Université de Montréal

L'altération des minéraux dans les sols forestiers du Bouclier Canadien : Quels facteurs environnementaux affectent la variabilité spatiale et temporelle de la mise en solution des cations basiques?

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Cette thèse intitulée :

L'altération des minéraux dans les sols forestiers du Bouclier Canadien : Quels facteurs environnementaux affectent la variabilité spatiale et temporelle de la mise en solution des cations basiques?

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RÉSUMÉ

Les processus d'altération des minéraux constituent un important pourvoyeur de nutriments pour les plantes et jouent parallèlement un rôle déterminant dans la neutralisation des dépositions acides dans les écosystèmes terrestres et aquatiques. Plus spécifiquement, l'altération des silicates et son couplage avec la végétation constituent également un puits de carbone et contrôle l'évolution à long terme du climat. Malgré la place centrale de ces processus dans le cycle biogéochimique global des éléments, il n'existe pas de méthode standard pour quantifier les taux d'altération des minéraux. De plus, l'impact des changements environnementaux sur ces processus demeure difficile à anticiper en milieu naturel. En effet, l'altération des minéraux résulte de l'interaction complexe de facteurs hydroclimatiques (précipitations, température, humidité des sols), biochimiques (pH, matière organique, activité biologique) et physiques avec les sols ou le matériel parental. Or, ce caractère multidimensionnel de l'altération des minéraux a rarement été considéré dans des études visant à analyser les impacts de variables environnementales sur ces processus en milieu naturel. De même, les méthodes permettant d'analyser les effets intégrés de plusieurs facteurs agissant simultanément ont été peu explorées. À travers cette thèse, nous avons : 1) quantifié les taux d'altération historiques et contemporains de cations basiques (Ca, Mg, Na et K) dans une vaste aire géographique au Québec; 2) évalué la concordance entre trois méthodes d'estimation des taux d'altération des minéraux; 3) développé une nouvelle approche pour obtenir des taux d'altération fiables sur des échelles de temps de l'ordre de l'année afin d'analyser la variabilité temporelle des taux d'altération des minéraux; et 4) examiné l'impact de certaines caractéritiques des bassins versants et de facteurs environnementaux sur la variabilité des taux d'altération.

Les résultats montrent que des variables reliées au climat expliquent jusqu'à 51.6% de la variation spatiale des taux d'altération contemporains des cations basiques. Des variables liées à la lithologie, aux dépôts acides et aux propriétés des sols captaient également une proportion significative de la variance. Quant aux taux d'altération historiques, certaines propriétés des sols, tels que la surface spécifique et la composition minéralogique, constituaient les principaux déterminants de leur variabilité spatiale dans l'aire d'étude. En ce qui concerne la variabilité temporelle des taux d’altération des cations basiques, les résultats de cette recherche montrent qu’ils dépendent essentiellement de l’évolution des conditions hydrocilimatiques. Dans l'ensemble, les taux d’altération des cations basiques sont positivement affectés par la température, la proportion de feuillus dans la canopée, les précipitations sous forme de pluie, les dépôts de sulfate et la surface spécifique des sols, alors qu’ils sont négativement affectés par les précipitations sous forme de neige et le nombre de jours de gel. Ces résultats représentent une contribution originale à la compréhension des processus d’altération des minéraux en milieu naturel et à l’amélioration des connaissances sur l’impact potentiel des changements climatiques sur l’altération des minéraux et, de là, sur la capacité des sols à soutenir l’apport en nutriments essentiels à la croissance forestière à long terme.

Mots clés : Altération des minéraux, podzols, écosystèmes forestiers, variabilité spatiale, variabilité temporelle, bilan élémentaire en profil, budget intrant-extrant en bassin, extraction séquentielle, facteurs environnementaux, climat, PROFILE, statistiques multivariées.

ABSTRACT

Mineral weathering is an important nutrient provider for plants, and these processes play a key role in the neutralization of acid inputs in terrestrial and aquatic ecosystems. Silicate weathering and its coupling with the vegetation also constitutes a carbon sink and controls the long-term evolution of the climate. Despite the central role of mineral weathering processes in the overall biogeochemical cycle of elements, there is no standard method for quantifying the rates at which minerals weather. Moreover, the impact of environmental changes on these processes remains difficult to anticipate in natural environments. Mineral weathering results from the complex interaction of hydro-climatic (precipitation, temperature, soil moisture), biochemical (pH, organic matter, biological activities) and physical factors with soils or parental material. However, the multidimensional nature of mineral weathering has rarely been considered in studies aiming at analyzing the impacts of environmental variables on these processes in the natural environments. Furthermore, approaches that allow to analyze the integrated effects of several simultaneously acting factors have been little explored. Through this thesis, we have: 1) analyzed the spatial variability of historical and contemporary weathering rates of base cations (Ca, Mg, Na and K) in a wide geographical area in Quebec; 2) evaluated the agreement between three methods for estimating mineral weathering rates; 3) developed a new approach for estimating base cation weathering rates on an annual time scale in order to analyze temporal variability in mineral weathering rates; and 4) examined the impact of the watershed characteristics and environmental factors on the variability of weathering rates.

The results show that climate-related variables accounted for up to 51.6% of the spatial variation in contemporary weathering rates of base cations. Variables related to ion sources (lithology, sulphate deposition and soil properties) also explained a significant proportion of the variation. As for historical base cation weathering rates, soil properties, such as surface area and mineralogical composition, were the main determinants of their spatial variability in the study area. Regarding the temporal variability of base cation weathering rates, the results of this research show that they depend essentially on the evolution of hydro-climatic conditions. Overall, base cation weathering rates are positively affected by temperature, percent deciduous canopy cover, precipitation as rain, sulphate deposition, and soil surface area, while they are negatively affected by precipitation as snow and the number of frost days. These findings provide an original contribution to the understanding of mineral weathering processes in natural environments, and they are likely to improve knowledge about the potential impact of climate change on mineral weathering and hence on the ability of soils to supply essential plant nutrients to sustain long-term forest growth.

Keywords: Mineral weathering, podzols, forest ecosystems, spatial variability, soil profile mass balance, watershed input-output budget, sequential extraction, environmental factors, climate, PROFILE, multivariate statistics.

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Chapitre 1. Introduction générale

1.1 Contexte et justification de la thèse

Appréhender la réponse des écosystèmes forestiers aux changements globaux nécessite un vaste effort de recherche. Compte tenu de la place centrale des sols dans ces écosystèmes, notamment comme réservoirs d'éléments nutritifs, toute démarche d'aménagement durable des écosystèmes forestiers suppose une meilleure compréhension de la manière dont les sols et les processus biogéochimiques qu'ils abritent sont affectés par les modifications de variables environnementales telles que l'activité biologique, la température, les régimes de précipitations et le pH des dépôts atmosphériques. En effet, les flux élémentaires au sein des écosystèmes forestiers sont très sensibles à ces variables. Dans de nombreuses situations, des changements intervenus au niveau de ces paramètres ont été mentionnés comme causes avérées ou potentielles de carences en cations basiques observées dans des sols forestiers du Nord-est des États-Unis et de l'Est canadien. Par exemple, les précipitations acides sont souvent citées comme l'un des facteurs qui prédisposent certaines espèces végétales au dépérissement en affectant leur nutrition (Duchesne et al. 2002, 2003; Houle et al., 2001). Plusieurs auteurs suggèrent également que le phénomène de l'envahissement du hêtre observé dans certaines érablières de l'Est canadien serait lié à des problèmes nutritionnels induits par l'acidification des sols et/ou les stress climatiques (Doyon et al. 2003; Duchesne et al. 2002, 2003; Nolet et al. 2008), bien que des perturbations liées aux phénomènes naturels (succession, chablis) et à la sylviculture pourraient également être en cause (Leak et Smith, 1996).

Plusieurs études réalisées dans des écosystèmes forestiers du Nord-est américain vers la fin du 20ème siècle et au début des années 2000 en relation avec la réduction des dépôts de sulfate ont montré que ces apports acides peuvent affecter la croissance forestière en modifiant l'acidité des sols et la biodisponibilité des cations basiques (Likens et al., 1996, 1998; Houle et al., 1997; Duchesne et al., 2003). Des travaux portant sur la nutrition forestière en lien avec l'épisode de dépérissement de l'érable à sucre du début des années 1980 (Bernier and Brazeau, 1988; Duchesne et al., 2002) ont également démontré l'importance du renouvellement du réservoir de cations échangeables du sol pour le maintien de la santé, la productivité et la stabilité des écosystèmes forestiers à long terme. L'impact des pratiques d'aménagement forestier sur le renouvellement des réservoirs échangeables de cations basiques a également fait l'objet de plusieurs études (Duchesne and Houle 2006, 2008). Parallèlement, l'évolution des réservoirs échangeables des sols en relation avec les modifications des paramètres environnementaux a reçu peu d'attention. Pourtant, plusieurs auteurs suggèrent qu'une modification de la température, accompagnée de changements du régime hydrique des sols, risquent d'influencer les processus d'altération des minéraux et ainsi affecter leur capacité à fournir des cations aux réservoirs échangeables des sols (Campbell et al. 2009).

L'altération des minéraux. Outre les dépôts atmosphériques, l'altération des minéraux constitue la principale source de cations basiques qui permet de renouveler à long terme les réservoirs échangeables des sols. Toutefois, les apports de nutriments à travers les processus d'altération des minéraux ont souvent été négligés dans les bilans nutritifs. En effet, quantifier les taux d'altération des minéraux en milieu naturel demeure un défi, à cause de l'absence d'une méthode standard. Les informations disponibles sur les taux d'altération des minéraux ont ainsi été obtenues grâce à l'utilisation d'une diversité d'approches méthodologiques dont des expériences de dissolution en laboratoire (Chou and Wollast, 1984; Oelkers et al., 1994; Amram and Ganor, 2005), la méthode des minéraux-tests (Ranger et al., 1990), l'utilisation du ratio isotopique du strontium (Åberg et al., 1989, Shand et al., 2007), la modélisation à l'aide de PROFILE (Sverdrup et Warfvinge, 1993, Sverdrup, 2009) ou MAGIC (Cosby et al., 2001, Whitfield et al., 2006), la méthode du budget intrant-extrant à l'échelle du bassin versant (Clayton, 1979, Velbel, 1985, White et Blum, 1995, Velbel et Price, 2007) et la méthode du bilan de masse en profil de sol (Brimhall et al., 1991a,b ; Egli et Fitze, 2000). L'approximation à partir de la texture du sol est une autre approche empirique qui a été utilisée pour estimer des taux d'altération dans des sols situés principalement au Canada et aux États-Unis (Koseva et al., 2010). L'ensemble de ces méthodes sont basées sur des postulats distincts et elles utilisent des données de base différentes pour estimer les taux d'altération des minéraux. Conséquemment, leur performance dépend en grande partie de l'adéquation entre les données et les conditions de site, d'une part, et les postulats des méthodes, d'autre part.

Plusieurs études comparatives des méthodes d'estimation de l'altération des minéraux ont été réalisées et des incohérences ont été relevées au niveau des résultats obtenus. Si certaines études ont montré peu de différences entre les taux d'altération estimés à l'aide de plusieurs méthodes pour un même site (Starr et al., 1998; Houle et al., 2012), d'autres ont fait état de différences significatives entre les taux estimés par différentes approches (Langan et al., 1995, 1996, 2001; Hodson and Langan, 1999; Watmough and Dillon, 2003; Futter et al., 2012). Par exemple, Starr et al. (1998) ont utilisé quatre méthodes différentes dont celle du bilan de masse en profil, la méthode du budget intrant-extrant et le modèle PROFILE pour estimer les taux d'altération de Ca et Mg dans le bassin versant de Hietajärvi (Parc National de Patvinsuo, à l'Est de la Finlande). Ces auteurs ont observé que les taux d'altération estimés par les différentes méthodes étaient similaires, bien que la méthode du bilan de masse en profil avait tendance à produire les valeurs les plus élevées alors que le modèle PROFILE simulait les plus faibles. D'un autre côté, en analysant les résultats d'un grand nombre d'études réalisées essentiellement dans des environnements granitiques en Europe et en Amérique du Nord, Langan et al. (1995) ont observé que les taux d'altération de cations basiques obtenus avec la méthode du bilan de masse en profil étaient significativement plus faibles que ceux simulés avec le modèle PROFILE. Futter et al. (2012) ont examiné des taux d'altération de minéraux silicatés provenant de 82 sites distribués sur trois continents. Ces auteurs ont observé que des différences de plus de 100% peuvent se produire lorsque des méthodes différentes sont utilisées pour estimer les taux d'altération, et ce principalement à cause des incertitudes liées aux intrants plutôt qu'en raison des différentes conceptions des processus d'altération associées aux méthodes. Sachant que des taux d'altération calculés à l'aide de méthodes différentes sont utilisés dans des études biogéochimiques, notamment pour évaluer des bilans nutritifs et pour le calcul de charges critiques, ces observations invitent à la prudence quand vient le temps de choisir une méthode pour estimer les taux d'altération des minéraux. Toutefois, les études comparatives réalisées jusqu'ici n'ont pas permis d'évaluer la performance relative des méthodes les unes par rapport aux autres ni leur degré de concordance/ discordance en relation avec les conditions de site.

En outre, des études biogéochimiques montrent que les taux d'altération des minéraux sont variables dans l'espace et qu'ils sont reliés aux propriétés du matériel parental, à l'activité biologique et aux conditions hydro-climatiques (Courchesne et al., 2002; Schaller et al., 2009; Egli et al., 2006; Riebe et al., 2004; Velbel, 1993; White et Blum, 1995). Par exemple, Courchesne et al (2002) ont estimé les taux d'altération des minéraux dans trois sols forestiers du Québec. La différence observée entre les taux estimés a été attribuée aux contrastes existant entre les différents sites au plan de la texture et la minéralogie des sols ainsi que du type de matériel parental. Dans des podzols alpins du Nord de l'Italie, Egli et al. (2006) ont observé que des variables telles que le flux d'eau et l'abondance de la végétation influençaient positivement l'altération des minéraux. De plus, dans la forêt expérimentale de Hubbard Brook (New Hampshire, États-Unis), Schaller et al. (2009) ont estimé des taux d'altération à long terme pour 13 sites à partir de 39 profils de sols. Ayant observé une faible corrélation négative entre les taux d'altération estimés et l'élévation des sites dans la zone d'étude, ces auteurs ont émis l'hypothèse que la variabilité spatiale des taux d'altération des minéraux était associée à des variations de température, de précipitation ou d'abondance de la végétation. Bien que ces études traitant de la variabilité spatiale des taux d'altération aient permis d'identifier un large éventail de facteurs pouvant affecter ces processus en milieu naturel, elles n'ont pas analysé les effets synergiques ou antagonistes de plusieurs facteurs considérés simultanément sur les taux d'altération des minéraux (Gordon, 2005).

Par ailleurs, s'il est évident que les propriétés des sols devraient demeurer relativement stables dans un futur proche, les tendances observées et des projections récentes montrent que des variables climatiques telles que la température et les précipitations changent et que l'amplitude de ces changements risque de croître à l'avenir (Ouranos, 2010 ; Houle et al. 2010 ; Campbell et al., 2009). Plusieurs auteurs sont d'avis que les modifications du climat à travers le temps sont susceptibles d'affecter les taux d'altération des minéraux et leur capacité à renouveler les réservoirs échangeables des sols (Campbell et al., 2009). Cependant, la variabilité temporelle des taux d'altération des minéraux reste peu documentée à cause des difficultés méthodologiques associées à l'obtention d'estimations fiables sur des échelles de temps très courtes (de l'ordre d'une année) pour un site donné. Parmi les rares travaux de recherche sur le sujet, citons l'étude conduite dans huit bassins hydrographiques du Nord-est de l'Islande (Gislason et al., 2009). Ces auteurs ont observé une augmentation des flux de Ca dissous dans les rivières au cours de la période 1964-2004. En se basant sur l'évolution temporelle de ces flux de Ca ainsi que sur la corrélation positive entre ces flux et la température de l'air, ils ont attribué cette augmentation à l'effet positif de l'augmentation de la température sur l'altération mécanique et chimique des minéraux dans ces bassins hydrographiques au cours de la période concernée. Toutefois, les auteurs reconnaissent que les résultats de cette étude, réalisée dans une île volcanique où l'impact des activités humaines est très faible et où les sols sont formés sur des basaltes peu résistants à l'altération, ne sont pas forcément transposables à des bassins versants dont le matériel parental est constitué majoritairement de roches silicatés, ayant une hydrologie différente et qui sont soumis à des émissions acides provenant d'activités humaines. Au Québec, Houle et al. (2010) ont rapporté des corrélations positives entre les concentrations de Na et la température moyenne annuelle de l'air pour 27 lacs d'un groupe de 30 pour lesquels des séries chronologiques continues sont disponibles entre 1989 et 2005. En se basant sur le comportement conservateur du Na dans les sols des bassins versants forestiers et les lacs (Bailey et al., 2003), ils ont émis l'hypothèse qu'une température plus élevée a pu favoriser des taux d'altération plus élevés dans les bassins versants, à la fois en raison de la dépendance des taux d'altération à la température (White et Blum, 1995) et, éventuellement, en raison de la réduction de la période pendant laquelle la couverture neigeuse reste en place (Riebe et al., 2004), facilitant ainsi le contact entre l'eau sous sa forme liquide et les sols.

Les méthodes utilisées couramment pour estimer les taux contemporains d'altération nécessitent généralement un suivi sur plusieurs années afin de minimiser l'impact de multiples sources d'erreur (notamment les erreurs d'échantillonnage et la variabilité spatiale des processus et propriétés en milieu naturel) sur les valeurs estimées. Toutefois, dans le contexte des changements globaux de l'environnement, l'appréciation de la variabilité temporelle contemporaine des taux d'altération des minéraux en milieu naturel est cruciale. Afin d'étudier la variabilité temporelle des taux d'altération des minéraux, en particulier sur de courtes périodes de temps, le développement d'une nouvelle approche s'impose. Un tel effort de recherche permettrait de produire de nouvelles connaissances pour faciliter non seulement la compréhension de la réponse des écosystèmes forestiers aux changements environnementaux mais également pour favoriser une gestion plus durable des ressources.

1.2 Question centrale et objectifs spécifiques de la thèse

La question centrale à laquelle cette thèse tente de répondre peut être formulée ainsi : dans les écosystèmes forestiers, comment les taux d'altération des cations basiques varient-ils dans l'espace et dans le temps, et quelles sont les principaux facteurs environnementaux qui déterminent ces variations?

Cette question est importante pour deux raisons principales : 1) l'altération des minéraux est une composante fondamentale de la biogéochimie des écosystèmes terrestres (Riebe et al. 2004; Sverdrup and Warfvinge 1988; Whitfield et al. 2010) et la quantification des variations spatiale et temporelle de cette réaction telle qu'elle se produit en milieu naturel assurera une meilleure compréhension du cycle des éléments dans ces écosystèmes; et 2) l'identification et la quantification des déterminants environnementaux de ces variations sont essentielles pour anticiper les impacts potentiels des changements environnementaux sur les écosystèmes terrestres et aquatiques.

Cette recherche a été construite à partir de plusieurs objectifs spécifiques qui ont guidé l'action et ont permis la production de l'ensemble des résultats rapportés dans le présent document. Les objectifs spécifiques poursuivis dans le cadre de ce travail sont de:

1) chiffrer les taux d'altération contemporains des cations basiques (Ca, Mg, Na et K) à l'aide de la méthode du budget intrant-extrant à l'échelle du bassin versant (WATERSHED) dans un large éventail (n=72) d'écosystèmes forestiers;

2) quantifier les taux d'altération à long terme de Ca, Mg, Na et K au moyen de la méthode du bilan de masse en profil de sol (PEDON) pour un sous-ensemble de 21 bassins versants forestiers;

3) établir la concordance/discordance entre trois méthodes d'estimation des taux d'altération de cations basiques (PEDON, WATERSHED et le modèle géochimique PROFILE (MODEL)), et analyser la performance relative de ces méthodes dans un éventail de conditions environnementales;

4) estimer la variabilité interannuelle des taux d'altération actuels des cations basiques à l'échelle d'un bassin versant forestier;
5) évaluer l'impact de la variabilité spatiale des facteurs environnementaux et des propriétés des sols agissant simultanément sur les taux d'altération des cations basiques et analyser les relations existant entre les fluctuations à court terme de ces taux d'altération et les changements temporels des conditions environnementales.

Les objectifs spécifiques de cette thèse doivent être placés dans une optique d'amélioration du savoir sur les processus d'altération des minéraux et de développement d'approches méthodologiques pour quantifier les taux d'altération. Plus particulièrement, c'est la question de la variabilité spatio-temporelle des taux d'altération des minéraux qui se trouve au cœur de cette thèse. La Figure 1.1 présente les liens entre les différents aspects des processus d'altération des minéraux des sols qui sont traités dans le cadre de la réalisation de cette thèse.

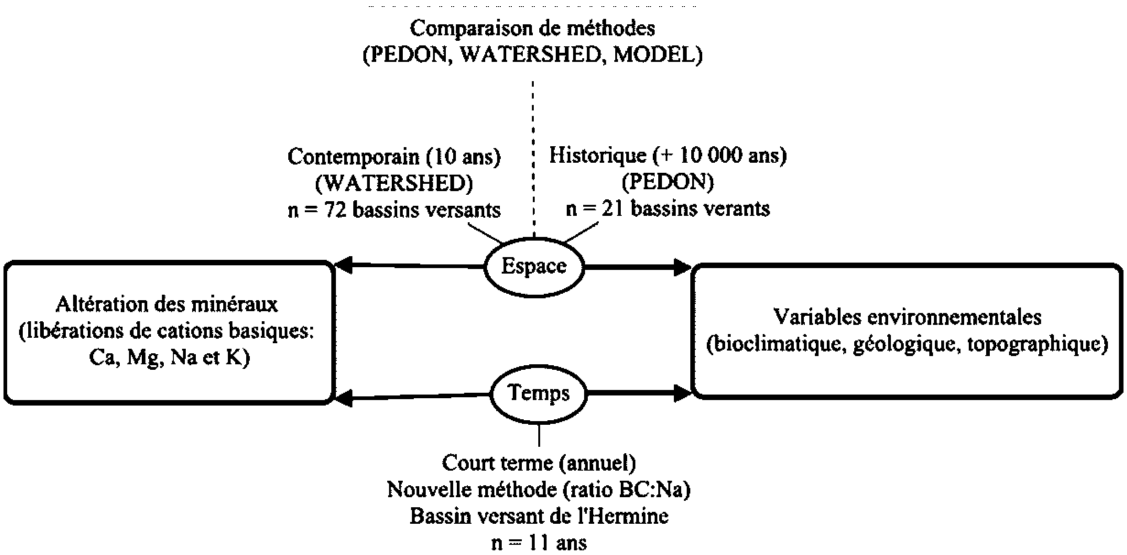

Figure 1.1 : Schéma conceptuel présentant l'ensemble du travail réalisé dans la thèse.

Les résultats de recherche reflétant la réalisation des divers objectifs spécifiques sont présentés dans des chapitres distincts, suivant un cheminement méthodologique élaboré de façon à ce que l'intégration des différentes parties de la thèse compose un ensemble cohérent.

1.3 Cheminement méthodologique

Trois stratégies expérimentales et d'échantillonnage ont été mises en œuvre pour collecter les données permettant de répondre à la question centrale de la thèse. Ces données originales sont complétées, lorsque nécessaire, par des informations disponibles dans la littérature scientifique. La première stratégie regroupe 72 bassins versants distribués de l'Outaouais à la Côte Nord du Québec de manière à définir d'importants gradients environnementaux, notamment des gradients climatiques et de végétation, et à couvrir des assemblages lithologiques variés. Les bassins versants sélectionnés font partie du réseau des lacs du Québec dont la physico-chimie fait l'objet de suivis par Environnement Canada depuis les années 1980. Cette stratégie a permis d'étudier la variabilité spatiale des **taux d'altération contemporains** (sur des dizaines voire des centaines d'années) des cations basiques. La seconde stratégie d'échantillonnage est basée sur un sous-échantillon de 21 bassins versants provenant du premier jeu de bassins. Ils sont distribués entre la rivière Saguenay et celle des Outaouais, au nord du fleuve Saint-Laurent, et ils ont été mis à profit pour l'analyse de la variabilité spatiale des **taux historiques d'altération** (à long terme, sur des milliers d'années) des cations basiques. Ce même jeu de bassins versants a été utilisé pour l'évaluation de la concordance entre trois méthodes d'estimation des taux d'altération des minéraux (PEDON, WATERSHED et MODEL). Quant à la troisième stratégie, elle repose sur un dispositif d'étude à long terme établi dans le bassin versant de l'Hermine (à 80 km au Nord de Montréal) depuis 1992, et elle a permis l'estimation de la variabilité temporelle des **taux actuels d'altération** (à court terme, au cours des années récentes) des minéraux.

Afin de mieux appréhender la complexité du milieu naturel, plusieurs méthodes d'estimation des taux d'altération ont été utilisées. Ainsi, la méthode du bilan de masse en profil de sol (Brimhall et al., 1991a,b ; Egli et Fitze, 2000) a été utilisée pour estimer les taux d'altération à long terme, alors que les taux d'altération contemporains ont été calculés à l'aide de la méthode du budget intrant-extrant à l'échelle du bassin versant (Clayton, 1979, Velbel, 1985, White et Blum, 1995, Velbel et Price, 2007). Par ailleurs, dans le cadre de l'analyse de la concordance entre les méthodes, des données d'altération simulées avec le modèle PROFILE (Sverdrup et Warfvinge, 1993, Sverdrup, 2009), et qui ont déjà fait l'objet d'une publication (Houle et al., 2012), ont été utilisées dans une perspective de comparaison. Cette thèse comporte de plus une composante expérimentale, dans le cadre de laquelle nous avons développé une nouvelle approche permettant d'estimer des taux d'altération sur une échelle de temps de l'ordre de l'année. Les résultats obtenus à partir de cette nouvelle approche, combinant des données de terrain et de laboratoire, ont permis la mise en relation de la variabilité temporelle des taux d'altération des minéraux avec l'évolution interannuelle des conditions hydro-climatiques au bassin versant de l'Hermine de 1995 à 2006.

1.4 Plan de la thèse

Dans l'optique de favoriser une diffusion rapide des principaux résultats de cette recherche, nous avons opté pour un mode de rédaction par articles à soumettre pour publication dans des revues scientifiques. Les chapitres 2 à 5 de cette thèse correspondent à ces articles, qui sont rédigés en anglais. Des ajustements mineurs, essentiellement sur la forme, ont été effectués dans les versions originales des différents articles pour les adapter au format de présentation de la thèse. Une section de transition est également insérée entre les différents chapitres afin d'intégrer un argumentaire qui fasse les liens entre eux et de mettre en évidence l'interdépendance des différents chapitres et leur intégration pour former un tout cohérent. Le chapitre 1 est une introduction où la problématique générale (contexte, justification, question centrale et objectifs spécifiques) de la recherche ainsi qu'une revue de la littérature qui contribue à la formulation du projet sont présentées. Dans ce chapitre, les grandes lignes du cheminement méthodologique déployé pour répondre à la question centrale de recherche sont énoncées, et l'organisation de la thèse est présentée.

Dans le chapitre 2, nous avons évalué les effets intégrés des variables climatiques, des dépôts atmosphériques acides et des caractéristiques pédologiques et topographiques des bassins versants sur les taux d'altération contemporains et les concentrations de cations basiques dans 72 lacs du Québec. Les taux d'altérations ont été estimés au moyen de la méthode du budget intrant-extrant à l'échelle du bassin versant (Clayton, 1979 ; Velbel, 1985 ; Velbel et Price, 2007) et des techniques statistiques multivariées ont été mises en œuvre.

Le chapitre 3 a été consacré à l'analyse de la variabilité spatiale des taux d'altération historiques des cations basiques dans une série de 21 bassins versants situés au Sud du Québec. Les taux d'altération historiques ont été estimés à l'aide de la méthode du bilan de masse en profil (Brimhall et al., 1991a,b; Egli and Fitze, 2000). L'analyse canonique de redondance a été utilisée pour identifier et quantifier les liens entre les taux d'altération estimés et des variables environnementales ainsi que les propriétés des sols.

Au chapitre 4, nous avons évalué la performance relative de trois méthodes d'estimation de l'altération des minéraux (PEDON, WATERSHED et MODEL). Des techniques d'analyse statistique non paramétriques telles que la régression de Passing et Bablok (Bablok et Passing, 1985) ainsi que le coefficient de corrélation de rang de Kendall ont été appliquées pour évaluer la concordance entre les méthodes. Dans cette perspective, la série de 21 bassins versants utilisés au chapitre 3 a été mise à profit. Ces bassins possèdent des caractéristiques variées au point de vue des conditions hydro-climatiques, de la couverture forestière et de certaines propriétés des sols.

Dans le chapitre 5, nous nous sommes intéressés à la variabilité temporelle des taux d'altération des minéraux au bassin versant de l'Hermine. Dans ce bassin versant situé au sud du Québec, un dispositif expérimental a été établi dès 1992 pour étudier la biogéochimie des éléments. Ce chapitre constitue également une composante expérimentale de la thèse. En effet, une nouvelle approche a été développée afin d'estimer des taux d'altérations actuels sur des échelles de temps de l'ordre de l'année. Pour y parvenir, nous avons réalisé une expérience de dissolution en laboratoire et des techniques d'extraction séquentielle ont été mises en œuvre pour solubiliser la fraction des cations basiques du sol qui peut être considérée potentiellement libérable par l'altération des minéraux. Ces données de laboratoire ont été combinées aux flux de Na dans les eaux de surface au bassin versant de l'Hermine entre 1995 et 2006 pour obtenir des taux d'altération de Ca, Mg et K pour chacune des années de cette période. Ensuite, les déterminants environnementaux de la variabilité temporelle des taux d'altération ont été analysés à l'aide du critère d'information d'Akaike corrigé pour les petits échantillons (AIC_C).

Enfin, dans le chapitre 6, nous revenons sur les principaux résultats de cette recherche, nous décrivons la contribution générale de la thèse et nous proposons des pistes de recherche pour des études futures.

1.5 Section de transition au chapitre 2

Le chapitre qui suit a été publié sous forme d'article dans la revue *Applied Geochemistry*[1]. Il traite de la variabilité spatiale des taux d'altération contemporains et de la concentration des cations basiques dans des lacs en relation avec certaines conditions environnementales et caractéristiques des bassins versants. Comme nous l'avons souligné dans le chapitre précédent, plusieurs variables ont été identifiées comme ayant un effet sur les taux d'altération des minéraux. Cependant, l'aspect multidimensionnel des processus d'altération des minéraux a rarement été considéré dans les analyses, en particulier en raison du faible nombre de sites utilisés dans les études. Le chapitre 2 de la thèse vise à contribuer à combler cette lacune en analysant les effets synergiques ou antagonistes de plusieurs facteurs considérés simultanément sur les taux d'altération des minéraux.

Ce chapitre s'emploie à répondre aux objectifs spécifiques 1 et 5 de la thèse. En utilisant des données provenant de 72 bassins hydrographiques du réseau des lacs du Québec, nous avons quantifié les taux d'altération contemporains de cations basiques à l'aide de la méthode du budget intrant-extrant à l'échelle des bassins versants. Ensuite, nous avons mis en œuvre des techniques statistiques multivariées dont celle de partition de variance pour analyser l'influence d'une série de facteurs (matériel parental, type de végétation, propriétés des sols, topographie, climat, etc.) sur les taux d'altération et les concentrations des cations basiques dans les lacs. L'utilisation de ces techniques statistiques a été rendue possible grâce à la stratégie expérimentale et d'échantillonnage utilisée qui nous a permis de retenir un grand nombre de sites distribués le long d'importants gradients environnementaux. Les résultats présentés dans ce chapitre font ressortir le rôle prépondérant des variables reliées au climat dans la variabilité spatiale des taux d'altération actuels et des concentrations des cations basiques dans les lacs. Dans un contexte de changement climatique,

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[1] Augustin, F., Houle, D., Gagnon, C., Couture, S., Courchesne, F. 2015. Partitioning the impact of environmental factors on lake concentrations and catchment budgets for base cations in forested ecosystems. Applied Geochemistry, 53: 1–12.

ces résultats représentent une importante contribution à la recherche sur les impacts potentiels de ces changements sur la capacité des sols à soutenir la croissance forestière à travers le renouvellement des réservoirs échangeables à long terme.

L’article a été réalisé en collaboration avec Daniel Houle, Christian Gagnon, Suzanne Couture et François Courchesne. J’ai effectué la recherche bibliographique et organisé les données hydro-chimiques pour calculer les taux d’altération. Les données environnementales ont été extraites de cartes ou simulées à la direction de la recherche forestière, au Ministère des Forêts, de la Faune et des Parcs du Québec. J’ai fait le travail de validation et d’organisation de ces données. J’ai également effectué les analyses statistiques et j’ai rédigé le manuscrit. Tout ce travail a été réalisé sous la supervision de François Courchesne et Daniel Houle (directeur et co-directeur du projet, respectivement) qui m’ont alimenté en idées et qui ont fait des recommandations. Les co-auteurs ont contribué à l’amélioration du manuscrit en faisant des corrections, des ajouts ou en me donnant des conseils.

Chapitre 2. Partitioning the impact of environmental factors on lake concentrations and catchment budgets for base cations in forested ecosystems

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2.1 Abstract

Seventy-two forested lake catchments were studied in Quebec (Canada) to examine the influence of climate, atmospheric deposition and catchment characteristics on base cation (BC) concentrations in lake waters (BC_C) and base cation budgets at the catchment scale (BC_Q). The catchments are located along a bioclimatic gradient in a vast (180000 km^2) study area underlained by the Canadian Shield. Multivariate statistical approaches are used to simultaneously assess the effects of multiple environmental factors on cation fluxes. Mean annual BC_C were 132, 40, 24 and 7 $\mu mol_c\ l^{-1}$ for Ca, Mg, Na and K, respectively. Mean annual BC_Q estimates showed exports of 0.826, 0.251, 0.135 and 0.043 $kmol_c\ ha^{-1}\ yr^{-1}$ for Ca, Mg, Na and K, respectively. There were strong similarities in the spatial variation of BC_C and BC_Q, and also in their links with environmental factors. We hypothesized that the spatial variability of both, BC_C and BC_Q, were strongly influenced by the spatial variability in the rates of mineral weathering reactions. Variance partitioning indicated that climate-related effects accounted for 51.6% and 52.7% of the variation in BC_Q and BC_C, respectively. Nonetheless, lake/catchment morphometry and variables linked to solutes sources (lithology, atmospheric deposition and soil properties) were also included in some models. Overall, BC_C and BC_Q were positively affected by temperature, precipitation as rain and sulphate depositions, and negatively influenced by precipitation as snow and the number of frost days. Multivariate models explaining up to 69% of variation in BC_C and BC_Q were developed. This study shows the strong impact of climatic drivers on base cation budgets and, thus, on mineral weathering at the regional scale on the Canadian Shield.

2.2. Introduction

Several authors reported that the capacity of an ecosystem to supply base cations (BC) through biogeochemical processes widely determines its sensitivity to nutrient enrichment and acidification (Cook et al., 1987; Kamenik et al., 2001; Watmough and Dillon, 2001; Stendera and Johnson, 2006). In undisturbed forested headwater catchments, Ca, Mg, K and Na concentrations in lakes and rivers are controlled by a range of environmental factors and biogeochemical processes including the chemistry of atmospheric depositions, the seasonality of hydrological flowpaths, the dynamics of forest growth and the geochemistry of soils and parent materials, in particular mineral weathering reactions (Bain et al., 1993; Egli et al., 2006; Hornung et al., 1995; Sverdrup et al., 1993; White and Blum, 1995).

