\delta^{15}$N, C:N and $\delta^{13}$C (Fig. 3.6) supports that the organic matter sources in our more eutrophic, polymictic and fast flushing lakes are more typically land derived and originating from vascular plants.

There was less of an apparent influence of terrigenous inputs on the seston as reflected in the $\delta^{13}$C signal of the SPOC in our deepest, stratified mesotrophic lake. Furthermore we found a relationship between $\delta^{15}$N of SPON and TDN concentrations in lake Bromont, suggesting that phytoplankton were a more significant fraction of the SPOM. Such relationships were also found in previous studies looking at $\delta^{15}$N as a proxy of nutrient utilization by phytoplankton but with either $NH_4^+$ or $NO_3^-$ concentrations (Teranes and Bernasconi 2000, Lehmann et al. 2004a, Kumar et al. 2011). In our lakes, the relationship with $\delta^{15}$N of SPON may be caused by various nutrient sources to phytoplankton including dissolved organic N forms. It has been reported that urea can be a particularly important N source supplying up to 50% of planktonic N uptake and favouring toxic cyanobacteria growth (Finlay et al. 2010, Solomon et al. 2010). Furthermore, cyanobacteria and bacteria are also capable of amino acid assimilation (Simon and Rosenstock 1992, Flores and

Herrero 2005). Given that the phytoplankton community of lake Bromont was dominated by cyanobacteria, it is most likely that component of the organic dissolved N pool contribute to the phytoplankton N uptake. However, it is not clear to what extent this pool was accessible given the lack of variability in the $\delta^{15}$N signature of DON. The latter would suggest that this pool is composed primarily of recalcitrant N, similarly to what has been observed in oceanographic studies (Knapp et al. 2005, Bourbonnais et al. 2009).

Even though we observed relationships with $\delta^{15}$N of SPON and nutrient concentrations for most of the samples collected in lake Bromont, low sestonic $\delta^{15}$N values were observed on two occasions (Fig. 3.5). The lower value in June might be due to N fixation, but DIN concentrations were still relatively high (> 5 μmol $L^{-1}$) at these dates and preliminary tracer experiment and molecular results indicate that N fixation is minimal in this lake (Monchamp and Massé pers. comm.). Given that there was no clear evidence of fixation in this system, one possible explanation of the low $\delta^{15}$N was a change to a more allochthonous organic matter composition or nutrient source linked to lake physical forcing. Indeed, meteorological data (see appendices Fig. C.I) indicate storm events prior to these two sampling dates.

The observed relationship with $\delta^{15}$N of SPON was not observed in our two shallower and more productive lakes. In addition to higher external organic matter inputs and internal sediment resuspension, the absence of a relationship in these lakes can be explained by the rapid draw down of inorganic nutrients by the fast growing phytoplankton (Fig. 3.2C,D). Under such conditions, the fractionation during assimilation would be minimal (Fogel and

Cifuentes 1993). Furthermore, with nutrients depleted, the phytoplankton were probably assimilating regenerated N from degraded organic matter and would therefore have similar $\delta^{15}$N than allochthonous inputs. Given the diversity of OM sources, future stable isotopic analysis of organic matter in small and shallow lakes should focus on specific compound isotope analysis, such as the determination of amino acid isotopic composition from algae (McClelland and Montoya 2002), to better understand phytoplankton nutrient utilization.

### *The use of dual $NO_3^-$ stable isotopes*

Nitrification is the process whereby ammonium is sequentially oxidized to nitrite and finally to nitrate. Nitrification is thus a key process regulating ammonium, nitrite and nitrate concentrations (Ward 2008). Our results showed the potential use of the dual stable isotopes of nitrate in the study of summertime lake nitrification. Indeed, in our mesotrophic lake, we found a strong deviation from the 1:1 $\delta^{15}$N and $\delta^{18}$O relationship expected if assimilation was the dominant process acting on $NO_3^-$ (Granger et al. 2004). Because the water column was constantly aerated, denitrification as a cause of this deviation can likely be ruled out. Furthermore, this deviation was observed in the euphotic zone and was maximal during summer and can thus be interpreted as simultaneous assimilation and nitrification, similarly to results from oceanographic studies (Wankel et al. 2007, DiFiore et al. 2009). Consistent with our observation, simultaneous nitrate assimilation and nitrification in the water column should result in a proportionally greater fractionation of $\delta^{18}$O as compared to the $\delta^{15}$N of the $NO_3^-$. Based on oceanographic studies in the euphotic zone, the $\delta^{18}$O from nitrification should also be higher than that of water. Therefore, further data on oxygen isotopic composition ($\delta^{18}O$) of lake water are needed to validate the hypotheses of occurrence of nitrification.

In our two eutrophic shallow lakes, we also observed that the $\delta^{18}O$ of $NO_3^-$ was consistently higher than the $\delta^{18}O$ observed in samples collected from the inlet. Measurements of $\delta^{18}O$ from water should also indicate the water source and whether the $\delta^{18}O$ of nitrate reflect internally produced nitrate or nitrate pollution from the catchment in these lakes, especially for Lake Petit St-François with values of $\delta^{18}O$ that can also be sign of fertilizer or atmospheric inputs. Moreover, we cannot infer from the literature if nitrification is important in these systems. Indeed, some studies on nitrification indicated that higher rates were measured in eutrophic waters compared to oligotrophic waters (Chen et al. 2010) whereas others have observed no apparent nitrification in the water columns and suggested that nitrification is mostly a sediment process in shallow lakes (Pauer and Auer 2000). In the case of negligible nitrification in highly productive systems, nitrate could be used as in studies in river systems were the dual isotopes are used to identify nitrate pollution sources (Nestler et al. 2011)

## CONCLUSIONS

In our study, we explored the potential application a multiple stable isotopic approach to better understand N cycle in small and shallow lakes. We showed that SPON from our dimictic lake can be used to assess assimilation. However, in fast flushing systems, the use of $\delta^{13}C$ in conjunction with $\delta^{15}N$ and C:N ratio is more useful in the determination of land derived organic matter sources. We also reported measures of dual nitrate isotopes. The deviation in the 1:1 relationship in the $\delta^{18}O$ and $\delta^{15}N$ indicates simultaneous assimilation and nitrification. Nitrification is an important process in freshwater whereby it can regulate the availability of dissolved inorganic nitrogen forms. Nitrification can also exacerbate eutrophication symptoms by its high consumption of oxygen that can lead to fish kills (Tanner et al. 2002, Grundle and Juniper 2011). Future measure of oxygen isotopic composition of water should confirm if nitrification is occurring. The confirmation of this process could lead to future analysis modelling the proportion of $NO_3^-$ internally produced by nitrification in lakes (e.g. DiFiore et al. 2009).

## TABLES AND FIGURES

Table III.I: Lake basin, watershed and chemical characteristics of the study systems. Chemical data for lake Bromont are representative of the epilimnion. Data on land use, morphometry and topography are taken from Chapter 2.

| | Bromont | Waterloo | Petit St-François |
|---|---|---|---|
| Mean depth (m) | 4.0 | 2.7 | 1.1 |
| Max depth (m) | 7.0 | 4.9 | 1.8 |
| Lake area (km$^2$) | 0.46 | 1.47 | 0.87 |
| Watershed area (km$^2$) | 24.8 | 28.7 | 19.5 |
| Volume (m$^3$) | $1.87 \times 10^6$ | $4.03 \times 10^6$ | $9.74 \times 10^5$ |
| Shoreline length (km) | 3.01 | 7.29 | 4.44 |
| Water residence time (d) | 39 | 117 | 22 |
| Population density (ind. km$^{-2}$) | 35 | 157 | 54 |
| Agricultural area (%) | 6.7 | 10.1 | 22.6 |
| Forested area (%) | 72.6 | 65.9 | 47.9 |
| Mean summer TP (µg L$^{-1}$) | 28.9 | 39.3 | 210.8 |
| Mean summer TN (µmol L$^{-1}$) | 33.9 | 41.7 | 162.9 |
| Mean summer $NO_3^-$ (µmol L$^{-1}$) | 3.0 | 0.4 | 0.1 |

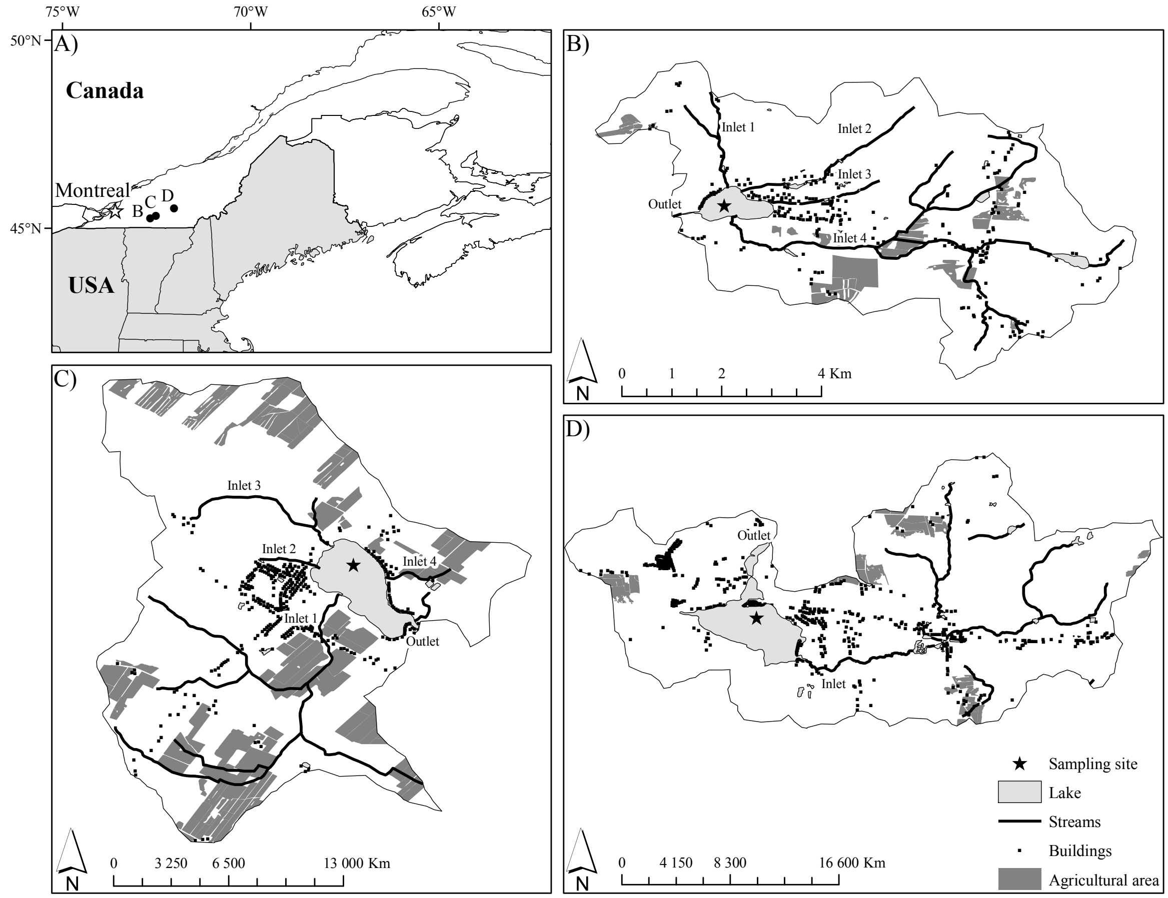


Figure 3.1: Map of the three study lakes. Lake location is presented in panel A). The three lakes and major features of their watersheds are represented in B) Lake Bromont; C) Lake Petit St-François and D) Lake Waterloo. The lake watersheds are represented with agricultural area in gray, the buildings in squares and the streams sampled.

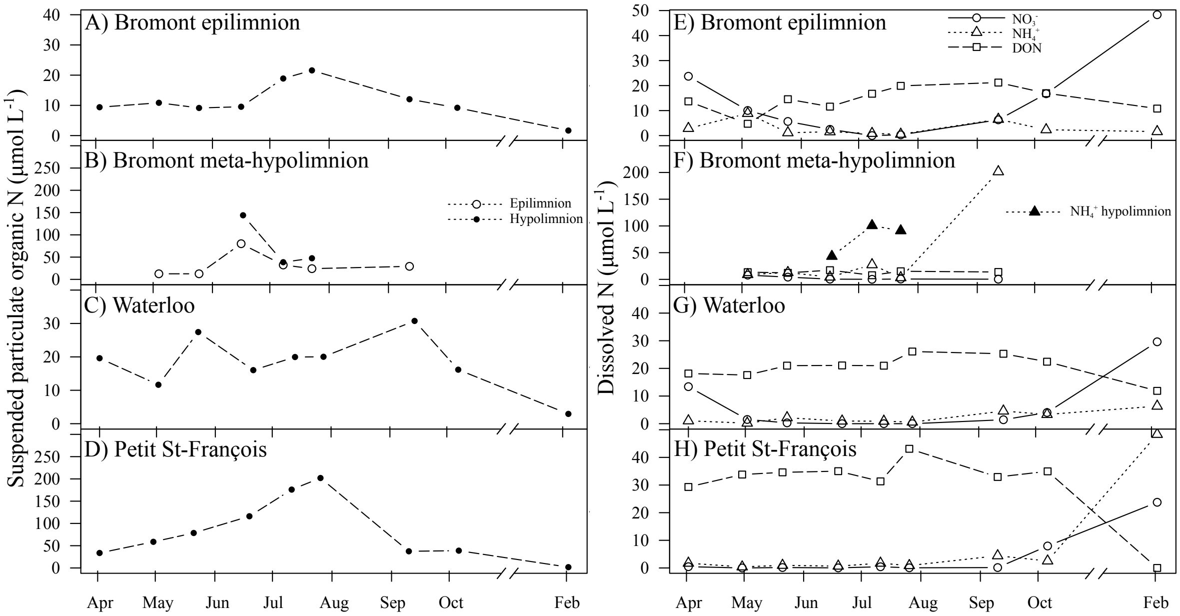


Figure 3.2: Temporal variation of the suspended particulate organic N (SPON) for lake A) Bromont epilimnion; B) Bromont metalimnion and hypolimnion; C) Waterloo and D) Petit St-François. Note the different y axis scale of panel B) and D) compare do A) and C). Temporal variation of the dissolved N ($NO_3^-$, $NH_4^+$, DON) for lake E) Bromont epilimnion; F) Bromont metalimnion and hypolimnion; G) Waterloo and H) Petit St-François. Note the different y axis scale of panel B) compare do A), B) and C) The x-axis are truncated between November 2010 and January 2011.

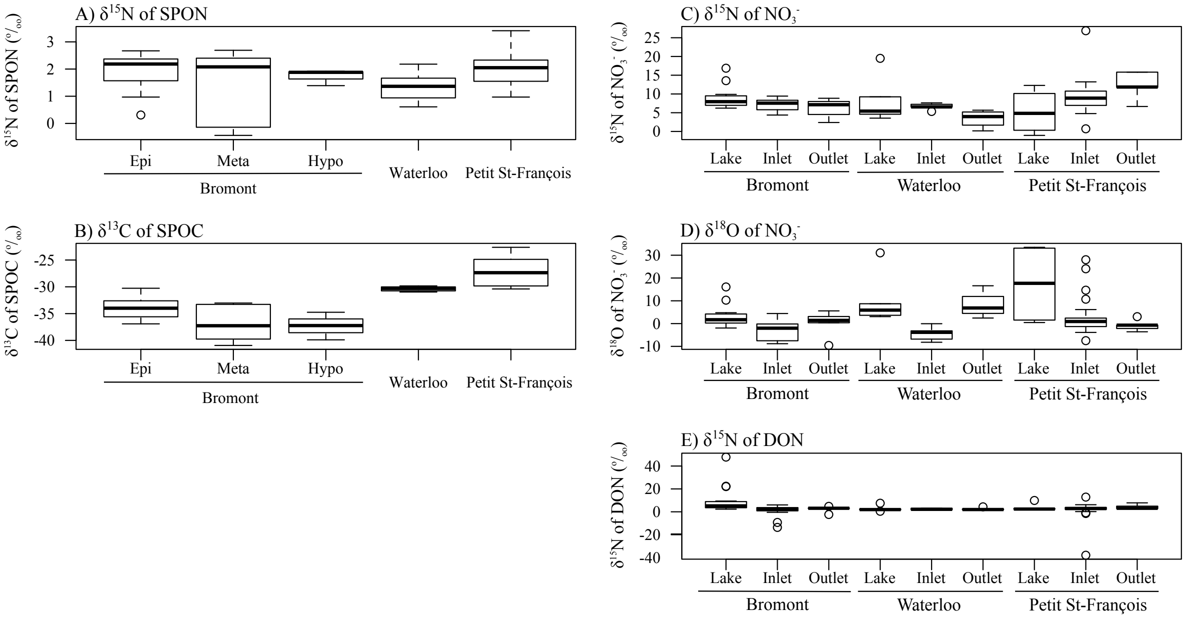


Figure 3.3: Box and whisker diagram representing the growing season isotopic ranges (excluding winter) of the three lakes and, when data is available, of their inlets and outlets. A) $\delta^{15}$N of Suspended particulate organic N (SPON); B) $\delta^{13}$C Suspended particulate organic C (SPOC); C) $\delta^{15}$N of nitrate; D) $\delta^{18}$O of nitrate and $\delta^{15}$N of dissolved organic N (DON). Solid horizontal line within each box indicates mean value. Box boundaries represent 25th and 75th and whisker extent represent 10th and 90th percentiles. Dots indicate sites exhibiting values outside of the 10th and 90th percentiles.