When base cations are released through weathering or displaced from the soil matrix, they are transported to adjacent surface waters or to regional groundwaters. Therefore, significant linkages exist across a range of environmental conditions in headwater catchments between the net BC transfer fluxes on hillslopes and the dissolved concentrations in lake waters (Schnoor and Stumm, 1986). Because long-term silicate and carbonate weathering is the main source of BC to the soils, it strongly contributes to BC export from soils to surface waters. As a result it regulates the long-term BC concentrations in surface waters. Positive relationships were observed between mineral weathering rates and BC concentrations in lake waters of southern Quebec (Houle et al., 2012). Marchetto et al. (1995) investigated the hydrochemistry of a variety of lakes in the Central Alps as a function of their catchment characteristics. They found that silicate and carbonate weathering were the main factors influencing lake chemistry. Because of biochemical reactions in the organic soil layer and modifications to cation exchange, natural disturbances such as forest wildfires or insect epidemics can further influence BC fluxes from catchments to water bodies or streams with potential impacts at the decadal scale (Nordin et al., 2007; Rask et al., 1993; Zhang and Wei, 2012).

On a short time-scale, other processes such as dust depositions and sea spray episodes may trigger ion exchange reactions and increase BC concentrations in runoff (Ballantyne et al., 2011; Chadwick et al., 1999). Dissolved anions (chloride (Cl), SO_4, NO_3) and dissolved organic substances fluxes may also temporarily induce increased BC fluxes from the soil matrix notably after prolonged periods of drought or disturbances of the vegetation cover

(Biron et al., 1999; Evans et al., 2001; Houle et al., 2004). Many studies on the biogeochemistry of watersheds also focused on the impact of atmospheric depositions on terrestrial and aquatic ecosystems (Cosby et al., 2001; Ouimet and Duchesne, 2009; Whitfield et al., 2010) and showed that acid inputs can promote the mobilization of base cations from catchment soils to surface waters. Over the past decades, changes in the chemical composition of atmospheric deposition occurred in eastern North America in response to reductions in anthropogenic emissions and resulted in the progressive recovery of some of the streams and lakes of the region with decreasing export of BC from catchment soils to surface waters (Driscoll et al., 2003; Houle et al., 2004, 2010).

The catchment input–output budget approach has been used to estimate the rates at which BC are released from soils, parent materials and bedrocks through carbonate and silicate mineral weathering (Clayton, 1979; Likens et al., 1967; Price et al., 2008; Velbel, 1985; Velbel and Price, 2007). This method assumes that BC release during soil formation and BC accretion in biomass are in a steady state. In this context, the method was found to yield reliable annual estimates of present day mineral weathering rates at the catchment scale (Kolka et al., 1996; Whitfield et al., 2006, 2010). At the Hubbard Brook Experimental Forest, Likens et al. (1977) derived mineral weathering rates from the difference between BC in atmospheric inputs and in stream outputs, assuming that the accretion of BC in the biomass balances their release in soils through the decay of dead tissues. However, this method also has limitations, because the steady state assumption for the individual biogeochemical compartments may be difficult to prove (Clayton, 1988; Cleaves et al., 1970). Yet, the magnitude of the error in weathering rates estimated with the catchment budget method has never been reported.

Several catchment studies highlighted the relationships existing between BC budgets or concentrations in water bodies and environmental factors such as soil properties, climate, hydrology, soil properties and catchment morphology (Bain et al., 1993; Sverdrup and Warfvinge, 1988; Velbel, 1993). Velbel (1993) observed a positive relationship between temperature and BC budgets for Coweeta Catchments in North Carolina. White and Blum

(1995) also reported a positive association between Na budgets and temperature, runoff and precipitation. The variability of BC concentrations in lake waters was also related to catchments characteristics and lake/catchment morphometry (D'Arcy and Carignan, 1997; Kamenik et al., 2001; Stendera and Johnson, 2006). However, there were few attempts to assess the simultaneous effects, either synergetic or antagonistic, of a spectrum of environmental variables across a vast geographic area on both the BC concentrations in lake waters and/or their annual budgets at the catchment scale (Kamenik et al., 2001; Pope et al., 1995; Stendera and Johnson, 2006). We hypothesized that the multiple environmental factors that determine BC concentrations in lake waters (BC_C) and BC budgets (BC_Q) in forested catchments are interrelated. By concurrently investigating BC_C and BC_Q for a suite of headwater lake catchments, we therefore aimed at identifying the similarities and contrasts in their control by environmental factors in forested ecosystems.

In this paper, we sought to: (1) assess the spatial variability of Ca, Mg, Na and K concentrations in lake waters and to estimate their annual budgets at the catchment scale in a wide spectrum of forested ecosystems and to (2) establish and quantify the significant links between BC_C and BC_Q, on the one hand, and a series of environmental and climatic factors, on the other hand. To do so, we used the data of 72 headwater forested catchments distributed over a vast geographic area extending along a 1000-km scale transect and located on the Grenville province of the Canadian Shield in Quebec.

2.3. Site characteristics and methodology

2.3.1. Catchment characteristics and geologic setting

The 72 lake catchments targeted for this study cover a large geographic area extending from 45° and 52° N to 65° and 79° W. They are distributed from the Outaouais region to the Côte Nord area of Quebec (Figure 2.1). The chemistry of these lakes has been monitored by Environment Canada over the last 30 years (Bouchard, 1997; Houle et al., 2004). The whole region is underlained by the Canadian Shield which consists of a variety of rocks formed during the Archean and Proterozoic eras, either igneous, mafic and ultramafic, metamorphic, sedimentary or volcanic rocks (D'Arcy and Carignan, 1997; Lachance et al., 1985). For the section of the Canadian Shield where the 72 catchments were selected, Kodama (1979) reported that the clay minerals in the subsoil were generally inherited from bedrocks available in the region. We therefore assumed that, for any given catchment, the lithology of the soil parent material reflects that of the underlying local bedrock with only negligible allochtonous contributions from sediments transported over long distances during the last glaciation. Ten among the most mineralized lakes are located in an area particularly rich in carbonate, located in the southernmost part of the study area in the Outaouais region.

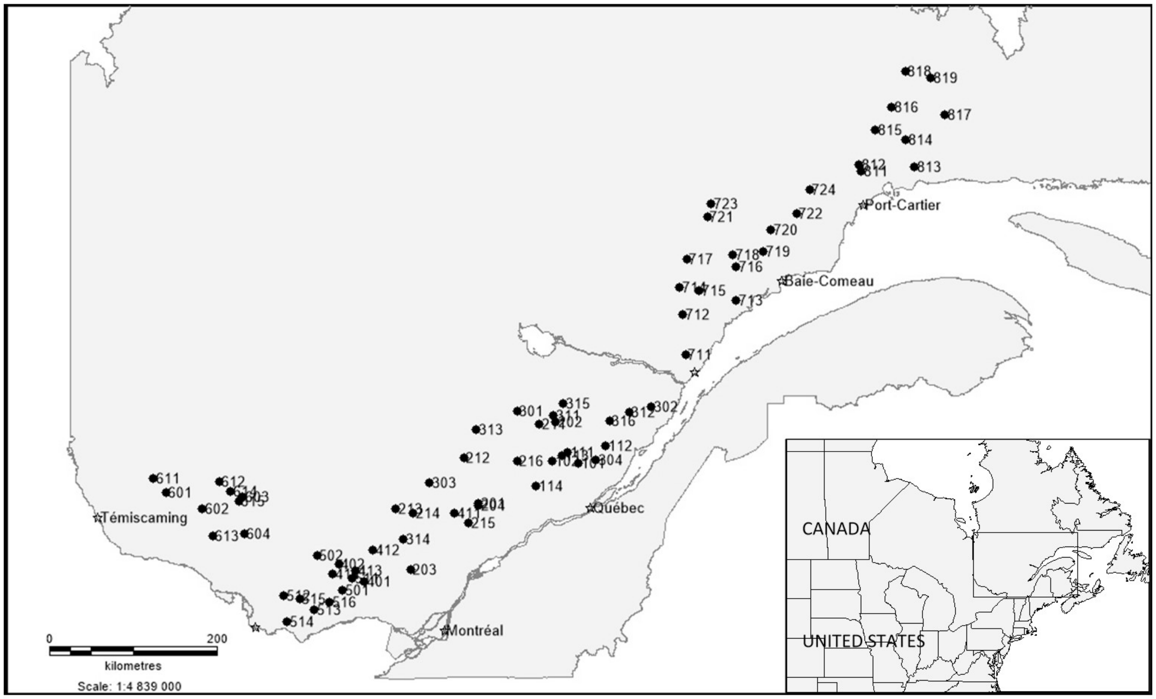

Figure 2.1. Distribution of the 72 lake catchments in the study area.

The soils in the 72 catchments are mostly orthic or gleyed humo-ferric or ferro-humic podzols, except for a few catchments where brunisols or regosols were present (Soil Classification Working Group, 1998). The vegetation ranges from deciduous forests dominated by sugar maple (Acer saccharum Marsh.) in the southwest part of the study area, to mixed forests dominated by either balsam fir (Abies balsamea L.) or black spruce (Picea mariana Mill.) in the northeast. The climate of the study area is characterized by long cold winters and short wet summers but the area is large enough as to cover a gradient of climatic conditions (Richard, 1995). The main axis of climatic variability extends from the southwestern part of the area, the Outaouais region, where the climate is dryer and warmer than in the northeastern catchments of the Côte Nord region located in the boreal zone.

2.3.2. Lake sampling and water analysis

The 72 catchments are distributed along an altitudinal gradient ranging from 145 to 975 m above sea level and have a total area of 25–696 ha (Table S2.1 in Appendix A). Each catchment has an undisturbed headwater lake with a small area (<202 ha) and a maximum depth ranging from 2 to 52 m. The lakes were sampled twice a year, at the end of May and at the end of November (during spring and autumn circulation), for each year from 1989 to 1996, for a total of 16 water samples per lake (except for the lakes located in the Côte Nord Region which were sampled once a year at the end of May, for a total of 8 water samples per lake). Integrated water samples (down to a 5 m deep) were collected for chemical analysis by helicopter at the geometric centre of the lake. When the lake was less than 5 m deep, the integration was performed 1 m from the bottom of the lake to the surface (Houle et al., 2004). All samples were kept cool after collection and sent to the laboratory within 24 h. From 1989 to 1991, the chemical analysis of water samples for Ca, Mg, Na and K concentrations was conducted using atomic absorption spectrophotometry. For samples collected after 1991, inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used (Environment Canada, 1994). A study comparing BC_C from both datasets revealed that the two methods produced similar results (Houle et al., 2004). For a given BC and sampling year, the data for lake water chemistry is the mean of the two samples collected during that year. The influence of climatic extremes on lake chemistry is expected to be small in this dataset because these first order headwater lakes have an average water residence time of 1 year and that the average of 8 years of sampling is used.

2.3.3. Atmospheric deposition fluxes of base cations

The annual atmospheric deposition fluxes for BC are those reported by Ouimet and Duchesne (2009). They mapped total atmospheric depositions for BC (annual average) for the period 1999–2002, using data obtained from a network of monitoring stations in southern Quebec. Although the present study covers the period 1989–1996, mean annual deposition data have not been adjusted to reflect the overall downward trends observed at the end of the 20th century, given the uncertainties associated with estimates of BC depositions. The georeferenced digital maps they produced for total annual BC deposition data with the ArcGIS software (Manjula et al., 2010) were used to position each of the 72 catchments. A mean, surface integrated, deposition value was then calculated for each BC and catchment within a radius (originating at the geometric centre of the lake) corresponding to that of a circle having the same area as the catchment of interest. For catchments located to the northeast of the Saguenay River, total atmospheric deposition data were adjusted to account for the deposition of sea salts. An average value was calculated for the first 10 catchments adjacent to the western shore of the Saguenay River and it was applied to all stations near the estuary of the St. Lawrence to correct for marine deposition.

2.3.4. Fluxes at the catchment outlet

For each individual BC, a mean annual lake concentration was calculated for the period 1989–1996 for each lake. A mean annual runoff was also obtained for the same period for each catchment by calculating the difference between total precipitations and potential evapotranspiration which have been simulated with the BioSIM model (Régnière, 1996; Régnière and Bolstad, 1994; Houle et al., 2012). The annual fluxes of BC at the outlet of the 72 catchments were then estimated by multiplying the mean annual lake concentrations by the annual runoff values. This approach assumes that BC concentrations at the centre of the lake are similar to concentrations at the lake outlet. Based on the fact that BC were generally far in excess of nutritional needs for plankton or macrophytes in oligotrophic lakes of the Canadian Shield (Houle et al., 2012), their behaviour was considered to be conservative in the lakes (Duchesne and Houle, 2008; Houle et al., 2012).

2.3.5. Input–output budgets at the catchment scale

The annual BC budget was estimated for each of the 72 lake catchments according to the elemental input–output approach (Clayton, 1979; Likens et al., 1967; Velbel and Price, 2007). This method yields an estimation of the net elemental flux at the outlet of a catchment by taking into account the main fluxes of dissolved materials entering (inputs) and leaving (outputs) a catchment area. For an unmanaged forest catchment, the inputs include total atmospheric depositions and mineral weathering whereas removals at the stream or lake outlet and storage changes in soils or in the biomass are the main outputs from the system (Velbel and Price, 2007). This is true for catchments underlain by impervious bedrock (Velbel, 1993), where losses to groundwater are negligible, and located at the head of a drainage network, thus eliminating the contribution of tributaries. For a given cation, input–output budget was calculated using the following equation (adapted from Clayton, 1979):

$$IOB_X = P_X - E_X \pm \Delta(B_X + S_X) \pm \Delta L_X$$

where IOB_X is the input–output budget of the cation X, P_X the total atmospheric deposition of the element X, E_X the export of the cation X at the stream outflow, $\Delta(B_X + S_X)$ the annual net change resulting from sequestration of the element X in the biomass and its storage in the soil (adsorption, desorption, exchanges), and ΔL_X is the annual net change resulting from sedimentation of the element X in the lake and the release of the element from sediment.

The study area is covered by unmanaged mature forests which have not been affected by burning or other significant disturbance for several decades. Assuming steady-state conditions for BC cycling in the catchment on an annual basis, further brings cation storage or release in soils and trees (thus the term $\Delta(B_X + S_X)$) close to zero. In three forested catchments of Quebec, this approach yielded weathering rates similar to simulations from MAGIC (Model of Acidification of Groundwater in Catchments) as reported by Ouimet and Duchesne (2005). Agreement was also recorded between rates calculated with the catchment budget method and those simulated with the model PROFILE for a subset of 21 of the 72 catchments studied here (Houle et al., 2012). It suggests that potential changes in the soil BC exchangeable pool as well as potential net BC immobilization in biomass were not of important magnitude or that both fluxes compensated each other.

We also assume that the concentrations of base cations in the centre of the lakes are similar to their concentrations at the outlet of the watershed. Base cations are generally present at concentrations well beyond the nutritional requirements for plankton or macrophytes compared with nitrates or phosphates which are limiting nutrients in oligotrophic Canadian

Shield lakes (Houle et al., 2012). Under these conditions, the behaviour of base cations is relatively conservative in these lakes (Duchesne and Houle, 2008; Houle et al., 2012), so that the term ΔL_X is negligible in the equation above. Therefore, the difference between total annual atmospheric deposition and removal at the stream or lake outlet yields a net flux (IOB_X) that can be interpreted as an estimate of the annual amount of BC release by weathering.

2.3.6. Acquisition of environmental data

Most of the environmental data were extracted from digital and georeferenced inventory maps, using the ArcGIS Software as was the case for the acquisition of the atmospheric deposition data. Before performing statistical analyses, each environmental variable was assigned to one of three variable groups: geographic variables (GEO), hydro-bioclimatic variables (CLM) or a third group including variables referring to solute sources (ION), as seen in Table S2.1. Lake morphometry and other catchment characteristics were computed using ArcGIS and the Digital Canadian Elevation Data of 90 m resolution (McDonnell and Kemp, 1995).

Bioclimatic variables were obtained first from BioSIM, a software developed at the Canadian Forest Service (Régnière, 1996). Using simple input data such as longitude, latitude, slope, aspect and elevation of the catchment, the software generates the climatic variables found in Table S2.1 for each individual catchment using climatological information gathered at a network of meteorological stations located within or in proximity to the boundaries of the study area. For each catchment, a maximum of four meteorological stations were used to generate the data. Minimum distance was the basic criterion for selecting the best sources of climatic data for a catchment. The vegetation data (percent deciduous or coniferous cover) was obtained from the digitized ecoforestry maps (1:20 000) of Quebec. They were produced from photo-interpretation conducted on the original photographs of the inventory of southern Quebec through the ecoforestry information system of the Ministry of Natural Resources of Quebec.

Regarding the group of environmental variables referring to ion sources (ION), atmospheric depositions of sulphate were obtained from Ouimet and Duchesne (2009). The eco-forestry map (1:20 000) of Quebec was used for data on surface deposits and drainage. The organic carbon content of the forest floor was taken from Tremblay et al. (2002) while humus and soil depths as well as soil clay and sand contents were obtained from the database of the Quebec Forest Ecosystem Research and Monitoring Network (Réseau d'Étude et de Surveillance des Écosystèmes Forestiers (RESEF)) (Gagnon et al., 1994), and the Quebec portion of the Soil profile and organic carbon database for Canadian forest and tundra mineral soils (Siltanen et al., 1997). According to the geological map (1:2 500 000) of Quebec produced by the Ministry of Natural Resources (MRN, 2003), twelve groupings of 26 different rocks are present in the study area. Each lithology group is characterized by a series of specific rocks and mineral types as indicated in Table S2.1. However, it was not possible to extract the terrestrial area covered by each rock type present in a given watershed from the available data. Therefore, the lithology of the catchments was described using a presence/absence matrix for the 12 rock groups identified in the study area.

2.3.7. Statistical analyses

All statistical analyses were performed using the R package (R Development Core Team, 2009). Univariate plots were used to visualize raw data and to check the normality of distributions. Prior to statistical analysis, BC_C and BC_Q data were log-transformed to satisfy parametric test assumptions. Due to the range in values and to reduce multicollinearity, all untransformed independent variables were standardized to a mean of 0 and a standard deviation of 1 to even their weight before performing the multivariate analyses. Principal Components Analysis (PCA) was first performed to outline the general structure of BC data and of environmental variables.

The relationships between environmental variables, on the one hand, and BC_C and BC_Q values, on the other hand, were then examined using several approaches. Variance partitioning was used to estimate the fraction of the total variation in BC concentration or budget data that could be explained by the three groups of environmental variables, and to partition the individual contribution of each group (Borcard et al., 1992). This statistical technique relies on the use of co-variables to estimate the fraction of variance in the dependant dataset explained by the groups of explanatory variables. For each group of variables, a forward selection procedure was run to detect the main environmental descriptors that could best explain the variability in BC_C and BC_Q. Each variable group was tested to determine the significance of individual variables using a Monte Carlo permutation test (with 999 unrestricted permutations). Only the significant variables ($\alpha = 0.05$) retained in the forward selection procedure were used in the variance partitioning analysis.

Redundancy analysis (RDA) was used to determine which of the significant environmental variables explained the majority of the variation in BC data and to quantify the discrete contribution of the individual descriptors. RDA is a constrained ordination method that uses two (or more) data tables, one of which includes a multivariate response matrix that depend linearly on descriptors contained in the other tables (Legendre and Legendre, 1998). This multivariate statistical method was chosen assuming that the relationships between variables to explain (BC concentrations and budgets) and descriptors (environmental variables) are linear. The forward.sel () function of the library Packfor was used to determine the best predictors amongst the significant environmental variables retained for the multivariate analyses. Multiple regression analyses were used to generate multivariate models for individual BC concentrations and budgets, as well as for the sum of base cation concentrations (ΣBC_C) or budgets (ΣBC_Q). Significant variables were chosen through a forward selection process that builds models by successively adding variables based solely on the t-statistics of their estimated coefficients. In order to focus on the most reliable models, only independent variables whose explanatory power represented at least 5% of the total variance explained were retained in the final models.

2.4. Results

2.4.1. Base cation concentrations in lake waters and input–output budgets at the catchment scale

Before calculating watershed budgets, the input and output data were closely examined (data not shown). In the study area, input fluxes varied from 0.01 to 0.16 kmol ha^{-1} yr^{-1} for all BC. For Mg, Na and K, the output fluxes mainly ranged from 0.01 to 0.98 kmol ha^{-1} yr^{-}

^{1}, while Ca was more variable with some catchments showing fluxes of up to 5.17 kmol ha^{-1} yr^{-1}. Base cation concentrations in lakes and estimates of input–output budgets are reported in Table 2.1. Concentrations were variable in the lakes and the ranking of BC_C followed the order: Ca > Mg > Na > K. The budgets for Ca, Mg, Na, and K (kmol ha^{-1} yr^{-1}) were all negative indicating that all the catchments were losing base cations. Globally, the ranking of BC_Q values was the same as for BC_C.

The results of the principal component analysis performed on log-transformed BC_C and BC_Q data (see Figure S2.1 in Appendix A for data distribution) showed that the first two principal component axes explained 82% of the variability in BC_C data and 79% of the variability of BC_Q in the study area (Table 2.2). For a given cation, loading coefficients for BC_C and BC_Q were very similar on the two first PCA axes, suggesting positive association between catchment budgets and concentrations for each cation. The PCA axis 1 was negatively linked to budget and concentration data for the four base cations and therefore contrasted catchments with high BC losses (or lakes with high BC concentrations) from those with lower BC depletion (Table 2.2). To the contrary, the PCA axis 2 was positively correlated with budget and concentration data for Ca and Mg, but negatively linked to Na and K budgets and concentrations (Table 2.2). The second PCA axis defined a contrast between catchments with high Ca and those with low Ca exports.

2.4.2. Spatial variations in environmental variables

Frequency histograms as well as normality test showed that the majority of the main environmental variable were not, or only slightly, skewed (Figure 2.2), so that raw data were not transformed. All independent variables were, however, standardized to even their weight prior to analysis. The environmental characteristics of the 72 catchments studied differed widely as seen in Tables S2.1 and 2.3.

Table 2.1: Summary statistics of BC catchment budgets and concentrations in lake waters over the study area.

Statistic	Catchment budget ($kmol_c\ ha^{-1}\ yr^{-1}$)				Concentration in lake waters ($\mu mol_c\ l^{-1}$)			
	Ca	Mg	Na	K	Ca	Mg	Na	K
Mean (SE)[a]	-0.826 (0.10)	-0.251 (0.03)	-0.135 (0.02)	-0.043 (0.01)	132 (16)	40 (5)	24 (3)	7 (1)
Median	-0.515	-0.206	-0.133	-0.040	86	33	24	7
Max	-0.087	-0.039	-0.038	-0.003	812	148	43	19
Min	-5.046	-0.945	-0.450	-0.116	21	10	11	2

[a]SE: standard error

Table 2.2: Eigenvalues, percent of inertia explained and loading coefficients oo the first two principal component axes, based on PCA analysis, for the lake BC concentrations and catchment budgets data of the study area.

Statistic	Cation	Concentration in lake waters		Catchment budget	
		PCA1	PCA2	PCA1	PCA2
Eigenvalues		2.51	0.77	2.33	0.84
Relative eigenvalues		0.63	0.19	0.58	0.21
Cumulative relative eigenvalues		0.63	0.82	0.58	0.79
Loading coefficients					
	Ca	-0.47	0.72	-0.48	0.68
	Mg	-0.57	0.18	-0.58	0.21
	Na	-0.47	-0.57	-0.46	-0.61
	K	-0.48	-0.35	-0.48	-0.36

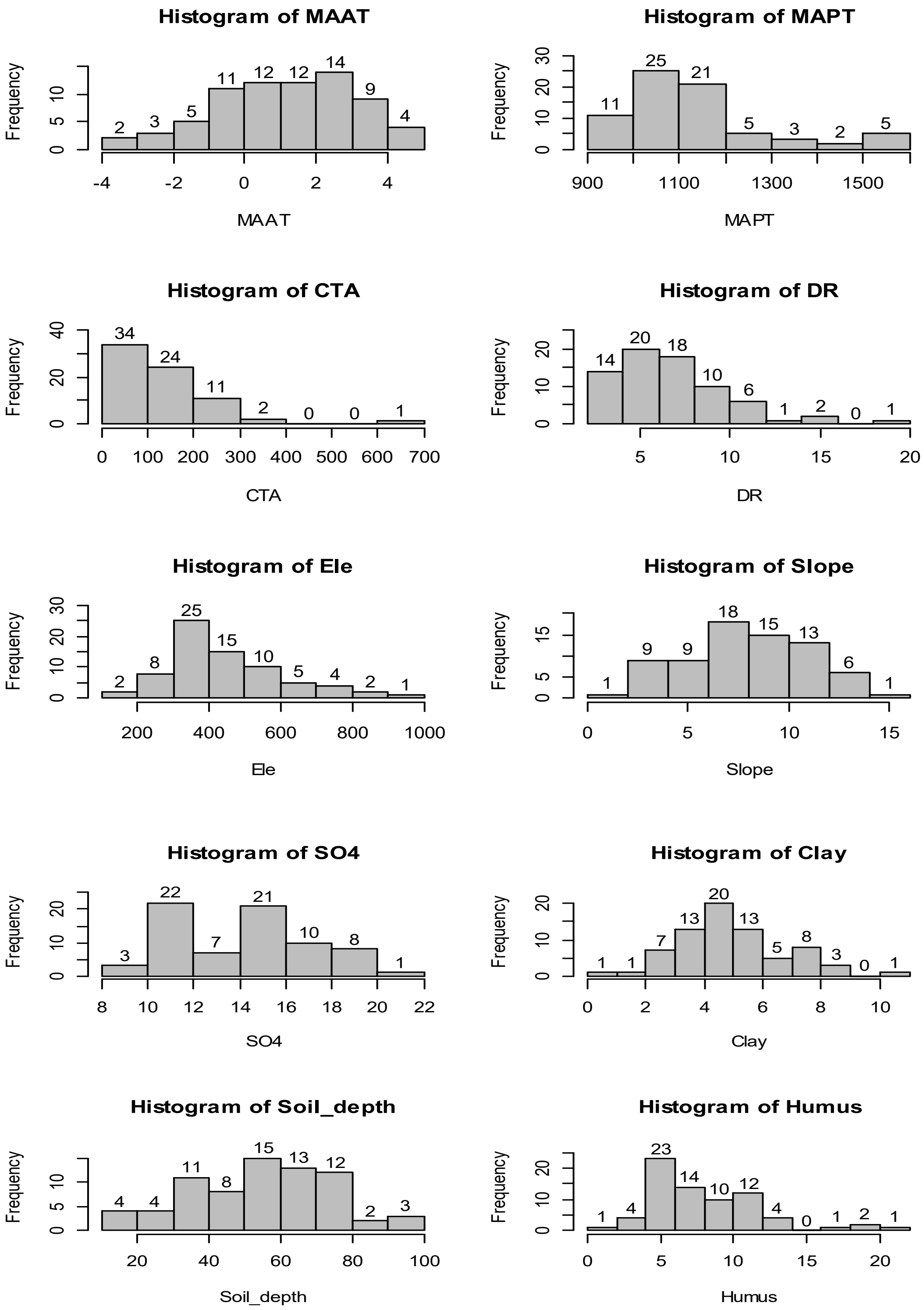

Figure 2.2. Histograms showing frequency distribution of selected environmental data in the study area. MAAT: mean annual air temperature (°C); MAPT: total annual precipitation (mm); CTA: catchment terrestrial area (ha); DR: drainage ratio; Ele: elevation (m); Slope: mean slope (°); SO_4: sulphate depositions (kg ha^{-1} yr^{-1}); Clay: soil clay content (%); soil depth (cm); Humus: humus depth (cm).

Table 2.3: PCA analysis on environmental variables for the 72 catchments. Scores are reported only for variables that have a loading coefficient of ±0.10 or more on the first two principal component axes.

Statistic	PCA1	PCA2
Eigenvalues	3276823	77879
Relative eigenvalues	0.97	0.02
Cumulative relative eigenvalues	0.97	0.99
Scores for environmental variables		
Longitude	1.21	1.00
Latitude	-0.70	-0.08
Elevation	-8.81	-0.01
Lake area	0.12	7.48
Lake depth	0.45	2.87
Number of Degree days	5.66	0.13
Number of frost days	-3.44	-8.92
Total radiation	0.04	-1.27
Mean annual air temprerature	0.61	0.79
Mean annual air temperature from May to october	0.38	0.88
Mean annual air temperature from November to April	0.84	0.69
Mean annual precipitation as rain	0.47	-0.65
Mean annual precipitation as snow	-0.14	-0.86
Relative humidity	0.20	-0.36
Drainage ratio	-0.32	-0.31
Aridity	-0.33	0.91
Organic carbon concentration of the forest floor	-3.43	-0.15
Soil clay content	-0.08	-0.66
Humus depth	-0.16	-0.42
Soil depth	2.66	-2.78
SO_4 deposits	1.19	-0.08
LITHO45	0.13	-0.08
LITHO46	-0.13	0.07
LITHO48	0.12	0.13
LITHO49	0.11	0.07
Bedrock	-0.13	0.02

The PCA run with all 48 environmental variables showed that 97% and 2% of the variation in the environmental variables was explained by axes 1 and 2, respectively (Table 2.3). Correlations were common between individual environmental variables and PCA axis 1 was positively correlated with variables such as longitude, number of degree days, air temperature (mean annual, mean from November to April and mean from May to October), total annual precipitations as rain, sulphate depositions and soil depth. The relationship was negative with latitude, elevation, number of frost days and organic carbon stock of the forest floor reflecting the existence of an altitudinal gradient mostly related to climate. PCA axis 2 had marked positive loadings for longitude, lake area, lake depth, air temperature and aridity, and strong negative loadings for soil clay content, soil depth and number of frost days. The second axis therefore mostly represented the presence of a longitudinal gradient in the study area. Of note are the strong relationships between some of the climatic variables (Table S2.2 in Appendix A). The regional climatic gradient is also superimposed on the spatial patterns in SO4 depositions and in the abundance of carbonate-rich substrates (LITHO49).

2.4.3. Relative contribution of environmental variables to variance

The results of the variance partitioning are summarized in Figure 2.3. A total of seven and eight significant ($p < 0.05$) variables were retained after the forward selection procedure for the concentration (elevation, lake area, lake perimeter, mean slope, mean annual air temperature, organic carbon content of the forest floor and SO_4 depositions) and the catchment budget data (elevation, catchment terrestrial area, lake perimeter, number of frost days, mean temperature from November to April, total annual precipitations as snow, SO_4 depositions and LITHO49), respectively. Adding the other variables did not improve the power of the model and these latter variables were thus excluded from subsequent RDA analyses. Clearly, the interactions among the three groups of descriptors accounted for the largest proportion of the total variance at 24.6% for BC_C and 26.3% for BC_Q (Figure 2.3). This represents 44% and 45% of the explained variation for BC_C and BC_Q, respectively. When only single effects were considered, climatic variables (7.5% for BC_C and BC_Q) explained more variance than either one of the other two groups of environmental variables.

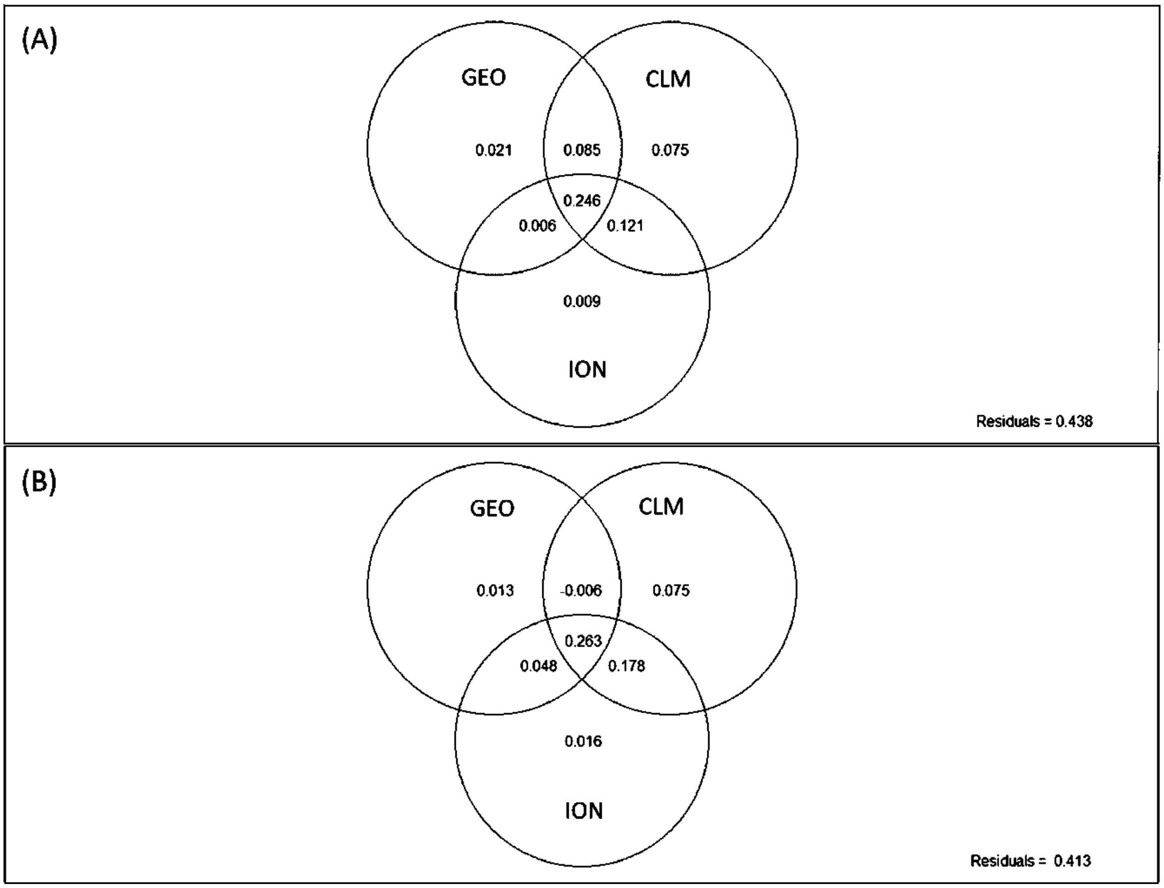

Figure 2.3. Percentage of the variation in $\mathrm{BC_C}$ (A) and $\mathrm{BC_Q}$ (B) explained (individual and shared effect computed from adjusted R2) for each group of environmental variables: geographic (GEO), bioclimatic (CLM), and solute sources (ION).

Within the context of a cumulative effects assessment, the variance decomposition also indicated that the climate component, either singly or in combination with other variables, explained up to 52.7% of the total variance (93.8% of the explained variation) for $\mathrm{BC_C}$. In the case of $\mathrm{BC_Q}$, climate-related effects captured 51.6% of the total variance and thus contributed 87.9% of the explained variation. Similarly, geographic characteristics accounted for 35.8% and 32.4% of the total variation in $\mathrm{BC_C}$ and $\mathrm{BC_Q}$, respectively. The third group of variables linked to solute sources in the environment (lithology, surface deposits, soil properties and other solute sources) explained, singly or in combination, 38.2% and 50.5% of $\mathrm{BC_C}$ and $\mathrm{BC_Q}$, respectively (Figure 2.3). The variation partitioning also showed that the interactions between CLM and ION predicted $\mathrm{BC_C}$ and $\mathrm{BC_Q}$ better than the GEO and CLM or the GEO and ION combinations.

2.4.4. Links between environmental variables and base cation concentrations and budgets

Redundancy analysis (RDA) allowed to identify the direction of the effects of individual environmental variables on BC_C and BC_Q in the study area (Table 2.4 and Figure 2.4). According to results from Monte Carlo permutation tests, only the first axis was significant for both BC_C ($F = 85.5$, $p = 0.001$) and BC_Q ($F = 123.6$, $p = 0.001$) (Table 2.4). This axis contrasts carbonate-containing catchments of the southwest where the temperature is higher and the growing season longer from carbonate-free catchments of the northeast where precipitation as snow is more abundant and the growing season shorter (Figure 2.4). The gradient in sulphate deposits across the study area is also reflected in RDA axis 1 (Figure 2.4A), with the southwestern part receiving more acid inputs than the northeastern part (Ouimet and Duchesne, 2009). The four BC_C were positively correlated with the first RDA axis. Calcium and Mg input–output budgets were also significantly associated to the first RDA axis. Positive correlations were observed between Ca and Mg concentrations and the variables sulphate deposits and mean annual air temperature; while watershed mean slope negatively influenced Na and K concentrations on the second RDA axis (Figure 2.4A). As for Ca and Mg budgets, they were positively correlated to mean temperature from November to April and the presence of charnockitic gneiss, orthopyroxene granitoids, limestones, marble, dolomite, shale and quartzite in the bedrock but negatively affected by total annual precipitations as snow and the number of frost days as seen on the first RDA axis (Figure 2.4B).

According to our results (data not shown), the major determinant for BC_C in the study area was mean annual air temperature (52% of the variation) while sulphate deposits (2%) had a small contribution. Mean temperature from November to April was the best predictor (45%) for BC_Q followed by the presence of a lithology composed of limestones, marble, dolomite, shale and quartzite (6%), total annual precipitations as snow (4%) and humus depth (3%).

Table 2.4: Statistical summary of RDA on base cation budgets and concentration in lakes waters, using forward selection of environmental variables at the 72 catchments. Scores for species and significant environmental variables are shown. (Monte Carlo permutation tests, 999 permutations; BC concentration in lakes: $R^2_{adj.} = 0.56$, $p = 0.001$; Catchment budget: $R^2_{adj.} = 0.62$, $p = 0.001$)

Statistic		BC catchment budget		BC concentration in lakes	
		RDA1	RDA2	RDA1	RDA2
Eigenvalues		0.0187	0.0006	0.1369	0.0107
Proportion explained		0.6347	0.0191	0.5335	0.0418
Cumulative proportion		0.6347	0.6538	0.5335	0.5753
Species score					
	Ca	-0.8966	0.0472	1.0780	0.2301
	Mg	-0.2909	-0.0601	0.7965	-0.0040
	Na	-0.1662	-0.1472	0.2837	-0.1188
	K	-0.0355	-0.0099	0.6326	-0.3338
Score for constrained variables					
	LITHO45	-0.4655	-0.1623	ns	ns
	LITHO49	-0.7024	0.3394	ns	ns
	Humus depth	0.1880	0.5142	ns	ns
	Number of frost days	0.7846	-0.0746	ns	ns
	Mean annual precipitation as snow	0.3739	-0.1629	ns	ns
	Mean annual air temperature for the winter season	-0.8512	-0.2906	ns	ns
	Mean annual air temperature	ns	ns	0.9993	-0.0039
	SO_4 deposits	ns	ns	0.7971	0.4418
	Mean slope	ns	ns	-0.2101	0.6907

ns: not statistically significant

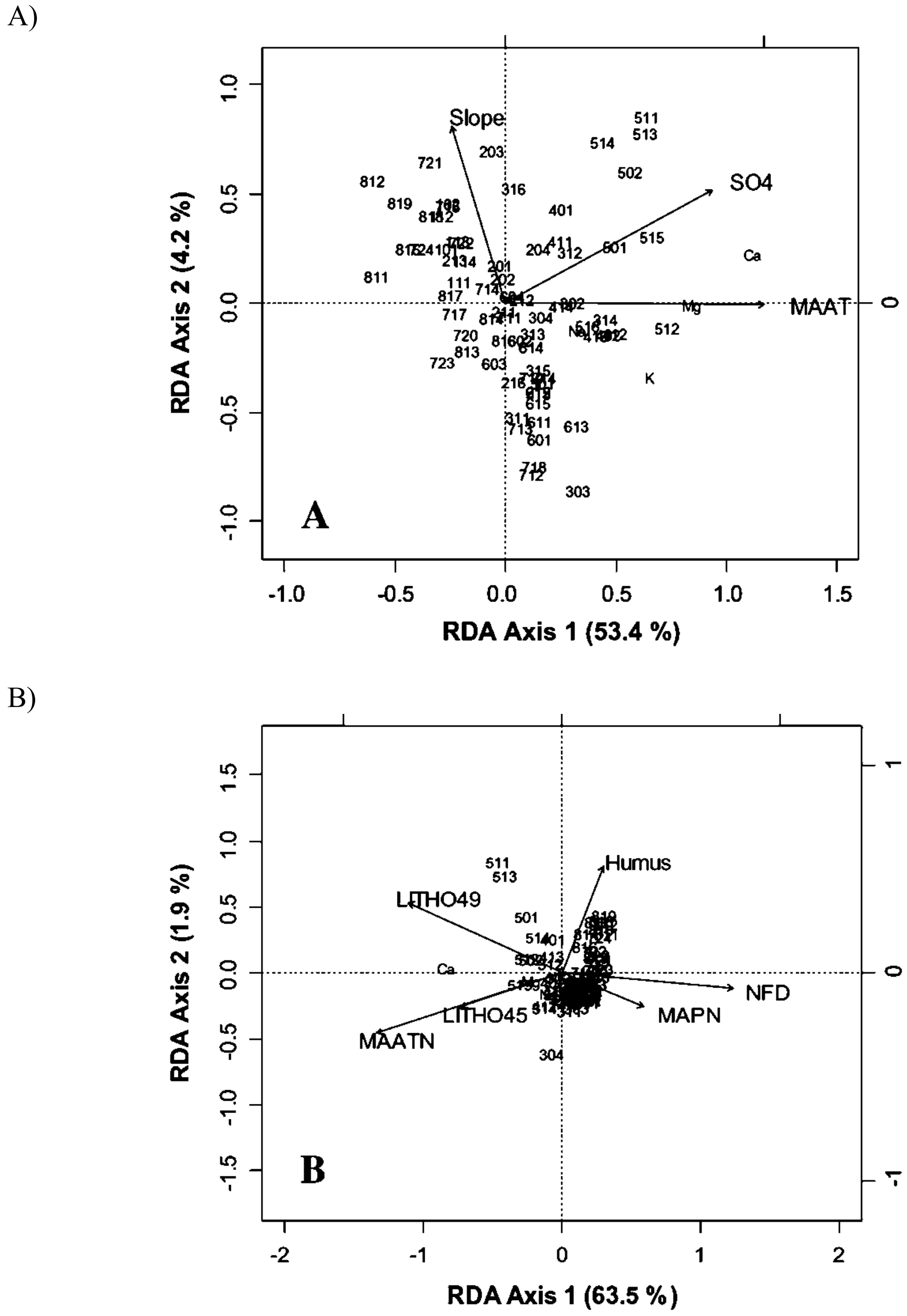

Figure 2.4. RDA biplots of BC_C (A) and BC_Q (B) and environmental variables: SO_4: sulfate deposits; MAAT: mean annual air temperature; LITHO49: Limestone and silicate rocks, marble, dolomite, shale and quartzite; Humus: humus depth; MAATN: Mean annual air temperature for the winter season; LITHO45: Charnockitic gneiss and orthopyroxene granitoids; MAPN: mean annual precipitations as snow; NFD: number of frost days.

2.4.5. Modelling individual base cation concentrations and budgets

We developed multivariate models for BC_C and BC_Q as well as for ΣBC_C and ΣBC_Q based upon stepwise multiple regression analyses. As indicated by the results reported in Tables 2.5 and 2.6, the power of the models was good (up to 69% of variation explained), with the exception of the model for K input–output budgets which accounted for 28% of the variance. The number of variables used to build the models ranged from one (for Mg concentrations) to three for Ca concentration, ΣBC_Q as well as Ca, Mg, Na, K budgets.

Models obtained for individual BC_C and BC_Q include either climatic, geographic or variables describing ion sources (Tables 2.5 and 2.6). Climatic variables were the most powerful determinant of BC_C and BC_Q, or ΣBC_C and ΣBC_Q, with the exception of Ca budgets (Table 2.6) that were mostly related to sulphate deposits. Air temperature, either mean annual temperature or mean temperature From November to April, was positively associated with concentrations for Ca, Mg, Na, K as well as ΣBC_C (Figure 2.5). Temperature was positively related to Mg, Na and K budgets and to ΣBC_Q. A positive correlation was also observed between total annual precipitations as rain and Na budgets, while soil humidity was positively correlated to K budgets.

Among environmental variables associated to soil properties, humus depth was positively related to ΣBC_C and ΣBC_Q. Calcium concentrations and budgets were positively linked to the presence of a lithology composed of limestones, marble, dolomite, shale and quartzite (LITHO49). Positive relationships were also observed between the presence of a lithology containing rocks such as charnockitic gneiss and orthopyroxene granitoids (LITHO45) and the budgets for Mg, as well as ΣBC_Q. As for catchment and lake characteristics, mean slope was associated to both concentrations and budgets for K (Tables 2.5 and 2.6). Other morphological variables such as drainage ratio (relative size of the catchment to that of the lake) and lake depth had a more accessory role. The drainage ratio was positively linked to Na concentrations (Table 2.5), while a negative correlation were observed between lake depth and Na budgets (Table 2.6). Table S2.3 in Appendix A summarize the strength of the correlations between all environmental data and BC concentrations.

Table 2.5: Summary of multiple regression analysis of base cation concentrations.

Cation	Overal model	Descriptor	Regression coefficient			Relative contribution of the descriptor
	$R^2_{adj.}$		Estimate	SE	*p*-value	Cummulative adjusted R^2
Calcium	0.69	MAAT	0.120	0.013	0.000	0.62
		LITHO49	0.210	0.069	0.003	0.66
		Soil clay content	0.032	0.012	0.010	0.69
Magnesium	0.61	MAAT	0.102	0.010	0.000	0.61
Sodium	0.37	MAATN	0.030	0.005	0.000	0.26
		Drainage ratio	0.014	0.004	0.001	0.37
Potassium	0.41	MAAT	0.075	0.013	0.000	0.35
		Mean slope	-0.021	0.008	0.009	0.41
Sum of base cations	0.66	MAAT	0.129	0.011	0.000	0.64
		Humus depth	0.014	0.006	0.015	0.66

MAAT: Mean annual air temperature

MAATN: Mean annual air temperature for the cold weather season

LITHO49: Limestone and silicate rocks, marble, dolomite, shale and quartzite

Table 2.6: Summary of multiple regression analysis of base cation budgets.

Cation	Overal model	Descriptor	Regression coefficient			Relative contribution of the descriptor
	$R^2_{adj.}$		Estimate	SE	*p*-value	Cummulative adjusted R²
Calcium	0.55	SO_4 deposits	0.014	0.005	0.014	0.46
		LITHO49	0.075	0.036	0.043	0.53
		NFD	-0.006	0.001	0.000	0.55
Magnesium	0.55	MAATN	0.014	0.002	0,000	0.49
		PERL	0.006	0.000	0.022	0.53
		LITHO45	0.020	0.010	0,045	0.55
Sodium	0.67	MAPP	0.002	0.000	0.000	0.51
		Lake depth	-0.001	0.000	0.000	0.58
		MAAT	0.007	0.002	0.000	0.67
Potassium	0.28	MAATN	0.002	0.000	0.000	0.16
		Humidity	0.005	0.002	0.002	0.24
		Mean slope	-0.001	0.000	0.033	0.28
Sum of base cations	0,64	MAATN	0.073	0.008	0,000	0.56
		LITHO45	0.070	0.026	0,016	0.61
		Humus depth	0.011	0.004	0,009	0.64

MAATN: Mean annual air temperature for the cold weather season;
MAAT: Mean annual air temperature
MAPP: Mean annual precipitations as rain;

LITHO49: Limestone and silicate rocks, marble, dolomite, shale and quartzite

LITHO45: charnockitic gneiss and orthopyroxene granitoids

NFD: Number of frost days

PERL: Lake perimeter

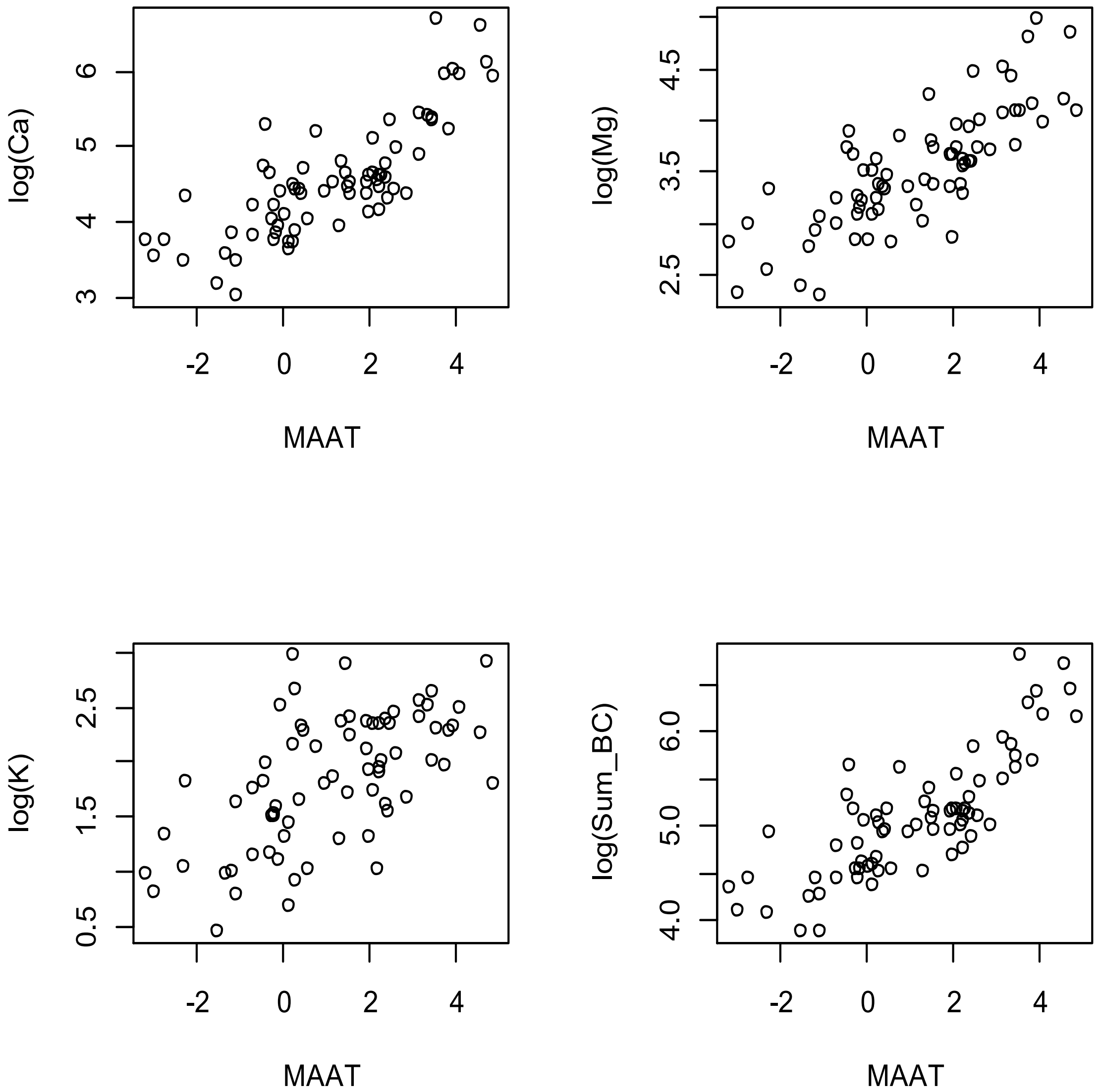

Figure 2.5. Scatter plots illustrating changes in BC concentrations and temperature (°C) across the study area.

2.5. Discussion

This study provide evidence that BC budgets and concentrations in lake waters were highly variable and showed similar spatial patterns within the study area, which is well illustrated by the strong correlation between catchment budgets and concentration in lake waters for each base cation and for the sum of base cations (Ca: $R = 0.95$, $p < 0.001$; Mg: $R = 0.91$, $p < 0.001$; Na: $R = 0.70$, $p < 0.001$; K: $R = 0.86$, $p < 0.001$; ΣBC: $R = 0.93$, $p < 0.001$). These correlations derive in part from the fact that BC_C represented the most important source of variation in the estimated BC_Q, being much more variable than BC deposition and runoff in the study area. The strong correlation further suggests that BC budgets at the watershed scale and BC concentrations in lake waters are controlled by similar drivers.

Net annual budgets at the catchment scale are often used as a method for estimating present day rates of mineral weathering assuming that steady state conditions, i.e. no annual BC losses or accumulations within the soil and biomass reservoirs, exist (Clayton, 1979). The values for individual cations and the sum of the BC budgets obtained here are comparable to weathering rates estimated for a range of forested catchments located across northeastern North America using either the soil profile mass balance method, the catchment input–output budget approach or simulations with the geochemical model PROFILE (Houle et al., 2012; Ouimet and Duchesne, 2005; Schaller et al., 2009; Watmough and Dillon, 2001; Whitfield et al., 2006). Yet, and because the existence of steady state conditions cannot be verified for each of the 72 catchments, some uncertainties exist in the absolute budget values reported here. Error sources associated with weathering estimates as well as limitation of this method have been discussed in previous studies (Kolka et al., 1996; Hodson and Langan, 1999; Velbel and Price, 2007). Nevertheless, it is well established that weathering rates often control BC concentrations in surface waters, and hence BC budgets at the watershed scale (Kamenik et al., 2001; Marchetto et al., 1995). Moreover, and as mentioned above, a good agreement was reported between the budget values and weathering rates estimated with the PROFILE model for a subset of 21 catchments (Houle et al., 2012) of the 72 catchments studied here. We therefore assumed that the spatial variability in BC concentrations and budgets was a good indicator of variations in BC weathering rates in the studied catchments and that the impact of the environmental factors on the variability of BC concentrations and budgets can be interpreted in terms of their impacts on the soil mineral weathering rates in the catchments.

Given the large number of sites sampled and the extended environmental gradients present in the study area, we were able to simultaneously examine the spatial variability of BC_C and BC_Q as a function of a variety of environmental factors. As a first step, we used RDA and variance partitioning as exploratory analyses to provide an integrated view on BC_C and BC_Q variations across the study area. Secondly, multiple regression techniques were used to develop multivariate models to constrain individual BC concentrations and budgets using key significant environmental factors.

2.5.1. Integrated view on base cation concentrations and budgets across the study area

According to the variance partitioning analysis, the responses of BC_C and BC_Q to the three groups of environmental variables were generally similar (Figure 2.3). The climatic component provided the largest part of the variance explanation for BC_C and BC_Q in the study area, closely followed by the ION group of variables. Lake chemistry is strongly influenced by the biogeochemical processes that occur in the surrounding soils, including mineral weathering (Hairston and Fussmann, 2002). In this context, it is likely that the factors affecting BC mineral weathering in the catchments also influenced the concentration of base cations in lakes. However, and despite the fact that the role of climate on the weathering processes has been highlighted in several studies (Velbel, 1993; White and Blum, 1995), its relative importance has often been downplayed compared to that of parent material and soil properties (Bain et al., 1993; Riebe et al., 2004). Our results are in good agreement with those previously reported in several studies relative to the role of climatic factors on soil mineral weathering and, hence, on BC exports and concentrations in lake waters (Boyle, 2008; Gislason et al., 2009; Houle et al., 2010). It should be noted that a significant part of the spatial variability in BC_C and BC_Q is related to the ION group that includes notably atmospheric sulphate deposition and underlying geology, both type of variables having a spatial pattern that may overlap the climate gradient in the study area. The influence of sulphate deposition on BC concentrations (Table 2.4 and Figure 2.4A) was expected since sulphate leaching is increasing BC exportations from soils to surface waters. Furthermore, Houle et al. (2012) identified that a few catchments with high calcite content were responsible for a strong spatial gradient of BC_Q (particularly for Ca) on a subset of 21 catchments among the 72 studied here. In the present study, detailed soil mineralogical data were not available for the 72 studied catchments and the possibility remains that the lack of such data in the analyses could have resulted in overestimating the climate effects to some extent. Nevertheless, we repeated the analysis after excluding twelve catchments where carbonate rocks were present (data not shown), which caused no substantial changes in the results while temperature remained the dominant factor. This may be an indication that the magnitude of the potential bias resulted from the lack of mineralogical data in the analyses is small. The strong linear relationships between mean annual air temperature (MAAT) and individual cations or the sum of BC concentrations are illustrated in Figure 2.5 and in Table S2.3.

Climate can affect mineral weathering either directly, via atmospheric precipitations and energy transfers, or indirectly, through its impact on vegetation and microbial activity. The presence of soil water and associated water fluxes are essential to initiate the chemical reactions responsible for mineral weathering and for the leaching of weathering products. Soil temperature further affects BC release from soil minerals and hence, BC concentrations in lake waters. In the presence of water, the rate of weathering reactions is hastened by higher temperatures (Riebe et al., 2004; Velbel, 1993). The positive relationships between temperature and BC_C (Figs. 4A and 5) are in-line with this statement. Redundancy analysis also showed strong negative associations between BC_Q and the number of frost days. These negative relationships stress the positive effect of the presence of soil water in the liquid phase (Riebe et al., 2004; Velbel, 1993) and of the length of the growing season on weathering. In the latter case, the longer they last, the longer the period during which weathering reactions can take place. In this study, the 72 watersheds are distributed over two vast bioclimatic domains (Richard, 1995): the northern temperate and the boreal zones. Our results clearly indicate that climatic conditions are more favourable to mineral weathering in the northern temperate zone of Quebec than in the boreal zone.

Climate also controls the presence, abundance and type of vegetation which (Shuman et al., 2004), in turn, influences mineral weathering through mostly biochemical mechanisms. The temperate zone where deciduous tree species abound receives more precipitation as rain compared to the boreal zone dominated by coniferous. Moreover, the higher air temperature of the temperate compared to the boreal zone stimulates biological activity and the decay of the soil organic matter more. Under favourable conditions of temperature and humidity, increases in soil microbial activity will increase the production of CO_2 and of a series of organic substances promoting the dissolution of soil minerals. In the boreal zone, a higher proportion of total precipitation falls as snow, soil temperatures are lower, frost days are more frequent and snow cover lasts longer. These bio-climatic conditions are less favourable to microbial activity, to the decomposition of organic matter and to the production of organic reagents involved in weathering reactions.

The results also illustrated the importance of the interaction between CLM and GEO, on the one hand, as well as between CLM and ION, on the other hand (Figure 2.3). The interaction between the three groups of explanatory variables was responsible for 44% and 45% of the explained variation in BC_C and BC_Q, respectively, in the study area. The combined effects of CLM and ION were the most pronounced with 12.1% and 17.8% of the variance explained for BC concentrations and budgets, respectively. This points to the structuring effect of lithology, and thus mineralogy, on the spatial variability of BC_C and BC_Q in this study.

Redundancy analysis further showed that Ca and Mg budgets were under some common influences. Similar observations were made for Ca and Mg concentrations in lake waters. The positive relationships between concentrations and budgets for Ca and Mg and the presence of substrates containing charnockitic gneiss and orthopyroxene granitoids, limestones, marble, dolomite, shale and quartzite (LITHO45 and LITHO49) is attributed to the mineralogical composition of these rocks. Such lithology is rich in carbonates, plagioclases, and amphiboles, a Ca- and Mg-rich mineral assemblage that has to be reflected in soil mineralogy. The negative association reported between BC_Q and both the number of frost days and the total annual precipitations as snow (Figure 2.4) is in good agreement with previous observations on the role of climate and reflects the fact that such environmental conditions are less favourable to mineral weathering (Riebe et al., 2004), mainly because higher number of frost days and persistent snow cover have negative consequences on biological activity in soils.

2.5.2. Describing individual base cation concentrations and budgets

The results of multiple regressions confirmed that climatic variables were key descriptors together with variables linked to solute sources or lake catchment morphometry of BC_C and BC_Q as well as of ΣBC_C and ΣBC_Q in the study area. The mean annual air temperature (or the mean air temperature from November to April) was present in all the models developed (Tables 2.5 and 2.6). The best descriptor was therefore air temperature (mean annual or mean from November to April), except for total annual precipitation as rain and sulphate depositions for Na and Ca budgets, respectively. Among all the models developed, the equation for K budgets had the lowest power (28% of variation explained). Contrary to Na which is considered to have a conservative behaviour in most catchments of northeastern North America (Williams et al., 2007), K is more strongly absorbed by vegetation and retained in plant biomass (Likens et al., 1994). Consequently, K exports from the watersheds may be very small compared to the amount of K released through soil mineral weathering in these ecosystems (Houle et al., 2012).

The positive link between both, BC_C and ΣBC_Q and mean annual temperature and/or total annual precipitations as rain reflects the processes outlined above. The presence of carbonate-rich rocks (LITHO49) in the watersheds was positively associated to Ca budgets and concentrations in lake waters. The Mg budgets, as well as the ΣBC_Q were also positively correlated to the presence of charnockitic gneiss and orthopyroxene granitoids (LITHO45). This lithological group can provide minerals that are important long-term sources of calcium and/or Mg in the soils via weathering, emphasizing the critical impact of the underlying bedrock and hence mineralogy on the spatial variability of BC_C and BC_Q.

Humus depth was selected as a predictor for ΣBC_C and ΣBC_Q. In forest ecosystems, the humus layer can impede surface runoff, restrict soil freezing, favour infiltration, and store considerable amounts of rainfall (Hart, 1960; Martens and Frankenberger, 1992), a series of conditions promoting mineral weathering. This may explain the positive link observed between humus depth and ΣBC_C and ΣBC_Q. Moreover, as suggested by D'Arcy and Carignan (1997), hydrogeological conditions of the Canadian Shield favour waterlogging on gentle slopes during periods of high runoff, thus increasing ion exports from top organic layers which are rich in K. As a result, a negative relationship was observed between mean catchment slope and K budgets and concentrations in lake waters. Lake morphometry variables (drainage ratio and lake perimeter and depth) were also present in the models. Drainage ratio is considered important in determining land-water linkage in lake catchment

(McEachern et al., 2000). Since a lake is the reflection of its watershed, the positive relationship between Na concentrations in lake waters and the drainage ratio is expected because of the conservative behaviour of Na. However, the negative relationship between lake depth and Na budgets may result from the collinearity between lake depth and lake area ($R = 0.57$; $p = 0.042$). Larger lakes have lower drainage ratio which, in turn, negatively affects Na concentration in lake waters and the estimated Na budgets at the catchment scale.

2.6. Conclusion

The spatial variability of BC concentrations in lake and of BC budgets was studied for 72 forested catchments of the Canadian Shield. In the study area, large environmental gradients allowed to analyze the simultaneous influence of several factors, including lithology, atmospheric depositions and climate, on these response variables. The results showed a significant similarity between spatial patterns of base cation budgets and concentrations, pointing to their dependence on common factors. We found that the single effects of the climatic group of variables were higher than those of the two other groups, and that a considerable amount of the variance explanation was shared by the interactions between two or three sets of variables. In regression analyses, up to 69% and 67% of the variation in individual BC_C and BC_Q or ΣBC_C and ΣBC_Q, respectively, was accounted for by the explanatory variables, with most of the variability being related to temperature, sulphate deposition and precipitations. Lithological variables and to a less extent, lake catchment morphometry were also related to BC_C and BC_Q variability.

Among the variables responsible for BC_C and BC_Q variation in the studied area, some are static in time such as mineralogy while some other (vegetation, soil types, etc.) will only change slowly. In this context, it seems that the mid-term catchments response to large scale drivers will be determined by the future temporal variations in atmospheric deposition and climate. Given that acidic deposition has decreased in Eastern North America and tended to stabilize over the recent years, and considering the fact that climate is warming at a substantial rate in the same region, the relative importance of climate changes on BC_C and BC_Q variation may increase in the next decades and overcome that of atmospheric inputs. In this context, the exclusive effect of hydro-climatic variables on biogeochemical processes such as soil mineral weathering need to be further investigated, in both time and space, to better isolate and quantify their contribution. This is needed for a better understanding of the potential impacts of climate changes on mineral weathering and on its ability to provide BC to the soil exchangeable reservoirs and to surface waters.

2.7. Acknowledgments

This work was funded by Environment Canada, the National Science Engineering Research Council of Canada (NSERC) and the Ouranos consortium. We thank Prof. Dr. Pierre Legendre for his advice on the multivariate analysis.

2.8 Appendix A

Supplementary data

Supplementary Table S2.1. Mean and range of selected environmental variables in the study area. This table contains the complete list of environmental variables used in univariate and multivariate analyses.

Supplementary Table S2.2: Coefficient of correlation among climatic variables in the 72 catchments. This table provides details on the strong correlations existing among the climatic variables used in the statistical analyses.

Supplementary Table S2.3: Coefficients of correlation between BC concentrations and environmental variables. The interactions presented in this table support the results of multivariate analyses.

Supplementary Figure S2.1: Frequency distribution of Ca, Mg, Na and K concentrations in the 72 lakes of the study area. These graphs allow to visually check the structure of the distributions. When needed, we used log transformation to obtain normal distributions for base cations concentrations as well as for budgets prior to statistical analyses.
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Table S2.1. Mean and range of selected environmental variables in the study area.

Environmental variable	Unit	Mean	Min - max
Geographic (GEO)			
Latitude	(decimal degree)	47.86	45.60 - 51.45
Longitude	(decimal degree)	72.1	65.55 - 78.20
Elevation	(m.a.s.l)	446	145 - 975
Lake area	(ha)	24	5 - 202
Catchment area	(ha)	137	25 - 696
Lake depth	(m)	18	2 - 52
Lake perimeter	(m)	3736	1120 - 9651
Mean slope	(°)	8	1.8 - 14.9
Weighted slope	(°)	7.4	1.8 - 16.9
Overland flow index		0.0004	0.0000 - 0.0026
Bioclimatic (CLM)			
Percent deciduous cover	(%)	29	0 - 80
Percent coniferous cover	(%)	34	0 -67
Degree-day	(°C)	122	78 - 170
Number of Frost day	(day)	211	177 - 243
Total radiation	(TJ/ha)	47.5	44.4 - 51.7
Mean annual air temperature	(°C)	1.2	-3.2 - 4.9
Mean annual air temperature from May to October	(°C)	11.5	8.2 - 14.5
Mean annual air temperature from November to April	(°C)	-9.1	-14.9 - -4.7
Total annual precipitation	(mm)	1136	922 - 1583
Precipitation as rain	(mm)	743	545 - 952
Precipitation as snow	(mm)	393	265 - 645
Potential evapotranspiration	(mm)	396	328 - 466
Runoff	(mm)	740	489 - 1224
Relative humidity	(%)	74	72 - 75
Aridity	mm	2.1	0.1 - 4.2
Drainage ratio		6.9	2.5 - 19.8
Lithology, surface deposits,soil properties and other sources of ions (ION) (Gagnon et al. 1994; MRN, 2003; Ouimet and Duchesne, 2009; Siltanen et al. 1997; Tremblay et al. 2002)			
Forest floor organic carbon concentration	(Mg/ha)	42	35 - 65
Soil clay content	(%)	5	1 - 10
Soil sand content	(%)	51	15 - 73
Soil depth	(cm)	55	13 - 100
Drainage class	Classified (0-60)	26	19 - 34
Humus depth	(cm)	8	2 - 21
Sulphate depositions (SO_4)	(kg ha^{-1} yr^{-1})	14.1	9.8 - 20.4

Table S2.1. (continued)

Environmental variable	Unit	Mean	Min - max
Lithology, surface deposits, soil properties and other sources of ions (ION)			
Glacial deposits	Binary variable		
Glaciofluvial deposits	Binary variable		
Organic deposits	Binary variable		
Bedrock	Binary variable		
LITHO43	Binary variable		
LITHO44	Binary variable		
LITHO45	Binary variable		
LITHO46	Binary variable		
LITHO48	Binary variable		
LITHO49	Binary variable		
LITHO52	Binary variable		
LITHO53	Binary variable		
LITHO54	Binary variable		
LITHO55	Binary variable		
LITHO56	Binary variable		
LITHO57	Binary variable		

LITHO43: plagioclase, biotite, hornblende, mafic gneiss, biotite and amphibolite

LITHO44: Granodiorite gneiss and granite, foliated or magmatized granitoids

LITHO45: charnockitic gneiss and orthopyroxene granitoids

LITHO46: Migmatite

LITHO48: Paragneiss, quartzite and amphibolite

LITHO49: Limestone and silicate rocks, marble, dolomite, shale and quartzite

LITHO52: Quartzite and schiste

LITHO53: Anorthosite and gabbronorite

LITHO54: Gabbro, pyroxenite, troctolite and amphibolite

LITHO55: Orthopyroxene granitoids: charnockite, mangerite, jotunite and hypersthene syenite

LITHO56: Syenite, monzonite, granodiorite and diorite

LITHO57: Granite and pegmatite

Table S2.2: Coefficient of correlation among climatic variables in the 72 catchments.

Variable	NDD	NFD	MAAT	MAATM	MAATN	MAPT	MAPP	MAPN
NDD								
NFD	-0.95***							
MAAT	0.96***	-0.95***						
MAATM	1.00***	-0.96***	0.96***					
MAATN	0.90***	-0.90***	0.98***	0.89***				
MAPT	-0.30**	0.29*	-0.13	-0.30*	-0.01			
MAPP	0.27*	-0.25*	0.44***	0.27*	0.54***	0.80***		
MAPN	-0.81***	0.77***	-0.72***	-0.80***	-0.64***	0.73***	0.18	1.00

* Significant at $p < 0.05$.

** Significant at $p < 0.01$.

*** Significant at $p < 0.001$.

NDD = Degree-day; NFD = Number of Frost Day; MAAT = Mean annual air temperature; MAATM = Mean annual air temperature from May to October; MAATN = Mean annual air temperature from November to April; MAPT = Total annual precipitation; MAPP = Total annual precipitation as rain; MAPN = Total annual precipitation as snow

Table S2.3: Coefficients of correlation between BC concentrations and environmental variables.

Environmental variable	Ca	Mg	Na	K	ΣBC
Elevation (m)	-0.41**	-0.49***	-0.30**	-0.48***	-0.46***
Lake area (ha)	-0.14	-0.03	-0.07	0.10	-0.10
Lake depth (m)	-0.00	-0.03	-0.30**	-0.06	-0.00
Mean slope (°)	-0.06	-0.14	-0.26*	-0.35**	-0.09
Weighted slope (°)	-0.08	-0.16	-0.23	-0.37**	-0.11
Overland flow index	-0.04	-0.01	0.29*	0.10	-0.02
Percent deciduous cover (%)	0.72***	0.68***	0.40***	0.51***	0.72***
Percent coniferous cover (%)	-0.69***	-0.67***	-0.39***	-0.59***	-0.70***
Degree-day (°C)	0.76***	0.76***	0.46***	0.59***	0.78***
Number of Frost day	-0.77***	-0.76***	-0.47***	-0.59***	-0.79***
Total radiation (TJ/ha)	-0.20	-0.32**	-0.18	-0.33**	-0.25*
Mean annual air temperature (°C)	0.79***	0.79***	0.51***	0.60***	0.81***
Mean annual air temperature from November to April (°C)	0.79***	0.78***	0.52***	0.58***	0.76***
Mean annual air temperature from May to October (°C)	0.74***	0.75***	0.47***	0.60***	0.80***
Total annual precipitation (mm)	-0.06	-0.21	-0.09	-0.18	-0.11
Precipitation as rain (mm)	0.37**	0.25*	0.20	0.17	0.34**
Precipitation as snow (mm)	-0.53***	-0.63***	-0.37**	-0.49***	-0.57***
Potential evapotranspiration (mm)	0.77***	0.77***	0.48***	0.60***	0.79***
Runoff (mm)	-0.21	-0.35**	-0.18	-0.28*	-0.26*
Relative humidity (%)	0.02	-0.04	-0.08	-0.01	-0.02
Aridity (mm)	0.07	0.18	0.03	0.16	0.11
Drainage ratio	0.04	0.10	0.33**	0.05	0.06
Forest floor organic carbon (Mg/ha)	-0.59***	-0.54***	-0.45***	-0.48***	-0.58***
Soil clay content (%)	0.09	-0.01	0.10	-0.03	0.06
Soil sand content (%)	-0.12	-0.19	0.05	-0.16	-0.14
Soil depth (cm)	0.06	0.02	0.20	0.13	0.04
Humus depth (cm)	-0.23	-0.27*	-0.28*	-0.19	-0.23
Sulphate depositions (kg SO_4 ha^{-1} yr^{-1})	0.72**	0.61***	0.31**	0.35**	0.69***
LITHO45	0.34**	0.30*	0.10	0.10	0.33**
LITHO46	-0.36**	-0.32**	-0.13	-0.22	-0.35**
LITHO48	0.50***	0.51***	0.20	0.32**	0.51***
LITHO49	0.58***	0.48***	0.19	0.25*	0.56***

* Significant at $p < 0.05$.