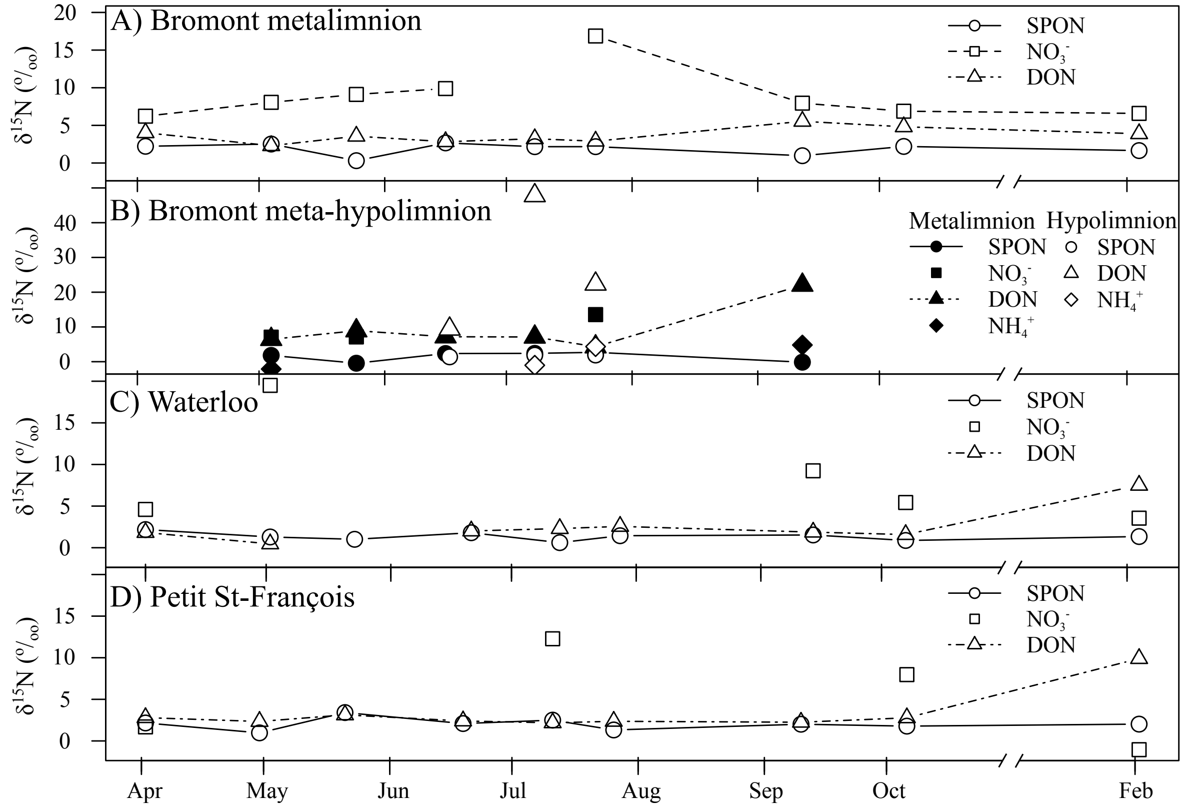


Figure 3.4: $\delta^{15}N$ temporal variation of suspended particulate organic N (SPON), nitrate ($NO_3^-$), ammonium ($NH_4^+$) and dissolved organic nitrogen (DON) from A) Bromont epilimnion; B) Bromont meta-hypolimnion; C) Waterloo and D) Petit St-François. Note the different y axis scale of panel B) compare do A), C) and D). The x-axis are truncated between November 2010 and January 2011.

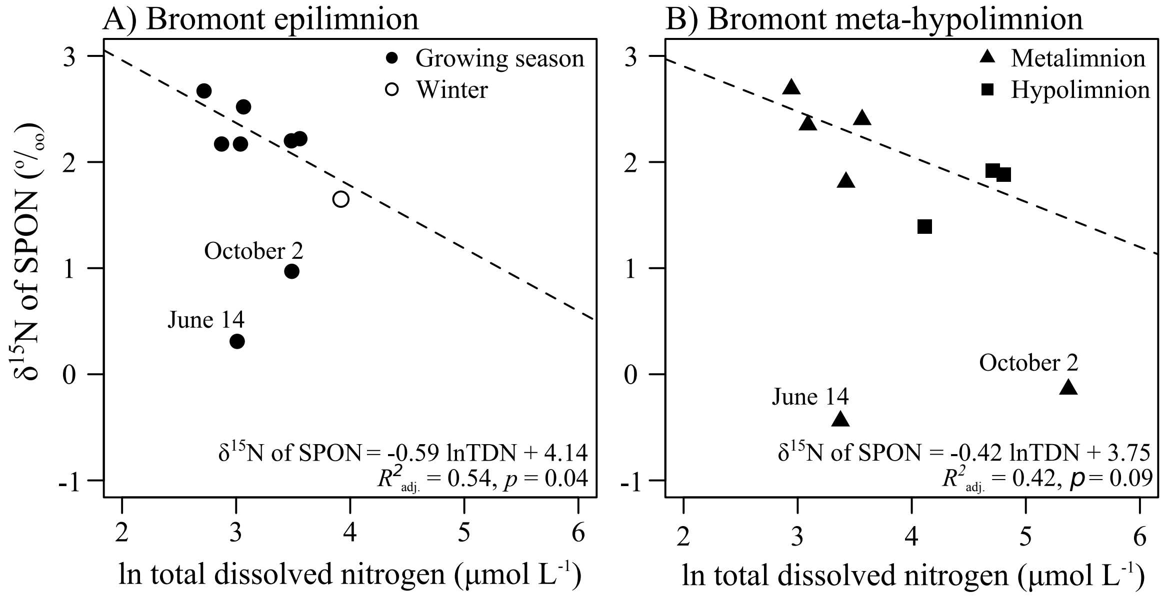


Figure 3.5: Relationships between $\delta^{15}$N of SPON and TDN for A) Bromont epilimnion; B) Bromont meta-hypolimnion.

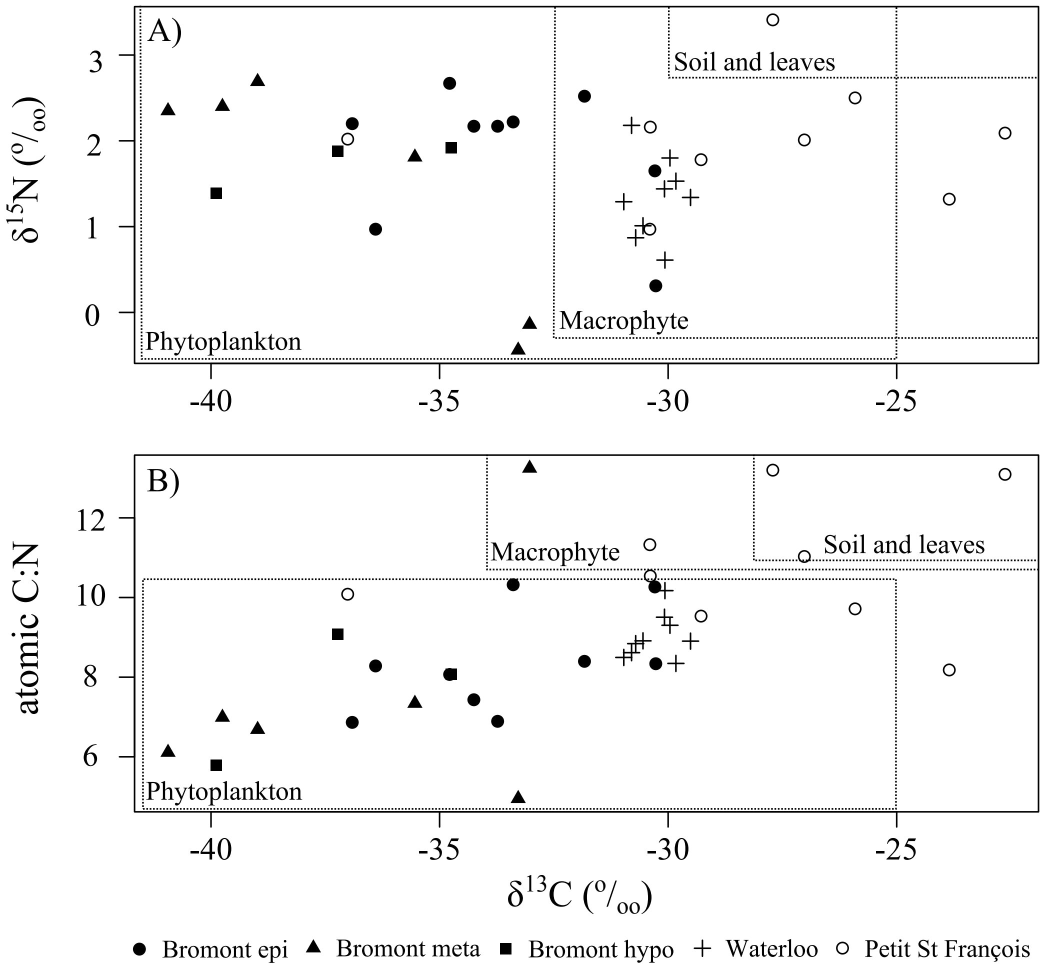
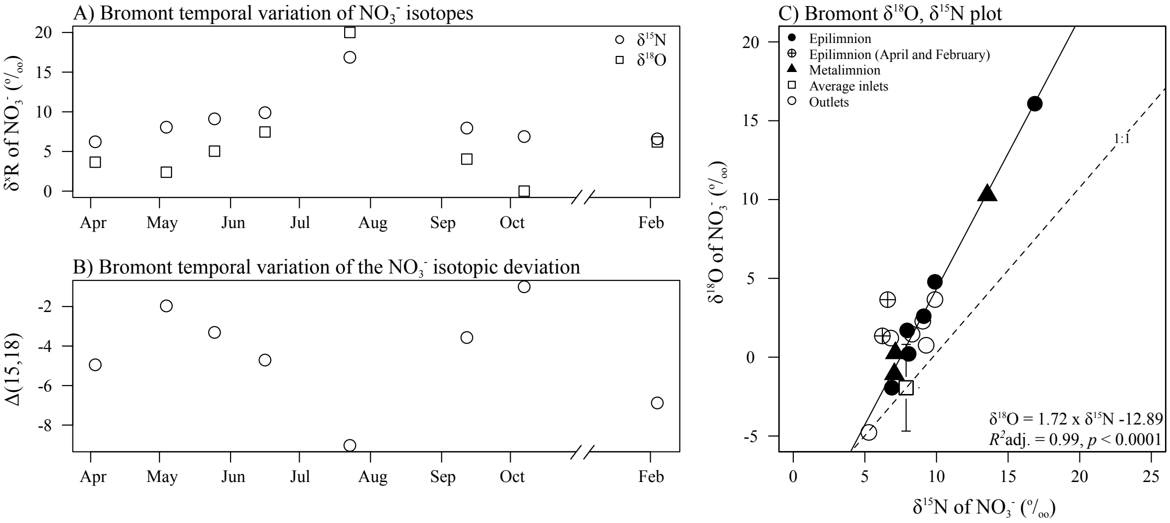


Figure 3.6: Source plot of A) $\delta^{15}N$ vs. $\delta^{13}C$ and B) atomic C:N vs. $\delta^{13}C$ from the suspended particulate organic matter (SPOM) for lake Bromont epilimnion, metalimnion, and hypolimnion as well as lake Waterloo and Petit St-François. The typical range of isotopic and elemental compositions of terrestrial organic matter versus phytoplankton are superimposed as modified from Finlay and Kendall (2007).


A) Bromont temporal variation of $NO_3^-$ isotopes

B) Bromont temporal variation of the $NO_3^-$ isotopic deviation

C) Bromont $\delta^{18}O$, $\delta^{15}N$ plot

Figure 3.8: Dual $NO_3^-$ stable isotopes plots for lake Bromont. A) Temporal variation of lake Bromont $\delta^{15}N$ and $\delta^{18}O$ values of $NO_3^-$. B) Temporal variation of the deviation calculated as the discrepancy from the 1:1 fractionation relationship expected for assimilation ($\Delta(15,18) = (\delta^{15}N - 7.88‰) – (\delta^{18}O – (-1.94‰))$). For A) and B) The x-axis are truncated between November 2010 and January 2011. C) Cross diagram of $\delta^{18}O$ vs. $\delta^{15}N$. The average isotopic signature of the inlet is calculated from our mixing model.

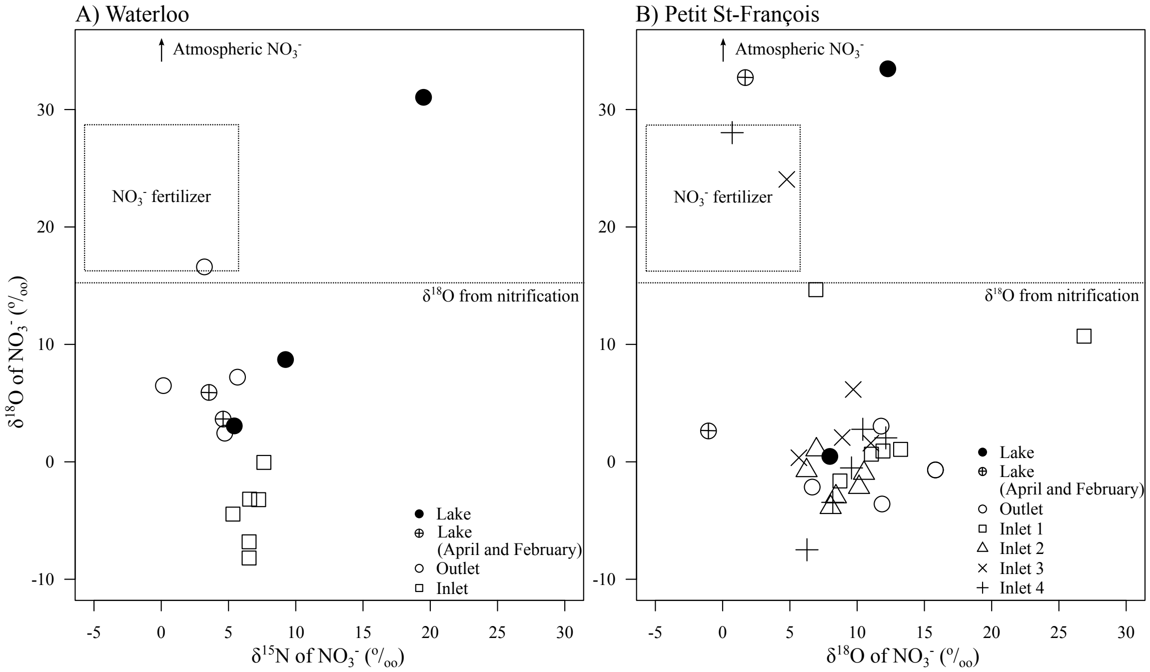


Figure 3.9: Dual NO$_3^-$ stable isotopes plots for lake A) Waterloo and B) Petit St-François. Winter and spring values are also symbolized to compare NO$_3^-$ signature in period of low biological productivity. The typical ranges of isotopic compositions are superimposed as modified from Kendall et al. (2007).

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# Conclusion

L'objectif global de ce mémoire était de caractériser les processus du cycle de l'azote et les sources d'azote aux lacs tempérés par l'utilisation d'isotopes stables. Nous avons exploré l'utilisation des isotopes stables d'azote des sédiments lacustres comme indicateur paléolimnologique des sources en azote aux lacs ainsi que les mesures de plusieurs isotopes stables de la matière organique particulaire et des nutriments pour la détermination des processus *in situ* du cycle de l'azote.

Dans le deuxième chapitre, nous avions comme objectif de déterminer quelles étaient les meilleures variables explicatives de la signature en isotope stable des sédiments. Les résultats ont démontré que ces variables sont la concentration en azote total (NT) et la proportion en azote des sédiments, le volume des lacs étant lui-même fortement corrélé à ces deux variables. Le %N des sédiments indiquerait que la diagenèse peut altérer la signature des sédiments de surface. Cependant, la charge en azote de sources anthropiques était elle même une bonne variable explicative du $\delta^{15}$N et du NT. Le $\delta^{15}$N des sédiments est donc un bon indicateur des changements des sources d'azote aux écosystèmes lacustres. L'utilisation du $\delta^{15}$N des sédiments pourrait être utilisé dans la compréhension des causes et des conséquences de l'eutrophisation des lacs à grande échelle temporelle.

Bien que le $\delta^{15}$N soit un bon indicateur des sources anthropiques à travers nos deux régions d'étude, notre modèle pour les lacs du Québec était moins puissant que pour l'Alberta. Cet effet pour le Québec est sans doute causé par l'importance de l'azote atmosphérique. En effet, selon nos estimations sommaires, jusqu'à 89 % de l'azote anthropique aux bassins versants pourrait être de nature atmosphérique. Afin de mieux comprendre les sources d'azote contrôlant de $\delta^{15}N$ des sédiments dans ces lacs, il serait intéressant d'estimer de façon plus détaillée les apports atmosphériques dans cette région, notamment par le biais de modèles. Les enregistrements sédimentaires pourraient ensuite être comparés à un modèle de mélange intégrant l'azote atmosphérique à l'azote provenant de l'utilisation du territoire. Cette utilisation des isotopes d'azote permettrait éventuellement d'évaluer à long terme l'effet de la déposition atmosphérique sur la biologie de ces lacs. Cette avenue est particulièrement prometteuse dans un contexte où l'importance de la déposition atmosphérique sur les lacs semble être à l'échelle globale (p. ex. Holtgrieve et al. 2011).