** Significant at $p < 0.01$.

*** Significant at $p < 0.001$.

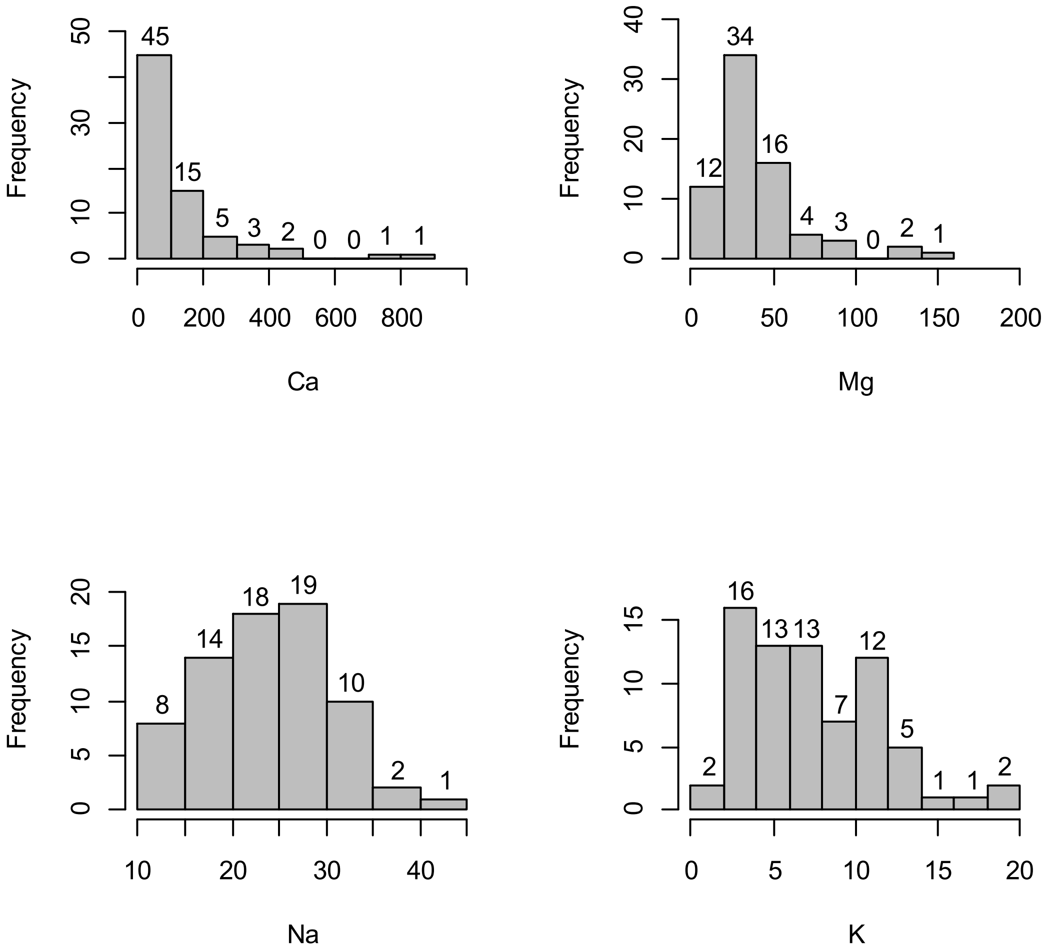

Figure S2.1: Frequency distribution of Ca, Mg, Na and K concentrations (μmol$_c$ l^{-1}) in the 72 lakes of the study area.

2.9 Section de transition 2-3

Le chapitre précédent a permis de mettre en évidence l'importance du climat dans la variabilité spatiale des taux d'altération contemporains des minéraux. Le chapitre suivant poursuit l'analyse de la variabilité spatiale des taux d'altération des minéraux, mais ce sont les taux d'altération historiques qui sont considérés. Ceux-ci ont été estimés à l'aide de la méthode du bilan de masse en profil de sol (Brimhall et al., 1991a,b; Egli et Fitze, 2000). Cette méthode permet d'estimer les taux d'altération en se basant sur la mesure des flux élémentaires tout en intégrant les effets des changements volumétriques que les sols ont subi depuis le début de la pédogénèse.

Dans le chapitre 3, consacré au traitement des objectifs spécifiques 2 et 5 de la thèse, un jeu de 21 bassins versants situés au sud du Québec (sous-échantillon des 72 bassins hydrographiques considéré dans le chapitre précédent) a été retenu dans notre stratégie expérimentale et d'échantillonnage. Ce nombre de sites demeure toutefois assez élevé et peu commun dans la littérature scientifique pour ce genre d'étude. Après avoir quantifié les taux historiques d'altération des minéraux, nous avons pu utiliser la méthode d'analyse canonique de redondance (RDA) pour analyser les liens entre des variables environnementales et certaines propriétés des sols d'un côté, et la variation spatiale des taux d'altération à long terme des cations basiques, de l'autre. Les résultats présentés dans ce chapitre montrent que les propriétés des sols, notamment la surface spécifique et la composition minéralogique des sols, expliquaient une grande proportion de la variation des taux d'altération à long terme. Toutefois, les variables reliées au climat expliquaient également une proportion significative de leur variation pour le jeu de données considéré. Étant donné que le climat devrait changer significativement dans un futur proche (notamment dans l'hémisphère nord), alors que les propriétés des sols sont appelées à demeurer relativement stables, ces résultats ont des implications majeures pour la compréhension des liens entre les facteurs environnementaux et l'altération des minéraux et sur notre capacité à anticiper l'impact des changements climatiques sur ces processus.

Le chapitre 3 a également été publié sous forme d'article dans la revue *Geoderma*[2]. La rédaction de cet article s'est faite en collaboration avec Daniel Houle, Christian Gagnon et François Courchesne. J'ai effectué la recherche documentaire, examiné et organisé les données d'analyse de sols pour calculer les taux d'altération à long terme. J'ai choisi des tests statistiques appropriés, effectué l'analyse des données et j'ai rédigé le manuscrit. Les différentes étapes qui ont conduit à la production du manuscrit ont été réalisées sous la supervision de François Courchesne et Daniel Houle (directeur et co-directeur du projet, respectivement). Les co-auteurs ont contribué à l'amélioration du manuscrit en faisant des corrections, des ajouts ou des recommandations.

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[2] Augustin, F., Houle, D., Gagnon, C., Courchesne, F. 2015. Long-term mineral weathering in forested catchments of the Canadian shield, Québec. Geoderma, 247–248: 12–23.

Chapitre 3. Long-term base cation weathering rates in forested catchments of the Canadian Shield

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3.1 Abstract

A number of methods exists for estimating mineral weathering rates. Yet, quantifying this crucial biogeochemical reaction in the field has always been a challenge because mineral weathering takes place in open systems whose initial state conditions are not well known and where material inputs and outputs vary in time and space. Here, using the soil profile mass balance method, we estimated long-term weathering rates of base cations (BC) for a set of 21 watersheds, and we investigated the links between environmental variables and soil properties and the spatial variation in BC weathering rates in the study area. The watersheds are located in southern Québec and vary with respect to hydro-climatic conditions, soil properties and forest cover. Average long-term estimates of annual BC weathering rates for the study area were 0.16, 0.10, 0.09 and 0.06 $\mathrm{kmol_c\ ha^{-1}\ yr^{-1}}$ for Ca, Mg, Na and K, respectively. Overall, redundancy analysis (RDA) indicated that soil surface area, percent deciduous canopy cover, elevation, as well as soil albite content were the most significant variables explaining together 56% of the total variation in BC weathering rates. Consistent with previous findings, our results showed that, beside soil properties, climate-related environmental variables played key roles in determining the variability of BC weathering rates in the study area. In the context of global climate change, more insights are needed for a better understanding of the effects of discrete climatic variables on BC weathering rates.

3.2. Introduction

Identifying the most important environmental factors that drive complex biogeochemical processes such as mineral weathering and relating them to the alteration mechanisms of soil minerals constitute a research frontier in the field of biogeochemistry. Meeting this challenge is essential for developing models capable of predicting mineral weathering rates as a function of projected future changes in environmental conditions. A crucial function of mineral weathering in terrestrial ecosystems is to provide essential plant nutrients, notably base cations (BC). In addition, mineral weathering contributes to the chemical composition of surface waters (Marchetto et al., 1995; Houle et al., 2012a). By influencing atmospheric CO_2 concentration, silicate wathering also influences climate change at the geologic time scale (Berner and Lasaga, 1989).

Several methods have been used to quantify weathering rates in terrestrial ecosystems (Clayton, 1979; Velbel, 1985; Brimhall et al., 1991a, 1991b; Sverdrup and Warfvinge, 1993; Egli and Fitze, 2000). In this study, we have focused on long-term average estimates of BC weathering rates at pedogenic time scale that have been estimated according to the profile mass balance method (Brimhall et al., 1991b; Egli and Fitze, 2000). This method is based on the geochemical behaviour of conservative elements such as Ti and Zr which are considered immobile during weathering processes (Cann, 1970; Floyd and Winchester, 1975). It takes into account pedogenic processes, including changes in soil chemical composition and volumetric soil expansion or contraction (Brimhall et al., 1991a, 1991b; Courchesne et al., 2002). The basic assumptions are that: 1) the actual chemical composition of the C horizon is identical to the composition of the initial parent material; 2) the total chemical composition of the parent material is uniform throughout its profile at the initiation of pedogenesis and; 3) additions of material to the soil surface through, for example, aeolian deposition, as well as losses of material through physical surface erosion are minimal, so that the present-day vertical variation in total chemical composition reflects the cumulative effects of mineral weathering in the soil profile over time. This estimation method has limitations because some assumptions notably those relative to the initial uniformity of the parent material and to the equivalence between the chemical composition of the unweathered parent material and the present C horizons cannot always be verified (Courchesne et al., 2002; Schaller et al., 2009). Despite these limitations, the soil profile mass balance has been considered a reliable method to estimate long-term weathering losses at pedogenic time scale (Ouimet, 2008), and was used in a number of studies (Kirkwood and Nesbitt, 1991; Taylor and Blum, 1995; Courchesne et al., 2002; Schaller et al., 2009).

There is a wide array of environmental factors and soil properties that are known to likely impact on BC weathering rates. These include topography, prevailing hydro-climatic conditions, vegetation type, biological activity in soils and the chemical (pH, organic matter), physical (surface area) and mineralogical properties of the soil and of the parent material, (Holmqvist et al., 2003; Wilson, 2004; Gordon, 2005; Egli et al., 2006). For example, Egli et al. (2006) reported that variables such as water flux, temperature and vegetation could be crucial in determining the rate at which minerals weather in Alpine podzols of northern Italy. Apart from studies carried out along climo-sequences, it is often difficult to relate the variability of estimated BC weathering rates to environmental factors because of the limited number of sites investigated at one time in a given study. A notable exception is the work of Schaller et al. (2009) who determined long-term mineral weathering rates from 39 soil profiles at 13 distinct sites within the Hubbard Brook Experimental Forest, in the White Mountains (New Hampshire, USA). These authors detected a weak negative correlation between mineral weathering rates and site elevation in the region, which led them to hypothesize that the spatial variability in weathering rates could be associated to variations in temperature, precipitation or vegetation type along an elevational gradient. However, the relative importance of each of these variables on long-term mineral weathering rates was not quantified.

The effects of environmental factors on mineral weathering rates have been tested under laboratory (Welch and Ullman, 2000) and field (White and Blum, 1995; Brady et al., 1999; Riebe et al., 2004) conditions. Yet, these studies investigated the effects of individual environmental factors, but did not consider their interactions and their simultaneous, synergetic or antagonistic, effects on mineral weathering rates (Gordon, 2005). Moreover, evidence from field research indicated that the presence of confounding factors often impedes our capacity to isolate and quantify the controls exerted by a discrete environmental factor on mineral weathering rates (Riebe et al., 2004). In this context, the objectives of this study were: i) to quantitatively estimate the long-term weathering rates of the cations Ca, Mg, Na and K in the soils of a series of 21 forested watersheds located in southern Quebec; and ii) to partition the impact of a range of environmental factors and soil properties acting simultaneously on the long-term weathering rates of Ca, Mg, Na and K. Working with a large number of field sites offers the opportunity to assess the *in situ* relationships between BC weathering rates with environmental conditions and soil properties and to investigate their simultaneous effects using multivariate statistical techniques.

3.3. Material and methods

3.3.1 Study area and sampling sites

The weathering rates of base cations were estimated for 21 watersheds that are part of the Québec lakes network (Houle et al., 2004). The watersheds were selected as to cover a wide range of geological, pedological and hydro-bioclimatic properties. They are located on the Canadian Shield, within a ~90 000 km^2 area in southern Québec that is parallel to the St. Lawrence River and bordered by the Ottawa and Saguenay rivers (Fig 3.1).

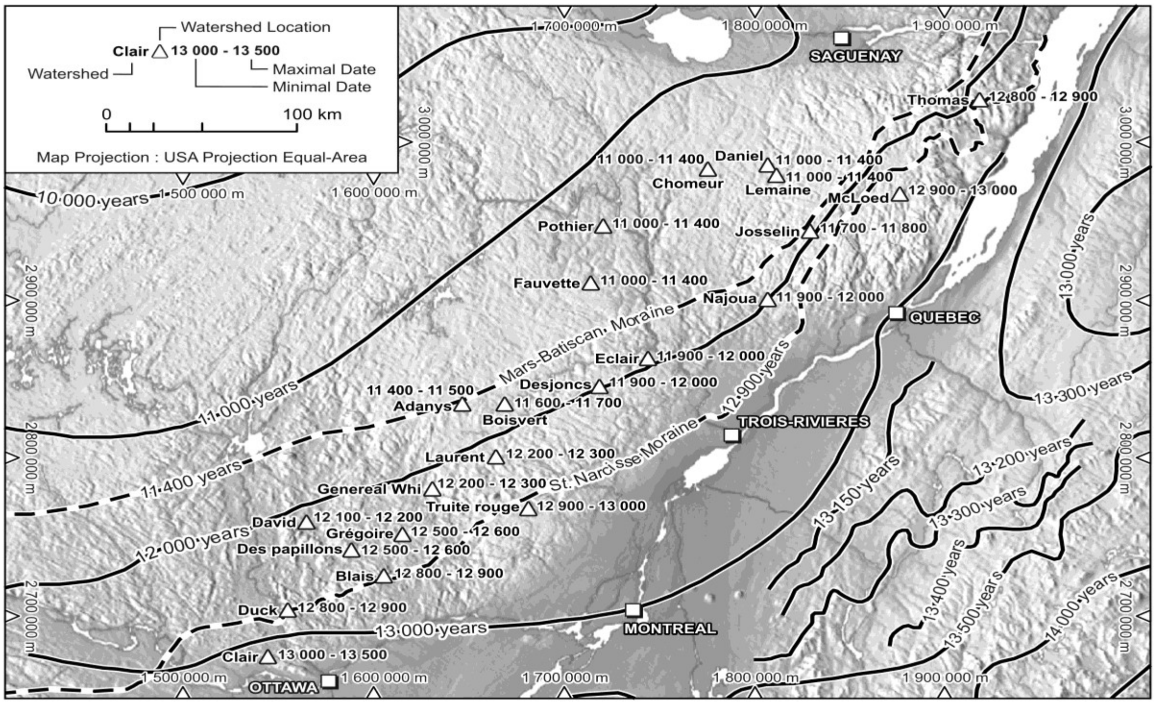

Figure 3.1: Location of the watersheds in southern Québec. The maximum and minimum number of years since the retreat of the Laurentian Ice Sheet are shown. The Saint-Narcisse morainic complex, the Mars-Batiscan moraine together with the main and late Younger Dryas isochrones of the Laurentide Ice Sheet ice margin are from Occhietti (2007).

In this area, the Canadian Shield is composed of bedrocks formed during the Precambrian era, which consists mainly of igneous (granite, syenite, anorthosite) and metamorphic (gneiss, granitic gneiss, paragneiss, marble) rocks (Lachance et al., 1985). The soils are classified as Podzols in the Canadian system of soil classification (Soil Classification Working Group 1998) and belong to the Spodosol order of the Soil Taxonomy (Soil Survey Staff. 2014).

The 21 watersheds are forested and free of major direct human activity. They are distributed along a southwest-northeast bioclimatic gradient between the northern temperate subzone of Québec and the lower boreal subzone, so that the vegetation ranges from deciduous forests dominated by sugar maple (*Acer saccharum* Marsh.) in the southwest, to mixed forests dominated by balsam fir (*Abies balsamea* L.) or black spruce (*Picea mariana* Mill.) in the northeast. These same forests were established in the area they currently occupy some 6,000 years ago although the relative abundance of some tree species differed from their modern distribution (Richard, 1995). In the study area, the climate is cold (mean annual air temperature of 2.0 °C) and wet (mean annual precipitation of 1163 mm) with long winters and short summers. The geographic and bioclimatic characteristics as well as the bedrock geology of each watershed are summarized in Table 3.1. Supplementary details on the watersheds of the Québec lakes network are found in Houle et al. (2004, 2006 and 2012a).

3.3.2 Data sources, variables assessed and methods

The watersheds included in this analysis are part of the Quebec portion of the Long-Range Transport of Airborne Pollutants (LRTAP) program. This network of watersheds was established and has been monitored since the early 1980. They have been the subject of numerous publications which presented detailed data about their geographic location, terrestrial area and topographic features (Gagnon et al., 1994; Siltanen et al., 1997; Houle et al., 2012a; Augustin et al., 2015). Most of the watershed characteristics were taken from Houle et al. (2012a) or computed using ArcGIS and the Digital Canadian Elevation Data of 90 meters resolution (McDonnell and Kemp, 1995).

Table 3.1: Characteristics of the 21 watersheds investigated.

Watershed	Lat	Long	Ele	W. area	Slope	SS	Dec	Con	MAST	MAAT	MAPT	Bedrock geology
	(°)	(°)	(m)	(ha)	(%)	(%)	(%)	(%)	(°C)	(°C)	(m)	
Adanys	46,81	-74,33	594	112	3	10	32	38	4.6	1.3	962	LITHO45; LITHO48; LITHO55; LITHO56
Blais	45,93	-75,17	244	129	8	10	62	16	5.2	4.1	1073	LITHO45; LITHO48; LITHO49
Boisvert	46,76	-74,04	472	168	4	20	61	12	5.8	2.1	964	LITHO45; LITHO48; LITHO56
Chomeur	47,83	-72,22	412	51	8	13	27	34	4.4	1.4	1135	LITHO43; LITHO49; LITHO53; LITHO54; LITHO55
Clair	45,60	-76,07	244	61	13	15	44	24	5.1	4.9	994	LITHO49; LITHO56
Daniel	47,79	-71,81	533	120	7	15	29	44	4.3	0.5	1202	LITHO43; LITHO55; LITHO57
David	46,31	-75,58	213	172	8	10	47	24	6.7	3.8	988	LITHO45; LITHO48; LITHO49
Des joncs	46,75	-73,38	366	79	10	25	34	39	6.6	2.1	1119	LITHO43; LITHO45; LITHO48; LITHO53; LITHO56
Papillons	46,11	-75,33	412	38	11	18	41	18	6.2	2.7	1072	LITHO45; LITHO48; LITHO49
Duck	45,84	-75,86	335	68	10	18	65	1	5.6	4.0	1221	LITHO48; LITHO49
Eclair	46,86	-73,00	320	42	9	20	47	22	5.3	2.4	1074	LITHO43; LITHO45; LITHO46
Fauvette	47,34	-73,23	396	249	8	23	50	30	5.7	1.5	1058	LITHO45
General-White	46,37	-74,68	366	218	12	35	49	16	5.6	3.2	1064	LITHO45; LITHO49; LITHO55; LITHO56
Josselin	47,37	-71,67	671	100	8	18	21	30	8.2	0.1	1602	LITHO45; LITHO55
Laurent	46,48	-74,20	457	59	9	22	62	27	5.6	2.5	1124	LITHO45; LITHO48; LITHO56
Lemaine	47,72	-71,77	549	81	9	40	31	31	6.9	0.4	1356	LITHO43; LITHO55
MacLeod	47,47	-70,98	975	88	12	23	1	64	2.8	-1.2	1434	LITHO45; LITHO46; LITHO53; LITHO56
Najoua	47,04	-72,08	366	80	8	33	29	38	4.7	2.0	1327	LITHO43; LITHO56; LITHO57
Pothier	47,64	-73,04	305	90	7	20	48	22	4.4	2.0	1187	LITHO43; LITHO44; LITHO45; LITHO48
Thomas	47,88	-70,24	625	93	9	35	29	27	3.3	0.8	1165	LITHO45; LITHO46; LITHO55
Truite-Rouge	46,15	-74,08	533	78	7	5	58	12	4.9	2.2	1299	LITHO43; LITHO49; LITHO53; LITHO55
Mean	46,86	-73,47	447	104	8	20	41	27	5.3	2.0	1163	
(SE)			(38)	(12)	(1)	(4)	(4)	(3)	(0.3)	(0.3)	(36)	

Lat = Latitude; Long = Longitude; Ele = mean elevation above sea level; W. area = Watershed area; Slope = mean slope; SS: Surface stoniness (% coarse fragments on surface); Dec = percent deciduous canopy cover; Con = percent coniferous canopy cover; MAST = mean annual soil temperature; MAAT = mean annual air temperature; MAPT = Mean annual precipitation total; LITHO43 = plagioclase, biotite, hornblende, mafic gneiss, biotite and amphibolite; LITHO44 = Granodiorite gneiss and granite, foliated or magmatized granitoids; LITHO45 = charnockitic gneiss and orthopyroxene granitoids; LITHO46 = Migmatite; LITHO48 = Paragneiss, quartzite and amphibolite; LITHO49 = Limestone and silicate rocks, marble, dolomite, shale and quartzite; LITHO53 = Anorthosite and gabbronorite; LITHO54 = Gabbro, pyroxenite, troctolite and amphibolite; LITHO55 = Orthopyroxene granitoids: charnockite, mangerite, jotunite and hypersthenes syenite; LITHO56 = Syenite, monzonite, granodiorite and diorite; LITHO57: Granite and pegmatite.

Lithological data were extracted from the geological map (1: 2 500 000) of Quebec produced by the Ministry of Natural Resources. Below, we present a brief overview of the methods of acquisition of data for climate, vegetation and soils.

3.3.2.1 Climate data

Average monthly precipitation and temperature were generated for each catchment with the BioSIM model (Régnière, 1996; Régnière and St-Amant, 2007). This model is based on a geo-referenced source of weather data (120 monitoring stations over the study area covering the last 30 years of data) to calculate the selected weather data for the specified latitude, longitude, elevation, slope, and aspect of a given watershed. The correlation coefficient between estimated and measured values of temperatures or precipitations is generally over 0.98 (Régnière and Bolstad, 1994). The weather data generated for each catchment in this study are robust as they are averages calculated from four meteorological stations. The monthly weather variables were in turn used to simulate soil temperature and soil moisture with the empirical models ForSTeM and ForHyM, respectively (Arp and Yin, 1992; Houle et al., 2002; Houle et al. 2012b). ForSTeM simulates heat transfer between the various soil layers, while ForHyM reproduces soil water contents in the watersheds. These models have been repeatedly validated on watersheds located in Ontario and Quebec which are similar to those selected for this study (Arp and Yin, 1992; Houle et al., 2002). The two models accurately reproduce soil temperature and moisture, especially when annual estimates are considered (Houle et al., 2012b).

3.3.2.2 Vegetation data

For each watershed, percent coniferous and deciduous canopy covers were obtained from forest geo-referenced maps (1: 20 000) of the third inventory program conducted by the Department of Natural Resources and Wildlife in the 1990s. The lake surface, as well as open area in the forest cover, was considered in the calculation, so that the sum of the relative abundance of the two main vegetation types is not 100%. Given the absence of detailed information on the historical evolution of the vegetation cover in the study area since glacial retreat, we assumed: 1) that natural or anthropogenic disturbances were occasional and equally likely to occur at any location over the studied territory, and 2) that forest composition has remained fairly stable over the last millennia (Richard, 1995).

3.3.2.3 Soil data

Soil sampling was conducted during the summer and fall of 2001 and 2002. For each watershed, three soil profiles evenly distributed on flat surfaces around the lake perimeter were dug approximately 50 m from the lake shore. A visual estimation of the percent volume of coarse fragments on land surface was made in the field. The soil profiles were described, the thickness of each horizon was recorded and soils were sampled by genetic horizons. The soil colors were characterized according to the Munsell Soil Color Chart (MacBeth Division of Kollmorgen Instruments Corporation, 1994).

Total chemistry. Soil samples were air dried and sieved to 2 mm prior to chemical analysis. For all horizons, the elemental composition of the soil solid phase was determined on 32-mm-diameter fused beads prepared from a 1:5 soil-lithium tetraborate mixture using an automated X-ray fluorescence (XRF) spectrometer system (Philips PW2440 4kW) with a Rhodium 60-kV end window X-ray tube. Soil pH was measured using a 1:2.5 soil:water ratio, with a pH electrode.

Soil organic matter. Organic matter content was estimated by combustion for three hours at 550 °C (Howard and Howard, 1990) on all horizons. Soil organic carbon was then computed by dividing soil organic matter content by 1.724 (van Bemmelen factor).

Bulk density. Stainless steel cylinders were inserted laterally in each mineral horizon to determine soil bulk density according to the core method described by Blake and Hartge (1986). Soil bulk density could be obtained for 252 soil samples (88% of all horizons) with the latter method. Regarding the remaining 12% (34 samples), a relationship between soil organic carbon content and bulk density was built from a subset of 17 soil profiles totaling 56 individual horizons. Bulk density (Bd) was a non-linear function of soil carbon (SC) content ($Bd = 3{,}978\ SC^{-0{,}363}$, $R^2 = 0.86$, $n = 56$) as previously observed in other studies (Huntington et al., 1989; Périé and Ouimet, 2008). This relation was then used for computing missing bulk density values for some thin mineral horizons which were impossible to sample with the core.

Creating a composite B horizon. A matrix of explanatory variables and sampled sites was assembled for statistical purposes. Given that geographic and hydro-climatic variables have a unique value for each watershed, the matrix required a unique corresponding soil value for each variable of concern. Accordingly, we produced a composite B horizon for each soil profile that includes all the B horizons. Because the uppermost mineral (A or E) horizons are highly weathered and absent in some soil profiles, we assumed that the bulk of the BC losses occurred mainly in the surface more weathered B horizons (Bhs, Bs and BC horizons) that overhang the C horizon. The amount of soil materials used from the individual B horizons of a given profile to form the composite B was calculated as a function of their thickness and density, using the following equation:

$$P = \frac{[\text{B horizon thickness (cm)} * \text{B horizon density (g m}^{-3})]}{\Sigma[\text{B horizon thickness (cm)} * \text{B horizon density (g m}^{-3})]}$$

where P refers to the proportion of soil to be used from the B horizon considered. It follows that soil particle-size distribution, soil surface area and mineralogical composition were determined on these composite B horizon samples for each soil profile. The composite B horizons were also analyzed for organic carbon content and pH, as described above. For a given soil property, a mean watershed value was obtained by averaging data for the composite B horizons of the different soil profiles within the catchment.

Particle-size distribution of the composite B horizon. Prior to particle-size distribution analysis, the composite B samples were digested with hydrogen peroxide (30% H_2O_2) in acid medium to remove organic matter coatings. Because the composite B horizons had lower levels of organic matter (and oxides) contents than most individual B horizons, complete oxidation was expected with the hydrogen peroxide treatment. Moreover, this reagent attacks the amorphous Fe and Mn oxides (Jackson, 1979; Filgueiras et al., 2002), thus solubilizing a substantial part of the organo-metallic coatings formed in these soils during podzolisation. Once the organic component and these amorphous oxides coatings were removed, the sand-size particles were separated from the soil samples (<2 mm) by wet sieving through a 63 µm sieve. The >63 µm fraction retained by the sieve was oven dried, sieved again using a sieve column and then weighted. A laser diffraction method was then used for determining the size distribution of particles <63 µm. This analysis was preceded by the dispersion of the soil particles with sodium metaphosphate.

Surface area of the composite B horizon. The soil surface area was estimated from soil bulk density and soil particle size distribution using the texture based soil type Eq. 25 from Sverdrup and Warfvinge (1995):

$$\mathrm{SSA} = (8.0 * x_{clay} + 2.2 * x_{silt} + 0.3 * x_{sand}) * \rho_{\mathrm{soil}}/1000$$

where SSA refers to the total mineral surface area (m^2/m^3), ρ_{soil} is the soil bulk density (kg m^{-3}) and x is the weight fractions of clay, silt and sand with the size fractions classified as follow:

x_{clay} = less than 2 µm fraction

x_{silt} = 2-63 µm fraction

x_{sand} = 63-250 µm fraction

Mineralogy of the composite B horizon. The data for soil mineralogy have been published previously (Houle et al., 2012a) and their method of acquisition was described in detail elsewhere (Houle et al., 2012a; Lafleur et al., 2013). Briefly, bulk elemental composition of the B composite samples was obtained by XRF, as above. The mineralogical composition of the soil samples was then quantitatively estimated from the bulk chemistry, using the stoichiometric model UPPSALA (Sverdrup 1990; Sandén et Warfvinge 1992; Houle et al., 2012a). This normative back-calculation model was developed for converting the bulk elemental (Na, K, Ca, Mg, P, Al, Si and Fe) contents of the soils into different soil minerals (Sverdrup 1990; Sandén et Warfvinge 1992). Results from semi-quantitative analysis by X-ray diffraction (XRD; Hillier, 1999; Kahle et al. 2002) were subsequently compared to those obtained using UPPSALA as a validation of the modelled data, and consistency was observed (Houle et al. 2012a). The mineralogical data formerly published in Houle et al. (2012a) are summarized in the supplementary Table S3.1 in Appendix B.

***Duration of pedogenesis*.** For each watershed, the duration of pedogenesis was estimated assuming: 1) that all the soil parent materials were of glacial or glaciofluvial origin, 2) that the materials were exposed to the atmosphere after the retreat of the Laurentian Ice Sheet of the Wisconsinian glaciation, and 3) that the weathering of soil materials has not been interrupted for a significant time since the glacial retreat. The duration of pedogenesis for each watershed was estimated by interpolation using the MapInfo software (Fig 3.1). The position of each watershed was first located on a geomorphological map containing the isochronous lines for the retreat of the Laurentian Ice Sheet together with the position of the Mars-Batiscan Moraine and the Saint-Narcisse morainic complexes, dated at 11 400 and 12 900 years before present, respectively (Occhietti, 2007). Because only two reference dates were available, an interpolation algorithm could not be used. The space between the two moraines was therefore divided in equidistant 100-years intervals, based on both geometric and arithmetic calculations, to estimate duration.

3.3.3 Estimation of long-term BC weathering rates in soil profiles

The soil mass balance method (Brimhall et al., 1991a, b; Egli and Fitze, 2000) takes into account both the chemical transformations and the physical deformations occurring during soil genesis (Anderson et al., 2002). Chemical changes at the profile scale are interpreted as the results of mineral weathering, which is one of the main processes responsible for the development of soil profiles (Johnson and Watson-Stegner, 1987; Brimhall et al., 1991b). Moreover, soil profiles are progressively deformed during pedogenic development, because of processes such as weathering, eluviation, illuviation, bioturbation and the incorporation of organic matter leading to volumetric changes (collapse/dilation) in weathered horizons (Brimhall et al., 1991b; Anderson et al., 2002; Courchesne et al., 2002). The neoformation of amorphous solid phases (Al and Fe oxyhydroxides), the growth of plant roots or the integration of organic substances generally produce horizon dilation. To the contrary, horizon collapse mostly results from mineral weathering and the subsequent leaching of dissolved elements from the soil profile. The mass balance model of Brimhall et al. (1991a) provides a mean to quantify the physical deformation (strain) in weathered soil horizons using conservative chemical elements as geochemical tracers to estimate change in soil thickness relative to the initial thickness of the parent material. Strain values are positive for soil dilation and negative when the partial collapse of soil horizons occurs (Egli et al., 2001; Minasny et al., 2008).

For the calculations of elemental mass balance, we selected Zr as the immobile element because its vertical distribution through the soil profiles was more predictable than that of Ti, showing a decreasing concentration with depth (Schaller et al., 2009) in 90% of the soil profiles compared to 76% for Ti. Prior to calculation, a critical examination was conducted for soil data collected from the 21 watersheds. Four watersheds had missing data for one soil profile and these four profiles were removed from the dataset. Of the remaining 59 soil profiles, ten were considered to be unsuitable for the application of the mass balance method because they did not meet the following two criteria: 1) total Zr concentrations should not increase with soil depth (Schaller et al., 2009) and 2) total elemental data should be available for a minimum of three weathered horizons for a given soil profile. BC weathering rates were then computed for the remaining 49 soil profiles. For a given catchment, site weathering rates were obtained by averaging data from all soil profiles. There were at least two profiles per catchment, except for the General-White watershed.

The integrated profile mass balance of Ca, Mg, Na and K since the initiation of pedogenesis was computed according to Equation 14 in Egli and Fitze (2000):

$$m_{j,flux}\ (Z_w) = \sum_{a=1}^{n} C_{j,p}\ \rho_p\ (1/(\epsilon_{i,w} + 1)\ \tau_{j,w}\ \Delta Z_w$$

where:

$m_{j,flux}\ (Z_w)$: changes in mass of element j (kg)

$C_{j,p}$: concentration of element j in the parent material (kg/t)

ρ_p : bulk density of the parent material (t/m^3)

$\epsilon_{i,w}$: strain, volumetric changes estimated by the ratio of volume difference during weathering with respect to the initial volume of the parent material

$\tau_{j,w}$: open-system mass transport function for the element j

ΔZ_w : weathered horizon height (m)

Equation 2 from Brimhall et al. (1991b) was used to calculate the volumetric changes ($\epsilon_{i,w}$):

$$\epsilon_{i,w} = ((\rho_p C_{i,p})/(\rho_w C_{i,w}))-1$$

with $C_{i,p}$ and $C_{i,w}$ as the concentrations of the immobile element (Zr) in the parent material and the weathered horizons, respectively. The open-system mass transport function ($\tau_{j,w}$) was obtained using the Eq. 4 from Brimhall et al. (1991b):

$$\tau_{j,w} = [((\rho_w C_{j,w})/(\rho_p C_{j,p}))\ (\epsilon_{i,w} + 1)] - 1$$

The average profile mass balance per year was then obtained by dividing the integrated mass balance by the duration of soil genesis. Annual elemental mass loss is interpreted as an estimate of the long-term average weathering rates at pedogenic time scale.

3.3.4 Data analysis

The statistical analysis was based on weathering rates for four base cations and on 31 environmental variables or soil properties for each of the 21 watersheds. We used redundancy analysis (RDA) with the vegan package in R (R Development Core Team, 2009) to link long-term BC weathering rates to explanatory variables. The RDA is an analog of multivariate linear regression analyses that uses matrices of dependent and explanatory variables. The dependent matrix is represented by BC weathering rates, and the explanatory data consisted of variables pertaining to the vegetation cover, the geographic and hydro-climatic characteristics of the sites as well as the physical, chemical and mineralogical properties of the soils in each watershed. This ordination method (RDA) allows dimension reduction, i.e. to reduce the data set to a 2-dimensional summary, which can be presented as an ordination diagram. The dependent variables were $\log_{10}(x+1)$ transformed to stabilize the variance and normalize their distribution. The forward.sel () function of the library packfor of the R package was used to evaluate the significance of the environmental variables, using Monte Carlo tests (ter Braak and Verdonschot, 1995), with 999 unrestricted permutations. Only variables with $p < 0.1$ were included in the final model. This function also calculates the cumulative proportion of variation explained in the weathering rates data by the explanatory variables selected in the multivariate model.

3.4 Results

3.4.1 Catchments and soils characteristics

The properties of the 21 watersheds are summarized in Table 3.1. Catchment sizes vary from 38 to 249 hectares, while mean slopes range from 3 to 13%. Elevation spans from 213 to 975 m above the sea level and almost covers the spectrum found in southern Quebec. Total annual precipitation levels are close to or exceed 1 m per year in the watersheds. Average annual air temperature varied from -1.2 to 4.9 °C while mean annual soil temperature fluctuated between 2.8 and 8.2 °C. Temperature increased along an overall northeast-southwest gradient while total incident precipitation increased in the opposite direction. Similarly, a strong geographical pattern was observed in the relative abundance of the two main vegetation types. The abundance of deciduous tree species was negatively related to longitude (R = -0.72; $p < 0.05$) and decreased from the western to the eastern part of the studied area whereas a positive correlation was observed for the abundance of coniferous species (R = 0.64; $p < 0.05$). In the study area, percent surface coverage of coarse fragments range from 10 to 40%. Eleven groupings of a total of 26 different rocks are present in the study area. Each lithology group is characterized by a series of specific rocks and mineral types (Table 3.1).

The common sequence of mineral horizons in soils is E or A–Bhs–Bs1–Bs2–BC–C, as illustrated in Table 3.2. The morphology and properties of the 14 soil profiles, whose horizon sequence is presented in this Table, are representative of the overall variability of the soils in the 21watersheds. The land surface is stony in the 21 watersheds. All soils had organic (O) surface horizons resting on either a light-colored eluvial (E) horizon or a darker A horizon. A podzolic B horizon follows, composed, from top to bottom, by thick reddish to brown (10YR or 7.5YR) illuvial Bhs horizons superimposed on orange-brown to yellowish (7.5YR to 5 YR) Bs horizons.

Table 3.2: Properties of 14 representative pedons from six of the 21 watersheds.

Profile	Horizon	Soil depth (cm)	Bulk density (g cm^{-3})	Color	pH (H_2O)	[a]Org. C (%)
Pothier (Podzol/Spodosol; estimated duration of pedogenesis: 11 200 years)						
Profile 1	A	0-4	0.80	10YR 6/2	4.33	3.29
*(*SS = 10%)*	Bhs	4-16	0.88	10YR 5/8	5.48	5.97
	Bs1	16-28	1.04	10YR 4/6	5.46	3.78
	Bs2	28-41	1.30	2.5Y 4/3	5.36	1.63
	C	41-78	1.30	2.5Y 4/2	5.24	0.74
Profile 2	E	0-5	0.80	5YR 6/1	5.02	1.58
(SS = 15%)	Bhs	5-15	0.89	2.5YR 3/6	5.26	7.59
	Bs1	15-27	1.04	7.5YR 3/4	5.25	4.85
	Bs2	27-40	1.23	10YR 4/4	5.29	2.13
	BC	40-50	1.30	--	5.28	2.18
Profile 3	E	0-5	0.80	10YR 7/1	4.32	1.71
(SS = 35%)	Bhs	5-17	0.86	7.5YR 4/6	5.11	7.96
	Bs1	17-39	0.95	10YR 5/8	5.27	3.38
	Bs2	39-63	1.04	10YR 4/3	5.34	1.42
	C	63-93	1.36	10YR 4/1	5.26	0.54
Boisvert (Podzol/Spodosol; estimated duration of pedogenesis: 11 650 years)						
Profile 1	E	0-8	0.80	7.5YR 5/2	4.38	2.52
(SS = 30%)	Bhs	8-28	0.78	5YR 3/3	4.90	5.64
	Bs	28-50	1.20	7.5YR 4/4	5.05	2.76
	C	50-87	1.30	2.5Y 5/4	5.18	0.96
Profile 3	E	0-4	0.80	7.5YR 6/2	4.30	2.76
(SS = 10%)	Bhs1	4-15	0.80	5YR 3/4	4.89	11.34
	Bhs2	15-33	1.16	7.5YR 4/6	4.99	5.55
	BC	33-53	1.25	10YR 5/3	5.10	2.31
David (Podzol/Spodosol; estimated duration of pedogenesis: 12 150 years)						
Profile 1	A	0-5	0.80	10 YR 4 / 2	--	4.37
(SS = 5%)	Bhs1	5-27	0.71	10 YR 3 / 3	5.27	9.91
	Bhs2	27-54	0.95	7.5 YR 2.5 / 3	5.17	8.54
	Bs	54-74	1.22	10 YR 3 / 3	5.22	3.78
	BC	74-84	1.51	2.5 Y 4 / 4	5.21	2.23
Profile 2	A	0-5	0.80	10 YR 3 / 1	--	3.98
(SS = 15%)	Bhs1	5-25	0.65	7.5 YR 2.5 / 2	5.31	7.02
	Bhs2	25-45	1.14	10 YR 2 / 2	5.31	5.73
	Bs	45-60	1.28	10 YR 3 / 3	5.41	4.88
	BC	60-70	1.28	2.5 Y 3 / 3	5.47	1.99

Table 3.2 (continued)

Profile	Horizon	Soil depth (cm)	Bulk density (g cm^{-3})	Color	pH (H_2O)	Org. C (%)
Papillons (Podzol/Spodosol; estimated duration of pedogenesis: 12 550 years)						
Profile 1	Bhs	0-26	0.77	7.5 YR 3 / 3	4.87	6.39
(SS = 10%)	Bs	26-49	1.01	10 YR 3 / 2	5.30	4.34
	BC	49-61	1.09	10 YR 3 / 4	5.53	2.84
	C	61-86	1.68	2.5 Y 4 / 2	5.44	1.47
Profile 2	A	0-4	0.80	10 YR 2 / 2	--	7.91
(SS = 30%)	Bhs	4-29	0.80	10 YR 3 / 2	4.55	6.89
	Bs	29-64	0.99	10 YR 3 / 3	5.10	4.56
	C	64-71	1.44	2.5 Y 3 / 3	5.56	1.37
Profile 3	A	0-3	0.80	10 YR 2 / 1	--	18.12
(SS = 15%)	Bhs1	3-26	0.79	10 YR 3 / 3	4.92	8.70
	Bhs2	26-46	1.08	10 YR 3 / 4	4.99	5.79
	Bs2	46-64	1.09	10 YR 3 / 4	5.11	--
	C	64-100	1.38	10 YR 4 / 4	4.99	--
Chômeur (Podzol/Spodosol; estimated duration of pedogenesis: 11 200 years)						
Profile 1	E	0-6	0.80	--	4.34	1.18
(SS = 10%)	Bhs	6-12	0.80	2.5YR 3/6	4.92	12.51
	Bs1	12-27	1.10	10YR 5/8	5.08	3.24
	Bs2	27-48	1.08	10YR 5/6	5.04	1.86
	C	48-83	1.47	2.5Y 4/3	5.20	1.82
Profile 2	E	0-8	0.80	7.5YR 6/2	4.38	1.37
(SS = 15%)	Bhs	8-18	0.80	2.5YR 3/4	5.02	16.95
	Bs1	18-36	1.17	7.5YR 4/6	5.03	2.95
	Bs2	36-70	1.08	--	5.06	2.03
	C	70-100	1.26	--	--	0.71
Blais (Podzol/Spodosol; estimated duration of pedogenesis: 12 850 years)						
Profile 1	E	0-9	0.80	10 YR 4 / 3	--	1.89
(SS = 10%)	Bhs	9-24	0.76	7.5 YR 3 / 4	4.73	7.34
	Bs	24-42	1.24	10 YR 4 / 4	4.97	2.20
	BC	42-57	1.48	10 YR 4 / 4	5.16	1.31
	C	57-100	1.52	2.5 Y 4 / 4	5.30	0.78
Profile 3	Bhs	0-25	0.70	10 YR 2 / 1	--	12.64
(SS = 10%)	Bs1	25-55	1.03	10 YR 3 / 3	5.71	2.69
	Bs2	55-77	1.45	10 YR 3 / 3	5.63	1.66
	C	77-100	1.57	2.5 Y 4 / 4	5.79	0.75

*SS: surface stoniness (% coarse fragments on land surface)

[a] Org. C: soil organic carbon content

The podzolic B grades into a transition BC horizons and then, into a grey (10YR to 2.5Y) C that can appear at depth as shallow as 40 cm for some profiles. Through the mineral soil profile, soil pH in water globally decreases towards the surface with the extent of acidification being less than one pH unit in the mineral soil. Bulk density is at a minimum in the top (E or A horizons) and increases towards the bottom of the soil profiles. This marked loosening of the top mineral horizons result from the cumulative effect of soil genesis, root growth and mineral weathering. The soil organic carbon content reaches a first maximum in the surface organic horizons (data not shown). Below the O horizons, the organic C content decreases sharply in the E, when present, and to a lesser extent in the A horizon. A second organic C peak is reached in the upper B horizon (Bhs) followed by a progressive decrease in the deeper B horizons and towards the C horizon (Table 3.2; Figure 3.2). Research conducted in similar soil profiles of the Canadian Shield have shown that vertical patterns in organically-complexed Al and Fe (Na-pyrophosphate extractable) closely follow those of organic carbon (Courchesne et al., 2005; Courchesne and Turmel, 2007). Overall, these observations are consistent with podzolization which is the main pedogenic process affecting the soils of the study area (Buurman, 1987; Egli et al. 2006).

The vertical distribution pattern of total element concentrations was similar for Ca and Mg in all profiles with concentrations decreasing towards the soil surface (Figure 3.2). For most soil profiles, we also recorded an overall decrease in Na and K concentrations from the C horizon towards the upper B followed by a subsequent increase to the surface (Figure 3.2). The Zr concentration was generally constant at depth, increased in the upper horizons and reached a maximum in the uppermost mineral horizon (A or E) of the profiles (Figure 3.2). The composite B horizons had a thickness ranging from 32 to 73 cm, a pH in water varying from 4.5 to 5.5 and a loamy sand to silty loam texture (Table 3.3) with low clay contents (0.8 to 3.5%). The soil surface area estimated according to the granulometric approach (Sverdrup and Warfvinge, 1995) varied from 0.70 to 1.64 $km^2\ m^{-3}$ (Table 3.3). Soil surface area was positively related to soil clay content ($R = 0.69$; $p < 0.05$) and both surface area and clay content followed a longitudinal gradient, decreasing from the southwest to the northeast in the study area. Soil surface area was also inversely related to elevation ($R = -0.70$; $p < 0.05$).

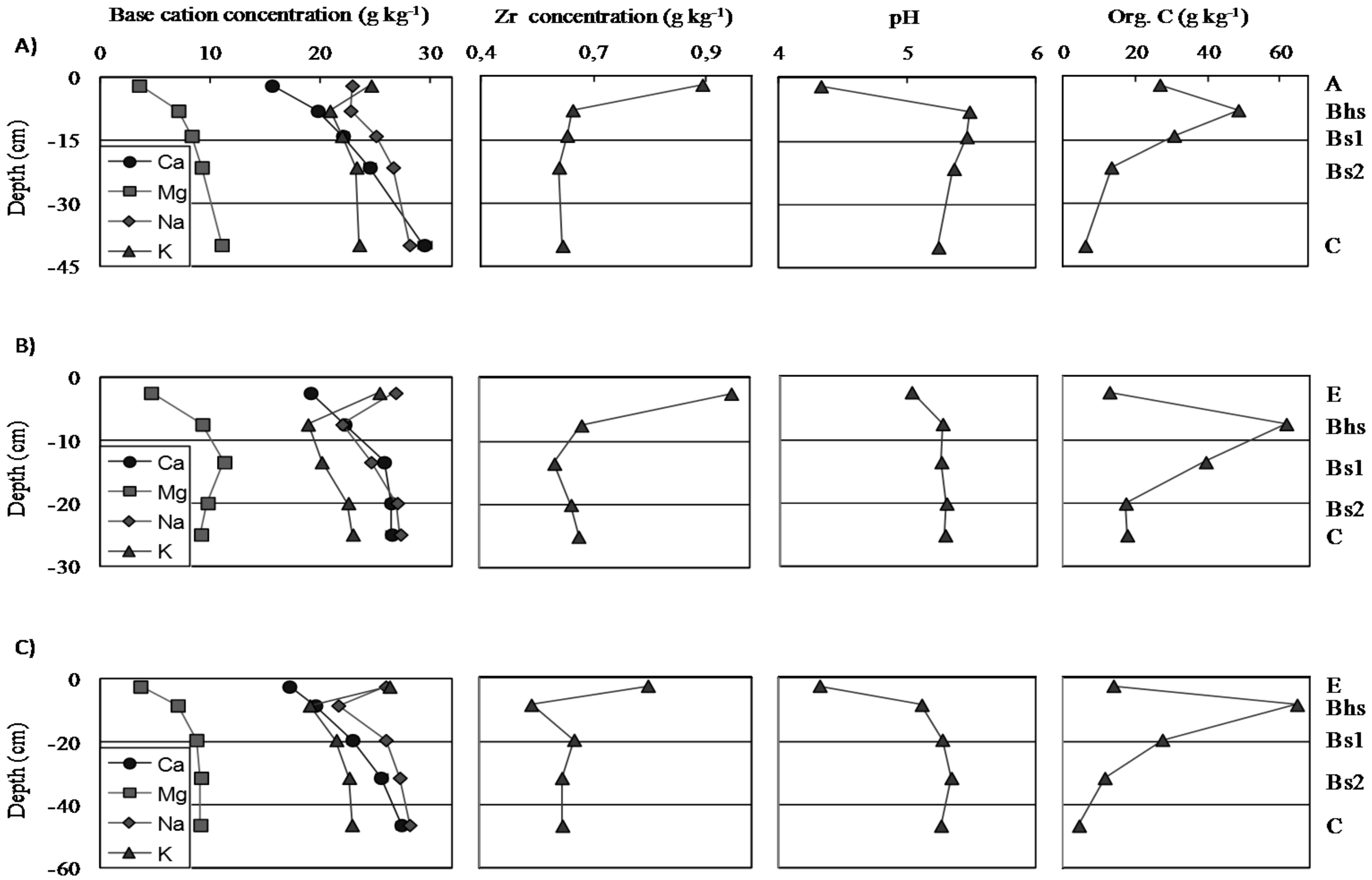

Figure 3.2: Vertical distribution of total elemental concentrations and pH in the three soil profiles (A, B and C) of the Pothier Watershed.

Table 3.3: Physical and chemical properties of the composite B horizon.

Watershed	Thickness (cm)	pH (in H_2O)	Water content[a] (%)	Org. C[b] (%)	Clay (%)	Silt (%)	Sand (%)	SSA[c] (km^2 m^{-3})
Adanys	50	4.6	27	5.16	1.7	28.1	70.2	0.96
Blais	50	4.6	19	6.65	1.6	33.4	65.0	1.27
Boisvert	39	4.7	16	4.39	1.4	36.4	62.2	1.09
Chomeur	43	4.9	25	2.38	1.5	36.9	61.6	1.04
Clair	73	4.7	19	6.65	2.0	38.3	59.6	1.29
Daniel	32	4.9	21	4.67	3.0	31.3	65.7	1.11
David	64	4.5	20	2.97	1.6	45.1	53.3	1.23
Des joncs	47	4.9	21	4.58	1.4	40.1	58.5	1.28
Papillons	59	4.8	21	3.27	1.9	36.5	61.6	1.09
Duck	59	4.6	21	4.64	3.5	46.5	50.0	1.64
Eclair	67	4.7	24	4.15	1.4	49.8	48.8	1.33
Fauvette	42	4.6	25	3.97	2.8	36.2	61.0	1.48
General-White	55	5.0	21	2.63	3.5	33.7	62.8	1.20
Josselin	39	4.9	23	3.92	1.1	35.9	63.0	0.99
Laurent	36	4.8	21	5.50	1.9	42.7	55.4	1.23
Lemaine	45	5.2	26	5.18	2.1	42.7	55.1	1.07
MacLeod	51	5.0	22	4.90	0.5	27.9	71.6	0.79
Najoua	55	5.2	25	2.81	1.2	31.4	67.4	0.93
Pothier	48	5.4	21	5.01	2.1	39.9	58.0	1.30
Thomas	33	5.3	25	3.76	0.8	22.1	77.1	0.70
Truite-Rouge	56	5.5	21	3.80	1.0	33.4	65.6	0.95
Mean	48.8		22	4.3	1.8	36.6	61.6	1.14
(SE)	(2.3)	4.9 (0.1)	(1)	(0.3)	(0.2)	(1.5)	(1.5)	(0.05)

[a]Water content: ForHyM-generated mean annual soil moisture content
[b]Org. C: soil organic carbon content
[c]SSA: soil surface area

Other positive relationships were observed between soil surface area and hornblende ($R = 0.55$; $p < 0.05$), pyroxene ($R = 0.61$; $p < 0.05$) and vermiculite ($R = 0.53$; $p < 0.05$) contents in soils although the relationship with soil feldspar content was negative ($R = -0.55$; $p < 0.05$). ForHyM-generated mean annual soil water content ranged from 16 to 27% (Table 3.3). The pH in water of the composite B was inversely correlated to longitude ($R = -0.43$, $p = 0.043$) whereas organic carbon followed no geographic or climatic pattern (Table 3.3).

3.4.2 Long-term estimates of base cation weathering rates

Annualized long-term mass balances for all sites in the study area averaged 0.16, 0.10, 0.09 and 0.06 kmol$_c$ ha^{-1} an^{-1} for Ca, Mg, Na and K, respectively (Table 3.4). On an individual cation basis, these mass balances showed that Ca had the highest weathering rates while the lowest rates were estimated for K.

Table 3.4: Mean annual mass balance estimated for the four cations in the soil profiles of the 21 watersheds.

Watershed	Ca	Mg	Na	K
	---------------------------- kmol$_c$ ha^{-1} yr^{-1} ---------------------------			
Adanys	0.13	0.05	0.14	0.08
Blais	0.22	0.12	0.06	0.05
Boisvert	0.08	0.21	0.05	0.07
Chômeur	0.13	0.06	0.10	0.05
Clair	0.18	0.01	-0.01	-0.03
Daniel	-0.09	-0.12	0.02	0.08
David	0.17	0.08	0.06	0.06
Des Joncs	0.17	0.10	0.13	0.06
Des Papillons	0.30	0.20	0.08	0.07
Duck	0.86	0.85	0.09	0.12
Éclair	0.17	0.09	0.16	0.07
Fauvette	0.23	0.18	0.15	0.07
Général-White	0.13	0.00	0.12	0.03
Josselin	0.03	0.02	0.02	0.02
Laurent	0.17	0.12	0.16	0.10
Lemaine	0.05	-0.01	0.08	0.05
MacLeod	0.13	0.03	0.10	0.06
Najoua	0.15	0.04	0.17	0.06
Pothier	0.12	0.05	0.06	0.02
Thomas	0.09	0.07	0.06	0.04
Truite-Rouge	0.03	-0.02	0.03	0.04
Mean (SE)	0.16 (0.04)	0.10 (0.04)	0.09 (0.01)	0.06 (0.01)

For a given cation, the weathering rates varied among sites, with the highest variations observed for Mg weathering rates (relative standard error of 40%) and the lowest for Na weathering rates (relative standard error of 11%). The relative cation fluxes were generally negative for each horizon and they decreased somewhat progressively with depth (Figure 3.3 A to C). However, some positive base cation fluxes were observed in the B horizon of a few profiles, as exemplified in Figure 3.3 B for the Pothier watershed.

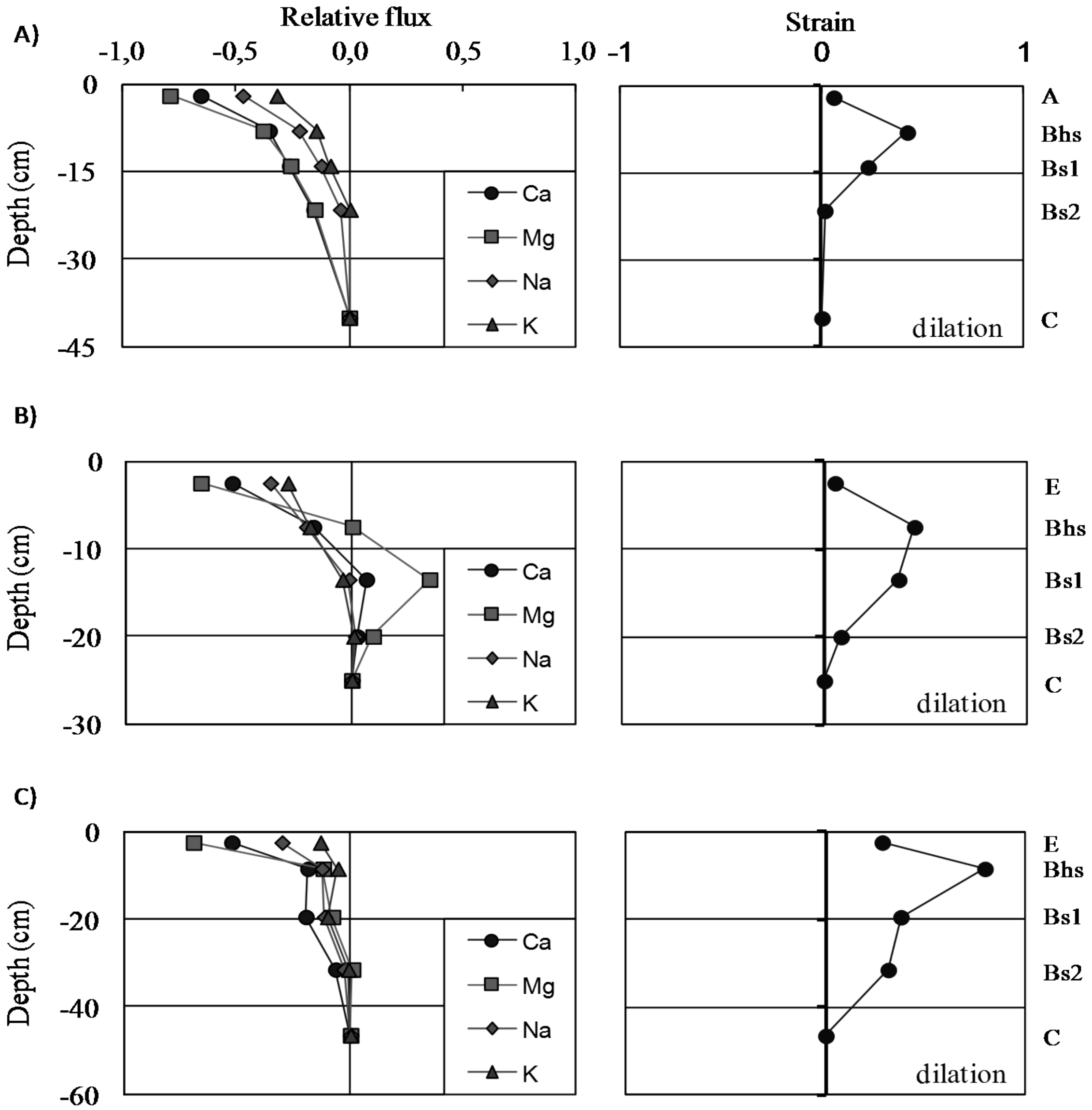

Figure 3.3: Relative fluxes for Ca, Mg, Na and K and calculated strain as a function of soil depth for the three soil profiles (A, B and C) of the Pothier watershed.

In rare cases, there was an apparent elemental accumulation (Table 3.4). This was particularly obvious for the Daniel watershed where significant accumulations of Ca and Mg were observed (Table 3.4). Strain values were generally close to zero at the base of soil profiles while volumetric changes, mostly soil dilation, were common in surface horizons where pedogenesis is more intense (Figure 3.3).

3.4.3 Linking base cation weathering rates to environmental factors and soil properties

The forward selection procedure using a Monte Carlo permutation test (n=999, $p<0.1$) identified soil surface area, percent deciduous canopy cover, elevation, as well as soil albite content as the most significant, among all 31 candidates, explanatory variables contributing to the spatial variations in BC weathering rates (Table 3.5).

Table 3.5: Summary statistics for the first four axes of the redundancy analysis (RDA) of environmental variables and BC weathering rates. Only environmental variables selected in the forward selection procedure are presented in the ordination.

Statistic	RDA1	RDA2	RDA3	RDA4
Eigenvalue	0.00419	0.00016	0.00005	0.00002
Proportion of variation explained	0.53780	0.01990	0.00586	0.00027
Cumulative percentage of variance	0.53780	0.55770	0.56360	0.56380
Score for base cations				
Ca	0.336	0.001	-0.030	0.003
Mg	0.314	0.004	0.030	-0.003
Na	0.015	-0.088	-0.001	-0.001
K	0.025	-0.010	0.023	-0.009
Score for environmental variables				
Soil Surface area (SSA)	0.783	-0.086	0.085	-0.613
Percent deciduous canopy cover (DEC)	0.675	-0.237	-0.662	0.223
Elevation (Ele)	-0.408	0.034	0.622	0.667
Albite	-0.543	-0.724	0.417	-0.083

The results indicated that up to 56.4% of the variance could be explained by these four environmental variables. The first ordination axis captured 53.8% of the variation while the second axis accounted for only 2.0% (Table 3.5, Figure 3.4). Only the first RDA axis was significant for the set of variables used (Monte Carlo test, 999 permutations, $F = 5.17$, $p = 0.006$), but we nonetheless reported the results for the first four canonical axis (Table 3.5). On the first RDA axis, Ca and Mg weathering rates were positively correlated to soil surface area and percent deciduous canopy cover, and negatively related to elevation and soil albite content. The K and Na weathering rates showed very little variation compared to Ca and Mg. They loaded negatively on the second RDA axis which was positively related to soil albite content (Figure 3.4).

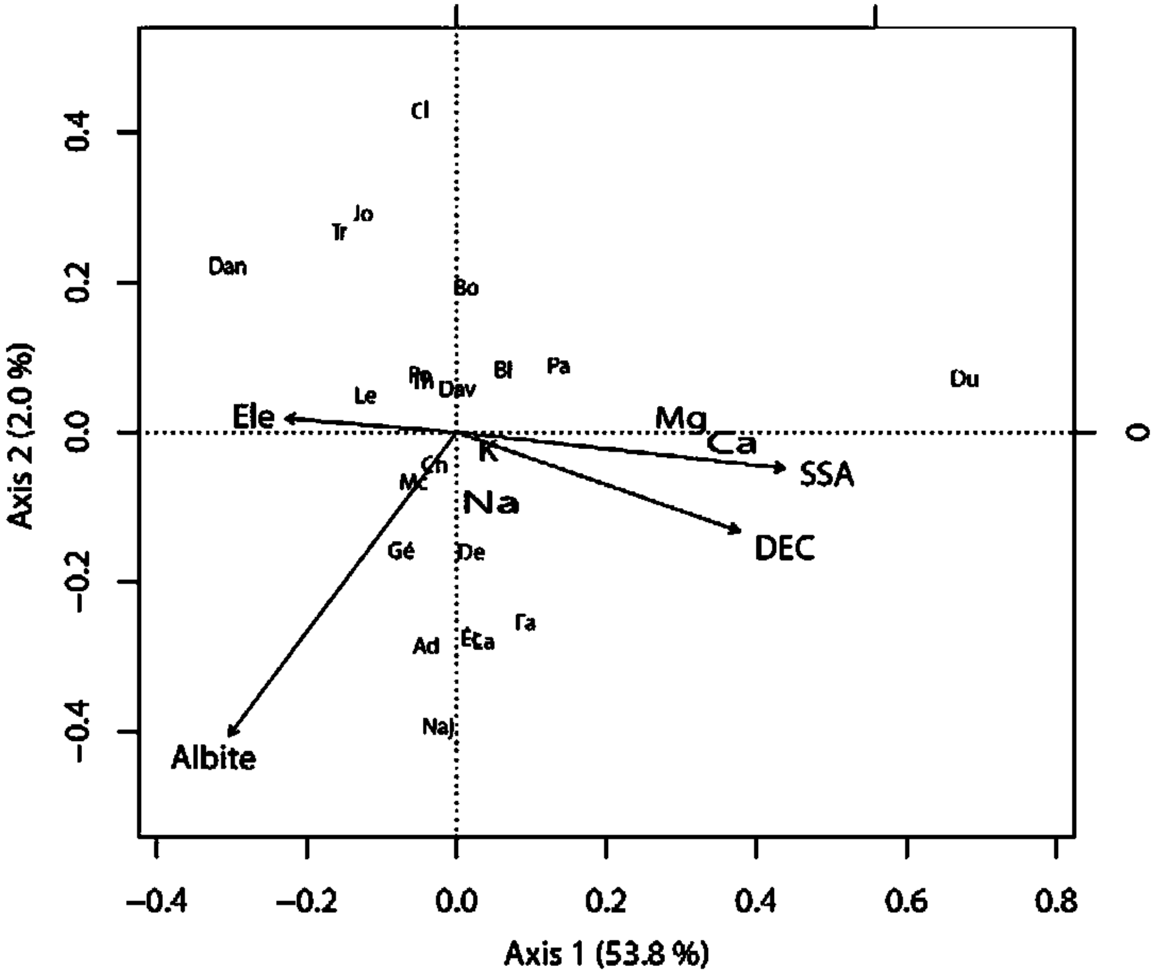

Figure 3.4: Ordination RDA diagram (Axes 1 and 2) of environmental variables and base cation weathering rates for the 21 watersheds. DEC = percent deciduous canopy cover; Ele = elevation; SSA = soil surface area; Albite = soil albite content.

3.5 Discussion

3.5.1 Distribution and long-term weathering fluxes of base cations in soil profiles

The vertical distribution patterns for base cations in the mineral horizons of most profiles is the result of the combined effects of mineral weathering reactions and of other pedogenic processes such as podzolization and elemental leaching (Buurman, 1987; Egli et al., 2006). These processes lead to cation release from soil minerals, to their progressive downward movement in the soil profile and are more pronounced in the upper mineral horizons compared to the lower section of the profile (Olsson and Melkerud, 2000; Courchesne et al., 2002). Biocycling is another key biogeochemical process acting on the profile redistribution of base cations (Jobbagy and Jackson, 2004). Contrary to the processes above, it results in a net upward movement of cations, notably K, following their uptake by plant roots from the mineral soil, transfer to the aboveground biomass and return to the soil surface as throughfall, stemflow, root exudates or litterfall (Gordon and Jackson, 2000; Jobaggy and Jackson, 2004).

Calculations showed that average long-term weathering rates of individual base cations estimated with the soil profile mass balance method ranged from 0.06 to 0.16 $\text{kmol}_c\ \text{ha}^{-1}\ \text{an}^{-1}$, with Ca being the most important contributor to total BC weathering (Table 3.4). These values are of the same order of magnitude as those obtained with the geochemical model PROFILE for the same study area (Houle et al. 2012a) although the model generally simulated more elevated weathering rates compared to the soil profile mass balance method.

The weathering rates reported here are in good agreement with published data for similar forested environments obtained using the soil profile mass balance method. For example, the estimates reported by Courchesne et al. (2002) for long-term weathering rates of individual base cations in southern Quebec ranged from 0.02 to 0.35 $\text{kmol}_c\ \text{ha}^{-1}\ \text{yr}^{-1}$ for three forested soils formed in contrasting parent materials. These authors attributed the observed differences in rates between sites to contrasts in the texture and mineralogy of the soil parent materials. Ouimet and Duchesne (2005) also published values that varied between 0.008 and 0.67 $\text{kmol}_c\ \text{ha}^{-1}\ \text{yr}^{-1}$ for long-term weathering rates of individual base cation in forested soils from Quebec. In the White Mountains of central New Hampshire, Schaller et al. (2009) estimated fluxes ranging from 0.10 to 0.30 $\text{kmol}_c\ \text{ha}^{-1}\ \text{yr}^{-1}$ for weathering rates of total BC in 13 sampling sites. They suggested that the spatial variability in weathering rates reflected differences in temperature, precipitation or vegetation type between sites.

Although the soil profiles that did not met the assumptions for mass balance calculations were rejected, our results nonetheless showed apparent accumulation in 7% of all calculations done for the four cations and the 21 catchments (Table 3.4). Some authors attributed soil enrichment in base cations to long-term exogenous material inputs such as mass wasting or aeolian deposition (Chadwick et al., 1999; Favilli et al., 2009; Bern et al., 2010). Based on geomorphologic and stratigraphic data, such addition are unlikely for our study area. Similarly, the atmospheric deposition of BC appears too low to compensate for BC losses due to leaching or tree uptake in the study area (Houle et al., 1997; Duchesne and Houle, 2008). Biocycling processes, which result in the net upward movement of some elements in the soil, could however influence estimates of base cation budgets, in particular those of K (Figure 3.2). Another possibility is that the assumption of the initial homogeneity of parent material was not met in some profiles with potential consequences on the estimated net cation fluxes, as it seems to be the case for Ca and Mg at the Daniel watershed. Possible heterogeneity of the initial material may also explain the enrichment of the surface horizons in Na at the Clair site. These results suggest that potential bias could be associated with the BC weathering rates estimated with the profile mass balance method (Futter et al., 2012). We nonetheless used the data for the 49 profiles in the subsequent statistical analysis of the relationships between BC weathering rates and environmental factors or soil properties. Note that the resulting statistical relationships were either unaffected or only weakly affected by the inclusion, or not, of the apparent BC accumulation values in the data set (data not shown).

3.5.2 Relationships between BC weathering rates and environmental conditions

Spatial variability in BC weathering rates involves complex interactions between environmental factors and soil properties (Pope et al., 1995). In this study, a total of four distinct environmental variables (elevation and percent deciduous canopy cover) and soil properties (soil surface area and soil albite content) were significantly associated to the spatial variations in the long-term BC weathering rates of individual base cations (Figure 3.4). The soil surface area was strongly correlated with BC weathering rates, notably Ca and Mg. Surface area has been found to correlate positively to BC release rates (Hodson et al., 1998; Holmqvist et al., 2003). The amount and density of exposed soil mineral surfaces accessible to the soil solution determine the intensity of weathering reactions because dissolution occurs on these wetted reactive surfaces (Velbel, 1985, 1993; Holmqvist et al., 2003).In addition, the surface area reflects not only the texture but also the mineralogical composition of soils which, in this study, are dominated by quartz, K-feldspars, plagioclases, albite and hornblende, with micas, pyroxenes, calcite and phyllosilicates as accessory minerals (Houle et al, 2012a). Of note, are the positive relationships between soil surface area and hornblende (R = 0.55; $p < 0.05$), pyroxene (R = 0.61; $p <0.05$) and vermiculite (R = 0.53; $p <0.05$) contents in our soils. Although these minerals were not found to be significant in the statistical analyses, hornblende and pyroxene nonetheless represent two major sources of Ca in soils whereas pyroxene and vermiculite are Mg providers (Houle et al., 2012a; Watmough and Aherne, 2008; White et al., 1999). The strong positive link between Ca and Mg rates, and surface area in Figure 3.4 in part reflects these relationships. Similarly, albite constitutes an important source of Na in the soils (Dorn, 1995) as illustrated by the positive association between Na weathering rates and soil albite content on axis 2 of the RDA (Figure 3.4).

The percentage of deciduous canopy cover was strongly positively linked to BC weathering rates. The 21 watersheds included in this study were distributed over two vast bioclimatic domains structured along a global southwest to northeast bioclimatic gradient: the northern temperate subzone, in the south,and the lower boreal subzone, in the north. The forest vegetation domains were already established in the study area some 6,000 years ago and they generally followed the same geographic distribution as today, a fact revealed by the analysis of pollens from stratified lake sediments (Richard, 1995). Their relative species composition varied to some extent through time but we can reasonably assume that the dominant vegetation types remained relatively stable. This millennium-scale geographic stability of major vegetation domains in southern Quebec suggests that vegetation had chemical and physical impacts on soils over the long-term in the study area and that the imprint of each vegetation domain was quite well constrained geographically.