Dans le troisième chapitre, nous avions comme objectif d'appliquer une approche isotopique croisée dans les lacs peu profonds et de déterminer si cette approche permet d'étudier l'assimilation par le phytoplancton et la nitrification *in situ*. Nous avons montré que l'utilisation des isotopes stables de la matière organique particulaire dans un lac mésotrophe était applicable pour comprendre l'assimilation, mais que cette utilisation est restreinte. Des mesures conjuguées avec les isotopes stables de carbones et du ratio C:N montrent plutôt que la matière organique provenant du bassin versant amenuise ce signal, notamment lors d'événements météorologiques importants (p. ex. de fortes pluies). Des études futures dans les lacs peu profonds pourraient se concentrer sur la mesure des isotopes stables sur des classes d'algues distinctes ou sur des composés spécifiques à celles-ci (p. ex. acides aminés). De telles études permettraient de déterminer quelles sont les préférences en terme de nutriment des différentes algues retrouvées en milieux naturels et dans quelles conditions celles-ci risquent de se retrouver. Bien que nous ayons montré qu'il y ait une assimilation reflétée par la matière particulaire dans le lac Bromont, une identification complète des cyanobactéries fixatrices de $N_2$ dans ce lac nous permettra également de confirmer si la fixation est importante dans ce système où si ce sont effectivement des évènements hydrologiques qui abaissent le $\delta^{15}N$ de la matière particulaire.

L'utilisation des isotopes stables du nitrate ($\delta^{15}N$ et $\delta^{18}O$) est également très prometteuse dans l'étude de la nitrification. En accord avec des observations faites par des études océanographiques, nous avons constaté une déviation linéaire de la relation 1:1 du $\delta^{15}N$ et $\delta^{18}O$ indicatrice de l'assimilation et de la nitrification simultanée du nitrate dans notre lac stratifié et mésotrophe. À notre connaissance, il s'agit de la première observation claire d'un tel phénomène en milieu lacustre. Cependant, le $\delta^{18}O$ de l'eau reste à mesurer pour confirmer si la nitrification a bien lieu. De plus, ces analyses permettront de déterminer si dans nos deux lacs eutrophes la composition en isotopes stables des nitrates est indicatrice du $NO_3^-$ produit dans le lac ou du $NO_3^-$ du bassin versant. Les données isotopiques de l'eau permettrons également de préciser l'importance de la nitrification. À l'aide de modèle de boîte, une prochaine étape serait de déterminer la proportion de nitrate provenant de la nitrification et comment cette proportion varie au cours de l'année. Cette utilisation permettra éventuellement de déterminer à quel niveau les communautés lacustres sont soutenues par un recyclage de nutriment dans le lac ou plutôt par des apports provenant du bassin versant. Étant donné l'importance de la nitrification dans le cycle de l'azote, son potentiel d'exacerber les effets de l'eutrophisation et sa méconnaissance en milieu lacustre, l’utilisation des isotopes de nitrate devrait grandement contribuer à l’évolution des connaissances dans ce domaine d’étude.

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# Annexe A : Informations supplémentaires pour le chapitre 2

Table A.I: Simple least square regression models for Quebec lakes to correct punctual limnological data (August sampling) to summer average and to fill missing data.

| x | y | $R^2$ adj. | *n* | *p* value |
|---|---|---|---|---|
| Mean TN (ln) | August TN (ln) | 0.86 | 13 | <0.001 |
| Mean TP (ln) | August TP (ln) | 0.86 | 13 | <0.001 |
| Mean DOC | August DOC | 0.77 | 13 | <0.001 |
| Mean Chla (ln) | August chla (ln) | 0.77 | 13 | <0.001 |
| Mean secchi (ln) | August secchi (ln) | 0.87 | 12 | <0.001 |
| Mean pH | August pH | 0.60 | 13 | 0.001 |
| Mean DP (ln) | August TP (ln) | 0.77 | 13 | <0.001 |
| Lake area (ln) | Lake volume (ln) | 0.77 | 34 | <0.001 |

Table A.II: Simple least square regression models to fill missing data for Alberta lakes.

| x | y | $R^2$ adj. | *n* | *p* value |
|---|---|---|---|---|
| TP (ln) | DP (ln) | 0.77 | 18 | <0.001 |
| TN (ln) | DOC (ln) | 0.93 | 13 | <0.001 |
| Lake area (ln) | Lake volume (ln) | 0.92 | 23 | <0.001 |

Table A.III: Summary of the environmental data from Quebec and Alberta regions. The regions are significantly different at $p < 0.005$ using a multivariate analysis of variance. Significantly different variables between the two regions were determined using t-test with Holm correction for multiple tests. *: variable is significant at $p < 0.05$, NS: variable is non-significant at $p > 0.05$.

| | Quebec | | | | Alberta | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Variables | Mean | Minimum | Maximum | Stdev | Mean | Minimum | Maximum | Stdev | Sig. |
| $\delta^{15}N$ | 2.5 | -3 | 5.2 | 1.9 | 4.1 | -0.8 | 8.6 | 1.9 | * |
| N sediments (%) | 1.3 | 0.2 | 3.5 | 0.9 | 2 | 0.5 | 3.7 | 0.9 | * |
| C sediments (%) | 12.4 | 2.5 | 29.4 | 6.6 | 14.6 | 4.8 | 25.3 | 5.9 | NS |
| C:N sediments | 10.6 | 5.1 | 15.5 | 2.6 | 7.8 | 4.6 | 10.8 | 1.7 | NS |
| TN (mg $L^{-1}$) | 0.4 | 0.2 | 1.2 | 1.9 | 1.7 | 0.4 | 13 | 2.4 | * |
| TP (µg $L^{-1}$) | 16.1 | 5.5 | 112.7 | 17.5 | 64 | 17.5 | 459 | 88.5 | * |
| DP (µg $L^{-1}$) | 6.5 | 3 | 31.3 | 4.8 | 25.7 | 5.9 | 241 | 46.7 | * |
| DOC (µg $L^{-1}$) | 7 | 3.4 | 14.9 | 2.8 | 20.1 | 6.3 | 122 | 22 | * |
| Chla (µg $L^{-1}$) | 6.4 | 1.6 | 41.8 | 6.9 | 19.8 | 3.8 | 114 | 22.8 | * |
| Secchi depth (m) | 3.3 | 0.5 | 7.1 | 1.3 | 2.5 | 0.5 | 4.8 | 1.1 | NS |
| pH | 7.8 | 7.3 | 8.7 | 0.3 | 8.7 | 7.9 | 9.4 | 0.3 | * |
| N:P | 29.9 | 10.2 | 58.2 | 10.8 | 30.9 | 9.2 | 58.8 | 12.7 | NS |
| N from fertilizer (kgN $yr^{-1}$) | $4.39 \times 10^4$ | 0 | $9.24 \times 10^5$ | $1.63 \times 10^5$ | $5.02 \times 10^5$ | 0 | $4.38 \times 10^6$ | $1.09 \times 10^6$ | * |
| N from population (kgN $yr^{-1}$) | $6.55 \times 10^3$ | 2.4 | $9.79 \times 10^4$ | $1.69 \times 10^4$ | $1.04 \times 10^4$ | 0 | $7.44 \times 10^4$ | $1.94 \times 10^4$ | NS |
| N from animal (kgN $yr^{-1}$) | $5.77 \times 10^4$ | 0 | $1.04 \times 10^6$ | $1.93 \times 10^5$ | $1.86 \times 10^5$ | 0 | $6.18 \times 10^5$ | $1.92 \times 10^5$ | * |
| Total anthropogenic N (kgN $yr^{-1}$) | $1.08 \times 10^5$ | 257,49 | $1.41 \times 10^6$ | $3.16 \times 10^5$ | $6.99 \times 10^5$ | 1600,17 | $4.77 \times 10^6$ | $1.23 \times 10^6$ | * |
| Buildings (number) | 515 | 3 | 8691 | 1427 | 235 | 0 | 1224 | 327 | NS |
| Agriculture area (%) | 4 | 0 | 26 | 7 | 13 | 0 | 62 | 18 | NS |
| Forested area (%) | 78 | 12 | 98 | 21 | 65 | 19 | 96 | 24 | NS |
| Water area (%) | 4 | 0 | 95 | 15 | 4 | 0 | 14 | 3.8 | * |
| Watershed area ($km^2$) | 85.7 | 0.6 | 1861.6 | 300.4 | 207 | 2.8 | 743.8 | 216.7 | * |
| Maximum watershed slope (°) | 32.1 | 12.8 | 84.5 | 12.9 | 14.7 | 6.8 | 26.5 | 5.3 | * |
| Mean watershed slope (°) | 5.6 | 2.4 | 13.1 | 2.7 | 2.2 | 0.7 | 10.6 | 2.2 | * |
| Lake area ($km^2$) | 1.5 | 0.1 | 14.8 | 2.8 | 16.2 | 0.1 | 81.2 | 21.4 | * |
| Mean depth (m) | 4,2 | 0,6 | 21,7 | 4,8 | 6,4 | 2 | 12.6 | 2.9 | * |
| Shore line length (km) | 6.2 | 1.2 | 23 | 5.4 | 27.3 | 3 | 86.6 | 21.9 | * |
| Lake volume ($m^3$) | $9.09 \times 10^6$ | $4.23 \times 10^4$ | $7.88 \times 10^7$ | $1.89 \times 10^7$ | $1.07 \times 10^8$ | $3.09 \times 10^5$ | $5.15 \times 10^8$ | $1.55 \times 10^8$ | * |
| Max depth (m) | 10.3 | 1.2 | 54.9 | 11.6 | 14.9 | 4.6 | 40 | 9 | * |
| Drainage ratio | 58.8 | 2 | 441.9 | 95.5 | 22.2 | 2.3 | 120.7 | 24.7 | NS |
| V:WA (km) | 0.5 | 0 | 3.6 | 0.9 | 0.8 | 0.1 | 4.1 | 1.1 | NS |
| IBP ($1 \times 10^6 m^3 km^{-1}$) | 1 | 0 | 6.9 | 1.5 | 2.9 | 0.1 | 11.8 | 3 | * |

# Annexe B : Tableaux des données brutes utilisées pour le chapitre 2

# Tableau B.I : Données sédimentaires et de la qualité de l’eau

| Lake | Region | $\delta^{15}N$ | Sediment N | Sediment organic C | Sediment C:N | Mixing | Average TN | Average TP | Average DP | Average DOC | Average chl*a* | Average secchi | Average pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Units* | *0 = Quebec<br>1 = Alberta* | *‰* | *% by mass* | *% by mass* | *by mass* | *0 = polymictic<br>1 = dimictic* | *mg L⁻¹* | *µg L⁻¹* | *µg L⁻¹* | *µg L⁻¹* | *µg L⁻¹* | *m* | |
| Araignees | 0 | 3.22 | 0.70 | 9.93 | 14.10 | 0 | 0.232 | 5.55 | 2.95 | 9.34 | 5.74 | 3.80 | 7.32 |
| Argent (Eastman) | 0 | 2.97 | 0.64 | 7.55 | 11.82 | 1 | 0.375 | 12.33 | 5.33 | 7.73 | 3.40 | 2.40 | 7.49 |
| Argent (St-Adolphe) | 0 | 4.66 | 0.68 | 6.19 | 9.09 | 1 | 0.472 | 8.12 | 3.96 | 4.97 | 2.17 | 4.54 | 7.85 |
| Baldwin | 0 | 2.17 | 1.48 | 17.50 | 11.83 | 1 | 0.276 | 8.14 | 3.97 | 5.01 | 3.92 | 3.26 | 7.85 |
| Bran de Scie | 0 | 1.79 | 0.44 | 6.77 | 15.54 | 1 | 0.303 | 14.50 | 5.50 | 6.30 | 3.75 | 2.20 | 7.53 |
| Brome | 0 | 3.29 | 1.04 | 8.54 | 8.23 | 0 | 0.349 | 14.50 | 6.00 | 5.20 | 7.00 | 3.00 | 7.82 |
| Bromont | 0 | 3.81 | 0.64 | 6.73 | 10.55 | 1 | 0.368 | 19.16 | 7.70 | 4.81 | 12.33 | 4.16 | 8.00 |
| Coulombe | 0 | 1.92 | 0.82 | 11.47 | 13.91 | 1 | 0.446 | 12.95 | 5.69 | 13.06 | 4.24 | 2.45 | 7.49 |
| Cristal | 0 | 2.53 | 3.45 | 25.02 | 7.25 | 0 | 0.340 | 10.98 | 5.00 | 4.77 | 4.56 | 3.97 | 7.90 |
| Drolet | 0 | 3.99 | 0.85 | 10.38 | 12.27 | 1 | 0.251 | 9.77 | 4.57 | 4.28 | 7.30 | 3.54 | 7.91 |
| Francais | 0 | -0.80 | 3.11 | 21.99 | 7.06 | 0 | 0.284 | 11.00 | 4.00 | 10.89 | 3.55 | 2.65 | 7.28 |
| Gale | 0 | -0.30 | 2.50 | 18.76 | 7.50 | 1 | 0.204 | 7.89 | 3.87 | 3.41 | 3.15 | 5.35 | 7.81 |
| Gilbert | 0 | 1.09 | 2.12 | 19.60 | 9.25 | 1 | 0.259 | 8.24 | 4.01 | 4.00 | 2.44 | 7.05 | 8.02 |
| Greenbay | 0 | 5.20 | 0.84 | 9.22 | 11.04 | 1 | 0.703 | 12.37 | 5.49 | 4.51 | 2.01 | 5.98 | 7.93 |
| Libby | 0 | 3.15 | 1.62 | 14.74 | 9.07 | 0 | 0.233 | 8.96 | 4.27 | 5.33 | 2.50 | 3.78 | 7.84 |
| Lindsay | 0 | 4.36 | 0.42 | 4.45 | 10.47 | 0 | 0.597 | 29.89 | 10.86 | 6.79 | 12.14 | 1.70 | 7.80 |
| Lippe | 0 | 1.13 | 1.92 | 11.47 | 5.99 | 0 | 0.683 | 25.21 | 9.51 | 6.71 | 15.36 | 1.47 | 8.15 |
| Louise | 0 | 4.10 | 0.19 | 2.51 | 13.43 | 0 | 0.408 | 15.40 | 6.50 | 9.86 | 4.10 | 2.80 | 7.75 |
| McKenzie | 0 | 3.59 | 0.95 | 11.75 | 12.36 | 0 | 0.325 | 13.72 | 5.94 | 9.32 | 7.74 | 3.36 | 7.58 |
| Miller | 0 | 2.57 | 1.02 | 12.32 | 12.06 | 0 | 0.241 | 10.59 | 4.87 | 4.65 | 3.47 | 4.28 | 7.76 |
| Monts | 0 | -0.46 | 2.31 | 18.34 | 7.94 | 1 | 0.337 | 9.50 | 5.00 | 7.04 | 2.55 | 2.90 | 7.50 |
| Nick | 0 | -0.50 | 3.11 | 22.20 | 7.14 | 0 | 0.262 | 9.00 | 5.00 | 4.06 | 2.75 | 2.80 | 8.20 |
| Orford | 0 | 4.37 | 0.58 | 5.88 | 10.08 | 1 | 0.243 | 6.00 | 3.00 | 3.78 | 1.55 | 5.25 | 7.99 |
| Orignal | 0 | 3.26 | 0.45 | 6.25 | 13.94 | 0 | 0.327 | 10.39 | 4.80 | 7.64 | 5.46 | 3.59 | 7.89 |
| Petit lac St-Francois | 0 | 2.91 | 0.72 | 6.16 | 8.56 | 0 | 1.154 | 112.67 | 31.33 | 11.06 | 41.77 | 0.50 | 8.72 |
| Rat-Musqué | 0 | -2.69 | 2.60 | 23.48 | 9.04 | 0 | 0.449 | 12.58 | 5.56 | 9.30 | 6.57 | 3.00 | 7.59 |
| Roxton | 0 | 3.61 | 1.08 | 15.67 | 14.46 | 0 | 0.611 | 34.33 | 14.67 | 6.98 | 13.87 | 1.60 | 7.99 |
| Sally | 0 | 2.47 | 1.97 | 23.03 | 11.71 | 0 | 0.313 | 9.98 | 4.65 | 4.59 | 4.26 | 3.26 | 8.17 |
| Simoneau | 0 | 2.27 | 0.92 | 13.25 | 14.43 | 1 | 0.216 | 8.00 | 4.00 | 4.64 | 1.80 | 4.70 | 7.54 |
| St-Georges | 0 | 4.89 | 0.91 | 8.47 | 9.35 | 0 | 0.473 | 26.12 | 9.78 | 9.08 | 9.80 | 2.06 | 7.76 |
| Stoke | 0 | 4.24 | 0.98 | 9.72 | 9.88 | 1 | 0.329 | 13.56 | 5.89 | 5.97 | 5.81 | 3.47 | 7.71 |
| Stukely | 0 | 2.90 | 0.41 | 5.29 | 12.82 | 1 | 0.264 | 8.00 | 3.83 | 4.61 | 1.70 | 4.75 | 7.64 |
| Sugarloaf | 0 | 2.08 | 1.21 | 10.50 | 8.68 | 1 | 0.180 | 12.56 | 5.55 | 3.80 | 3.73 | 3.26 | 7.78 |
| Trois-Lacs | 0 | 4.53 | 0.62 | 3.13 | 5.07 | 0 | 0.701 | 32.60 | 13.60 | 9.97 | 4.34 | 1.30 | 7.54 |
| Trois-Milles | 0 | 3.07 | 0.91 | 8.16 | 8.95 | 0 | 0.250 | 6.51 | 3.34 | 7.68 | 4.76 | 3.39 | 7.90 |
| Trousers | 0 | 2.92 | 0.75 | 9.94 | 13.19 | 0 | 0.387 | 10.98 | 5.00 | 7.89 | 3.30 | 3.87 | 7.74 |
| Truite (Ham Sud) | 0 | 2.36 | 0.98 | 13.06 | 13.34 | 0 | 0.418 | 14.46 | 6.19 | 14.86 | 3.86 | 2.90 | 7.60 |
| Truite (Orford) | 0 | 1.52 | 1.23 | 14.95 | 12.12 | 1 | 0.408 | 8.58 | 4.13 | 6.90 | 4.08 | 3.80 | 7.84 |
| Waterloo | 0 | 3.26 | 1.26 | 12.91 | 10.26 | 0 | 0.621 | 33.33 | 9.67 | 7.36 | 16.27 | 1.13 | 7.94 |
| Whitton | 0 | -2.97 | 3.28 | 29.36 | 8.96 | 0 | 0.371 | 6.90 | 3.49 | 10.58 | 5.24 | 3.26 | 7.90 |
| Baptiste North | 1 | 4.83 | 1.68 | 12.95 | 7.70 | 1 | 1.368 | 90.28 | 47.51 | 18.54 | 36.05 | 2.43 | 8.62 |
| Clear | 1 | 2.68 | 1.81 | 13.32 | 7.34 | 1 | 0.940 | 24.00 | 9.40 | 9.80 | 5.40 | 3.20 | 8.70 |
| Cooking | 1 | 8.58 | 1.68 | 18.08 | 10.79 | 0 | 13.000 | 459.00 | 241.00 | 122.00 | 114.00 | 0.45 | 9.40 |
| Crane | 1 | 5.03 | 2.12 | 13.36 | 6.31 | 1 | 0.985 | 21.60 | 10.40 | 13.70 | 5.89 | 3.05 | 8.90 |
| Elkwater | 1 | 5.62 | 0.53 | 4.80 | 9.14 | 0 | 0.750 | 41.40 | 14.21 | 8.65 | 7.97 | 2.15 | 8.60 |
| Ethel | 1 | 3.47 | 2.67 | 18.21 | 6.83 | 1 | 0.692 | 24.89 | 8.50 | 10.99 | 7.32 | 3.35 | 8.42 |
| Fishing | 1 | 3.52 | 2.96 | 16.32 | 5.51 | 0 | 1.235 | 26.90 | 7.35 | 16.00 | 22.85 | 1.51 | 8.84 |
| Gregoire | 1 | 3.96 | 0.97 | 8.41 | 8.72 | 0 | 0.726 | 37.35 | 12.78 | 11.70 | 17.93 | 1.58 | 7.95 |
| Gull | 1 | 3.99 | 1.52 | 10.98 | 7.25 | 0 | 1.621 | 36.29 | 12.41 | 20.24 | 8.51 | 1.86 | 9.17 |
| Hilda | 1 | 3.28 | 3.57 | 23.02 | 6.46 | 1 | 1.333 | 22.67 | 7.97 | 21.00 | 3.80 | 2.77 | 8.93 |
| Long Island North | 1 | 3.26 | 2.55 | 22.97 | 9.01 | 1 | 0.879 | 25.50 | 8.50 | 11.74 | 8.74 | 3.43 | 8.28 |
| Long Island South | 1 | 2.59 | 2.27 | 22.13 | 9.73 | 1 | 1.000 | 27.50 | 11.00 | 13.16 | 12.30 | 3.78 | 8.27 |
| Mons | 1 | 3.73 | 2.21 | 13.24 | 6.00 | 0 | 1.658 | 44.50 | 26.00 | 22.50 | 20.50 | 1.85 | 8.85 |
| Moose | 1 | 4.10 | 2.53 | 16.88 | 6.68 | 0 | 1.525 | 48.25 | 14.00 | 19.17 | 27.50 | 2.18 | 8.90 |
| Muriel | 1 | 5.11 | 1.55 | 14.56 | 9.38 | 0 | 2.322 | 54.67 | 22.83 | 27.87 | 9.90 | 1.17 | 9.25 |
| Pine | 1 | 6.83 | 1.26 | 10.47 | 8.34 | 0 | 1.809 | 72.80 | 30.38 | 22.32 | 28.98 | 2.06 | 8.68 |
| Reesor | 1 | 3.49 | 0.52 | 4.76 | 9.10 | 1 | 0.756 | 47.78 | 16.48 | 6.65 | 14.92 | 1.97 | 8.45 |
| Sante | 1 | 8.27 | 1.10 | 10.65 | 9.68 | 1 | 2.305 | 61.00 | 21.19 | 27.68 | 7.33 | 4.75 | 9.15 |
| Skeleton | 1 | 3.32 | 3.72 | 23.83 | 6.40 | 0 | 1.158 | 29.00 | 8.40 | 14.00 | 12.00 | 2.30 | 8.70 |
| Spruce Coulee | 1 | 3.39 | 0.98 | 8.51 | 8.69 | 0 | 0.439 | 17.53 | 5.86 | 6.33 | 4.79 | 4.07 | 8.39 |
| Steele | 1 | 4.46 | 2.87 | 25.32 | 8.84 | 0 | 1.688 | 172.17 | 61.73 | 20.98 | 46.24 | 1.83 | 8.50 |
| Sylvan | 1 | 3.36 | 1.28 | 6.02 | 4.69 | 0 | 0.694 | 75.25 | 7.00 | 9.51 | 5.95 | 4.63 | 8.84 |
| Tucker | 1 | 2.96 | 2.24 | 16.50 | 7.36 | 0 | 1.257 | 70.00 | 17.00 | 16.14 | 28.50 | 1.55 | 8.55 |
| Wolf | 1 | -0.79 | 2.74 | 17.79 | 9.61 | 1 | 0.828 | 20.50 | 7.45 | 14.00 | 3.95 | 3.40 | 8.55 |
| Wizard | 1 | 3.48 | 1.85 | 12.64 | 4.62 | 0 | 1.300 | 48.40 | 13.60 | 16.63 | 32.60 | 1.33 | 8.30 |