The strong positive association between the nature of vegetation cover and BC weathering rates results from the combined effect of the biochemical and biomechanical activities of tree roots in the soils (Egli et al., 2006, 2008). The vegetation abundance, density and composition impact on the production by roots of acidic and complexing compounds in soils, a class of substances favoring mineral dissolution reactions (Wilson, 2004; Egli et al., 2006, 2008; Williams et al., 2007). The production of organic substances, from low molecular weight organic acids to complex humic substances, during the decomposition of leaf and root litter is also known to promote mineral weathering (Buurman, 1987; Drever, 1994). One of the key plant-driven processes contributing to the generation of corrosive conditions in soils is the uptake of cationic nutrients by tree roots (Hinsinger and Courchesne, 2008). Because cation uptake by plants is balanced by the release of an equivalent amount of protons to the soil solution, higher plant activity will stimulate the dissolution of minerals in the root zone of the soil, hence favoring the release of base cations (Hinsinger and Courchesne, 2008).

One of the main contrasts between vegetation domains are the climatic conditions under which they prevail. Although total precipitation increases along a southwest to northeast gradient in the study area, the northern temperate subzone of the southwest receives proportionally more precipitation as rain and has a higher mean air temperature than the lower boreal subzone of the northeast. In the latter subzone, frost days are more frequent, snow cover lasts longer and the growing season is shorter compared to the southwest. It follows that biological productivity, in a general sense, and the decay of soil organic matter and the associated production of acidic organic compounds, in particular, are more intense in the watersheds covered by deciduous vegetation than in the coniferous-dominated lower boreal subzone. Previous results from a soil climosequence in the Alps of northern Italy (Egli et al., 2003) have however shown that the combined effect of temperature, water percolation rate and vegetation have led to increased weathering rates in the alpine site covered by mature coniferous forests as compared to subalpine areas. In short, and although master climate variables like temperature and precipitation were not significantly associated to weathering rates in this study, it appears that the impact of vegetation on weathering is, at least in part, mediated by underlying climatic factors controlling the geographic distribution of vegetation domains and the intensity of biological activity and organic matter decay at the scale of millennia.

In the study area, watershed elevation was negatively correlated to both soil surface area (R = -0.69; $p < 0.05$) and the percent deciduous canopy cover (R = -0.55; $p < 0.05$) and, consequently to Ca and Mg weathering rates (Figure 3.4). The negative relationship between elevation and BC weathering rates is consistent with observations from Riebe *et al.* (2004) reporting decreasing rates of mineral weathering with increasing elevation for sites located along a two-km ridgeline transect in the Santa Rosa Mountains, Nevada. In our study area, average elevation was higher in catchments of the lower boreal subzone of the northeast than in the northern temperate subzone of the southwest. The negative relationships between elevation and BC weathering rates may thus be due in part to the fact that the rate of organic matter decay was higher at lower elevation sites (Wang *et al.*, 2000; Riebe et al., 2004). Therefore, and similar to the effect of vegetation, the underlying impact of climatic conditions need to be considered when interpreting the role of elevation on weathering rates. Not only does temperature decreases and precipitation as snow increases with altitude but the duration of active pedogenesis also decreases while going up on a toposequence (Birkeland, 1999). As such, and despite the fact that the mineralogy of the parent material was not uniform through our 90 000 km^2 study area, the coarser soil texture observed in our 49 profiles at higher than at lower altitude is considered to reflect less intense soil formation dynamics. The same interpretation is valid for the presence of shallower solum at more elevated sites. Indeed, because the mean soil temperature decreases with elevation, water remains in the solid state longer than at lower elevation thus reducing the period of time during which organic matter decomposition, mineral dissolution and solute leaching processes can be active on a yearly basis. In such context, one of the most probable results will be less intense weathering and pedogenesis at higher sites. The repetition and integration of this elevation-climate effect on soil formation at the scale of centuries or millennia contributes to explain the negative link between elevation and BC, here Ca and Mg, weathering rates in this study.

3.6 Conclusion

Elemental mass balance calculations showed that Ca, Mg, Na and K weathering rates in podzols of southern Quebec averaged 0.16, 0.10, 0.09 and 0.06 kmol_c ha^{-1} an^{-1}, respectively, since the end of the last glaciation. A strong spatial gradient was found in BC weathering rates across the studied area. Redundancy analysis (RDA) was performed to constrain BC weathering rates using key environmental factors and soil properties. According to our results, soil surface area, percent deciduous canopy cover, elevation, as well as soil albite content were the main determinants of BC weathering rates. In the study area, elevation and latitude jointly determine the climatic conditions whereas the proportion of deciduous and coniferous is influenced by the hydro-climatic conditions. Because they are so strongly interconnected, the singular effects of precipitation, temperature and vegetation type on weathering rates cannot be unequivocally separated.

While soil properties should remain relatively stable in the near future, climatic conditions are expected to change considerably faster during this period in the northern hemisphere. In this context, new methodological approaches are needed to isolate and quantify the exclusive contribution of hydro-climatic variables on soil mineral weathering, in both time and space. This is required to favour a better understanding of the potential impacts of climate changes on mineral weathering and on its ability to provide the soluble base cations needed to populate the soil exchangeable complex reservoirs and to satisfy the nutritional needs of the vegetation.

3.7 Acknowledgments

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3.8 Appendix B

Supplementary data

Table S3.1: Mineralogical composition[1] (%) of the composite B-horizons for the 21 watersheds. Mean (SE) are reported.

Watershed	K-Feldspar	Plagioclase	Albite	Hornblende	Pyroxene	Garnet	Biotite	Muscovite	Fe-Chlorite	Vermiculite	Apatite	Kaolinite	Calcite	Quartz
Adanys	16.7 (0.8)	10.0 (0.8)	25.6 (0.8)	8.6 (0.9)	1.4 (0.5)	0.3 (0.5)	2.1 (0.1)	3.0 (0.4)	0.0 (0.0)	0.8 (0.5)	0.6 (0.1)	0.3 (0.2)	0.0 (0.0)	30.6 (1.8)
Blais	15.3 (0.5)	6.6 (0.1)	4.7 (0.0)	18.7 (0.6)	1.9 (0.0)	0.9 (0.0)	3.8 (0.2)	0.0 (0.0)	0.0 (0.0)	0.7 (0.4)	0.6 (0.4)	0.3 (0.1)	2.0 (0.8)	44.8 (1.1)
Boisvert	16.3 (0.3)	9.7 (1.0)	20.4 (2.4)	10.3 (1.4)	1.6 (0.2)	0.9 (0.1)	4.4 (0.9)	0.0 (0.0)	0.0 (0.0)	0.5 (0.7)	0.5 (0.2)	0.0 (0.1)	0.0 (0.0)	35.3 (4.1)
Chomeur	17.5 (0.6)	9.9 (0.7)	24.9 (0.3)	8.7 (1.3)	1.6 (0.2)	0.4 (0.3)	0.0 (0.0)	5.0 (1.1)	0.0 (0.0)	0.8 (0.7)	0.7 (0.2)	0.1 (0.2)	0.0 (0.0)	30.5 (2.1)
Clair	16.4 (1.2)	7.7 (0.6)	5.1 (1.4)	23.6 (3.5)	2.4 (0.3)	1.0 (0.3)	0.7 (1.2)	3.1 (1.5)	0.2 (0.3)	1.0 (1.4)	0.6 (0.2)	0.4 (0.5)	2.6 (1.1)	35.1 (4.4)
Daniel	18.1 (0.6)	10.3 (0.1)	25.5 (0.8)	9.1 (0.3)	1.7 (0.0)	0.6 (0.2)	0.9 (0.1)	3.0 (0.1)	0.0 (0.0)	1.9 (0.0)	0.6 (0.0)	0.3 (0.4)	0.0 (0.0)	28.1 (1.0)
David	14.2 (1.4)	7.3 (0.8)	4.9 (0.8)	20.9 (2.1)	2.2 (0.3)	0.4 (0.4)	0.9 (0.8)	3.2 (1.3)	0.5 (0.8)	0.5 (0.6)	0.6 (0.2)	0.1 (0.1)	2.2 (0.5)	42.1 (4.4)
Des joncs	15.1 (0.3)	11.6 (0.4)	24.1 (0.6)	12.1 (0.7)	2.0 (0.1)	0.7 (0.4)	0.0 (0.0)	3.3 (0.3)	0.0 (0.0)	1.0 (0.5)	0.6 (0.2)	0.0 (0.0)	0.3 (0.3)	29.2 (1.5)
Despapillons	16.7 (1.4)	7.1 (0.6)	5.4 (0.2)	19.3 (1.5)	2.0 (0.2)	1.0 (0.3)	3.9 (0.4)	0.0 (0.0)	0.0 (0.0)	1.0 (0.3)	0.6 (0.1)	0.3 (0.3)	1.8 (0.7)	41.0 (0.9)
Duck	16.0 (0.3)	6.7 (0.1)	4.5 (0.1)	20.1 (0.2)	2.0 (0.1)	1.2 (0.6)	0.0 (0.0)	2.8 (1.2)	0.1 (0.2)	1.9 (1.2)	1.0 (0.5)	0.8 (0.4)	1.1 (1.0)	41.9 (1.3)
Eclair	15.9 (0.5)	12.7 (0.1)	27.0 (1.2)	12.7 (0.6)	2.19	1.0 (0.9)	0.0 (0.0)	4.6 (0.8)	0.0 (0.0)	0.0 (0.0)	0.5 (0.1)	0.0 (0.0)	0.0 (0.0)	23.5 (1.3)
Fauvette	15.1 (0.8)	12.8 (0.6)	24.7 (0.7)	16.4 (2.9)	2.5 (0.3)	0.6 (0.6)	1.5 (0.7)	2.1 (0.5)	0.2 (0.4)	1.1 (1.0)	0.7 (0.5)	0.8 (0.7)	0.0 (0.0)	21.5 (2.5)
General-	16.8 (1.5)	10.0 (0.5)	19.2 (1.3)	11.6 (0.2)	1.7 (0.1)	0.6 (0.6)	3.1 (1.5)	0.0 (0.0)	1.3 (0.3)	2.0 (1.0)	0.7 (0.3)	0.6 (0.6)	0.3 (0.5)	32.1 (0.9)
Josselin	20.1 (0.6)	9.4 (0.5)	23.8 (0.5)	8.3 (0.9)	1.5 (0.1)	0.5 (0.9)	6.2 (1.2)	0.0 (0.0)	0.0 (0.0)	0.4 (0.3)	1.0 (0.2)	0.2 (0.1)	0.0 (0.0)	28.6 (0.8)
Laurent	19.4 (4.2)	9.5 (1.1)	19.2 (2.8)	11.1 (2.3)	1.6 (0.3)	2.0 (0.6)	0.6 (1.1)	3.1 (1.2)	0.3 (0.5)	0.8 (0.9)	0.4 (0.1)	0.3 (0.5)	0.0 (0.0)	31.6 (1.6)
Lemaine	18.0 (1.2)	10.0 (0.6)	25.4 (1.4)	9.3 (2.3)	1.7 (0.3)	1.4 (0.5)	2.9 (0.5)	1.4 (1.3)	0.0 (0.0)	0.7 (0.8)	1.1 (0.8)	0.1 (0.2)	0.0 (0.0)	28.1 (2.0)
McLoed	20.9 (1.2)	10.3 (1.0)	22.4 (0.9)	11.0 (1.4)	1.8 (0.2)	1.0 (0.9)	0.0 (0.0)	6.3 (0.5)	0.0 (0.0)	0.1 (0.0)	1.3 (0.4)	0.1 (0.1)	0.0 (0.0)	25.0 (2.3)
Najoua	17.7 (1.6)	9.5 (0.7)	23.0 (0.5)	8.9 (1.4)	1.6 (0.2)	0.3 (0.6)	0.0 (0.0)	5.5 (1.3)	0.0 (0.0)	0.4 (0.4)	0.4 (0.1)	0.0 (0.0)	0.0 (0.0)	32.7 (2.2)
Pothier	15.1 (0.5)	13.2 (0.6)	26.2 (0.4)	14.1 (1.4)	2.3 (0.1)	1.0 (0.9)	0.0 (0.0)	2.6 (1.0)	0.3 (0.5)	1.5 (0.6)	0.8 (0.2)	0.0 (0.0)	0.0 (0.0)	23.1 (1.4)
Thomas	17.3 (0.6)	11.3 (0.3)	24.3 (0.2)	11.6 (0.4)	1.9 (0.1)	1.1 (0.1)	0.0 (0.0)	4.7 (0.3)	0.0 (0.0)	0.3 (0.4)	0.7 (0.1)	0.0 (0.1)	0.0 (0.0)	26.7 (0.8)
Truite-Rouge	15.5 (0.6)	5.8 (0.4)	4.8 (0.2)	15.1 (1.9)	1.5 (0.2)	0.0 (0.0)	1.2 (0.0)	4.4 (0.1)	0.0 (0.0)	0.4 (0.4)	0.6 (0.3)	0.1 (0.0)	0.5 (0.5)	50.3 (2.4)
Mean (SE)	16.9 (1.7)	9.6 (2.1)	18.3 (9.0)	13.4 (4.7)	1.9 (0.3)	0.8 (0.4)	1.5 (1.8)	2.8 (1.9)	0.1 (0.3)	0.9 (0.6)	0.7 (0.2)	0.2 (0.2)	0.5 (0.9)	32.5 (7.7)

[1] Average weighted mineralogy (weight %) according to the UPPSALA model (adapted from Houle *et al.*, 2012)

3.8 Section de transition 3-4

Dans le chapitre précédent, nous avons estimé des taux d'altération de cations basiques à l'aide de la méthode du bilan de masse en profil de sol (PEDON). Ces taux d'altération étaient généralement inférieurs à ceux obtenus au moyen de la méthode du budget intrant-extrant (WATERSHED) rapportés dans le chapitre 2 pour les 21 bassins versants situés au sud du Québec. Ils étaient également inférieurs à ceux simulés à l'aide du modèle géochimique PROFILE (MODEL) dans une étude antérieure (Houle et al., 2012) pour les mêmes bassins versants. Des analyses préliminaires sur les facteurs qui pourraient expliquer ces différences ont suggéré que les estimations inférieures obtenues avec la méthode du bilan de masse en profil de sol n'étaient pas systématiques sur l'ensemble des 21 sites et avaient tendance à être associées aux bassins hydrographiques contenant de la calcite et ayant les plus grands réservoirs échangeables parmi ceux étudiés.

Dans le chapitre 4, nous avons comparé les trois méthodes pour mieux comprendre leur fonctionnement, permettant ainsi de répondre à l'objectif spécifique 3 de la thèse. Nous avons utilisé des techniques statistiques non paramétriques (coefficient de corrélation de rang de Kendall, analyse de régression de Passing et Bablok) pour examiner la concordance entre les trois méthodes et nous avons comparé leur performance relative en relation avec des conditions de site. Les résultats présentés dans le chapitre 4 montrent une bonne concordance entre les méthodes WATERSHED et MODEL, alors que la concordance entre ces méthodes et PEDON est faible. Par ailleurs, ayant observé que les taux d'altération estimés par la méthode PEDON n'étaient significativement corrélés ni à l'abondance de calcite dans les sols ni à la taille du pool de cations échangeables, contrairement aux taux estimés par les deux autres méthodes, nous avons émis l'hypothèse que les taux d'altérations sont sous-estimés par la méthode PEDON dans les sites contenant la calcite. Ces résultats ont des implications importantes au niveau du choix des méthodes d'estimation des taux d'altération des cations basiques dans des études géochimiques. Le choix de certaines méthodes doit tenir compte non seulement des objectifs de l'étude, mais également des conditions de site.

Le chapitre 4 de la thèse a fait l'objet de publication sous forme d'article dans la revue *Catena*[3]. L'article a été réalisé en collaboration avec Daniel Houle, Christian Gagnon et François Courchesne. J'ai effectué la recherche et compilé l'ensemble des données pour analyse. J'ai fait le

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[3] Augustin, F., Houle, D., Gagnon, C., Courchesne, F. 2016. Evaluation of three methods for estimating the weathering rates of base cations in forested catchments. Catena, 144 :1–10

choix de tests adéquats pour réaliser les analyses statistiques, et j'ai rédigé le manuscrit. Tous les travaux ont été réalisés sous la supervision de François Courchesne et Daniel Houle (directeur et co-directeur du projet, respectivement). Les co-auteurs ont contribué à l'amélioration du manuscrit en faisant des corrections, des ajouts et des recommandations.

Chapitre 4. Evaluation of three methods for estimating the weathering rates of base cations in forested catchments

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4.1 Abstract

This paper investigates three techniques that are commonly used to generate estimates of base cation (BC) weathering rates, i.e. the profile mass balance (PEDON), the watershed input-output budget (WATERSHED) and the PROFILE model (MODEL). These methods were compared for their relative performance in estimating BC weathering rates for 21 watersheds located in southern Quebec that vary with respect to hydro-climatic conditions, soil properties and forest cover. Average total BC weathering rates for the 21 watersheds were 0.41± 0.09 (± SE), 1.20± 0.17 and 1.71± 0.22 $\text{kmol}_c\ \text{ha}^{-1}\ \text{yr}^{-1}$ for PEDON, WATERSHED and MODEL, respectively. Passing and Bablok regression analysis demonstrated good agreement between WATERSHED and MODEL {regression formula: WATERSHED = -0.08 + 0.74 MODEL, with 95% CI for intercept [-1.13; 0.25] and for slope [0.40; 1.43]}, while poorer agreements were observed between these two methods and PEDON. Contrary to the WATERSHED and the MODEL methods, BC weathering rates obtained with PEDON were not significantly associated with the spatial variation of the soil calcite content and of the size of the soil exchangeable BC pools. We hypothesized that in the calcite-containing watersheds, the performance of PEDON was negatively impacted by environmental conditions that favored the partial dissolution and leaching of the calcite contained in the initial parent material, including in the material situated at the base of the profile (C horizon).

4.2. Introduction

Soil mineral weathering is a key component of biogeochemical cycles in terrestrial ecosystems (Sverdrup and Warfvinge, 1988; Riebe et al., 2004; Whitfield et al., 2010). It involves major changes in the mineral assemblage, chemical composition and physical properties of soils (Murakami et al., 2003; Whitfield et al., 2006), and therefore contributes chiefly to soil development. Mineral alteration, notably silicate weathering, is recognized as an important long-term control on atmospheric CO_2 (Berner and Lasaga, 1989). It also plays a central role on plant nutrition by releasing nutrients, like base cations (BC = Ca, Mg, K, Na), from minerals into an available form that can be taken up by plants. The weathering process further contributes to the neutralization of acidic compounds in soils (Bain et al., 1993; Mortatti and Probst, 2003; Whitfield et al., 2010). Therefore, quantifying long-term mineral weathering rates is crucial to improve our understanding of the biogeochemical cycling of elements in terrestrial ecosystems, to evaluate the relative sensitivity of ecosystems to environmental stresses and to further develop sustainable forest management strategies.

The evaluation of BC weathering rates requires reliable quantitative methods of analysis. However, there is no recognized standard procedure for quantifying the rate at which minerals release BC under field conditions. Estimates of BC weathering rates have been obtained from a number of methodological approaches such as laboratory dissolution experiments (Chou and Wollast, 1984; Oelkers et al., 1994; Huertas et al., 1999; Amram and Ganor, 2005), test-mineral techniques (Ranger et al., 1990), strontium isotope ratio methods (Åberg et al., 1989; Shand et al., 2007), geochemical modeling using PROFILE (Sverdrup and Warfvinge, 1993; Whitfield et al., 2006, 2010; Sverdrup, 2009; Houle et al., 2012; Whitfield and Reid, 2013) or MAGIC (Cosby et al., 2001; Whitfield et al., 2006), watershed input-output budgets (Clayton, 1979; Velbel, 1985; White and Blum, 1995; Velbel and Price, 2007) and soil profile mass balance calculations (Brimhall et al., 1991a; White et al., 1998; Egli and Fitze, 2000; Anderson et al., 2002). The empirical clay-based Soil Texture Approximation was also used to assess weathering rates in Canada and the United States (Koseva et al., 2010). Each estimation method is based on specific assumptions, and their performance therefore largely depends on how far the data and field conditions can meet these requirements.

It is generally accepted that several environmental factors act simultaneously to influence the rates at which BC are released through the weathering of minerals. The main factors include variables related to soil properties, biotic activity and climatic conditions (Sverdrup and Warfvinge, 1988; Courchesne et al., 2002; Wilson, 2004; Gordon, 2005; Egli et al., 2006; Ouimet, 2008; Augustin et al., 2015a, 2015b). However, no single estimation method integrates all these factors specifically. Comparing the performance of the methods under different site conditions is thus needed to better understand the functioning of the methods and to identify possible bias that can be induced by some field conditions. Amongst the methods cited above, the watershed input-output budget, the soil profile mass balance and the geochemical model PROFILE are recurring in the scientific literature, and have been used, alone or in combination, at diverse geographic locations. The first approach takes into account pedogenic processes occurring at the scale of the catchment, whereas the other two methods are based on soil data collected from the rhizosphere, at the scale of the soil profile. Moreover, modelling with PROFILE and the watershed budget method are considered to reflect contemporary weathering fluxes, whereas soil mass balances yield historic weathering rates covering the total duration of soil genesis.

Several authors conducted comparative analyses across estimation methods (Kolka et al., 1996; Starr et al., 1998; Hodson and Langan, 1999; Ouimet and Duchesne, 2005; Whitfield et al., 2006; Houle et al., 2012). Such comparison is of interest because, for example, critical loads estimates (Hodson and Langan, 1999; Mongeon et al., 2010; Futter et al., 2012) are often based on weathering rates obtained from methods that differ across studies. On the one hand, some studies have shown that, for a given watershed, little overall difference was found between the weathering rate estimates when different methods were used (Starr et al., 1998; Houle et al., 2012). For example, Starr et al. (1998) calculated weathering rates for four soil profiles using three different methods (soil profile mass balance, Ca + Mg/temperature sum regression, and the PROFILE model). They observed that the weathering rates calculated by the three methods were similar, although the soil profile mass balance method gave the highest values and PROFILE the lowest. On the other hand, many studies found significant differences in weathering rates calculated using different methods simultaneously (Langan et al., 1995, 1996, 2001; Hodson and Langan, 1999; Watmough and Dillon, 2003). Langan et al. (1995) observed that BC weathering rates obtained with the soil profile mass balance method were significantly lower than those simulated with PROFILE in Scottish soils. With a few exceptions, these studies were performed for a limited number of sites and their results were often not analyzed statistically. Houle et al. (2012) evaluated base cation weathering rates in 21 watersheds located on the Canadian Shield that were part of the Québec lakes network, using both the watershed input-output budget and the geochemical model PROFILE. They found that Ca and Mg weathering rates simulated with the PROFILE model were significantly correlated with rates estimated using the watershed budget method. The BC weathering rates reported by Augustin et al. (2015) for southern Quebec using the soil profile mass balance method were, however, generally lower than those obtained by Houle et al. (2012) for the same 21 catchments with the watershed input-output model and PROFILE model. Preliminary investigations (Houle, unpublished data) into the factors explaining these differences suggested that the lower estimates yielded by the soil profile mass balance method were not systematic across sites and tended to be associated with catchments containing soil calcite and having the largest soil exchangeable BC reservoirs among the studied watersheds.

Overall, the above considerations suggest that our understanding of the relative performance of these commonly used methods for estimating BC weathering rates is still incomplete. In this context, the primary objective of this analysis was to compare the soil profile mass balance method with both the watershed input-output budget calculation and the geochemical model PROFILE. In this endeavour, we seek: 1) to establish the concordance/discordance between the methods for estimating the sum of Ca, Mg, Na and K weathering rates (or total BC weathering rates), and 2) to explain their relative performance under a spectrum of environmental conditions.

4.3. Materiel and methods

4.3.1. Site description

The study area encompasses twenty-one (21) forested catchments of the Québec lakes network (Houle et al., 2004). Briefly, the watersheds cover a wide range of geological, pedological and hydro-bioclimatic conditions (Lachance et al., 1985; Augustin et al., 2015a). They are located on the Canadian Shield, within a ~90 000 km^2 area in southern Québec that is parallel to the St. Lawrence River and bordered by the Ottawa and Saguenay rivers (Figure 4.1). According to Lachance et al. (1985), there are two main types of geological substrates in the area: igneous (granite, syenite, anorthosite) and metamorphic (gneiss, granitic gneiss, paragneiss, marble) rocks. In the southwestern part of the study area, nearly half of the studied watersheds are located in an area where carbonates are present in the soil parent material (Augustin et al., 2015a, 2015b). Most soils have been classified as orthic and gleyed humo-ferric or ferro-humic podzols (Soil Classification Working Group, 1998). They are medium to coarse textured, shallow and acidic. The vegetation is mostly mixed forests dominated by deciduous species such as sugar maple (*Acer saccharum* Marsh.) in the southwest, and by coniferous species, predominantly balsam fir (*Abies balsamea* L.) or black spruce (*Picea mariana* Mill.) in the northeast. In the region, total annual precipitation averages 1162 mm, of which about a third falls as snow. The mean annual air temperature was 2.0 ºC over the last three decades. The characteristics of the studied catchments are described in detail elsewhere (Houle et al., 2004, 2006, 2012; Augustin et al., 2015a, 2015b).

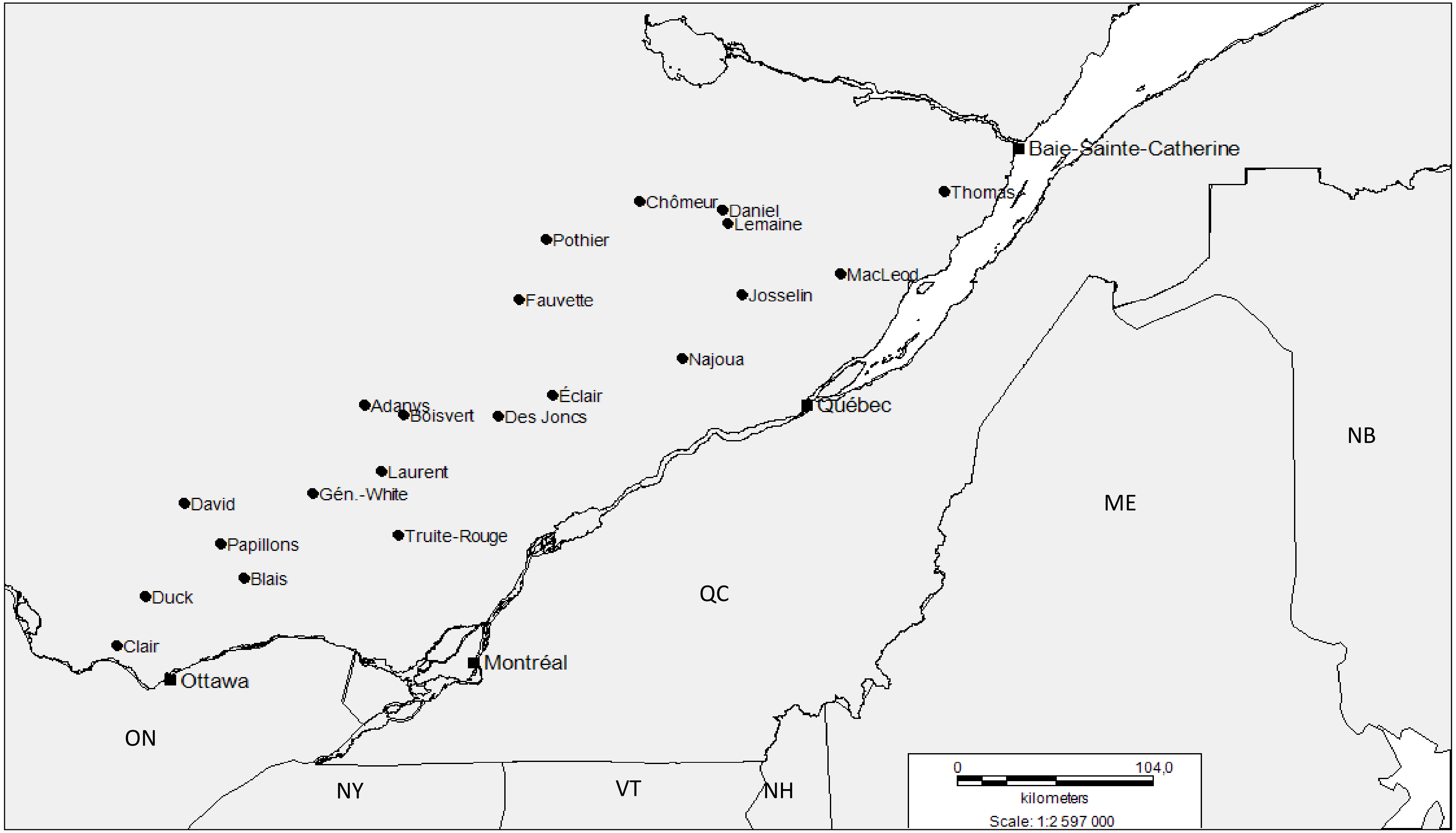

Figure 4.1. Location of the 21 watersheds in southern Québec

4.3.2 Data sources and estimation methods

The total BC weathering fluxes reported in this study for each of the 21 catchments have been calculated from weathering rate data obtained for individual base cations (Ca, Mg, Na and K) using three different estimation methods. The BC weathering rates simulated with the geochemical model PROFILE (Sverdrup and Warfvinge, 1993) as well as those obtained using the watershed input-output budgets (Clayton, 1979; Velbel, 1985; Velbel and Price, 2007) were published in Houle et al. (2012) for the 21 catchments. The soil surface area and mineralogical composition data, used as key inputs to PROFILE, were acquired as described in in Houle et al. (2012) and Augustin et al. (2015a). Briefly, soil mineral surface area was obtained from soil bulk density and soil particle size distribution according to the texture based - Eq. 25 from Sverdrup and Warfvinge (1995). The mineralogical composition of the soil samples was quantitatively estimated from the bulk chemistry, using the stoichiometric model UPPSALA (Sverdrup 1990; Sandén et Warfvinge 1992; Houle et al., 2012; Augustin et al., 2015). The BC weathering rates estimated with the soil profile mass balance method (Anderson et al., 2002; Brimhall et al., 1991a; Egli and Fitze, 2000) were presented in Augustin et al. (2015a). Detailed information on sample collection and handling can be found in Houle et al., (2012) and in Augustin et al. (2015a). For the soil rooting zone, the amounts of NH_4Cl-exchangeable Ca, Mg and K were also determined as described in Houle et al. (2012). The three methods for estimating mineral weathering rates investigated in this study have been described in details and their respective advantages and limitations discussed in several publications (Bain et al., 1993; Hodson et al., 1997, 1998; Hodson and Langan, 1999; Holmquist et al., 2003; Futter et al., 2012; Houle et al., 2012). Here, we summarize the main characteristics and special features of the three methods.

Geochemical model PROFILE (MODEL). The geochemical model PROFILE was developed by Sverdrup and Warfvinge (1988, 1993) for estimating current mineral weathering rates at the soil profile scale. It is a mechanistic mathematical steady-state model where the soil profile is stratified in layers or horizons, each showing different properties. The model estimates base cation weathering rates using independent input data on vegetation, mineralogy, soil properties, atmospheric deposition and climatic conditions. In order to reflect processes occurring under field conditions, properties such as mineral surface area, soil mineralogical composition and effective soil wetting and bulk density have a key role in the estimation of weathering rates with PROFILE (Barkman and Alveteg, 2001; Holmqvist et al., 2003; Sverdrup, 2009). Given constrains associated with the estimation of the input data, PROFILE outputs were shown to bear some uncertainties (Hodson et al., 1997, 1998; Hodson and Langan, 1999). Yet, the PROFILE model was often used to predict weathering rates in studies assessing critical loads for forest soils, notably in Europe and North America (Foster et al., 2001; Skeffington, 2006; Whitfield et al., 2006, 2010; Mongeon et al., 2010; Watmough and Dillon, 2004).

Watershed input-output budget (WATERSHED). The calculation of watershed input-output budgets yields a contemporary estimation of the net annual elemental fluxes at the scale of the whole catchment (Clayton, 1979; Likens et al., 1967; Velbel, 1985; Velbel and Price, 2007). For impervious and unharvested forested catchments where both erosion and sedimentation are negligible, the input fluxes include all forms of atmospheric depositions plus elemental additions due to mineral weathering. The elemental outputs are represented by dissolved and particulate removals in streamflow and by the net annual elemental storage in plants. Under the assumption that the exchangeable soil cation pool and forest biomass are at steady state, the difference between inputs from the atmosphere and outputs in streamwater is interpreted as an estimate of the present-day weathering rate, for a given base cation. Over the last decades, the watershed budget method has been applied in many studies to document mineral weathering rates (Clayton, 1979; Velbel, 1993). Of note is that neglecting the biomass term in the calculations may cause mineral weathering rates to be under- or over-estimated for watershed where biomass is not at steady-state (Cleaves et al., 1970; Velbel and Price, 2007).

Soil profile mass balance (PEDON). The mass balance method (Brimhall et al., 1991a, 1991b; Egli and Fitze, 2000) estimates gains and losses of chemical elements in the weathered horizons of a soil profile, as compared to the unaffected parent material, the C horizon. This method uses the observed vertical variations in total chemical composition to estimate net long-term elemental fluxes in soil profiles since the initiation of pedogenesis. Conservative elements, such as Ti and Zr, are used as geochemical tracers to estimate physical deformations (*i.e* change in soil thickness relative to the initial thickness of the parent material) occurring during soil genesis (Brimhall et al., 1991a, 1991b; Anderson et al., 2002). The mass balance method is based on the following assumptions: 1) the actual geochemical composition of the C horizon is identical to the initial composition of the parent material; 2) the total geochemical composition was uniform throughout the sedimentary column, at the beginning of pedogenesis and 3) the addition of material to the soil surface through atmospheric deposition or sedimentation, as well as losses due to physical surface erosion are minimal, so that the present geochemical profile reflects alteration over time. Annualized historic elemental losses are considered to result from mineral alteration, which is one of the main processes responsible for the development of soil profiles (Johnson and Watson-Stegner, 1987; Brimhall et al., 1991b), and are thus interpreted as weathering rates.

4.3.3 Statistical analysis

Statistical analysis, including descriptive statistics, was performed using MedCalc 9.2.0.0 software (MedCalc, Mariakerke, Belgium). The weathering rates for the sum of the four BC estimated by the three methods were analyzed for central tendency. In order to get a better handle on spatial variation, the relative standard deviation in the sum of BC weathering rates was calculated for each method. A W*ilcoxon* signed-rank test was also performed to evaluate the significance of the difference between the estimates obtained with the three methods.

The Wilcoxon signed-rank test is ideal for the evaluation of a constant difference (bias) between two groups of data (Linnet, 1999; Hawkins, 2002). However, it cannot detect systematic proportional bias. We used Kendall rank correlation coefficient to test if the rank order of BC weathering rates was the same across the study area regardless of the estimation method used (Zar, 1999; Legendre, 2005). It is a non-parametric (resistant to outliers) method that evaluates the strength of the correspondance between two rankings given to the same set of objects. To quantify the agreement between pairs of methods we also used the Passing and Bablok regression analysis (Bablok and Passing, 1985), which is one of the most-cited standard statistical techniques in studies on method comparison. The Passing and Bablok analysis of agreement was performed to establish whether total BC weathering rates values calculated from pairs of methods were statistically comparable. In this non-parametric regression procedure, all possible pairs of x, y points are connected; the slopes of the resulting connecting lines are then ranked, and the median slope is taken to be that of the best-fitting line (Ludbrook, 2010). The intercept is also determined by the medians. According to this linear regression technique, which takes into account the variation in both variables, the slope of the line of best fit is an estimate of the proportional error (agreement), while the intercept is indicative of systematic error between the two methods. If the 95% confidence interval (CI) of the intercept included the value of 0 (meaning that there was no constant systematic bias between the methods compared) and the 95% CI of the slope included the value 1 (indicating that the estimates between the compared methods were free from proportional systematic bias), the methods are considered to be in agreement

(Bablok and Passing, 1985). The Passing and Bablok approach has no special assumptions regarding the distribution of the samples and the measurement errors, and it is robust against outliers (Ludbrook, 2010).