# Tableau B.II : Données morphométriques et topographiques

| Lake | Region | Latitude | Longitude | Lake area | Watershed area | Max watershed slope | Mean watershed slope | Lake volume | Maximum slope | Mean slope | Shoreline length | Water residence time | WSA:LA | IBP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Units* | *0 = Quebec*<br>*1 = Alberta* | *DD* | *DD* | $km^2$ | $km^2$ | ° | ° | $m^3$ | *m* | *m* | *km* | *yr* |  | $(10^6 m^3 km^{-1})$ |
| Araignees | 0 | 45.4759 | -70.8094 | 8.74 | 142.25 | 84.47 | 6.21 | 19361328 | 10.67 | 2.21 | 18.89 | NA | 16.27 | 1.03 |
| Argent (Eastman) | 0 | 45.3103 | -72.3137 | 1.05 | 65.04 | 41.84 | 5.24 | 4672008 | 15.24 | 4.44 | 4.66 | 0.15 | 61.76 | 1.00 |
| Argent (St-Adolphe) | 0 | 45.6423 | -71.5950 | 0.71 | 65.04 | 26.36 | 6.54 | 15465233 | 54.86 | 21.70 | 4.75 | NA | 91.29 | 3.26 |
| Baldwin | 0 | 45.0185 | -71.8875 | 0.48 | 5.10 | 34.24 | 3.78 | 1042060 | 7.62 | 2.18 | 2.54 | 0.03 | 10.65 | 0.41 |
| Bran de Scie | 0 | 45.4060 | -72.2020 | 0.12 | 41.09 | 46.91 | 5.69 | 535070 | 9.14 | 4.30 | 2.51 | 0.80 | 330.29 | 0.21 |
| Brome | 0 | 45.2504 | -72.5199 | 14.76 | 173.52 | 38.58 | 4.29 | 78040239 | 12.19 | 5.29 | 23.03 | NA | 11.76 | 3.39 |
| Bromont | 0 | 45.2662 | -72.6713 | 0.46 | 24.84 | 39.15 | 9.49 | 1873542 | 7.00 | 4.04 | 3.01 | NA | 53.52 | 0.62 |
| Coulombe | 0 | 45.8387 | -71.4649 | 0.68 | 24.94 | 32.99 | 4.46 | 3556272 | 12.19 | 5.21 | 4.07 | NA | 36.52 | 0.87 |
| Cristal | 0 | 45.0300 | -72.0776 | 0.34 | 1.98 | 16.23 | 3.10 | 717557 | 5.49 | 2.13 | 2.29 | NA | 5.88 | 0.31 |
| Drolet | 0 | 45.7384 | -70.8806 | 6.37 | 12.96 | 30.79 | 4.48 | 26917383 | 7.62 | 4.23 | 13.00 | NA | 2.03 | 2.07 |
| Francais | 0 | 45.0810 | -71.6437 | 0.06 | 2.45 | 19.86 | 6.01 | 42339 | 1.22 | 0.66 | 1.19 | NA | 38.31 | 0.04 |
| Gale | 0 | 45.2697 | -72.6949 | 0.11 | 0.62 | 32.98 | 13.10 | 228624 | 9.14 | 2.12 | 1.36 | NA | 5.79 | 0.17 |
| Gilbert | 0 | 45.2185 | -72.2915 | 0.18 | 4.71 | 30.64 | 7.41 | 17002696 | 12.00 | 6.00 | 2.48 | NA | 26.55 | 6.87 |
| Greenbay | 0 | 45.1640 | -72.2950 | 0.47 | 49.49 | 35.88 | 5.38 | 78811760 | 24.38 | 17.42 | 14.29 | NA | 105.28 | 5.52 |
| Libby | 0 | 45.2763 | -72.3677 | 0.39 | 5.52 | 15.32 | 3.84 | 547541 | 3.05 | 1.39 | 4.62 | NA | 14.04 | 0.12 |
| Lindsay | 0 | 45.1822 | -71.5440 | 0.62 | 29.92 | 32.07 | 5.31 | 1102860 | 4.88 | 1.78 | 4.45 | NA | 48.40 | 0.25 |
| Lippe | 0 | 45.0978 | -71.6564 | 0.13 | 0.99 | 29.27 | 10.53 | 177311 | 2.44 | 1.37 | 1.73 | NA | 7.70 | 0.10 |
| Louise | 0 | 45.5624 | -71.5649 | 4.21 | 1861.65 | 44.72 | 3.03 | 1391769 | 2.00 | 1.42 | 16.61 | NA | 441.91 | 0.08 |
| McKenzie | 0 | 45.5646 | -71.0190 | 0.59 | 23.08 | 19.52 | 4.14 | 770240 | 3.66 | 1.30 | 5.25 | NA | 38.95 | 0.15 |
| Miller | 0 | 45.4884 | -72.1860 | 0.20 | 0.75 | 22.48 | 8.11 | 555824 | 4.27 | 2.81 | 2.11 | NA | 3.80 | 0.26 |
| Monts | 0 | 45.4040 | -72.1865 | 0.29 | 44.57 | 46.91 | 5.58 | 312991 | 7.62 | 1.09 | 4.15 | 0.01 | 155.72 | 0.08 |
| Nick | 0 | 45.2119 | -72.3280 | 0.54 | 5.99 | 29.72 | 7.39 | 1459391 | 6.00 | 3.00 | 3.86 | 0.31 | 11.17 | 0.38 |
| Orford | 0 | 45.2947 | -72.2691 | 1.28 | 9.22 | 41.84 | 10.12 | 20615825 | 48.77 | 16.05 | 8.40 | 3.82 | 7.17 | 2.45 |
| Orignal | 0 | 45.6103 | -70.9055 | 0.22 | 44.65 | 24.88 | 3.32 | 641277 | 4.88 | 2.91 | 2.48 | NA | 202.46 | 0.26 |
| Petit lac St-Francois | 0 | 45.5380 | -72.0376 | 0.87 | 19.54 | 16.27 | 2.81 | 974002 | 1.83 | 1.12 | 4.44 | 0.06 | 22.57 | 0.22 |
| Rat-Musqué | 0 | 45.7070 | -70.8990 | 1.12 | 10.90 | 29.59 | 3.47 | 647767 | 1.22 | 0.58 | 5.37 | NA | 9.69 | 0.12 |
| Roxton | 0 | 45.4675 | -72.6526 | 1.93 | 14.64 | 17.23 | 2.62 | 5745401 | 5.49 | 2.97 | 7.44 | 0.56 | 7.57 | 0.77 |
| Sally | 0 | 45.1238 | -72.3336 | 0.18 | 3.33 | 36.64 | 10.54 | 2963993 | 2.00 | 1.00 | 2.30 | NA | 19.01 | 1.29 |
| Simoneau | 0 | 45.4120 | -72.1940 | 0.45 | 4.66 | 33.40 | 5.55 | 4376542 | 22.86 | 9.63 | 3.54 | 0.41 | 10.25 | 1.24 |
| St-Georges | 0 | 45.6454 | -71.8822 | 0.51 | 7.71 | 12.79 | 2.42 | 1156995 | 4.27 | 2.25 | 2.88 | NA | 15.00 | 0.40 |
| Stoke | 0 | 45.5179 | -71.8102 | 0.38 | 12.27 | 20.83 | 4.43 | 1904989 | 9.14 | 5.07 | 2.84 | NA | 32.65 | 0.67 |
| Stukely | 0 | 45.3750 | -72.2536 | 4.02 | 16.31 | 46.91 | 6.35 | 51388158 | 30.48 | 12.79 | 17.17 | 4.03 | 4.06 | 2.99 |
| Sugarloaf | 0 | 45.1238 | -72.3336 | 0.23 | 1.16 | 39.78 | 12.71 | 714904 | 8.53 | 3.10 | 2.57 | NA | 5.05 | 0.28 |
| Trois-Lacs | 0 | 45.7998 | -71.8773 | 2.40 | 511.33 | 39.92 | 3.37 | 6664972 | 10.97 | 2.78 | 15.69 | 0.01 | 213.32 | 0.42 |
| Trois-Milles | 0 | 45.6878 | -70.9197 | 1.02 | 14.25 | 28.95 | 5.38 | 1073464 | 2.44 | 1.05 | 4.54 | NA | 13.98 | 0.24 |
| Trousers | 0 | 45.2455 | -72.3387 | 0.59 | 118.83 | 43.17 | 4.90 | 1217636 | 10.67 | 2.06 | 6.33 | NA | 200.87 | 0.19 |
| Truite (Ham Sud) | 0 | 45.8061 | -71.5869 | 0.33 | 10.33 | 32.25 | 4.59 | 420774 | 4.57 | 1.29 | 2.12 | NA | 31.63 | 0.20 |
| Truite (Orford) | 0 | 45.3449 | -72.1511 | 0.78 | 3.32 | 27.26 | 4.41 | 3875449 | 15.24 | 4.95 | 4.64 | NA | 4.24 | 0.83 |
| Waterloo | 0 | 45.3350 | -72.5220 | 1.47 | 28.66 | 25.60 | 2.81 | 4032009 | 4.88 | 2.75 | 7.29 | 0.32 | 19.54 | 0.55 |
| Whitton | 0 | 45.6283 | -71.0507 | 0.59 | 9.67 | 15.19 | 2.90 | 519664 | 2.00 | 0.88 | 6.14 | NA | 16.36 | 0.08 |
| Baptiste North | 1 | 54.7382 | -113.5490 | 9.72 | 295.73 | 13.00 | 1.46 | 90361250 | 27.50 | 9.30 | 24.05 | 6.00 | 30.42 | 3.76 |
| Clear | 1 | 52.7651 | -110.6009 | 0.78 | 11.18 | 13.49 | 2.75 | 4232226 | 18.60 | 5.45 | 3.88 | NA | 14.39 | 1.09 |
| Cooking | 1 | 53.4375 | -113.0117 | 36.43 | 289.14 | 6.80 | 0.88 | 71982500 | 4.60 | 1.98 | 73.77 | >100 | 7.94 | 0.98 |
| Crane | 1 | 54.5176 | -110.5253 | 9.93 | 53.14 | 12.21 | 1.54 | 83391250 | 25.91 | 8.39 | 18.65 | >100 | 5.35 | 4.47 |
| Elkwater | 1 | 49.6700 | -110.2981 | 2.31 | 16.09 | 25.23 | 6.71 | 8520000 | 8.40 | 3.68 | 13.22 | 6.00 | 6.95 | 0.64 |
| Ethel | 1 | 54.5316 | -110.3491 | 4.93 | 595.37 | 15.67 | 0.97 | 37640000 | 30.00 | 7.63 | 11.17 | 2.50 | 120.72 | 3.37 |
| Fishing | 1 | 53.9038 | -110.2069 | 6.93 | 254.65 | 12.03 | 1.34 | 39463953 | 14.00 | 5.70 | 19.82 | NA | 36.75 | 1.99 |
| Gregoire | 1 | 56.4617 | -111.1459 | 26.52 | 205.83 | 19.48 | 1.89 | 95520643 | 7.20 | 3.60 | 30.45 | 4.00 | 7.76 | 3.14 |
| Gull | 1 | 52.5083 | -113.9661 | 81.22 | 188.54 | 8.89 | 1.36 | 515311250 | 11.00 | 6.34 | 52.99 | NA | 2.32 | 9.72 |
| Hilda | 1 | 54.5219 | -110.4304 | 3.56 | 96.48 | 12.43 | 1.44 | 25196250 | 14.00 | 7.08 | 13.61 | NA | 27.10 | 1.85 |
| Long Island North | 1 | 54.4708 | -113.7880 | 1.41 | 4.34 | 6.79 | 1.12 | 15681250 | 14.00 | 11.16 | 18.65 | NA | 3.09 | 0.84 |
| Long Island South | 1 | 54.4708 | -113.7880 | 0.82 | 13.81 | 8.57 | 0.99 | 10278750 | 14.00 | 12.57 | 18.65 |  | 16.89 | 0.55 |
| Mons | 1 | 54.1902 | -112.3601 | 2.68 | 16.66 | 9.75 | 2.74 | 14267842 | 7.00 | 7.00 | 6.66 | NA | 6.22 | 2.14 |
| Moose | 1 | 54.2592 | -110.9653 | 40.52 | 743.79 | 21.95 | 1.53 | 218466250 | 19.80 | 5.39 | 86.63 | 7.50 | 18.35 | 2.52 |
| Muriel | 1 | 54.1504 | -110.6813 | 61.82 | 376.82 | 19.22 | 1.90 | 469813750 | 10.70 | 7.60 | 58.94 | >100 | 6.10 | 7.97 |
| Pine | 1 | 52.0848 | -113.4403 | 4.05 | 154.75 | 17.38 | 1.89 | 23637500 | 12.20 | 5.84 | 20.05 | 9.00 | 38.20 | 1.18 |
| Reesor | 1 | 49.6655 | -110.1107 | 0.44 | 2.84 | 26.54 | 10.62 | 1045782 | 5.50 | 2.35 | 4.58 | 6.00 | 6.39 | 0.23 |
| Sante | 1 | 53.8411 | -111.5441 | 11.25 | 375.30 | 15.53 | 1.12 | 105217500 | 24.38 | 9.36 | 39.61 | NA | 33.37 | 2.66 |
| Skeleton | 1 | 54.6225 | -112.7443 | 8.79 | 67.72 | 10.20 | 1.21 | 56943750 | 16.66 | 6.48 | 24.84 | 61.50 | 7.71 | 2.29 |
| Spruce Coulee | 1 | 49.6740 | -110.1810 | 0.12 | 4.56 | 16.89 | 5.10 | 308820 | 6.00 | 2.52 | 2.99 | 3.00 | 37.19 | 0.10 |
| Steele | 1 | 54.6502 | -113.7720 | 7.22 | 288.51 | 11.66 | 0.72 | 24680000 | 4.57 | 3.42 | 19.02 | 2.00 | 39.97 | 1.30 |
| Sylvan | 1 | 52.3575 | -114.1623 | 42.29 | 105.82 | 14.60 | 1.77 | 432067500 | 18.30 | 10.22 | 36.55 | NA | 2.50 | 11.82 |
| Tucker | 1 | 54.5343 | -110.5996 | 6.66 | 296.29 | 12.94 | 1.02 | 19550000 | 6.30 | 2.93 | 16.73 | NA | 44.46 | 1.17 |
| Wolf | 1 | 53.1133 | -113.8551 | 31.33 | 684.89 | 15.58 | 0.84 | 307708750 | 40.00 | 9.82 | 50.89 | 9.20 | 13.09 | 6.05 |
| Wizard | 1 | 54.6965 | -110.9942 | 2.59 | 33.88 | 20.05 | 1.82 | 11472500 | 10.64 | 4.43 | 16.32 | 13.50 | 21.86 | 0.70 |

# Tableau B.III : Données d’utilisation du territoire et de charge en azote aux bassins versants

| Lake | Region | Number of buildings | Agricultural area | Forested area | Water area | Fertilizer N load | Population | Population 1 km around lake | Population 0.5 km around lake | Population 0.25 km around lake | Population 0.5 km around lake | Population N load | Animal N load | Atmospheric deposition N load | Anthropogenic N load | Total N deposition / anthropogenic N load |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Units* | *0 = Quebec*<br>*1 = Alberta* | | *% of watershed* | *% of watershed* | *% of watershed* | *kg yr⁻¹* | *ind.* | *ind.* | *ind.* | *ind.* | *ind.* | *kg yr⁻¹* | *kg yr⁻¹* | *kg yr⁻¹* | *kg yr⁻¹* | *%* |
| Araignees | 0 | 39 | 0.00 | 97.10 | 0.18 | 0.00 | 74.90 | 59.65 | 57.72 | 57.72 | 46.18 | 419.46 | 14280.47 | 120792.52 | 135492.45 | 89.15 |
| Argent (Eastman) | 0 | 113 | 0.42 | 11.93 | 2.87 | 5041.80 | 165.06 | 620.63 | 506.06 | 350.10 | 221.20 | 924.36 | 9169.23 | 52878.22 | 68013.61 | 77.75 |
| Argent (St-Adolphe) | 0 | 864 | 6.19 | 73.13 | 0.12 | 3526.02 | 1375.08 | 140.23 | 127.09 | 100.79 | 64.27 | 7700.44 | 7492.14 | 52605.65 | 71324.25 | 73.76 |
| Baldwin | 0 | 11 | 0.05 | 43.32 | 0.00 | 469.48 | 87.51 | 63.64 | 63.64 | 15.91 | 0.00 | 490.03 | 10753.12 | 4461.80 | 16174.43 | 27.59 |
| Bran de Scie | 0 | 436 | 0.00 | 77.13 | 17.50 | 0.00 | 940.37 | 125.94 | 106.57 | 101.72 | 77.50 | 5266.04 | 10826.74 | 32969.79 | 49062.58 | 67.20 |
| Brome | 0 | 1956 | 3.76 | 75.84 | 0.53 | 34604.74 | 4105.84 | 1477.88 | 1209.83 | 1023.89 | 748.60 | 22992.69 | 128528.51 | 150622.28 | 336748.22 | 44.73 |
| Bromont | 0 | 259 | 6.71 | 72.60 | 0.73 | 9308.20 | 873.90 | 362.94 | 257.57 | 156.10 | 85.86 | 4893.82 | 148038.67 | 20246.24 | 182486.92 | 11.09 |
| Coulombe | 0 | 37 | 0.00 | 92.25 | 0.98 | 0.00 | 35.73 | 18.35 | 17.38 | 13.52 | 3.86 | 200.08 | 1160.34 | 20496.98 | 21857.41 | 93.78 |
| Cristal | 0 | 54 | 25.62 | 16.22 | 0.20 | 3101.97 | 109.71 | 91.80 | 68.37 | 32.79 | 4.13 | 614.36 | 4531.54 | 1851.83 | 10099.70 | 18.34 |
| Drolet | 0 | 137 | 0.85 | 65.42 | 0.62 | 1553.32 | 273.52 | 253.56 | 237.59 | 211.63 | 183.68 | 1531.73 | 7451.87 | 15461.58 | 25998.50 | 59.47 |
| Francais | 0 | 3 | 0.61 | 84.99 | 95.32 | 347.63 | 4.33 | 4.33 | 0.00 | 0.00 | 0.00 | 24.27 | 1706.45 | 2013.41 | 4091.77 | 49.21 |
| Gale | 0 | 7 | 0.32 | 82.12 | 0.00 | 271.76 | 27.32 | 27.32 | 27.32 | 23.42 | 7.81 | 152.98 | 592.89 | 586.21 | 1603.85 | 36.55 |
| Gilbert | 0 | 14 | 0.00 | 97.23 | 2.01 | 0.00 | 19.94 | 17.09 | 12.82 | 12.82 | 7.12 | 111.64 | 145.86 | 3906.53 | 4164.03 | 93.82 |
| Greenbay | 0 | 483 | 1.05 | 88.56 | 4.75 | 2260.14 | 683.16 | 44.08 | 32.75 | 29.90 | 18.51 | 3825.68 | 1569.52 | 39971.66 | 47627.00 | 83.93 |
| Libby | 0 | 117 | 0.00 | 85.43 | 0.44 | 0.00 | 173.23 | 168.79 | 149.54 | 133.25 | 118.45 | 970.08 | 0.00 | 4730.70 | 5700.78 | 82.98 |
| Lindsay | 0 | 144 | 11.78 | 70.13 | 0.10 | 10950.78 | 235.89 | 31.12 | 29.49 | 29.49 | 18.02 | 1320.96 | 0.00 | 24431.85 | 36703.58 | 66.57 |
| Lippe | 0 | 58 | 1.35 | 87.68 | 0.00 | 643.03 | 83.79 | 83.79 | 83.79 | 83.79 | 78.01 | 469.23 | 758.93 | 898.00 | 2769.19 | 32.43 |
| Louise | 0 | 8691 | 4.72 | 73.59 | 6.05 | 270360.88 | 17483.75 | 692.85 | 553.28 | 391.29 | 311.53 | 97909.01 | 1039600.81 | 1492688.76 | 2900559.45 | 51.46 |
| McKenzie | 0 | 42 | 0.09 | 93.81 | 0.01 | 1682.72 | 94.60 | 49.61 | 49.61 | 45.12 | 45.12 | 529.78 | 5552.47 | 18940.09 | 26705.07 | 70.92 |
| Miller | 0 | 50 | 0.00 | 94.27 | 0.00 | 0.00 | 96.13 | 96.13 | 96.13 | 94.20 | 94.20 | 538.30 | 773.82 | 761.12 | 2073.23 | 36.71 |
| Monts | 0 | 509 | 0.00 | 77.77 | 16.45 | 0.00 | 1117.17 | 249.46 | 217.98 | 203.29 | 48.44 | 6256.14 | 11576.41 | 35887.99 | 53720.54 | 66.80 |
| Nick | 0 | 52 | 0.00 | 97.05 | 2.39 | 0.00 | 70.67 | 62.52 | 33.98 | 20.39 | 6.80 | 395.76 | 527.61 | 5223.56 | 6146.92 | 84.98 |
| Orford | 0 | 201 | 0.00 | 91.85 | 0.45 | 0.00 | 313.64 | 309.57 | 250.85 | 183.26 | 119.86 | 1756.40 | 777.30 | 8400.37 | 10934.07 | 76.83 |
| Orignal | 0 | 198 | 6.46 | 80.14 | 0.05 | 22083.28 | 498.59 | 135.96 | 109.66 | 66.57 | 61.81 | 2792.13 | 14766.93 | 35899.70 | 75542.04 | 47.52 |
| Petit lac St-Francois | 0 | 403 | 22.64 | 47.89 | 0.10 | 21168.06 | 1050.72 | 849.96 | 417.16 | 273.76 | 174.69 | 5884.02 | 20197.70 | 16328.88 | 63578.65 | 25.68 |
| Rat-Musqué | 0 | 91 | 1.00 | 79.84 | 0.76 | 2234.29 | 169.16 | 86.39 | 46.02 | 42.20 | 38.54 | 947.28 | 5190.77 | 9618.74 | 17991.08 | 53.46 |
| Roxton | 0 | 329 | 0.47 | 61.79 | 0.47 | 1140.21 | 1064.81 | 877.09 | 796.18 | 601.99 | 601.99 | 5962.95 | 87725.21 | 13256.37 | 108084.74 | 12.26 |
| Sally | 0 | 19 | 0.00 | 97.62 | 1.22 | 0.00 | 26.47 | 26.47 | 26.47 | 26.47 | 18.11 | 148.22 | 2417.66 | 2806.55 | 5372.42 | 52.24 |
| Simoneau | 0 | 18 | 0.00 | 96.25 | 2.48 | 0.00 | 43.60 | 41.17 | 41.17 | 41.17 | 36.33 | 244.13 | 1426.76 | 4091.86 | 5762.75 | 71.01 |
| St-Georges | 0 | 113 | 10.84 | 55.95 | 0.00 | 6133.74 | 181.24 | 163.59 | 147.56 | 115.48 | 48.12 | 1014.93 | 0.00 | 6581.25 | 13729.91 | 47.93 |
| Stoke | 0 | 137 | 13.19 | 73.72 | 0.18 | 1843.55 | 385.65 | 261.79 | 191.42 | 149.19 | 98.52 | 2159.65 | 9944.27 | 10116.99 | 24064.45 | 42.04 |
| Stukely | 0 | 151 | 0.00 | 97.87 | 0.46 | 0.00 | 252.15 | 247.99 | 239.20 | 203.29 | 122.84 | 1412.03 | 5316.73 | 16263.95 | 22992.72 | 70.74 |
| Sugarloaf | 0 | 34 | 0.00 | 96.01 | 0.00 | 0.00 | 39.55 | 39.55 | 39.55 | 37.22 | 27.91 | 221.45 | 505.28 | 1115.86 | 1842.60 | 60.56 |
| Trois-Lacs | 0 | 2555 | 20.20 | 57.43 | 0.07 | 425892.76 | 7281.43 | 1600.86 | 866.60 | 523.17 | 300.70 | 40775.99 | 676508.34 | 410983.55 | 1554160.64 | 26.44 |
| Trois-Milles | 0 | 130 | 3.19 | 86.49 | 0.01 | 1377.94 | 237.54 | 171.76 | 166.28 | 164.45 | 158.97 | 1330.23 | 6083.73 | 12212.45 | 21004.34 | 58.14 |
| Trousers | 0 | 1321 | 0.43 | 84.26 | 3.87 | 5342.86 | 2059.47 | 144.36 | 100.87 | 88.52 | 66.55 | 11533.05 | 14015.93 | 95539.14 | 126430.99 | 75.57 |
| Truite (Ham Sud) | 0 | 6 | 0.00 | 94.48 | 0.00 | 0.00 | 7.68 | 7.68 | 7.68 | 7.68 | 3.84 | 43.03 | 2101.10 | 8525.31 | 10669.45 | 79.90 |
| Truite (Orford) | 0 | 77 | 0.00 | 95.22 | 0.38 | 0.00 | 186.49 | 186.49 | 167.11 | 150.16 | 79.92 | 1044.35 | 754.30 | 3282.67 | 5081.32 | 64.60 |
| Waterloo | 0 | 547 | 10.08 | 65.85 | 0.51 | 923524.59 | 4487.40 | 2309.75 | 1721.42 | 1046.77 | 642.92 | 25129.42 | 50829.19 | 24102.46 | 1023585.67 | 2.35 |
| Whitton | 0 | 155 | 1.72 | 85.52 | 0.00 | 2106.48 | 368.51 | 19.02 | 19.02 | 19.02 | 19.02 | 2063.65 | 3208.11 | 8205.80 | 15584.04 | 52.66 |
| Baptiste North | 1 | 367 | 7.65 | 80.64 | 1.68 | 159308.24 | 692.02 | 578.45 | 556.10 | 532.47 | 400.70 | 3875.30 | 147067.69 | 122180.61 | 432431.84 | 28.25 |
| Clear | 1 | 61 | 11.55 | 46.97 | 1.98 | 12971.25 | 97.24 | 94.82 | 94.82 | 93.22 | 71.96 | 544.54 | 13339.57 | 4780.69 | 31636.06 | 15.11 |
| Cooking | 1 | 1031 | 18.50 | 43.36 | 9.96 | 156500.69 | 13287.26 | 3914.86 | 2633.63 | 1537.47 | 441.31 | 74408.68 | 427005.68 | 130229.70 | 788144.75 | 16.52 |
| Crane | 1 | 46 | 0.94 | 86.30 | 4.03 | 2617.19 | 214.25 | 205.19 | 205.19 | 205.19 | 132.82 | 1199.78 | 30877.21 | 25229.42 | 59923.60 | 42.10 |
| Elkwater | 1 | 38 | 2.05 | 67.00 | 0.45 | 6798.39 | 86.68 | 79.84 | 61.59 | 25.09 | 2.28 | 485.40 | 8782.07 | 7360.95 | 23426.81 | 31.42 |
| Ethel | 1 | 172 | 0.85 | 83.41 | 11.13 | 24995.47 | 389.36 | 38.20 | 35.96 | 33.72 | 26.98 | 2180.40 | 231836.58 | 240119.76 | 499132.22 | 48.11 |
| Fishing | 1 | 46 | 0.16 | 82.27 | 5.89 | 982.85 | 106.76 | 67.18 | 55.96 | 42.69 | 20.20 | 597.85 | 208237.98 | 104633.20 | 314451.88 | 33.27 |
| Gregoire | 1 | 102 | 0.00 | 95.42 | 3.53 | 0.00 | 5831.15 | 4731.27 | 3899.61 | 2491.74 | 63.89 | 32654.45 | 0.00 | 92940.64 | 125595.09 | 74.00 |
| Gull | 1 | 448 | 61.62 | 23.19 | 1.52 | 2439193.42 | 1065.72 | 613.05 | 274.55 | 64.03 | 19.70 | 5968.06 | 617694.67 | 107905.69 | 3170761.84 | 3.40 |
| Hilda | 1 | 67 | 1.47 | 77.43 | 13.57 | 7139.05 | 255.06 | 33.67 | 31.43 | 20.20 | 4.49 | 1428.36 | 55801.89 | 40015.24 | 104384.54 | 38.33 |
| Long Island North | 1 | 29 | 0.71 | 84.55 | 3.05 | 277.57 | 51.81 | 51.81 | 51.81 | 48.23 | 37.52 | 290.12 | 23127.80 | 2298.36 | 25993.85 | 8.84 |
| Long Island South | 1 | 82 | 1.13 | 89.10 | 2.10 | 277.57 | 98.73 | 98.73 | 98.73 | 98.73 | 50.84 | 552.89 | 7450.72 | 5850.26 | 14131.44 | 41.40 |
| Mons | 1 | 30 | 15.81 | 52.45 | 1.20 | 13791.02 | 37.99 | 21.53 | 12.66 | 6.33 | 3.80 | 212.74 | 12893.76 | 7733.57 | 34631.09 | 22.33 |
| Moose | 1 | 1223 | 28.58 | 41.95 | 4.76 | 885661.04 | 6546.67 | 1169.63 | 1073.10 | 873.08 | 401.48 | 36661.33 | 578635.93 | 313726.23 | 1814684.53 | 17.29 |
| Muriel | 1 | 418 | 12.89 | 66.11 | 7.26 | 112975.05 | 1282.51 | 610.78 | 586.08 | 563.33 | 557.19 | 7182.06 | 313167.02 | 175455.35 | 608779.47 | 28.82 |
| Pine | 1 | 198 | 31.06 | 44.54 | 1.51 | 4379099.26 | 637.15 | 348.51 | 322.63 | 286.39 | 193.37 | 3568.03 | 387649.82 | 63520.13 | 4833837.24 | 1.31 |
| Reesor | 1 | 0 | 0.00 | 39.30 | 1.17 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 1600.17 | 1314.83 | 2914.99 | 45.11 |
| Sante | 1 | 649 | 37.70 | 22.47 | 11.31 | 1834316.23 | 5959.64 | 102.47 | 98.24 | 77.07 | 26.95 | 33374.00 | 465007.17 | 154618.29 | 2487315.69 | 6.22 |
| Skeleton | 1 | 261 | 0.79 | 86.02 | 0.79 | 1764.22 | 485.01 | 431.02 | 421.71 | 374.96 | 143.14 | 2716.07 | 39486.39 | 30602.44 | 74569.12 | 41.04 |
| Spruce Coulee | 1 | 0 | 2.95 | 67.85 | 0.48 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 2277.77 | 1871.50 | 4149.27 | 45.10 |
| Steele | 1 | 20 | 1.58 | 83.42 | 4.68 | 11636.19 | 43.24 | 10.42 | 2.60 | 0.00 | 0.00 | 242.13 | 117021.33 | 118290.66 | 247190.31 | 47.85 |
| Sylvan | 1 | 539 | 55.95 | 18.95 | 0.17 | 2323621.98 | 9031.90 | 7386.39 | 3178.19 | 3178.19 | 1764.06 | 50578.67 | 335698.17 | 59247.12 | 2769145.94 | 2.14 |
| Tucker | 1 | 6 | 0.46 | 88.10 | 3.59 | 3418.17 | 13.47 | 2.24 | 2.24 | 2.24 | 0.00 | 75.43 | 166795.61 | 121182.06 | 291471.28 | 41.58 |
| Wolf | 1 | 64 | 1.16 | 90.63 | 4.72 | 131776.05 | 8.98 | 0.00 | 0.00 | 0.00 | 0.00 | 50.29 | 245138.25 | 286487.81 | 663452.40 | 43.18 |
| Wizard | 1 | 4 | 26.78 | 65.05 | 1.85 | 51000.38 | 145.52 | 115.66 | 113.33 | 108.65 | 81.26 | 814.91 | 214524.87 | 14588.24 | 280928.41 | 5.19 |