The lack of agreement between two measurement methods is often due to interactions between one method, or the other, with environmental factors (Peterson & Black, 1994). Soil (and in some cases bedrock geology) properties are one of the primary reason for spatial variability in lake chemistry (Marchetto et al., 1995). Houle et al. (2012) reported that catchments containing calcite in the soils were responsible for a strong spatial gradient of BC weathering rates obtained with MODEL for the study area. The lakes were more mineralized and they had higher BC concentrations in the calcite-containing catchments. Moreover, BC concentrations in lake waters were dominated by Ca. Indeed, carbonate rocks weather more readily than the metamorphic rocks mentioned above. We investigated whether soil calcite content across the study area could impact on the performance of the methods and could thus affect the spatial pattern in BC weathering rates. For this purpose, we used analysis of covariance to compare the slopes of the regression lines obtained when soil calcite content is regressed against the weathering rate values estimated with each method. This was motivated by the fact that preliminary analyses showed significant spatial discrepancies between weathering rate estimates obtained with PEDON and those calculated using the WATERSHED or the MODEL method, notably for the southwestern watersheds whose soil mineralogical composition contains calcite and where the vegetation is dominated by deciduous species. Regression analyses were also performed to examine the relationships between the sum of Ca, Mg and K weathering rates obtained with each estimation method, on the one hand, and the size of the soil exchangeable Ca, Mg and K reservoirs, on the other hand.

4.4. Results

4.4.1 Annual BC fluxes from mineral weathering

The total BC weathering rates for the 21 catchments estimated with the three methods were 0.41 (range -0.11 to 1.92), 1.20 (range 0.24 to 3.11) and 1.71 (range 0.58 to 4.46) $\text{kmol}_c\ \text{ha}^{-1}\ \text{yr}^{-1}$ for the PEDON, WATERSHED and MODEL methods, respectively (Table 4.1). The calculated relative standard errors (RSE) varied from 13% (MODEL) to 21% (PEDON), reflecting the elevated spatial variability of BC weathering rates within the study area (Table 4.1).

Yet, significant differences were observed between the BC weathering rates obtained with the three methods, with MODEL yielding the highest value and PEDON the lowest (Table 4.1). Of note is that for specific sites such as Blais, Clair, Daniel, David, Josselin, Truite-rouge, General-White and Lemaine, the PEDON method gave weathering rates that were much lower than those obtained with the two other methods (Table 4.1).

Table 4.1: Weathering rates estimated for the the sum of base cations (Ca+Mg+Na+K) in 21 forested watersheds using three methods.

Watershed	Estimation methods		
	PEDON	WATERSHED	MODEL
	---------------- $\mathrm{kmol_c\ ha^{-1}\ yr^{-1}}$ ----------------		
Adanys	0.40	0.24	1.26
Blais	0.45	2.66	2.52
Boisvert	0.41	0.69	0.77
Chômeur	0.34	0.94	1.06
Clair	0.15	1.76	4.46
Daniel	-0.11	0.55	0.75
David	0.37	2.08	3.36
Des Joncs	0.46	1.24	1.66
Des Papillons	0.65	1.16	2.44
Duck	1.92	3.11	3.24
Éclair	0.49	0.69	2.00
Fauvette	0.63	0.57	2.00
Gén.-White	0.28	2.07	1.70
Josselin	0.09	0.81	1.18
Laurent	0.55	1.92	1.02
Lemaine	0.17	0.80	1.39
McLoed	0.32	0.49	0.77
Najoua	0.42	0.55	1.20
Pothier	0.25	0.76	1.44
Thomas	0.26	1.48	0.58
Truite-Rouge	0.08	0.66	1.12
Median	0.36	1.18	0.81
Mean*	0.41[a]	1.20[b]	1.71[c]
SE[d]	0.09	0.17	0.22
RSE[e]	21	14	13

*Mean values with same superscripts do not differ significantly ($p < 0.05$)

[d] Standard Error

[e] Relative Standard Error (%)

4.4.2 Agreement between the three methods

Based on the Kendall concordance coefficient (K = 0.33; $p < 0.05$), the rank order of total BC weathering rates among sites was quite similar for the method pair WATERSHED/MODEL (Table 4.2). By contrast, the rank order of BC weathering rates varied depending on the method used for the pairs PEDON/WATERSHED and PEDON/MODEL (Table 4.2). The agreement between method pairs was also tested with the linear Passing and Bablok regression analysis. The cumulative sum (CUSUM) test for linearity showed no significant deviation from linearity ($p > 0.05$) for all relationships (Figure 4.2), thus supporting the use of the Passing and Bablok approach.

Table 4.2: Assessment of agreement between the method pairs according to Kendall rank correlation coefficient and the Passing and Bablok technique.

Method Y	Method X	K	Passing and Bablok regression analysis		
			Equation	95% CI Slope	95% CI Intercept
PEDON	WATERSHED	0.18^{a}	y = 0.13 + 0.22 x	[0.06; 0.66]	[-0.35; 0.30]
PEDON	MODEL	0.30^{a}	y = 0.14 + 0.20 x	[0.05; 0.44]	[-0.38; 0.30]
WATERSHED	MODEL	0.33*	y = -0.08 + 0.74 x	[0.40; 1.43]	[-1.13; 0.25]

Note: the Cusum test showed no significant deviation from linearity for all the regression lines ($p < 0.05$)
K: Kendall rank correlation coefficient
^{a}Not significant; $^{*}p < 0.05$

Despite a notable dispersion of data points around the regression line (Figure 4.2), analysis with the Passing and Bablok technique showed the absence of constant difference and proportional bias for the WATERSHED/MODEL pair (Table 4.2; Figure 4.2), thus indicating a significant agreement between the two methods, although some discrepancies can be observed between absolute weathering rate values for some specific sites. However, for the WATERSHED/PEDON and the MODEL/PEDON pairs, large deviations from the 1:1 slope suggested that estimated absolute weathering flux values were not in agreement (Table 4.2; Figure 4.2).

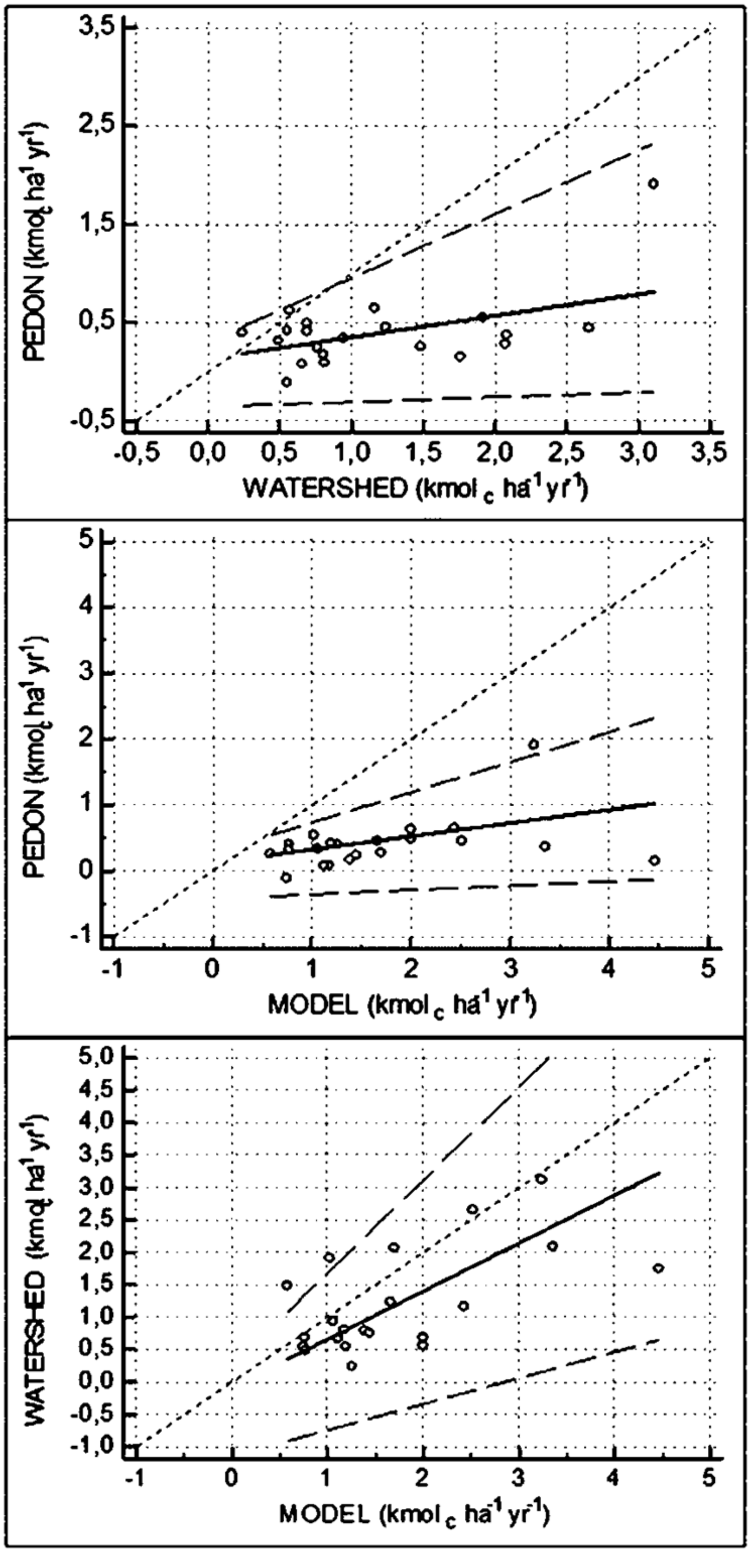

Figure 4.2. Passing and Bablok analyses of method pairs for the estimation of weathering rates for the sum of base cations. A scatter diagram is shown for each method pair, with the regression line (solid line), the confidence interval for the regression line (dashed lines) and the 1:1 line (dotted line).

4.4.3 Spatial pattern of BC weathering rates across the study area

The weathering rate data followed a latitudinal gradient as expressed by the generally decreasing trend observed from the southwest to the northeast of the study area. The relationship between BC weathering rates and latitude was relatively strong for rates simulated with MODEL (R = -0.72; $p < 0.001$) or calculated with WATERSHED (R = -0.62; $p = 0.003$). However, this link was not significant for estimates obtained with PEDON (R = -0.41; $p = 0.066$).

Regression analyses also revealed significant positive slopes for the MODEL-calcite and the WATERSHED-calcite relationships (Figure 4.3). To the contrary, no significant linear regression slope was observed for the PEDON-calcite relationships. Moreover, the 95% confidence intervals for the slope coefficients overlap across the two first relationships, indicating a similar sensitivity of the WATERSHED and MODEL methods to variation in soil calcite content (Figure 4.3). Furthermore, significant positive relationships were observed between the log of the sum of soil exchangeable Ca, Mg and K reservoirs and the sum of Ca, Mg and K weathering rates obtained with MODEL (Figure 4.4A) and WATERSHED (Figure 4.4B), while the relationship was not significant for weathering rates estimated with PEDON (Figure 4.4C). Note that including an outlier in Figure 4.4C led to a significant R^2 of 0.26 (inset).

4.5. Discussion

4.5.1 Quantitative comparison of the three methods

To analyze the relative performance of three methods that are frequently used for estimating mineral weathering rates, a data set of 21 watersheds covering extensive gradients in parent material mineralogy, soil pH, climatic conditions and forest cover was used. These environmental gradients are responsible for a significant part of the spatial variability in the total BC weathering rates reported here, regardless of the method considered (Velbel et al., 1993; Schaller et al., 2009; Houle et al., 2012; Augustin et al., 2015a).

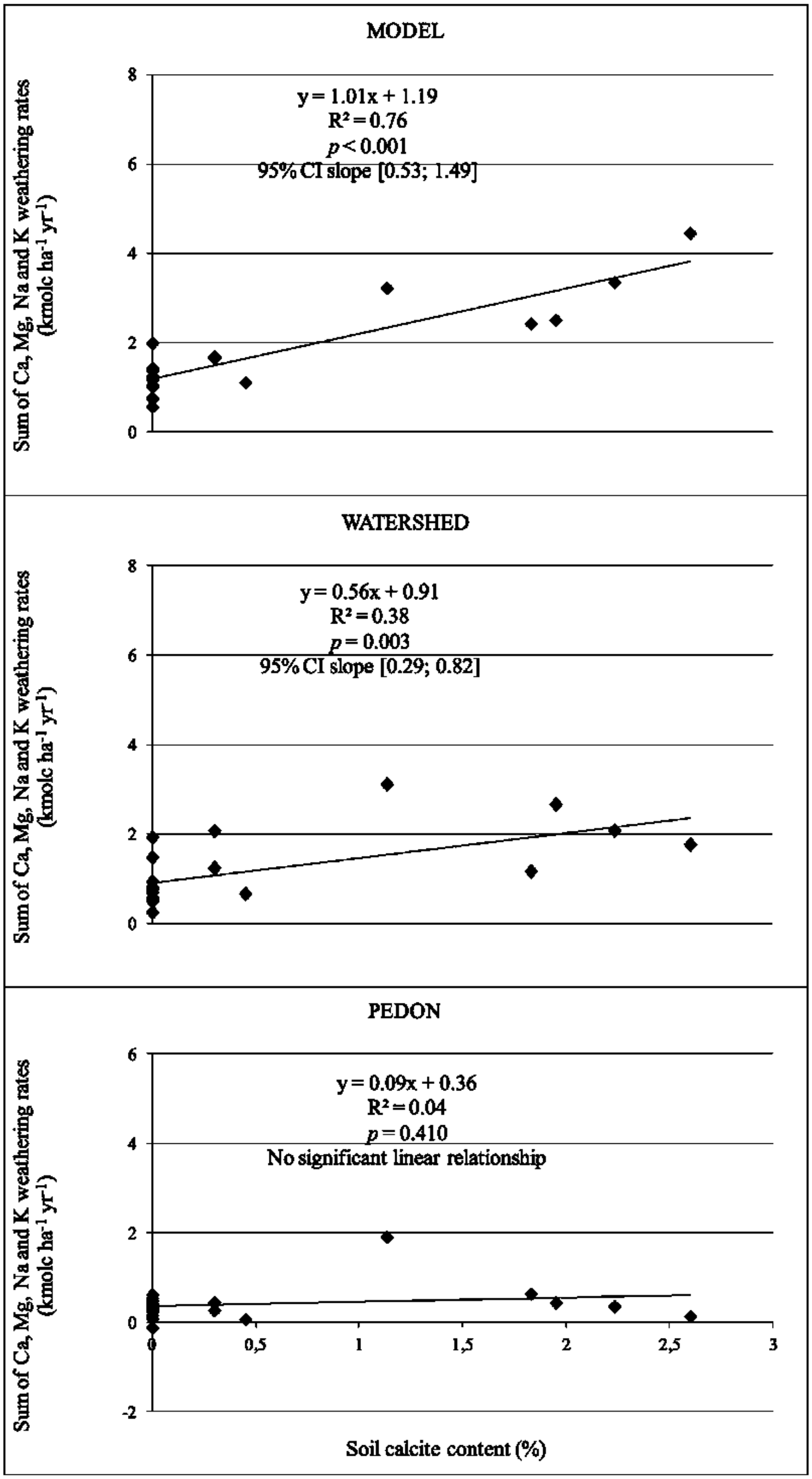

Figure 4.3. Relationships between soil calcite content and the sum of Ca, Mg, Na and K weathering rates estimated using PEDON, WATERSHED and MODEL.

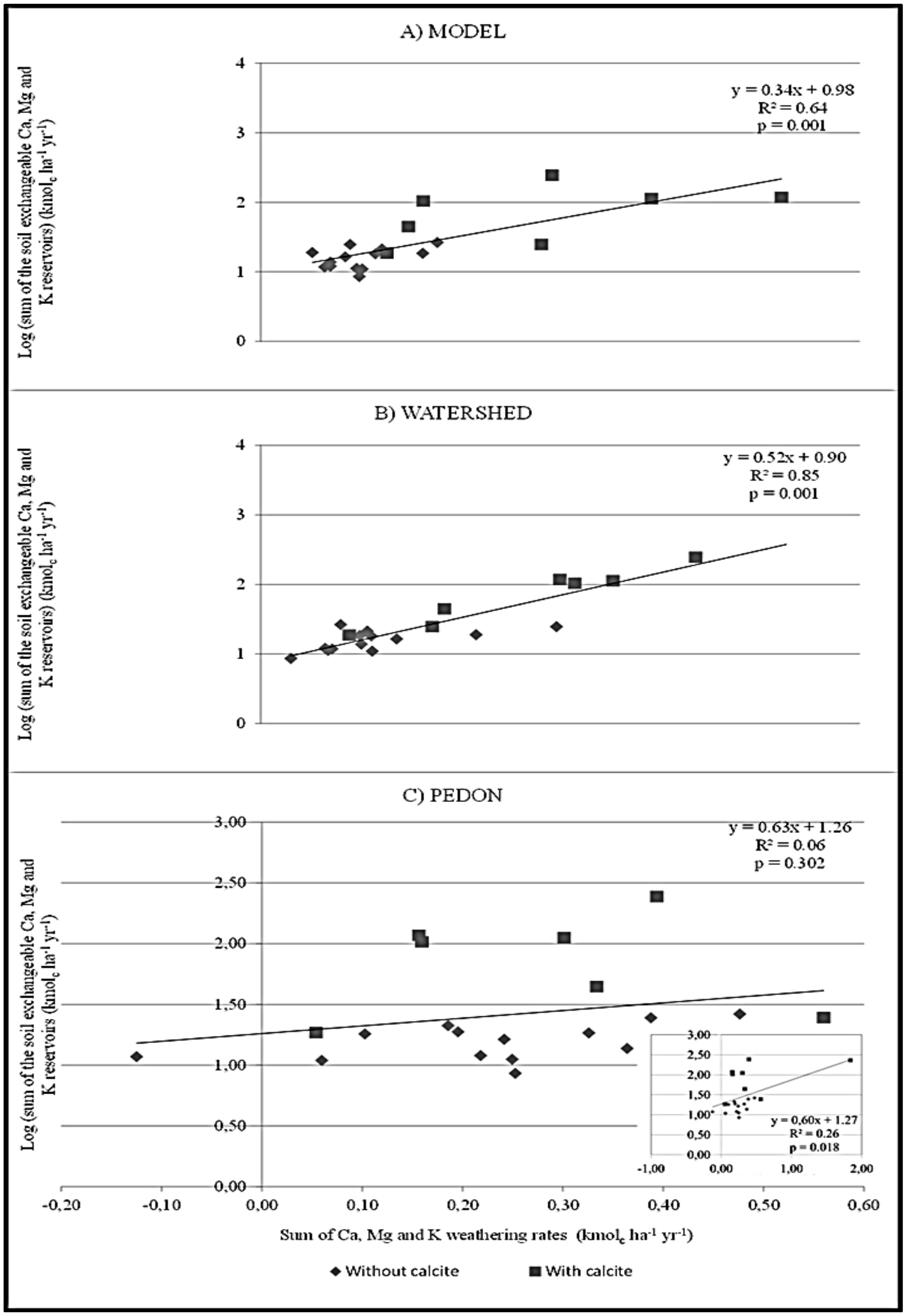

Figure 4.4. Relationships between the sum of Ca, Mg and K weathering rates estimated according to the three methods and the log of the sum of soil exchangeable Ca, Mg and K. Note that filled squares correspond to the eight (8) watersheds containing calcite. For PEDON (Figure 4.4C), the graph in the inset is the relationship obtained by including an outlier that was dropped from the main graph.

Although the three methods yield significantly different average BC weathering rates (Table 4.1), these values are relatively close to each other (averages ranging from 0.41 to 1.71 kmol$_c$ ha^{-1} yr^{-1} while median values range from 0.38 to 1.18 kmol$_c$ ha^{-1} yr^{-1}) considering the fact that the three methods are based on totally different approaches that do not share common input data except for soil horizon thickness that is used by the PEDON and MODEL methods. However, horizon thickness, similar to soil depth, was not a major source of variation in the weathering rates obtained with PEDON in the studied area as compared to the variation explained by factors like soil specific surface area and mineralogy (Augustin et al., 2015a). Therefore, the use of thickness data cannot be invocated as a potential bias favoring a better agreement between the PEDON and MODEL methods. To the contrary, these two methods were in poor agreement (see below).

The concordance or discordance between the methods can be further compared with both the Kendall correlation coefficient and the Passing and Bablok regression approach. The agreement observed between the MODEL and the WATERSHED methods has been reported in Houle et al. (2012), although with a different approach, for the same study area. Rank order of BC weathering rates as assessed with the Kendall correlation coefficient showed a significant agreement between the two techniques. Similarly, the Passing and Bablok regression also showed that weathering rates from MODEL and WATERSHED did not differ by a constant value (95% CI of intercept includes 0). Given the robustness of both the Kendall rank correlation coefficient and the Passing and Bablok regression to outliers, the difference detected between MODEL and WATERSHED methods by the W*ilcoxon* signed-rank test may be attributed to random error.

Despite some discrepancies for specific sites in absolute weathering rate values between the MODEL and WATERSHED methods, they both rank BC weathering rates following a similar order. To the contrary, the PEDON method yields lower total BC weathering rates and showed a lack of agreement with the other two methods. This could be partly explained by the fact that the PEDON method estimates weathering based on long-term changes in total BC content in soil profiles. In the area, soil formation began 10,000 to 13,000 years ago, after glacial retreat (Occhietti, 2007). In contrast, the WATERSHED and MODEL methods yield contemporary BC weathering rate estimates that are calculated from present-day elemental fluxes in watersheds or contemporary soil properties (mineralogy, surface area, chemistry, bulk density and moisture), respectively. Although consistent with data reported for similar environments (Langan et al., 1995, 1996), our results, showing that long-term weathering rates were generally lower than contemporary rates, contrast with weathering estimates for proglacial chronosequences where weathering intensity and BC leaching decreased with time (Anderson, 2007; Miková, 2012). Because of the presence of unweathered, easily weatherable minerals in the exposed fresh till or of the abundance of fine particles, thus exposing large surface area for weathering reactions, rates were higher in the initial stages of soil formation of recently deglaciated soils (Anderson et al., 1997, 2000; Miková, 2012). Moreover, West et al. (2005) reported that weathering rates decreased with the duration of exposure to the weathering environment. Therefore, marked rate discrepancies for some watersheds (particularly those located in the southwest portion of the study area) cannot be resolved by invoking time-scale differences between estimation methods.

4.5.2 Investigating potential sources of discordance between the methods

4.5.2.1 Non-uniformity of the parent material

Compliance with some assumptions of the soil profile mass balance method, notably that relative to the initial uniformity of the parent material, is often imperfect (Schaller et al., 2009). Occurrence of heterogeneity in the parent material may lead to an underestimation of the BC weathering rates obtained with the PEDON method (Courchesne et al., 2002; Augustin et al., 2015). Indeed, because possible exogenous material inputs like aeolian deposition and physical erosion or mass wasting of the soil surface may result in PEDON underestimating BC weathering rates (Chadwick et al., 1999; Favilli et al., 2009; Bern et al., 2010), Schaller et al. (2009) suggested to consider the long-term BC weathering rates estimated as minimum values. However, based on close examination of the geomorphology of soil sampling sites and of soil stratigraphic data, major sedimentation or erosion scenarios are unlikely for our study area (Augustin et al., 2015b).

4.5.2.2 Zr dissolution and migration

Another potential process leading to an underestimation of the BC weathering rates by the PEDON method is the downward migration of Zr in the soil profiles. Migration of Zr towards deeper soil horizons and the associated decrease in Zr concentrations in the surface horizons has been reported for soils under temperate and tropical conditions (Cornu et al., 1999; Shahid et al., 2013). As compared to the sites investigated in these studies, the duration of pedogenesis in southern Québec is however much shorter (10,000 to 13,000 years versus 100,000 to 3,000,000 for the sites investigated in the Cornu and Shahid papers). It follows that the downward mobility of Zr as a result of weathering and leaching processes must be extremely low in our study area. Even if hydro-climatic conditions were globally more favourable to weathering in the calcite-containing southwestern watersheds, we argue that the pH and climatic gradients were not strong enough to significantly increase the dissolution of an insoluble mineral like Zr in the southern part as compared to the rest of the study area. Hodson (2002) conducted an experimental work on Zr mobility and the impact it may have on the calculation of mineral weathering rates in podzols. The results suggested that the level of uncertainty associated with BC weathering rate estimates, when Zr is assumed to be immobile, would probably not be significant in the field.

4.5.2.3 A possible explanation linked to calcite

The 21 watersheds included in this study are distributed along an overall southwest to northeast gradient of decreasing soil calcite content (Houle et al., 2012; Augustin et al., 2015). For instance, Houle et al. (2012) reported that the presence or absence of soil calcite was an important source of variation in total BC concentrations in lake waters across the study area and that its presence is expected to positively influence BC weathering rates. In turn, BC weathering rates are hypothesized to control, at least to some extent, the size and chemical composition of the soil exchangeable BC reservoir in the watersheds (Campbell et al., 2009). Because no absolute reference approach exists to measure BC weathering rates, the results obtained with the three methods, as well as the difference between methods, were investigated in the light of their relationships with relevant soil variables like soil calcite content and the size of the soil exchangeable Ca, Mg and K pools.

Estimates of BC weathering rates obtained with the WATERSHED and the MODEL methods are significantly correlated with soil calcite content but such is not the case for the PEDON method (Figure 4.3). Similarly, the linear relationships between the sum of Ca, Mg and K weathering rates calculated with the WATERSHED and the MODEL methods and the log of the sum of soil exchangeable Ca, Mg and K pools was positive and significant, while no significant linear relationship was observed with the sum of Ca, Mg and K weathering rates obtained with the PEDON method (Figure 4.4). Moreover, the differences in the BC weathering rates obtained between the WATERSHED and PEDON, and between the MODEL and PEDON methods, respectively, were significantly positively correlated to soil calcite content (Figure 4.5). Overall, these data suggest that the discordance between PEDON and the two other methods is somehow the consequence of PEDON underestimating BC weathering rates in soils where calcite is present in the mineralogical assemblage.

Given the spatial gradient in soil calcite content (catchments with calcite are located in the southwestern portion of the study area), a strong gradient is observed in the differences between methods across the study area (Figure 4.6). The catchments of the southwestern portion of the studied area have a vegetation dominated by deciduous species, a higher average annual temperature and a longer growing season, so that biological activity is more intense and their productivity higher than in the northeastern sites. However, site productivity by itself cannot explain the underestimation of BC weathering rates with the PEDON method in the southwestern half of the study area.

Because carbonate is dissolving orders of magnitude faster than silicate minerals such as plagioclase, hornblende or biotite, one should estimate significantly higher BC weathering rates for calcite-containing soils compared to soils developed on granitic material (White et al., 1999; Schroth and Friedland, 2007). Moreover, field studies demonstrated that the carbonate content decreases with increasing age of the soils developed on calcite-containing terrains (White et al., 1999, 2005; Egli and Fitze 2001).

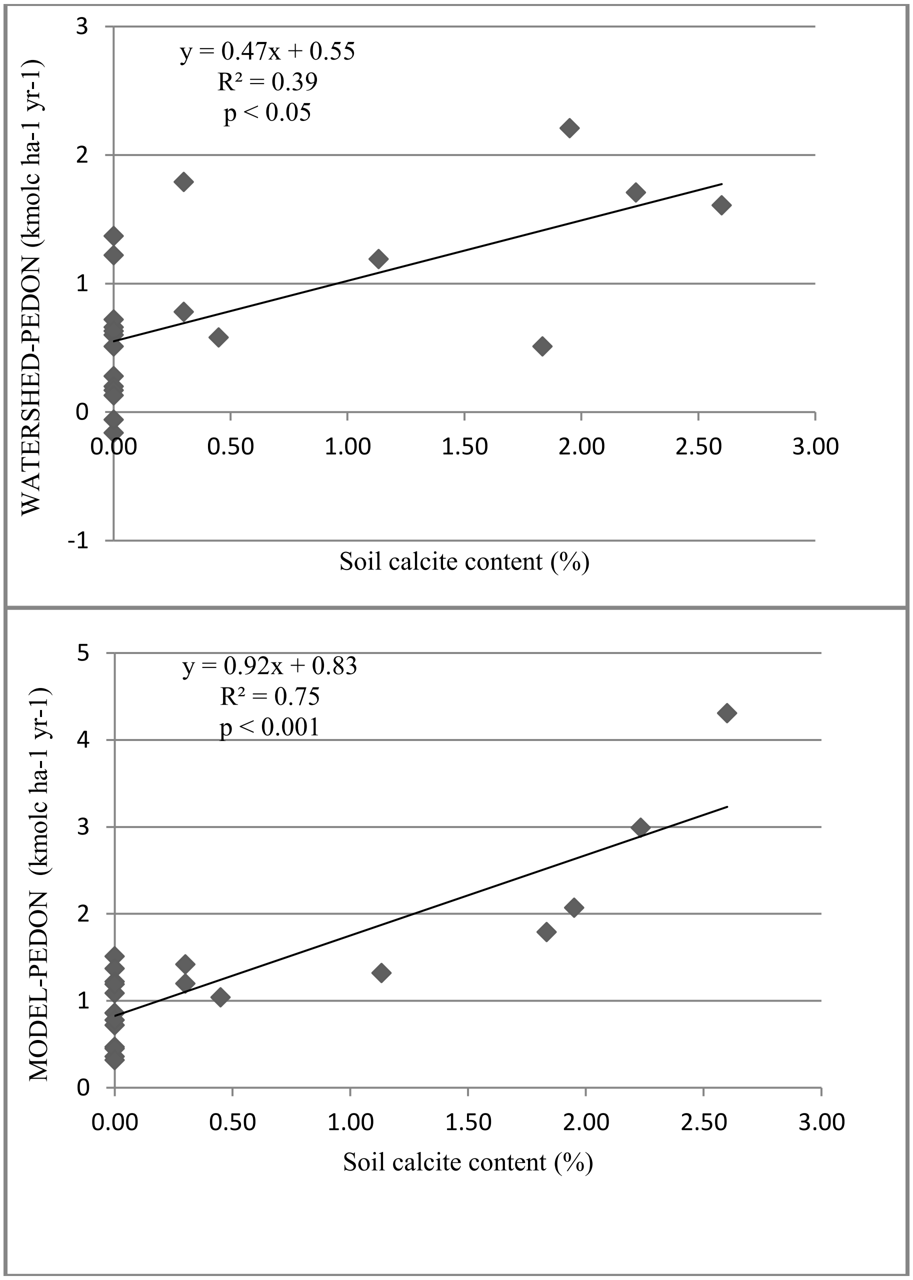

Figure 4.5. Relationships between soil calcite content and the differences between total BC weathering rates obtained with PEDON and the two other methods (WATERSHED and MODEL).

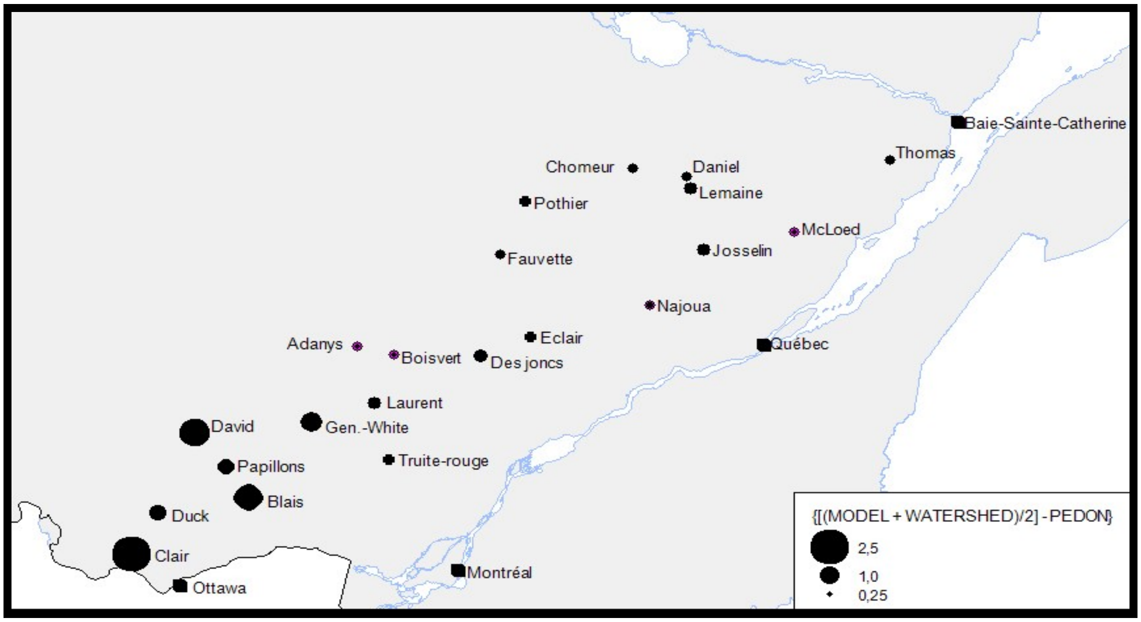

Figure 4.6: Distribution of the difference between the average of BC weathering rates obtained with MODEL and WATERSHED methods and those obtained with PEDON {[(MODEL + WATERSHED)/2] - PEDON} in the study area.

Our observations, suggesting a role for calcite in the underestimation of weathering rates with the PEDON method, are in-line with those of Schroth and Friedland (2007) who found that the PEDON method underestimated long-term weathering rates for soils containing calcite in their parent material compared to soils of similar environment but developed on purely granitic material. These authors argued that calcite in the soil profile would be depleted relative to the original parent material, notably in the lower part of the profile, because of the development of recurring hydrologic conditions favoring calcite weathering and leaching in till-mantled landscapes. These conditions are favored by the presence of a marked contrast in hydraulic conductivity in the soil profile that could be due to the presence of a high-density horizon, of a cemented layer or of impervious bedrock. In sandy permeable soils, such as the podzols of our study area, where water infiltration is rapid, the creation of underground saturated conditions during a hydrologic event can occur on top of such low permeability layers or horizons (James and Roulet, 2009; Ali et al., 2010). In these soils, the saturated, or almost saturated, deep layer represents a second weathering environment in the soil profile (the first one being located at the top of the mineral profile where the high soil acidity leads to intense calcite dissolution), in particular if the saturation process is recurrent. In an aluminosilicate-dominated soil where such a weathering environment is created at depth, the abundance of a soluble mineral like calcite would be progressively reduced compared to that of feldspars and quartz. This would result in a C-horizon that is, at least partly, calcite-depleted, and, consequently, has a lower weathering rate. Of note is that these weathering environments at depth in the profile can be made even more aggressive to minerals by the presence of thick root mats which represent a high H^+ ion source, because the development of the root network is strongly impacted by the presence of high-density or cemented soil layers or by bedrock.

4.6. Conclusion

In this study, three methods commonly used for estimating BC weathering rates were compared using a data set including 21 watersheds varying in soil properties, climate and forest cover. These methods, namely the PEDON, the WATERSHED and the MODEL, yielded significantly different average weathering rates with respective values of 0.41, 1.20 and 1.71 $kmol_c\ ha^{-1}\ yr^{-1}$. However, despite these discrepancies, absolute estimates of weathering rate values were relatively close. Overall, our analysis based on Kendall correlation coefficient and the Passing and Bablok techniques indicated that WATERSHED and MODEL showed good agreement, while PEDON was in poor agreement with the two other methods. The PEDON method also yields weathering rates that were not coherent with regards to the relationships that can be expected with soil calcite content and the size of the soil exchangeable BC reservoirs, contrary to the WATERSHED and MODEL methods. We therefore submit that the discordance between PEDON and the two other methods results from the fact that PEDON appears to underestimate weathering rates for the calcite-containing watersheds located in the southwest part of the area. More research is needed to further investigate these aspects.

4.7 Acknowledgments

This work was funded by Environment Canada (grant number K8C13-09-0301), the National Science Engineering Research Council of Canada (NSERC) (grant number 42251-2010) and the Ouranos consortium (grant number 530010).