# Annexe C : Informations supplémentaires pour le chapitre 3

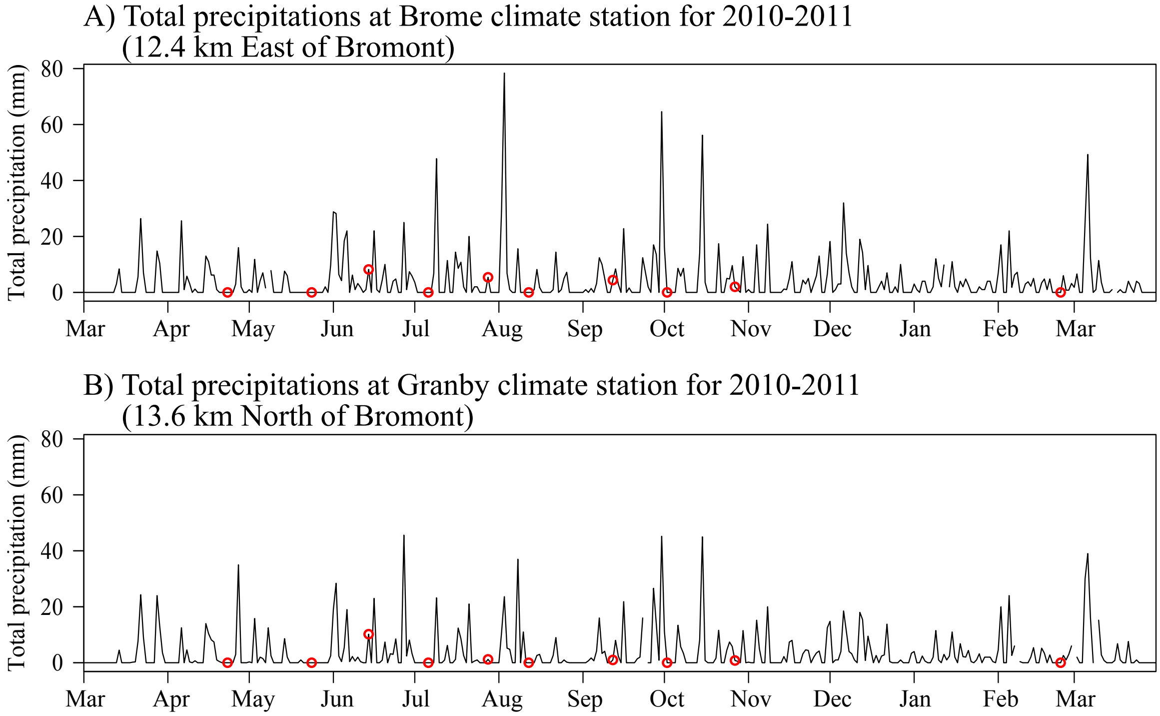
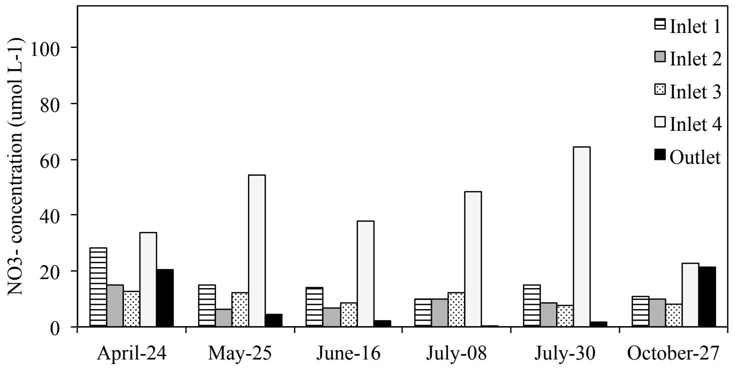
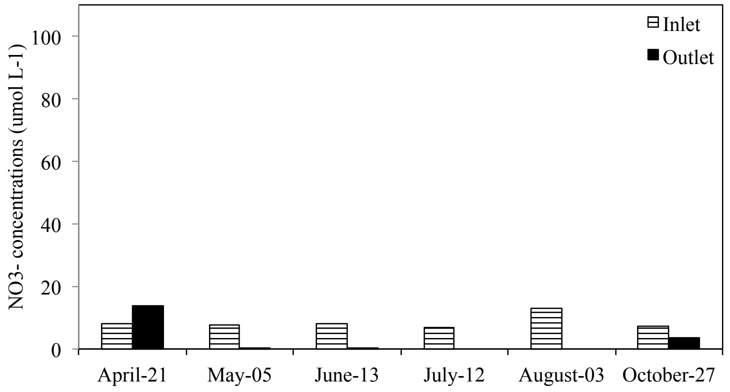


Figure C.I: Total precipitations from April 1st 2010 to March 31th 2011 at the nearest climate stations from lake Bromont. A) Brome and B) Granby climate stations. The circles represent the sampling dates. Data are taken from the Environment Canada National Climate Data and Information Archive (http://climate.weatheroffice.gc.ca/).

A) Bromont



B) Waterloo



C) Petit St-François

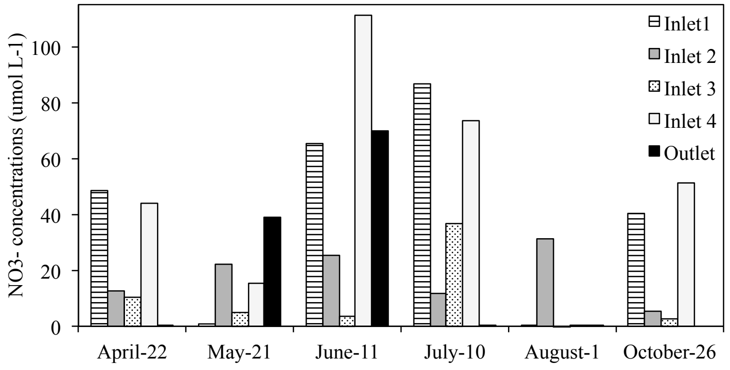


Figure C.II: Nitrate concentrations from inlets and outlets of lake A) Bromont, B) Waterloo and C) Petit St-François.

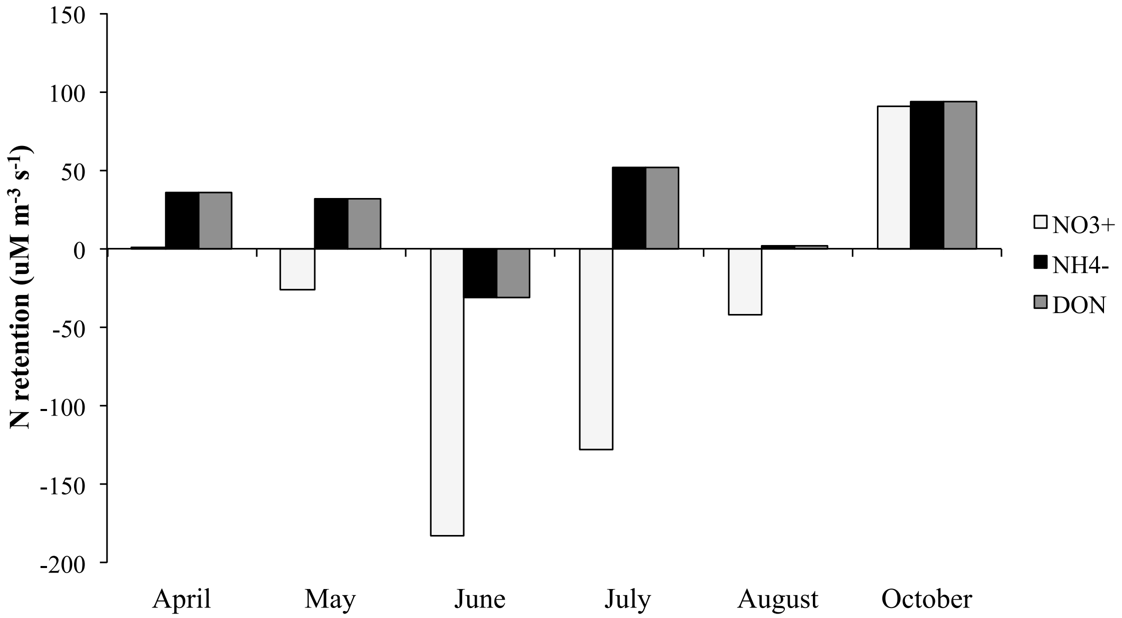


Figure C.III: Nitrogen budgets for lake Bromont.

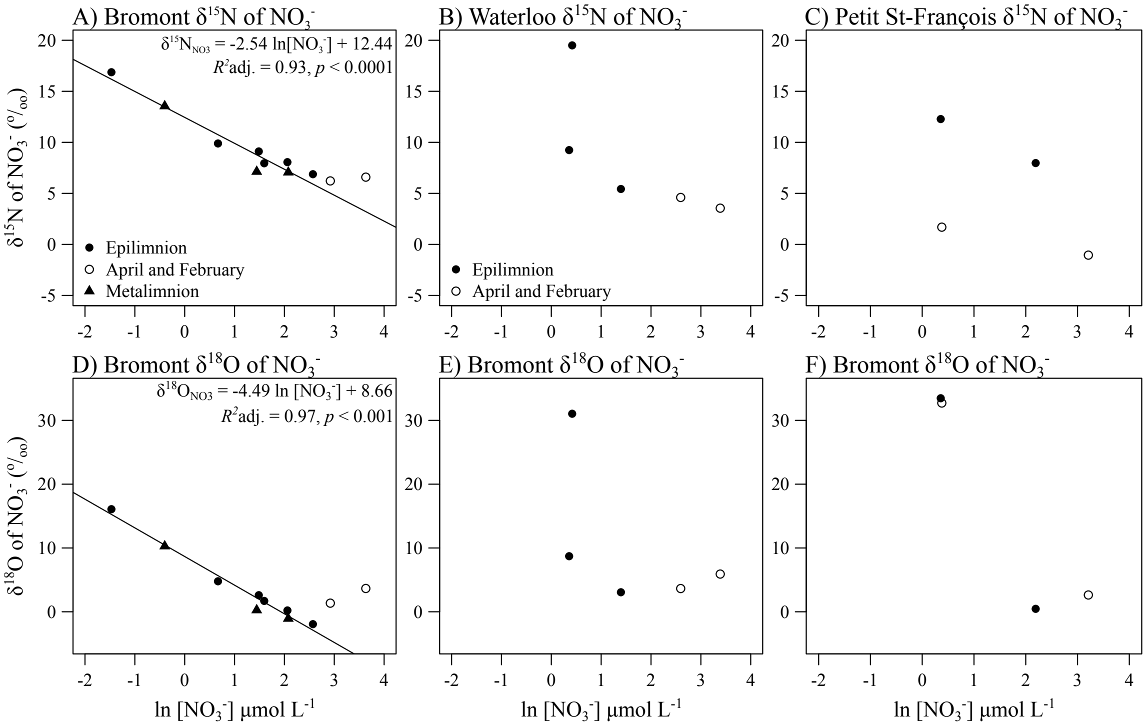


Figure C.IV: Nitrate isotopes fractionation plot for $\delta^{15}N$ of A) Bromont; B) Waterloo; C) Petit St-François and for $\delta^{18}O$ of D) Bromont; E) Waterloo and G) Petit St-François.

# Annexe D: Tableaux des données brutes utilisées pour le chapitre 3

Tableau D.I : Données isotopiques pour les trois lacs d'étude.

| Code | Site | Date | $\delta^{15}N$ of $NO_3^-$ | $\delta^{18}O$ of $NO_3^-$ | $\delta^{15}N$ of $NH_4^+$ | $\delta^{15}N$ of SPON | $\delta^{13}C$ of SPOC | $\delta^{15}N$ of TDN | $\delta^{15}N$ of DON | $\Delta$(15,18) |
|---|---|---|---|---|---|---|---|---|---|---|
|  | *Units* | *yyyy-mm-dd* | ‰ | ‰ | ‰ | ‰ | ‰ | ‰ | ‰ | ‰ |
| IBRO1 | epi | 2010-04-23 | 6.22 | 1.35 | NA | 2.22 | -33.39 | 4.85 | 4.02 | -4.95 |
| IBRO2 | epi | 2010-05-24 | 8.06 | 0.21 | NA | 2.52 | -31.83 | 4.41 | 2.30 | -1.97 |
| IBRO3 | epi | 2010-06-14 | 9.11 | 2.6 | NA | 0.31 | -30.27 | 4.77 | 3.56 | -3.31 |
| IBRO4 | epi | 2010-07-06 | 9.89 | 4.78 | NA | 2.67 | -34.78 | 3.74 | 2.83 | -4.71 |
| IBRO5 | epi | 2010-07-28 | NA | NA | NA | 2.17 | -34.25 | 3.22 | 3.22 | NA |
| IBRO6 | epi | 2010-08-12 | 16.87 | 16.08 | NA | 2.17 | -33.73 | 2.9 | 2.90 | -9.03 |
| IBRO7 | epi | 2010-10-02 | 7.95 | 1.7 | NA | 0.97 | -36.4 | 5.91 | 5.54 | -3.57 |
| IBRO8 | epi | 2010-10-27 | 6.88 | -1.94 | NA | 2.2 | -36.91 | 5.64 | 4.81 | -1 |
| IBRO9 | epi | 2011-02-24 | 6.59 | 3.65 | NA | 1.65 | -30.29 | 5.92 | 3.89 | -6.88 |
| MBRO1 | meta | 2010-05-24 | 7.06 | -1.07 | NA | 1.81 | -35.54 | 6.6 | 6.44 | -1.69 |
| MBRO2 | meta | 2010-06-14 | 7.13 | 0.26 | NA | -0.44 | -33.28 | 8.66 | 8.92 | -2.95 |
| MBRO3 | meta | 2010-07-06 | NA | NA | NA | 2.35 | -40.94 | 7.18 | 7.18 | NA |
| MBRO4 | meta | 2010-07-28 | NA | NA | NA | 2.4 | -39.75 | 7.09 | 7.11 | NA |
| MBRO5 | meta | 2010-08-12 | 13.55 | 10.28 | NA | 2.69 | -38.98 | 4.63 | 4.30 | -6.55 |
| MBRO6 | meta | 2010-10-02 | NA | NA | 4.8 | -0.14 | -33.03 | 5.92 | 22.04 | NA |
| HBRO1 | meta | 2010-07-07 | NA | NA | NA | 1.39 | -39.89 | 9.4 | 9.40 | NA |
| HBRO2 | meta | 2010-07-28 | NA | NA | -1.03 | 1.88 | -37.23 | 7.6 | 47.80 | NA |
| HBRO3 | meta | 2010-08-12 | NA | NA | 4.34 | 1.92 | -34.75 | 7.59 | 22.35 | NA |
| PSF1 | epi | 2010-04-22 | 1.69 | 32.72 | NA | 2.16 | -30.39 | 2.78 | 2.8 | NA |
| PSF2 | epi | 2010-05-20 | NA | NA | NA | 0.97 | -30.4 | 2.34 | 2.34 | NA |
| PSF3 | epi | 2010-06-10 | NA | NA | NA | 3.41 | -27.71 | 3.13 | 3.13 | NA |
| PSF4 | epi | 2010-07-09 | NA | NA | NA | 2.09 | -22.63 | 2.4 | 2.4 | NA |
| PSF5 | epi | 2010-07-31 | 12.28 | 33.47 | NA | 2.5 | -25.91 | 2.31 | 2.18 | NA |
| PSF6 | epi | 2010-08-15 | NA | NA | NA | 1.32 | -23.85 | 2.36 | 2.36 | NA |
| PSF7 | epi | 2010-09-30 | NA | NA | NA | 2.01 | -27.02 | 2.25 | 2.25 | NA |
| PSF8 | epi | 2010-10-26 | 7.97 | 0.46 | NA | 1.78 | -29.28 | 3.68 | 2.78 | NA |
| PSF9 | epi | 2011-02-22 | -1.05 | 2.63 | NA | 2.02 | NA | 5.54 | 9.9 | NA |
| WAT1 | epi | 2010-04-21 | 4.6 | 3.64 | NA | 2.18 | -30.8 | 2.97 | 1.83 | NA |
| WAT2 | epi | 2010-05-22 | 19.5 | 31.04 | NA | 1.29 | -30.97 | 1.96 | 0.46 | NA |
| WAT3 | epi | 2010-06-12 | NA | NA | NA | 1.01 | -30.55 | NA | NA | NA |
| WAT4 | epi | 2010-07-11 | NA | NA | NA | 1.8 | -29.96 | 2.01 | 2.01 | NA |
| WAT5 | epi | 2010-08-02 | NA | NA | NA | 0.61 | -30.07 | 2.3 | 2.3 | NA |
| WAT6 | epi | 2010-08-17 | NA | NA | NA | 1.44 | -30.08 | 2.56 | 2.56 | NA |
| WAT7 | epi | 2010-10-04 | 9.24 | 8.71 | NA | 1.53 | -29.83 | 2.2 | 1.87 | NA |
| WAT8 | epi | 2010-10-27 | 5.43 | 3.06 | NA | 0.87 | -30.71 | 2.1 | 1.58 | NA |
| WAT9 | epi | 2011-02-24 | 3.55 | 5.91 | NA | 1.34 | -29.51 | 5.07 | 7.5 | NA |

Tableau D.II : Concentrations des différentes formes d’azote et proportion d’azote et de carbone particulaire pour les trois lacs d’étude.

| Code | Site | Date | %N SPOM | %C SPOM | C:N SPOM | SPON | SPOC | TN | TDN | $NH_4^+$ | $NO_3^- + NO_2^-$ | $NO_3^-$ | $NO_2^-$ (µM) | DON (µM) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | *Units* | *yyyy-mm-dd* | *% atom* | *% atom* | *per atom* | *µmol $L^{-1}$* | *µmol $L^{-1}$* | *µmol $L^{-1}$* | *µmol $L^{-1}$* | *µmol $L^{-1}$* | *µmol $L^{-1}$* | *µmol $L^{-1}$* | *µmol $L^{-1}$* | *µmol $L^{-1}$* |
| IBRO1 | epi | 2010-04-23 | 0.24 | 2.45 | 10.32 | 9.39 | 96.90 | 44.50 | 35.11 | 2.86 | 18.56 | 18.56 | 0.005 | 13.68 |
| IBRO2 | epi | 2010-05-24 | 0.38 | 3.19 | 8.40 | 10.85 | 54.58 | 32.28 | 21.43 | 8.86 | 7.85 | 7.85 | 0.002 | 4.72 |
| IBRO3 | epi | 2010-06-14 | 0.42 | 3.46 | 8.34 | 9.14 | 74.51 | 29.41 | 20.27 | 1.13 | 4.59 | 4.42 | 0.166 | 14.55 |
| IBRO4 | epi | 2010-07-06 | 0.45 | 3.66 | 8.07 | 9.54 | 76.35 | 24.69 | 15.16 | 1.52 | 2.06 | 1.95 | 0.103 | 11.58 |
| IBRO5 | epi | 2010-07-28 | 0.51 | 3.78 | 7.43 | 18.89 | 141.12 | 36.57 | 17.68 | 0.87 | 0.08 | -0.02 | 0.090 | 16.73 |
| IBRO6 | epi | 2010-08-12 | 0.52 | 3.58 | 6.89 | 21.58 | 150.06 | 42.44 | 20.86 | 0.53 | 0.45 | 0.23 | 0.215 | 19.88 |
| IBRO7 | epi | 2010-10-02 | 0.28 | 2.34 | 8.28 | 12.03 | 96.41 | 44.75 | 32.72 | 6.50 | 5.02 | 4.93 | 0.090 | 21.20 |
| IBRO8 | epi | 2010-10-27 | 0.37 | 2.53 | 6.86 | 9.20 | 59.94 | 41.80 | 32.60 | 2.34 | 13.32 | 13.09 | 0.215 | 16.95 |
| IBRO9 | epi | 2011-02-24 | 0.15 | 1.53 | 10.27 | 1.67 | 17.25 | 51.99 | 50.32 | 1.59 | 37.93 | 37.82 | 0.103 | 10.80 |
| MBRO1 | meta | 2010-05-24 | 0.36 | 2.61 | 7.34 | 12.53 | 85.99 | 43.21 | 30.68 | 9.04 | 8.15 | 7.99 | 0.153 | 13.49 |
| MBRO2 | meta | 2010-06-14 | 0.55 | 2.72 | 4.95 | 12.56 | 62.14 | 41.79 | 29.23 | 12.76 | 4.25 | 4.24 | 0.015 | 12.22 |
| MBRO3 | meta | 2010-07-06 | 0.64 | 3.92 | 6.11 | 80.08 | 536.14 | 102.05 | 21.97 | 4.28 | 0.47 | 0.44 | 0.025 | 17.22 |
| MBRO4 | meta | 2010-07-28 | 0.44 | 3.09 | 6.99 | 32.36 | 227.31 | 67.70 | 35.34 | 27.40 | 0.18 | 0.14 | 0.043 | 7.76 |
| MBRO5 | meta | 2010-08-12 | 0.50 | 3.32 | 6.68 | 24.09 | 162.83 | 43.10 | 19.01 | 3.17 | 0.68 | 0.67 | 0.004 | 15.17 |
| MBRO6 | meta | 2010-10-02 | 0.11 | 1.50 | 13.24 | 29.26 | 371.12 | 244.85 | 215.59 | 201.38 | 0.38 | 0.35 | 0.028 | 13.83 |
| HBRO1 | meta | 2010-07-07 | 0.78 | 4.49 | 5.79 | 143.92 | 894.13 | 205.08 | 61.16 | 43.17 | 0.24 | 0.20 | 0.042 | 17.75 |
| HBRO2 | meta | 2010-07-28 | 0.24 | 2.15 | 9.08 | 38.56 | 367.72 | 160.83 | 122.27 | 100.66 | 0.05 | 0.05 | 0.002 | 21.56 |
| HBRO3 | meta | 2010-08-12 | 0.31 | 2.46 | 8.07 | 47.43 | 368.97 | 158.47 | 111.04 | 91.02 | 0.16 | 0.16 | 0.007 | 19.86 |
| PSF1 | epi | 2010-04-22 | 0.25 | 2.61 | 10.54 | 33.63 | 356.57 | 65.11 | 31.48 | 1.72 | 0.46 | 0.46 | 0.000 | 29.30 |
| PSF2 | epi | 2010-05-20 | 0.27 | 3.11 | 11.33 | 58.70 | 736.29 | 92.86 | 34.16 | 0.39 | -0.03 | -0.03 | 0.001 | 33.80 |
| PSF3 | epi | 2010-06-10 | 0.27 | 3.62 | 13.20 | 78.55 | 1060.11 | 114.25 | 35.70 | 0.95 | 0.16 | 0.15 | 0.006 | 34.60 |
| PSF4 | epi | 2010-07-09 | 0.22 | 2.82 | 13.09 | 116.12 | 1537.26 | 151.84 | 35.72 | 0.66 | 0.04 | 0.03 | 0.010 | 35.02 |
| PSF5 | epi | 2010-07-31 | 0.35 | 3.44 | 9.72 | 176.00 | 1699.77 | 209.50 | 33.50 | 1.72 | 0.44 | 0.43 | 0.014 | 31.33 |
| PSF6 | epi | 2010-08-15 | 0.41 | 3.39 | 8.18 | 201.99 | 1669.61 | 246.02 | 44.03 | 0.86 | 0.07 | 0.06 | 0.005 | 43.11 |
| PSF7 | epi | 2010-09-30 | 0.35 | 3.85 | 11.03 | 37.44 | 412.47 | 74.91 | 37.47 | 4.41 | 0.14 | 0.14 | 0.000 | 32.92 |
| PSF8 | epi | 2010-10-26 | 0.29 | 2.74 | 9.53 | 38.86 | 378.89 | 84.44 | 45.58 | 2.54 | 8.09 | 7.95 | 0.127 | 34.96 |
| PSF9 | epi | 2011-02-22 | 0.13 | 1.27 | 10.08 | 1.79 | 18.18 | 61.46 | 59.67 | 48.33 | 23.94 | 23.76 | 0.168 | 0.00 |
| WAT1 | epi | 2010-04-21 | 0.39 | 3.36 | 8.62 | 19.60 | 168.84 | 52.20 | 32.60 | 1.04 | 13.41 | 13.40 | 0.003 | 18.15 |
| WAT2 | epi | 2010-05-22 | 0.41 | 3.51 | 8.50 | 11.65 | 101.37 | 30.97 | 19.32 | 0.20 | 1.52 | 1.52 | 0.000 | 17.59 |
| WAT3 | epi | 2010-06-12 | 0.38 | 3.42 | 8.91 | 27.43 | 247.17 | 50.89 | 23.46 | 2.16 | 0.30 | 0.30 | 0.001 | 21.00 |
| WAT4 | epi | 2010-07-11 | 0.38 | 3.52 | 9.30 | 16.03 | 151.55 | 38.06 | 22.03 | 0.96 | 0.00 | 0.00 | 0.001 | 21.07 |
| WAT5 | epi | 2010-08-02 | 0.33 | 3.39 | 10.17 | 19.96 | 201.83 | 41.84 | 21.88 | 0.90 | 0.00 | -0.01 | 0.006 | 20.98 |
| WAT6 | epi | 2010-08-17 | 0.29 | 2.76 | 9.51 | 20.03 | 192.84 | 46.71 | 26.68 | 0.58 | 0.00 | 0.00 | 0.001 | 26.10 |
| WAT7 | epi | 2010-10-04 | 0.38 | 3.20 | 8.34 | 30.76 | 276.18 | 62.10 | 31.34 | 4.58 | 1.47 | 1.43 | 0.046 | 25.29 |
| WAT8 | epi | 2010-10-27 | 0.40 | 3.52 | 8.84 | 16.17 | 139.10 | 46.05 | 29.88 | 3.34 | 4.12 | 4.04 | 0.075 | 22.42 |
| WAT9 | epi | 2011-02-24 | 0.29 | 2.61 | 8.90 | 2.93 | 27.99 | 51.18 | 48.25 | 6.34 | 30.04 | 29.62 | 0.405 | 11.87 |

Tableau D.III : Données sur la physico-chimie des trois lacs d’étude.

| Code | Site | Date | TP | SRP | Chl*a* | DOC | Secchi | K | Zeu | Intermediate $O_2$ | Intermediate water temperature | Air temperature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *Units* | *yyyy-mm-dd* | *µg L⁻¹* | *µg L⁻¹* | *µg L⁻¹* | *mg L⁻¹* | *m* | | *m* | *%* | *° C* | *° C* |
| IBRO1 | epi | 2010-04-23 | 17.13 | NA | 4.34 | NA | 1.78 | 1.24 | 3.53 | 62.30 | 11.46 | 11.60 |
| IBRO2 | epi | 2010-05-24 | 16.07 | 5.66 | 5.61 | 2.63 | 2.73 | 0.67 | 6.65 | 111.19 | 18.47 | 21.80 |
| IBRO3 | epi | 2010-06-14 | NA | 6.52 | 5.02 | 6.30 | 2.72 | 0.77 | 5.92 | 106.38 | 19.10 | 15.00 |
| IBRO4 | epi | 2010-07-06 | 27.91 | 23.07 | 7.28 | 106.10 | 2.56 | 0.75 | 5.96 | 129.44 | 25.90 | 29.10 |
| IBRO5 | epi | 2010-07-28 | 26.34 | 4.55 | 14.17 | 23.64 | 2.31 | 1.10 | 4.02 | 108.31 | 24.01 | 26.40 |
| IBRO6 | epi | 2010-08-12 | 46.57 | 6.12 | 9.49 | 4.87 | 1.61 | 1.37 | 3.01 | 117.22 | 22.10 | 22.10 |
| IBRO7 | epi | 2010-10-02 | NA | 8.908 | 5.79 | NA | 1.15 | 1.56 | 2.55 | 76.59 | 15.17 | 7.50 |
| IBRO8 | epi | 2010-10-27 | 71.98 | 9.046 | 4.49 | NA | 1.875 | NA | NA | 96.13 | 8.20 | 15.10 |
| IBRO9 | epi | 2011-02-24 | NA | NA | NA | 2.78 | NA | NA | NA | 78.54 | 0.40 | 3.70 |
| MBRO1 | meta | 2010-05-24 | 27.25 | 5.79 | NA | 2.50 | NA | NA | NA | 24.11 | 9.28 | 21.80 |
| MBRO2 | meta | 2010-06-14 | NA | NA | 6.88 | 6.29 | NA | NA | NA | 10.98 | 10.47 | 15.00 |
| MBRO3 | meta | 2010-07-06 | 40.85 | 6.46 | 11.93 | 102.54 | NA | NA | NA | 38.76 | 11.75 | 29.10 |
| MBRO4 | meta | 2010-07-28 | 60.87 | 16.73 | 40.30 | NA | NA | NA | NA | 19.83 | 16.15 | 26.40 |
| MBRO5 | meta | 2010-08-12 | 65.80 | 8.97 | 20.30 | NA | NA | NA | NA | 4.97 | 13.63 | 22.10 |
| MBRO6 | meta | 2010-10-02 | NA | NA | NA | 9.72 | NA | NA | NA | 11.99 | 13.49 | 7.50 |
| HBRO1 | meta | 2010-07-07 | 136.20 | 6.68 | 34.28 | 8.24 | NA | NA | NA | 5.26 | 10.07 | 29.10 |
| HBRO2 | meta | 2010-07-28 | 96.16 | NA | NA | 9.61 | NA | NA | NA | 5.70 | 12.48 | 26.40 |
| HBRO3 | meta | 2010-08-12 | 89.47 | NA | NA | 5.26 | NA | NA | NA | 4.57 | 11.24 | 22.10 |
| PSF1 | epi | 2010-04-22 | 63.71 | 21.90 | 8.12 | 7.64 | 0.90 | NA | NA | 111.41 | 9.90 | 12.90 |
| PSF2 | epi | 2010-05-20 | NA | 26.15 | 11.23 | 9.07 | 1.65 | 1.20 | 3.72 | 104.39 | 16.37 | 21.00 |
| PSF3 | epi | 2010-06-10 | 134.80 | NA | 29.03 | 12.26 | 0.46 | 2.89 | 1.48 | 140.55 | 17.72 | 14.00 |
| PSF4 | epi | 2010-07-09 | 281.48 | 81.46 | 53.38 | 10.86 | 0.35 | 3.19 | 1.40 | 149.86 | 28.00 | 30.00 |
| PSF5 | epi | 2010-07-31 | 276.76 | 28.34 | 81.79 | 16.17 | 0.32 | 6.01 | 0.68 | 92.19 | 20.57 | 28.00 |
| PSF6 | epi | 2010-08-15 | 274.83 | 16.492 | 61.61 | 12.74 | NA | 6.24 | 0.65 | 141.04 | 22.16 | 19.70 |
| PSF7 | epi | 2010-09-30 | 77.33 | NA | 13.50 | NA | 0.265 | 5.98 | 0.69 | 84.67 | 15.09 | 17.20 |
| PSF8 | epi | 2010-10-26 | 115.11 | 19.250 | 9.72 | 11.26 | 0.495 | NA | NA | 106.65 | 7.00 | 17.40 |
| PSF9 | epi | 2011-02-22 | NA | NA | NA | 10.54 | NA | NA | NA | 29.71 | 1.37 | -2.80 |
| WAT1 | epi | 2010-04-21 | 34.13 | NA | 5.08 | NA | 1.43 | NA | NA | 110.19 | 9.56 | 20.00 |
| WAT2 | epi | 2010-05-22 | 21.45 | 8.24 | 5.79 | 5.30 | 0.56 | 1.06 | 3.71 | 118.45 | 15.79 | 22.00 |
| WAT3 | epi | 2010-06-12 | NA | 6.45 | 26.03 | 7.32 | 0.82 | 1.84 | 2.42 | 105.42 | 17.43 | 15.00 |
| WAT4 | epi | 2010-07-11 | 55.14 | 7.87 | 8.52 | 7.19 | 1.17 | 1.58 | 2.84 | 93.34 | 25.78 | 30.80 |
| WAT5 | epi | 2010-08-02 | 32.27 | 10.43 | 11.46 | 15.70 | 1.15 | 1.11 | 3.48 | 111.47 | 21.95 | 21.30 |
| WAT6 | epi | 2010-08-17 | 40.21 | 5.90 | 14.77 | 6.95 | 1.41 | 1.75 | 2.59 | 91.19 | 22.40 | 23.90 |
| WAT7 | epi | 2010-10-04 | NA | 5.736 | 11.12 | 10.51 | 1.94 | 1.98 | 1.94 | 87.15 | 13.06 | 6.80 |
| WAT8 | epi | 2010-10-27 | 160.29 | 50.139 | 6.21 | 13.08 | 1.045 | NA | NA | 95.17 | 8.50 | 17.40 |
| WAT9 | epi | 2011-02-24 | NA | NA | NA | 11.21 | NA | NA | NA | 68.77 | 0.82 | 6.7 |

Tableau D.IV : Concentrations des différentes formes d’azote, débits et données isotopiques aux charges et décharges du lac Bromont.

| Code | Site | Date | TN | $NO_3^-$ | TDN | $NH_4^+$ | DON | $NO_2^-$ | Discharge | $\delta^{15}N$ of $NO_3^-$ | $\delta^{18}O$ of $NO_3^-$ | $\delta^{15}N$ of TDN | $\delta^{15}N$ of DON |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *Units* | *yyyy-mm-dd* | *$\mu mol\ L^{-1}$* | *$\mu mol\ L^{-1}$* | *$\mu mol\ L^{-1}$* | *$\mu mol\ L^{-1}$* | *$\mu mol\ L^{-1}$* | *$\mu mol\ L^{-1}$* | *$m^3\ s^{-1}$* | *‰* | *‰* | *‰* | *‰* |
| WBRO1 | Inlet 1 | 2010-04-23 | 30.33 | 28.94 | 37.76 | 0.67 | 8.15 | 0.612 | 1.25 | 8.05 | 1.71 | 6.062 | -0.47 |
| WBRO2 | Inlet 1 | 2010-05-25 | 28.59 | 14.99 | 27.86 | 0.60 | 12.28 | 0.139 | 1.03 | 8.35 | -3.94 | 6.127 | 3.54 |
| WBRO3 | Inlet 1 | 2010-06-16 | 28.37 | 14.47 | 29.30 | 1.25 | 13.58 | 0.287 | 1.13 | 7.96 | -5.94 | 6.145 | 4.37 |
| WBRO4 | Inlet 1 | 2010-07-08 | 34.99 | 12.32 | 53.14 | 0.59 | 40.24 | 2.420 | 0.04 | 8.57 | 4.27 | 6.611 | 6.02 |
| WBRO5 | Inlet 1 | 2010-07-30 | 31.26 | 15.35 | 31.05 | 1.14 | 14.56 | 0.099 | 0.11 | 9.07 | -6.79 | 6.876 | 4.73 |
| WBRO6 | Inlet 1 | 2010-10-27 | 59.00 | 10.79 | 25.93 | 0.38 | 14.76 | 0.120 | 0.10 | 9.43 | 1.20 | 6.309 | 4.08 |
| WBRO7 | Inlet 2 | 2010-04-23 | 21.21 | 15.14 | 21.12 | 0.54 | 5.45 | 0.275 | 0.00 | 7.20 | -1.03 | 5.421 | 0.93 |
| WBRO24 | Inlet2 | 2010-05-25 | 14.11 | 6.26 | 14.24 | 0.27 | 7.71 | 0.122 | 0.71 | 4.38 | -7.58 | 3.508 | 2.83 |
| WBRO8 | Inlet 2 | 2010-06-16 | 17.27 | 7.16 | 12.29 | 0.47 | 4.65 | 0.151 | 2.81 | 4.83 | -7.82 | 3.151 | 0.81 |
| WBRO9 | Inlet 2 | 2010-07-08 | 19.42 | 10.01 | 22.36 | 0.47 | 11.88 | 0.123 | 0.03 | 4.81 | -8.09 | 4.334 | 3.95 |
| WBRO10 | Inlet 2 | 2010-07-30 | 15.98 | 8.47 | 17.15 | 0.84 | 7.84 | 0.092 | 0.03 | 6.18 | -8.66 | 4.077 | 2.03 |
| WBRO11 | Inlet 2 | 2010-10-27 | 19.20 | 9.90 | 18.79 | 0.24 | 8.65 | 0.099 | 0.04 | 7.85 | 0.69 | 4.817 | 1.44 |
| WBRO12 | Inlet 3 | 2010-04-23 | 20.79 | 12.74 | 21.80 | 0.82 | 8.24 | 0.183 | NA | 5.91 | -1.06 | 3.817 | 0.88 |
| WBRO13 | Inlet 3 | 2010-05-25 | 19.72 | 12.32 | 20.79 | 1.00 | 7.47 | 0.232 | 2.39 | 5.68 | -8.33 | 3.900 | 1.31 |
| WBRO14 | Inlet 3 | 2010-06-16 | 19.45 | 9.01 | 19.84 | 0.90 | 9.93 | 0.338 | 0.00 | 5.41 | -7.48 | 3.741 | 2.35 |
| WBRO15 | Inlet 3 | 2010-07-08 | 41.92 | 13.29 | 33.26 | 3.93 | 16.04 | 0.966 | 0.00 | 5.38 | -7.12 | 4.444 | 3.82 |
| WBRO16 | Inlet 3 | 2010-07-30 | 21.07 | 7.88 | 18.08 | 1.06 | 9.14 | 0.076 | 0.00 | 6.82 | -8.82 | 3.861 | 1.57 |
| WBRO17 | Inlet 3 | 2010-10-27 | 37.12 | 8.30 | 17.19 | 0.29 | 8.60 | 0.099 | 0.11 | 6.09 | 4.42 | 3.149 | 0.40 |
| WBRO18 | inlet 4 | 2010-04-23 | 45.99 | 33.89 | 36.31 | 0.72 | 1.71 | 0.169 | 1.27 | 7.24 | -1.85 | 5.843 | -13.64 |
| WBRO19 | Inlet 4 | 2010-05-25 | 60.47 | 54.78 | 60.49 | 0.58 | 5.13 | 0.399 | 0.00 | 8.08 | -2.18 | 6.437 | -9.29 |
| WBRO20 | Inlet 4 | 2010-06-16 | 50.30 | 38.35 | 50.09 | 0.92 | 10.82 | 0.264 | 4.66 | 7.98 | -1.62 | 6.043 | -0.30 |
| WBRO21 | Inlet 4 | 2010-07-08 | 63.56 | 48.41 | 62.89 | 0.42 | 14.06 | NA | 2.69 | 8.29 | -1.34 | 7.055 | 2.93 |
| WBRO22 | Inlet 4 | 2010-07-30 | 75.71 | 64.78 | 78.25 | 1.01 | 12.47 | 0.192 | 0.61 | 8.85 | -1.44 | 7.875 | 3.17 |
| WBRO23 | Inlet 4 | 2010-10-27 | 94.97 | 22.84 | 35.32 | 0.35 | 12.14 | 0.134 | 4.63 | 8.53 | 1.11 | 6.300 | 2.23 |
| WBRO25 | outlet | 2010-04-23 | 42.69 | 20.74 | 33.76 | 0.61 | 12.41 | 0.315 | 3.87 | 6.61 | 1.63 | 3.152 | -2.35 |
| WBRO26 | Outlet | 2010-05-25 | 22.98 | 4.76 | 20.47 | 1.76 | 13.95 | 0.237 | 4.85 | 7.99 | 0.36 | 4.154 | 2.99 |
| WBRO27 | Outlet | 2010-06-16 | 24.93 | 2.24 | 19.85 | 1.30 | 16.32 | 0.207 | 2.44 | 8.85 | 5.58 | 3.847 | 3.21 |
| WBRO28 | Outlet | 2010-07-08 | 22.17 | 0.61 | 19.16 | 1.38 | 17.18 | 0.107 | 5.34 | 4.53 | 1.18 | 3.335 | 3.30 |
| WBRO29 | Outlet | 2010-07-30 | 28.99 | 2.07 | 23.69 | 2.61 | 19.00 | 0.148 | 0.59 | 2.39 | -9.59 | 4.551 | 4.76 |
| WBRO30 | Outlet | 2010-10-27 | 82.71 | 22.14 | 40.40 | 1.25 | 17.01 | 0.692 | 9.00 | 7.66 | 3.11 | 5.532 | 2.95 |

Tableau D.V : Concentrations des différentes formes d’azote, débits et données isotopiques aux charges et décharges du lac Waterloo.

| Code | Site | Date | TN | $NO_3^-$ | TDN | $NH_4^+$ | DON | $NO_2^-$ | Discharge | $\delta^{15}N$ of $NO_3^-$ | $\delta^{18}O$ of $NO_3^-$ | $\delta^{15}N$ of TDN | $\delta^{15}N$ of DON |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *Units* | *yyyy-mm-dd* | *µmol L⁻¹* | *µmol L⁻¹* | *µmol L⁻¹* | *µmol L⁻¹* | *µmol L⁻¹* | *µmol L⁻¹* | $m^3\ s^{-1}$ | *‰* | *‰* | *‰* | *‰* |
| WWAT1 | Inlet | 2010-04-21 | 43.49 | 8.41 | 26.37 | 0.82 | 17.14 | 0.190 | 4.58 | 6.57 | -3.18 | 3.288 | 1.75 |
| WWAT2 | Inlet | 2010-05-23 | 29.34 | 7.83 | 28.49 | 0.73 | 19.92 | 0.300 | 0.47 | 6.36 | -2.63 | 3.537 | 2.47 |
| WWAT3 | Inlet | 2010-06-13 | 39.44 | 8.52 | 38.24 | 0.70 | 29.02 | 0.290 | 5.58 | 6.69 | -8.75 | 3.935 | 3.15 |
| WWAT4 | Inlet | 2010-07-12 | 50.63 | 7.45 | 43.10 | 1.22 | 34.44 | 0.440 | 8.68 | 6.53 | -6.81 | 3.076 | 2.35 |
| WWAT5 | Inlet | 2010-08-03 | 42.78 | 13.14 | 40.72 | 0.49 | 27.09 | 0.180 | 0.26 | 5.33 | -4.45 | 3.793 | 3.06 |
| WWAT6 | Inlet | 2010-10-27 | 23.01 | 7.45 | 24.50 | 0.30 | 16.76 | 0.120 | 4.86 | 7.24 | -3.22 | 3.333 | 1.63 |
| WWAT7 | Outlet | 2010-04-21 | 28.18 | 14.04 | 31.58 | 0.63 | 16.92 | 0.250 | 8.89 | 4.72 | 2.44 | 3.168 | 1.93 |
| WWAT8 | Outlet | 2010-05-23 | 62.85 | 0.53 | 22.84 | -0.07 | 22.38 | 0.110 | 2.90 | 0.16 | 6.49 | 2.437 | 2.49 |
| WWAT9 | Outlet | 2010-06-13 | 43.76 | 0.29 | 23.46 | 0.46 | 22.72 | 0.070 | 7.42 | 0.44 | 16.60 | 2.059 | 2.08 |
| WWAT10 | Outlet | 2010-07-12 | 45.30 | -0.04 | 23.27 | 0.20 | 23.10 | 0.150 | 4.93 | NA | NA | 1.742 | 1.74 |
| WWAT11 | Outlet | 2010-08-03 | 48.47 | 0.51 | 45.37 | 0.51 | 44.35 | 2.420 | 1.20 | NA | NA | 4.348 | 4.35 |
| WWAT12 | Outlet | 2010-10-27 | 38.11 | 3.69 | 31.19 | 0.30 | 27.21 | 0.150 | 8.97 | 5.67 | 7.21 | 2.066 | 1.58 |

Tableau D.VI : Concentrations des différentes formes d'azote, débits et données isotopiques aux charges et décharges du Petit lac St-François.

| **Code** | **Site** | **Date** | **TN** | **$NO_3^-$** | **TDN** | **$NH_4^+$** | **DON** | **$NO_2^-$** | **Discharge** | **$\delta^{15}N$ of $NO_3^-$** | **$\delta^{18}O$ of $NO_3^-$** | **$\delta^{15}N$ of TDN** | **$\delta^{15}N$ of DON** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *Units* | *yyyy-mm-dd* | *μmol $L^{-1}$* | *μmol $L^{-1}$* | *μmol $L^{-1}$* | *μmol $L^{-1}$* | *μmol $L^{-1}$* | *μmol $L^{-1}$* | *$m^3$ $s^{-1}$* | *‰* | *‰* | *‰* | *‰* |
| WPSF1 | Inlet 1 | 10-04-22 | 73.59 | 48.80 | 69.62 | 0.32 | 20.51 | 0.230 | 0.38 | 26.87 | 10.70 | 7.481 | -37.95 |
| WPSF2 | Inlet 1A | 10-05-21 | 27.50 | 2.63 | 24.15 | 0.49 | 21.03 | 0.260 | NA | 8.72 | -1.63 | 4.470 | 3.95 |
| WPSF3 | Inlet 1B | 10-05-21 | 43.01 | 0.68 | NA | NA | NA | NA | NA | NA | NA | | NA |
| WPSF4 | Inlet 1 | 10-06-11 | 92.59 | 65.49 | 96.31 | 1.05 | 29.77 | 0.340 | NA | 11.92 | 0.92 | 9.482 | 4.30 |
| WPSF5 | Inlet 1 | 10-07-10 | 161.70 | 86.95 | 141.76 | 1.03 | 53.78 | 0.460 | 4.53 | 13.23 | 1.06 | 9.183 | 2.77 |
| WPSF6 | Inlet 1 | 10-08-01 | 746.48 | 0.60 | 71.01 | 1.75 | 68.66 | 0.420 | NA | 7.64 | 14.91 | 1.744 | 1.69 |
| WPSF7 | Inlet 1 | 10-10-26 | 24.07 | 40.75 | 65.87 | 0.36 | 24.75 | 0.200 | 0.24 | 11.06 | 0.65 | 8.025 | 3.10 |
| WPSF8 | Inlet 2 | 10-04-22 | 25.36 | 12.79 | 25.85 | 12.53 | 0.53 | 0.190 | NA | 8.42 | -2.97 | 5.216 | 2.08 |
| WPSF9 | Inlet 2 | 10-05-21 | 34.77 | 22.54 | 31.37 | 0.63 | 8.20 | 0.440 | NA | 6.97 | 1.03 | 4.771 | -0.84 |
| WPSF10 | Inlet 2 | 10-06-11 | 39.47 | 25.54 | 38.89 | 0.88 | 12.47 | 0.280 | NA | 8.03 | -3.88 | 6.343 | 3.11 |
| WPSF11 | Inlet 2 | 10-07-10 | 63.76 | 11.97 | 53.58 | 1.68 | 39.93 | 0.200 | 0.22 | 6.24 | -0.74 | 3.664 | 2.92 |
| WPSF12 | Inlet 2 | 10-08-01 | 39.46 | 31.67 | 40.01 | 1.13 | 7.20 | 0.240 | NA | 10.14 | -2.17 | 8.749 | 3.45 |
| WPSF13 | Inlet 2 | 10-10-26 | 18.91 | 5.34 | 23.21 | 0.18 | 17.69 | 0.100 | 0.06 | 10.51 | -0.97 | 4.651 | 2.90 |
| WPSF14 | Inlet 3 | 10-04-22 | 31.44 | 10.64 | 30.78 | 1.34 | 18.80 | 0.270 | NA | 8.85 | 2.49 | 2.107 | -1.46 |
| WPSF15 | Inlet 3 | 10-05-21 | 40.50 | 5.12 | 32.43 | 0.67 | 26.64 | 0.200 | NA | 11.02 | 1.59 | 3.846 | 2.50 |
| WPSF16 | Inlet 3 | 10-06-11 | 82.72 | 3.74 | 36.69 | 0.85 | 32.10 | 0.170 | NA | 9.50 | 7.92 | 2.900 | 2.15 |
| WPSF17 | Inlet 3 | 10-07-10 | 176.64 | 38.12 | 139.79 | 52.09 | 49.59 | 1.280 | 0.78 | 4.77 | 24.05 | 5.801 | 6.19 |
| WPSF18 | Inlet 3 | 10-08-01 | 427.15 | 0.10 | 37.82 | 1.17 | 36.56 | 0.100 | NA | NA | NA | 2.717 | 2.72 |
| WPSF19 | Inlet 3 | 10-10-26 | 16.50 | 2.81 | 36.11 | 0.54 | 32.76 | 0.150 | 0.00 | 5.67 | 0.35 | 2.388 | 2.11 |
| WPSF20 | Inlet 4 | 10-04-22 | 80.69 | 44.67 | 72.30 | 1.40 | 26.23 | 0.640 | NA | 10.42 | 2.77 | 6.504 | 0.18 |
| WPSF21 | Inlet 4 | 10-05-21 | 56.66 | 15.75 | NA | 1.59 | NA | 0.350 | NA | 6.27 | -7.49 | 4.469 | 3.72 |
| WPSF22 | Inlet 4 | 10-06-11 | 143.33 | 112.26 | 146.68 | 1.39 | 33.04 | 1.010 | NA | 12.13 | 2.04 | 10.469 | 5.04 |
| WPSF23 | Inlet 4 | 10-07-10 | 187.15 | 74.12 | 162.44 | 2.99 | 85.32 | 0.780 | 0.51 | 8.19 | -3.45 | 7.053 | 6.10 |
| WPSF24 | Inlet 4 | 10-08-01 | 250.82 | 0.16 | 44.71 | 1.15 | 43.40 | 0.070 | 0.00 | NA | NA | 2.716 | NA |
| WPSF25 | Inlet 4 | 10-10-26 | 37.44 | 51.38 | 104.35 | 0.79 | 52.18 | 0.310 | 0.05 | 9.58 | -0.52 | 6.877 | 4.25 |
| WPSF26 | Outlet | 10-04-22 | 55.20 | 0.55 | 29.61 | 0.29 | 28.78 | 0.110 | 3.83 | 0.71 | 28.03 | 3.552 | 3.61 |
| WPSF27 | Outlet | 10-06-11 | 159.73 | 70.90 | 129.32 | 1.23 | 57.20 | 0.900 | 0.11 | 11.78 | 3.04 | 6.573 | 0.25 |
| WPSF28 | Outlet | 10-10-26 | 38.93 | 10.96 | 58.81 | 5.14 | 42.70 | 0.390 | 1.08 | 6.66 | -2.15 | 5.348 | 5.05 |
| WPSF29 | Outlet | 10-05-21 | 113.91 | 45.39 | 91.61 | 7.86 | 38.36 | 6.030 | NA | 15.82 | -0.69 | 11.785 | 7.82 |
| WPSF30 | Outlet AD | 10-07-10 | 122.31 | 0.11 | 42.25 | 0.50 | 41.64 | 0.080 | NA | NA | NA | 2.827 | 2.83 |
| WPSF31 | Outlet AD | 10-08-01 | 147.60 | 9.44 | 57.02 | 0.81 | 46.78 | 0.740 | NA | 11.85 | -3.59 | 4.650 | 3.22 |
| WPSF32 | Outlet BD | 10-07-10 | 120.52 | 0.09 | 43.29 | 0.51 | 42.69 | 0.080 | NA | NA | NA | 2.459 | 2.46 |
| WPSF33 | Outlet BD | 10-08-01 | 129.05 | 0.18 | 43.83 | 0.92 | 42.73 | 0.090 | 0.09 | NA | NA | 2.820 | 2.82 |