4.8 Section de transition 4-5

Cette recherche nous a amené à examiner la variabilité spatiale des taux d’altération contemporains et historiques des cations basiques et à évaluer la performance relative des méthodes d’estimation des taux d’altération des minéraux en relation avec des conditions de site (chapitres 2, 3 et 4). Les résultats obtenus jusqu’ici nous ont permis de comprendre que le climat joue un rôle important (en plus de plusieurs autres caractéristiques des bassins versants) dans la variabilité des taux d’altération des minéraux. Cependant, la grande variabilité des conditions de sites dans l’aire d’étude, tant au niveau des type de sol, de matériel parental, de type de végétation, de topographie et d’autres caractéristiques des bassins, entraine une superposition de gradients, limitant ainsi notre capacité à bien isoler et quantifier l’impact exclusif des facteurs hydro-climatiques sur les taux d’altération des minéraux. En effet, dans la zone d'étude, l'altitude et la latitude des sites déterminent conjointement les conditions climatiques alors que la proportion de feuillus et de conifères est influencée par les conditions hydro-climatiques. L’interconnexion de ces variables fait en sorte que les effets singuliers de variables discrètes (précipitation, la température, humidité, etc.) sur les taux d'altération ne peuvent être séparés sans équivoque. De ce fait, une analyse de la variabilité temporelle des taux d’altération des minéraux paraissait nécessaire afin de regarder tout cela sous un autre angle. Par contre l’étude de la variabilité temporelle des taux d’altération des minéraux exige l’utilisation d’une méthode capable d’estimer des taux d’altération fiables sur des échelles de temps très courtes (par exemple, sur une base annuelle). C’est ce travail qui a été fait à travers le cinquième chapitre, répondant ainsi aux objectifs spécifiques 4 et 5 de la thèse. Dans ce chapitre 5, une nouvelle approche méthodologique a été développée pour estimer les taux d’altération à l’échelle du bassin versant sur des périodes de temps d’un an. Cette nouvelle méthode a été appliquée au bassin versant de l’Hermine pour quantifier les taux d’altération des minéraux au cours de la période de 1995 à 2006. Ensuite, des techniques d’analyse multivariées ont été mises en œuvre pour examiner l’impact de variables hydro-climatiques sur l’évolution temporelle des taux d’altération dans le site au cours de cette période.

Ce chapitre est rédigé sous forme d'article. Le manuscrit est soumis pour publication à la revue *Biogeochemistry*[4]. L'article est réalisé en collaboration avec François Courchesne et Daniel Houle qui agissent également à titre de superviseurs de recherche. J'ai effectué la recherche bibliographique, et j'ai mis au point le protocole expérimental pour les analyses d'extraction séquentielle. J'ai effectué un échantillonnage de sols supplémentaire et j'ai réalisé des analyses au laboratoire. J'ai également effectué tout le travail de validation et d'organisation des données avant de procéder aux analyses statistiques et à la rédaction du manuscrit. Co-auteurs du manuscrit, mes superviseurs de recherche m'ont apporté un soutien inconditionnel dans les différentes étapes de ce travail et ils ont contribué en faisant des recommandations, en apportant de nouvelles idées et en corrigeant le texte du manuscrit.

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[4] Augustin, F., Courchesne, F., Houle, D. (*in prep*.). A new approach at estimating current base cation weathering rates: A case study for the Hermine watershed, Canada.

Chapitre 5: An approach at estimating current base cation weathering rates: A case study for the Hermine watershed, Canada

***Authors*: Fougère Augustin, Daniel Houle and François Courchesne**

Publication: Soumis à Science of the Total Environment
Source:

5.1 Abstract

A new methodological approach is described for estimating Ca, Mg and K fluxes from soil mineral weathering. This method combines fluxes of base cations (BC) in surface waters in the Hermine watershed with BC:Na molar ratios from the soil weatherable pool obtained using sequential extraction method. Comparison of BC:Na molar ratios of the weatherable pool with those from other compartments of the watershed suggests possible accumulation of base cations in some areas of the watershed, while losses or minimal changes are observed in others. On average, current Na weathering rates estimated using the watershed input-output budget method was 0.26 (range: 0.16 to 0.36) $\text{kmol}_c\ \text{ha}^{-1}\ \text{yr}^{-1}$, over the period of 1995 to 2006. For Ca, Mg and K, current weathering rates estimated with the new methodological approach averaged 0.44 (range: 0.27 to 0.60), 0.11 (range: 0.07 to 0.15) and 0.02 (range: 0.01 to 0.02) $\text{kmol}_c\ \text{ha}^{-1}\ \text{yr}^{-1}$, respectively. These values are within the range of present day rates previously calculated for forested soils from similar granitic environments using other methods. Candidate models for predicting BC weathering rates on individual annual observations were developed using Akaike's information criterion. The best model, includes the number of frost days (inverse relationship) and explained 51% of the variation in total BC weathering rates. The newly developed method may be applicable to other watersheds, providing yearly estimates of nutrient BC at the watershed scale.

5.2 Introduction

As a major source of nutrients to soils and as an essential regulator of their long-term concentrations in surface waters, mineral weathering plays a key role in the global flux and cycling of elements in terrestrial ecosystems. Environmental changes that alter the rates at which soil minerals weather thus having the potential to influence plant nutrition and the neutralization of acidic compounds in soils and surface waters (Bain et al. 1993; Whitfield et al. 2010). In the last decades, soil mineral weathering rates have been found to be associated with several climatic variables in field studies addressing the spatial variability of mineral weathering rates across large geographical areas (Schaller et al., 2009; Houle et al., 2012; Augustin et al., 2015a, 2015b). Results from these studies suggest that the variability in BC weathering rates is mainly attributed to soil properties (soil parent material/mineralogy and soil surface area), amounts of acid inputs and climate-related variables such as water fluxes, soil temperature and vegetation type. Direct links between chemical weathering and temperature have also been reported in catchment studies (Velbel, 1993; White and Blum, 1995; Millot et al., 2003) and laboratory experiments (Oelkers and Schott, 2001; Oelkers and Gislason, 2001).

While soil properties are relatively stable at the decadal scale, patterns in climatic variables such as temperature and precipitations are changing and they are expected to change significantly in the future, thus potentially altering mineral weathering rates (Campbell et al., 2009). Over the time period 1964-2004, Gislason et al. (2009) observed an increasing Ca fluxes, among others, in eight north-east Icelandic river catchments. They attributed the increase in Ca outflux to the positive effect of temperature on mineral weathering in the watershed over the time period. Such study monitoring the temporal variability of cation fluxes over a significant period is quite rare. Yet, long-term studies on the annual variation in mineral weathering rates are required to quantify trends in rates and to identify the climatic drivers influencing weathering. However, estimating current base cation weathering rates on an annual timescale has always been a challenge. Present day BC weathering rates have been obtained from a number of methodological approaches such as modelling with PROFILE (Sverdrup and Warfvinge, 1993; Sverdrup, 2009) or MAGIC (Cosby et al., 2001) and calculation using the watershed input-output budget or the mass balance method (Likens et al., 1967; Clayton, 1979; Velbel, 1985). These methods are thought to provide reliable estimates of current BC weathering rates, but several years of monitoring are necessary in order to minimize the impact of multiple error sources.

The Ca:Na molar ratio of the underlying bedrock has been used to interpret Ca weathering rates at the watershed scale (Mast et al., 1990; Likens, 1996, 1998; Horton et al., 1999; Bailey et al., 2003). At the Hubbard Brook Experimental Forest, Bailey et al. (2003) used this approach to refine the mass balance method for geochemical studies. This approach minimized the error introduced by the assumption of biomass steady-state, among others, notably on granitic environments where the weathering of plagioclase feldspars is a dominant source of Ca and Na (Clayton 1988, Hyman et al. 1998; Bailey et al. 2003). Blum et al. (2002) performed a four-step sequential extraction experiment on C-horizon soil samples to identify the weathering sources of Ca and to determine the availability of Ca pools at Hubbard Brook. They used increasingly potent solutions to displace the exchangeable pool (1 M NH_4Cl, pH = 7) and to successively digest apatite (1 M HNO_3 at room temperature), hornblende and pyroxene (1 M HNO_3 at 200 ºC) and plagioclase and K-feldspar (concentrated HF and HNO_3, at 210 ºC). Nezat et al. (2004, 2007) subsequently applied the same approach to weathered horizons to provide insight into the role of soil-forming processes on weathering reactions. A sequential extraction protocol similar to that used by Blum et al. (2002) and Nezat et al. (2004, 2007) has also been applied to lower B horizon soil samples from the Hermine watershed to constrain elemental ratios as well as $^{87}Sr/^{86}Sr$ of soil minerals (Bélanger et al., 2012). In order to determine the contribution of atmospheric deposition and soil mineral weathering as sources to the Ca pools in trees, measured $^{87}Sr/^{86}Sr$ ratios of trees, soil solutions, atmospheric deposition, stream water and soil leachates were combined with Ca/Sr ratio in a mass balance (Bélanger et al., 2012).

This study focus on temporal patterns in net BC fluxes from mineral weathering at the Hermine catchment (1995-2006). We consider that, in the short term, the mineral phases of the B horizons, where the active tree roots are present, are more representative base cation sources from chemical weathering than the C horizon or the underlying bedrock. Based on this assumption, we developed a method for estimating base cation weathering rates at the watershed scale. Our approach draws its foundation from the assumption of conservative behavior of Na in forest ecosystems (Likens and Bormann, 1995; Horton et al., 1999; Bailey et al., 2003). Under the conditions that this assumption is true, Na weathering flux from mineral weathering equals stream output minus bulk precipitation input, according to the small watershed approach (Likens and Bormann, 1995). Ca, Mg and K weathering fluxes, respectively, are then obtained by multiplying Na weathering flux by Ca:Na, Mg:Na and K: Na molar ratios characteristic of the mineral soil horizons where chemical weathering is currently active. These molar ratios are determined in the laboratory via a soil extraction procedure. This methodological approach was subsequently tested for a decadal period using soils and solutions data from the Hermine watershed, a forested catchment of southern Quebec, Canada, with the overall objectives of: a) establishing the inter-annual variability in BC weathering rates at the catchment scale and b) identifying the relationships existing between these short-term variations in weathering rates and the temporal changes in climatic conditions.

5.3 Materials and methods

5.3.1 The Hermine watershed

The Hermine catchment is situated about 80 km North of Montreal in southern Quebec, Canada (45° 59'N, 74° 01'W) at an altitude of 400 m above sea level. An intermittent first-order stream drains this 5.1 ha headwater forested catchment. The total annual precipitation averages 1150 mm (±136 mm) for the last three decades, of which about 30% falls as snow (Biron et al., 1999). For the same period, mean annual air temperature was 3.9 ° C (± 0.7 ° C), with the maximum (in July) and the minimum (in January) daily temperatures averaging 25 ° C and -30 ° C, respectively (Ali et al., 2010). The underlying bedrock is an igneous and impervious feldspar-rich Precambrian anorthosite of the Morin series (McGerrigle, 1976), covered by a shallow glacial till (less than 2 m) derived from the local rocks. Soils are mostly classified as sandy orthic or gleyed humo-ferric and ferro-humic Podzols (Soil ClassificationWorking Group, 1998). A dense and compact layer present at a 50 to 65 cm depth slows water infiltration in soils and favors the formation of a saturated zone on top of the layer. The proportion of sand varies from 45 to 73%, whereas clay content never exceeds 20% in any of the soil horizons (Courchesne et al., 2005).

The forest has an average basal area of 28 m² ha^{-1} and is dominated by sugar maple (Acer saccharum Marsh., 78% of total basal area), American beech (Fagus grandifolia Ehrn., 9%) and yellow birch (*Betula alleghaniensis* Britton, 6%). The accompanying species are balsam fir (Abies balsamea (L.) Mill.), white birch (*Betula papyrifera* Marsh.), trembling aspen (*Populus tremuloides* Michx.) and large-toothed aspen (*Populus grandidentata* Michx.). The last timber harvesting reported for the area was a selective thinning performed at the turn of the 20th century (Savage, 2001). Three sampling zones were selected in the catchment based on topography and the floristic composition of the forest. Zone 1 is located in the downstream portion of the watershed and occupies a downslope position, a few meters above the main stream channel on the northwestern-facing slope. Zone 3 is situated upslope from Zone 1, close to the divide, whereas Zone 2 is in the upstream end of the watershed near an intermittent gully that is active during spring melt and major rainfalls. Tree coring indicated that the stand in Zone 3 was affected by a fire disturbance that occurred around the mid-1920s, while Zones 1 and 2 were then spared (Bélanger et al., 2002a, 2002b).

5.3.2 Soil sampling and analysis

5.3.2.1 Collection of soils and preparation of composite samples

Three soil profiles were dug in the fall of 1993 within nine circular 300-m² plots that had been delineated in each of the three zones of the catchment: Zone 1 (plots 1, 2, 3), Zone 2 (plots 3, 4, 5) and Zone 3 (plots 7, 8, 9). Within a given zone, the three plots were separated by less than 100 m and were considered as field replicates (Courchesne et al. 2005). The nine soil profiles were described in the field and samples were collected in all genetic horizons (Soil ClassificationWorking Group, 1998). Volumetric samples were also taken with a corer to estimate bulk density. In order to obtain sufficient soil material to run preliminary dissolution experiments, a supplementary soil profile was sampled in Zone 1 during the summer of 2015. All soil samples were air-dried and sieved to 2 mm before analyses.

For the purpose of estimating the weatherable soil BC pools, composite samples were produced for the three main soil horizons (E, Bs and C) and for each of the three watershed zones using three soil profiles per zone and taking into account horizon thickness and density (Augustin et al., 2015a). The B horizon comprised soil materials from below the lower frontier of the E to a depth of 50 cm from the soil surface. For the C-horizon (soil parent material), one weighted composite sample was created for the whole watershed by mixing the C-horizons sampled from the three zones. Therefore, a total of seven composite horizon samples (three E, three B and one C) were included in the experiment.

5.3.2.2 Mineralogical composition of soils

Soil mineralogy was determined for the clay (<2 µm) and fine silt (2–20 µm) fractions of the E, Bs and C horizons of the soil profile sampled in Zone 1 in 2015. Organic carbon coatings were removed by a sodium hypochlorite (pH = 9.5) pre-treatment. The clay and fine silt fractions were then saturated with Mg, Mg-ethylene glycol and K. The saturated samples were mounted on glass slides by sedimentation. The mineralogy was determined by X-ray powder diffraction method (XRD) using a Rigaku Miniflex diffractometer at a scanning speed of 2°/min from 2° to 30° or 70°. After a first run at room temperature, the K-saturated slides were heated at 550 °C and reanalyzed. Diffractogram peaks were interpreted according to data from Whittig and Allardice (1986) and Amonette and Zelazny (1994). The relative abundance of minerals was determined semi-quantitatively by normalizing XRD peak heights among samples and treatments by calculating the Ix/Iqz intensity ratio for each mineral using the height of its XRD peak (Ix) divided by the height of the 0.426 nm peak (Iqz) according to Courchesne & Gobran (1997).

5.3.2.3 Chemical properties of soils

Soil pH was determined in water at a 1:2 soil: solution ratio (Hendershot et al. 2007a). Soil organic matter content was measured by the loss-on-ignition (LOI) method of Combs and Nathan (1998). Soil organic carbon was computed by multiplying organic matter content by the van Bemmelen factor 1.724. The total cation concentration (expressed as Al_2O_3, CaO, Fe_2O_3, K_2O, MgO, Na_2O and SiO_2) was determined on 32-mm-diameter fused beads prepared from a 1:5 soil-lithium tetraborate mixture using an automated X-ray fluorescence (XRF) spectrometer system with a Rhodium 60-kV end window X-ray tube. The analysis was performed on air-dried soil samples (fine earth sieved through a 2 mm mesh).

5.3.2.4 Extracting the weatherable soil BC pool

Two experiments were carried out to quantify the BC:Na molar ratios of the potentially weatherable soil BC pools that were used to estimate BC weathering rates in the soils of the Hermine catchment. First, a dissolution experiment was conducted to determine the most suitable HNO_3 molarity for extracting the potentially weatherable soil BC pools from the E, B and C horizons. The selected molarity was then used as one of the steps of a sequential extraction experiment to characterize the BC:Na molar ratios of different soil fractions.

5.3.2.4.1 The suitable HNO_3 molarity for extracting the potentially weatherable BC pool.

Three soil samples from three horizons (E, B and C) of one soil profile were first subjected to batch treatments to remove the BC exchangeable fraction as well as BC bound to organic matter (step 1) or sorbed to oxide coatings (step 2). In step 3, the pretreated soil material was then subjected to 11 different HNO_3 molarities. The overall procedure was as follows:

Step 1: Sixty g of soil was placed in a 750 ml container and 600 ml of sodium hypochlorite solution (pH 9.5) were added and mixed with a glass rod. The containers were heated in a water bath to 80°C for 1 hour. Samples were then cooled and centrifuged at 2000 rpm for 10 min. The supernatant was carefully decanted and discarded. This step was repeated three times, until the supernatant was pink or pale yellow. The soil residue was washed three times by adding 600 mL of Milli-Q water, shaking and centrifuging at 2000 rpm for 10 min. The supernatant was decanted and discarded prior to the next step.

Step 2: A 600 mL volume of 0.2 M ammonium oxalate (pH=3) was added to the soil residue from step 1. The mixture was shaken in the dark for 1 hour at ambient temperature. The supernatant was separated from the solids by centrifugation (2200 rpm for 20 min) and decantation. This step was repeated twice and sand grains were afterwards examined with a binocular microscope to ensure that oxide coatings had indeed been removed. The soil residue was washed as in step 1, and the supernatant was discarded. The soil residue was then oven-dried at 30°C for 24 hours. The dry soil material was transferred to an agate mortar and gently crushed only to break up aggregates that formed during drying.

Step 3: The dried soil material resulting from step 2 was reacted in triplicate with solutions of 11 different HNO_3 molarities (10^{-5} M; 5 x 10^{-5} M; 10^{-4} M; 5 x 10^{-4} M; 10^{-3} M; 5 x 10^{-3} M; 10^{-2} M; 5 x 10^{-2} M; 10^{-1} M; 5 x 10^{-1} M; 1 M). One gram of soil was placed in a 50-mL centrifuge tube and 35 mL of HNO_3 solution of a given molarity was added. The tubes were then lightly shaken mechanically at room temperature for 96 hours. The resulting soil-solution mixture was centrifuged at 2200 rpm for 15 min. The supernatant was carefully decanted and filtered through Fisherbrand Q8 filter paper and kept cool for elemental analysis. Extracts were analyzed for Al, Si, Fe, Ca, Mg, Na and K concentrations by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Analytical grade reagents were used to prepare standard solutions and 5-point calibration curves for all the analyses.

5.3.2.4.2 The sequential extraction experiment

For the seven composite samples (three E, three B and one C), exchangeable cations were first displaced from a 1-g soil sample for 2 hours using 30 mL of unbuffered 0.1 M $BaCl_2$ (Hendershot et al., 2007b). Another treatment was then performed with sodium hypochlorite solution (pH 9.5) to remove organic matter from the samples prior to the removal of Fe and Al oxide coatings using 0.2 M ammonium oxalate (pH=3) as in steps 1 and 2 above. Potentially weatherable BC pools were then extracted from these treated soil materials as in step 3 above using 5 x 10^{-4} M HNO_3, based on the results of the dissolution experiment with 11 HNO_3 molarities. The main criterion used for determining the most suitable HNO_3 molarity for the extraction of the weatherable BC pool from the soils was a BC:Na molar ratio value that was relatively stable over a significant range of HNO_3 molarities. In the presence of such BC:Na ratio plateau, the molarity resulting in the least acidic extraction pH was selected.

5.3.3 Solution sampling and analysis

In the fall of 1993, zero-tension lysimeters were installed at 0 cm (under the organic LFH horizons) and at 50 cm (in the B horizon below the rooting zone) in the nine soil profiles used to collect soil samples (Courchesne et al. 2005). Only data from the 50 cm-lysimeters will be discussed in this paper. A gauging station and an automatic water sampler located at the watershed outlet provided continuous streamflow measurements and daily streamwater samples. From May to November of 1994 to 2002 inclusively, a composite streamwater sample was produced and nine 50-cm depth soil solutions were collected every two weeks, except for 1998, when solutions were not sampled regularly. Incident precipitation depth and the chemical composition of bulk deposition were provided by a weather station located 1 km north of the Hermine and operated by the Quebec Ministry of the Environment. Stream and soil solutions were analyzed for pH before filtration through a 0.45-µm poly-carbonate membrane. Calcium and Mg concentrations were determined by atomic absorption spectrophotometry whereas Na and K were measured by ion chromatography. Reference water samples from the National Water Research Institute (Burlington, ON, Canada) were used as external quality controls.

5.3.4 Calculating current BC weathering rates in the field

The method presented here for estimating current BC weathering rates is based on the use of Na as an indicator of weathering because of its conservative behavior in forested ecosystems (Likens and Bormann, 1995; Horton et al., 1999; Bailey et al., 2003). According to the small watershed approach (Likens and Bormann, 1995), the mass balance for Na could be derived from the formula given by Bailey et al (2003; Eq. 1):

$$P_{Na} + W_{Na} = S_{Na} + B_{Na} + M_{Na} \pm \Delta A_{Na} \qquad (1)$$

where:

P_{Na}: Na inputs through atmospheric deposition (mol ha^{-1} yr^{-1}),

W_{Na}: Na mineral weathering flux (mol ha^{-1} yr^{-1}),

S_{Na}: Na in stream output (mol ha^{-1} yr^{-1}),

B_{Na}: changes in Na ecosystem pools, including net biomass uptake (mol ha^{-1} yr^{-1}),

M_{Na}: Na retained in secondary mineral formation (mol ha^{-1} yr^{-1}),

ΔA_{Na}: change in available Na soil pools (mol ha^{-1} yr^{-1})

In these ecosystems, Na storage in elemental pools including biomass, forest floor, secondary minerals, and the soil exchangeable phase is low, so that potential short-term changes in storage do not contribute significantly to total ecosystem loss in streamwater compared to Na released from weathering (Likens et al. 1996, 1998; White et al., 2009). In such conditions, Bailey (2003) suggested to simplify Eq. 1 to:

$W_{Na} = S_{Na} - P_{Na}$ (2)

The contribution of Na from weathering to the observed Na concentration in the stream water can thus be determined from Eq. 2. For soils formed in granitic material where plagioclase feldspars release Ca and Na, Ca weathering fluxes have been estimated by multiplying the net watershed input-output budget of Na by the Ca: Na molar ratio of bedrock samples (Bailey, 2003). Instead of bedrock molar ratios, we elected to use BC:Na molar ratios calculated for the potentially weatherable soil pool to better constrain BC weathering flux estimates. The BC:Na molar ratios in the potentially weatherable soil pool are determined on soil samples free of organic matter and oxide coatings, so that the dilute HNO_3 can interact directly with the mineral surfaces. Based on the notion of potentially weatherable pool of BC, the weathering fluxes of Ca, Mg and K are calculated as follows:

$W_{BC} = W_{Na} * PWSP_{(BC/Na)}$ (3)

where W_{BC} refers to the mineral weathering flux (mol ha^{-1} yr^{-1}) of the base cations Ca, Mg or K; W_{Na} is the Na weathering flux (mol ha^{-1} yr^{-1}) estimated using the mass balance method (see above); and $PWSP_{(BC/Na)}$ is the BC:Na molar ratio (unitless), for any BC, in the potentially weatherable soil pool (PWSP). This methodological approach was applied to the field data recorded at the Hermine in order to determine BC weathering rates.

5.3.5 Explanatory variables

Bioclimatic variables (average growing season temperature, number of degree-day, cooling season precipitation, number of consecutive days without frost, number of frost days, aridity, growing season length, snowfall proportion, mean annual air temperature, number of growing degree-day, total radiation and ratio of growing season to total precipitation) were obtained for the period 1995 to 2006 from BioSIM 10.3.1.2, (Régnière et al., 2014). This software uses input data such as longitude, latitude, slope, aspect and elevation of a given catchment, to simulate a set of bioclimatic variables, based on climatological information gathered at meteorological stations located within or close to the study area. Data from four Environment Canada and Quebec Ministry of the Environment weather stations were used, with minimum distance as the basic criterion for selecting the stations. We used a hydrological year that extends from October 1st to September 30th. Note that the label of hydrological years is designated by the calendar year in which it ends, so that the 1995 water year started on October 1, 1994 and ended on September 30, 1995. We used the monthly values to calculate means or sums and to generate annual data.

5.3.6 Data analysis

Box and whisker plot graphs were used to visually contrast the base cation concentration distributions in incident precipitation, soil solution and streamwater. The data set also allowed testing for trends (1994-2006) in precipitation, soil solution, stream water chemistry and estimated weathering rates using the Mann-Kendall method. The magnitude of trends in the data was determined using the non-parametric Sen's estimator method. Student's t–test was used to assess whether the means of BC:Na molar ratios from two different compartments of the Hermine catchment were statistically different from each other. We used an information theoretic approach, the Akaike's Information Criterion with small sample correction (AICc), to evaluate the weight of evidence for probable models of the effects of environmental variables on the BC weathering rates (Anderson 2008; Burnham and Anderson 2002). Analyses were performed using the model.select_0.3.R function in the R package. All the models with an AICc.w (model AICc weight, i-e the relative probability for a particular model to be selected as the best fit in the set of models and conditional to the dataset used) higher than 5% or with ΔAICc (difference between the AICc of a given model and the AICc of the best model) values lower than 2 were considered as plausible models (Burnham and Anderson 2002).

The forward.sel() function of the library packfor of the R package was used to calculate the cumulative proportion of variation explained in BC weathering rates data for each selected model as assessed by Monte Carlo permutation tests using 999 unrestricted permutations (ter Braak and Verdonschot 1995). The data for environmental variables were log-transformed (x+1) to meet the assumptions of normality and to balance the effect of different measurement units. Scatter plots were also reported to visualize the relationships between the significant (or marginally significant) environmental variables and BC weathering rates. All the analyses were performed using the statistical software package R (R Development Core Team, 2016).

5.4 Results

5.4.1 Soil chemical properties, mineralogical composition and weatherable BC pools

5.4.1.1 Soil chemical properties

The CEC was dominated by exchangeable Al and Fe, and varied from 0.85 g kg^{-1} (C horizon) to 3.21 g kg^{-1} (E horizons) with the highest value always measured in the E horizon (Table 5.1). The base saturation was low at less than 15% in the soil materials of all zones except for a 55.2% level in the C horizon. The organic matter content of the three horizons ranged from 2.2 to 22.7% and was much lower in the E and C horizons than in the composite B. The soils were acidic, with pH in water values increasing from the top (E) to the bottom (C) of the mineral profile.

5.4.1.2 Mineralogical composition of the soils

In the fine silt fraction of the E, Bs and C horizons, plagioclase and K-feldspar were dominant followed by quartz and smectite with amphibole, pyroxene, chlorite, vermiculite and hydroxyl-interlayed vermiculite present at lower levels (Table 5.2). Yet, quartz was more abundant than plagioclase and K-feldspar in the E horizon, a common feature of podzols. Similarly, smectite was more abundant in the E horizon compared to deeper horizons whereas pyroxene, chlorite and vermiculite were not detected in the E. With the exception of amphibole, the same minerals were detected in the clay fraction and similar patterns existed with depth in the soil (Table 5.2). However, smectite and hydroxyl-interlayed vermiculite were relatively more abundant than in the silts; a reverse trend was observed for plagioclase and K-feldspar. The major minerals reported here for the silt and clay fractions were also detected by McCourt (1993) who used a combination of X ray Diffraction (XRD) and X-Ray Fluorescence (XRF) for total chemical analysis.

5.4.1.3 Weatherable BC pools – determining the HNO_3 molarity used for the extraction

The BC concentrations and final pH of the batch experiment conducted to establish the appropriate HNO_3 molarity to conduct the dissolution reaction are presented in Figure 5.1 as a function of HNO_3 molarity.

Table 5.1: Element concentration in the three fractions for the three soil horizons

Soil horizon	Zone	Fraction	Al	Si	Fe	Ca	Mg	Na	K	CEC^{o}	BS^{p}	OM^{q}	pH$_{(H2O)}$
							(g kg^{-1})				(%)	(%)	
E horizon	Zone 1	5 x 10^{-4} M HNO_3-extractable	0.10	0.12	0.15	0.04	0.02	0.04	0.02				
		$BaCl_2$-exchangeable	1.89	0.26	0.69	0.24	0.03	0.07	0.03	3.21	11.4	7.51	4.11
		Total element concentration in soils	49.8	327	31.6	10.4	4.64	13.6	20.7				
	Zone 2	5 x 10^{-4} M HNO_3-extractable	0.07	0.10	0.06	0.03	0.02	0.03	0.01				
		$BaCl_2$-exchangeable	1.30	0.33	0.59	0.18	0.03	0.08	0.03	2.53	12.5	6.39	4.09
		Total element concentration in soils	50.5	337	22.5	8.43	3.50	14.5	22.8				
	Zone 3	5 x 10^{-4} M HNO_3-extractable	0.08	0.09	0.08	0.02	0.01	0.03	0.02				
		$BaCl_2$-exchangeable	0.93	0.30	0.38	0.16	0.01	0.06	0.02	1.87	13.5	3.05	4.06
		Total element concentration in soils	48.5	356	26.2	7.29	3.44	13.6	21.7				
Composite B	Zone 1	5 x 10^{-4} M HNO_3-extractable	0.11	0.09	0.02	0.06	0.01	0.11	0.01				
		$BaCl_2$-exchangeable	1.28	0.15	0.24	0.05	0.01	0.08	0.02	1.83	8.48	17.27	4.95
		Total element concentration in soils	77.8	248	41.6	17.5	8.20	15.9	16.7				
	Zone 2	5 x 10^{-4} M HNO_3-extractable	0.48	0.23	0.07	0.15	0.02	0.09	0.01				
		$BaCl_2$-exchangeable	0.78	0.16	0.23	0.04	0.01	0.07	0.02	1.31	10.5	11.49	4.98
		Total element concentration in soils	74.9	283	35.6	15.5	7.54	17.7	20.1				
	Zone 3	5 x 10^{-4} M HNO_3-extractable	0.73	0.37	0.14	0.15	0.03	0.07	0.01				
		$BaCl_2$-exchangeable	1.21	0.19	0.33	0.08	0.01	0.08	0.02	1.93	10.2	22.72	4.99
		Total element concentration in soils	82.1	226	40.0	13.7	6.39	14.7	15.8				
C horizon	Watershed	5 x 10^{-4} M HNO_3-extractable	0.28	0.61	0.09	0.96	0.18	0.11	0.03				
		$BaCl_2$-exchangeable	0.05	0.14	0.19	0.12	0.02	0.07	0.26	0.85	55.2	2.24	5.12
		Total element concentration in soils	72.4	322	34.1	19.7	7.66	20.2	22.3				

^{o}Cation exchange capacity; ^{p}Base saturation; ^{q}Organic matter

Table 5.2: Semi-quantitative (Ix/Iqz)[a] mineralogical assemblage of the soils at the Hermine catchment.

Size fraction	Horizon	Intensity ratio (Ix/Iqz) for soil minerals								
		Quartz	K-feldspar	Plagioclase	Amphibole	Pyroxene	Chlorite	Vermiculite	HIV[b]	Smectite
Fine silt (2–20 µm)	E	1.00	0.80	0.80	0.06	n.d.	n.d.	n.d.	0.04	0.43
(Zone 1)	Bs	1.00	1.55	2.25	0.09	0.13	0.13	n.d.	0.07	0.15
	C	1.00	1.43	2.12	0.06	0.18	0.11	0.11	nd	0.09
Clay (<2 µm)	E	1.00	0.42	0.31	n.d.	n.d.	n.d.	n.d.	0.27	1.04
(Zone 1)	Bs	1.00	1.03	1.10	n.d.	0.13	0.15	0.13	0.25	0.21
	C	1.00	1.00	1.29	n.d.	0.17	0.14	0.06	0.17	0.09

[a] Ix/Iqz = Intensity ratio calculated for mineral using the height of its XRD peak (Ix) divided by the height of the 4.267 Å quartz peak (Iqz)

[b] HIV = Hydroxyl-interlayed vermiculite

[c] n.d. = not detected

Quartz = 4,267 Å; K-feldspar = 3,264 Å; Plagioclase = 3,218 Å; Amphibole = 8,499 Å; Pyroxene =2,583 Å; Chlorite = 14,717 Å; Vermiculite = 14,017 Å; HIV = 12,267 Å; Smectite = 13,181 Å or 16,351 Å in Mg-EG

Note that plots of molar BC to Na ratios according to HNO_3 molarity are illustrated in Figure S5.1 (see Appendix C). The cation concentration increased with increasing HNO_3 molarity for all elements and horizons although cation release level was much lower in the E compared to Bs or C horizons. The difference between horizons differed with the studied cation and reached a factor of three for K and Na up to a factor of 92 for Mg. Overall, the highest concentrations were measured for Al and Si at all HNO_3 molarities followed by Fe (in particular above 10^{-2} M HNO_3), Mg and Ca. This cation sequence was similar for the Bs and C horizons but Na was released at a higher rate than the other base cations in the E whereas Fe decreased markedly in the E compared to the Bs and C. As expected, solution pH decreased with increasing acid concentration with an abrupt pH drop occurring in the $5x10^{-5}$to 10^{-4}M HNO_3 range.

A base cation concentration plateau in the range of 10^{-4} M and $5x10^{-3}$ M HNO_3 was observed for the three horizons studied (Figure 5.1). A second plateau appeared above 0.5 M HNO_3. These plateaus represent molarity ranges over which the BC concentrations are quasi-invariant reflecting some level of stability in the solid-solution system. In agreement with our main criterion (invariant BC:Na molar ratios over a range of HNO_3 molarity), and because of its less acidic final pH compared to the other molarities forming the plateau, the $5x10^{-4}$ HNO_3 molarity was selected to further perform sequential extraction on soils from the watershed.

5.4.1.4 Weatherable BC pools – the element concentrations and BC:Na molar ratios

In the E horizons of the three zones of the watershed, the amounts of the individual elements Al, Si, Fe, Ca, Mg, Na and K extracted with HNO_3 $5x10^{-4}$ M was below 1% of the total concentrations obtained by XRF (Table 5.1). They represented 0.04 to 0.89% of total amounts in the composite B horizons and 0.14 to 2.32% in the C horizon. The HNO_3–extracted BC concentrations were generally lower than the $BaCl_2$-exchangeable fraction in the E horizons.

In the B and C horizons, HNO_3-extracted Fe and K were lower than their exchangeable counterpart whereas HNO_3-extracted Ca, Mg and Na were higher or similar to the exchangeable fractions (Table 5.1). The amount of Si dissolved with HNO_3 was higher than the $BaCl_2$-exchangeable fraction in the B and C horizons, except for the B horizon in zone 1. Regarding the HNO_3-extracted Al, it was lower in the B horizons and higher in the C, compared to its exchangeable fraction (Table 5.1).

5.4.2 Trends in precipitation, soil solution and stream water chemistry

Although this study takes several more years of sampling into account, our results support the major trends previously reported by Courchesne et al. (2001) and Courchesne et al. (2005) for BC concentrations in solutions (incident precipitations, soil solutions and stream water) at the Hermine catchment (Table S5.1 and Figure S5.2 in Appendix C). Briefly, significant decreasing trends in individual Ca and Mg concentrations were detected with the Mann-Kendall test in incident precipitations, stream water and soil solutions, except for Ca in incident precipitations. In contrast, increasing trends in Na concentrations series were observed in soil solutions in zones 1 and 2. The Mann-Kendall test also revealed a significant decreasing trend in total BC concentration in incident precipitations while K concentrations were stable. With respect to mean annual concentration values, significant increasing Na trends were detected with the Sen's slope estimator in soil solutions for the three zones, while decreasing trends were observed for Ca (zones 1 and 3) and Mg (zones 1 and 2). No trend existed for mean annual K and total BC.

5.4.3 Investigating BC:Na molar ratios from different sources in the watershed

The BC:Na molar ratios in incident precipitations were always higher than the corresponding ratios in soil solutions, in stream water and in the soil pools, except for K/Na in the soil exchangeable pool (Table 5.3). In the soil solutions and stream water, Ca:Na and Mg:Na were higher than in the weatherable pools in Zone 1, while they were lower compared to the weatherable pools for other areas of rhe watershed (except for Ca/Na in Zone 3). As for K:Na, the ratios were higher in the weatherable pools than in soil solutions, except for Zone 3. However, they remained almost unchanged when compared to the stream water.

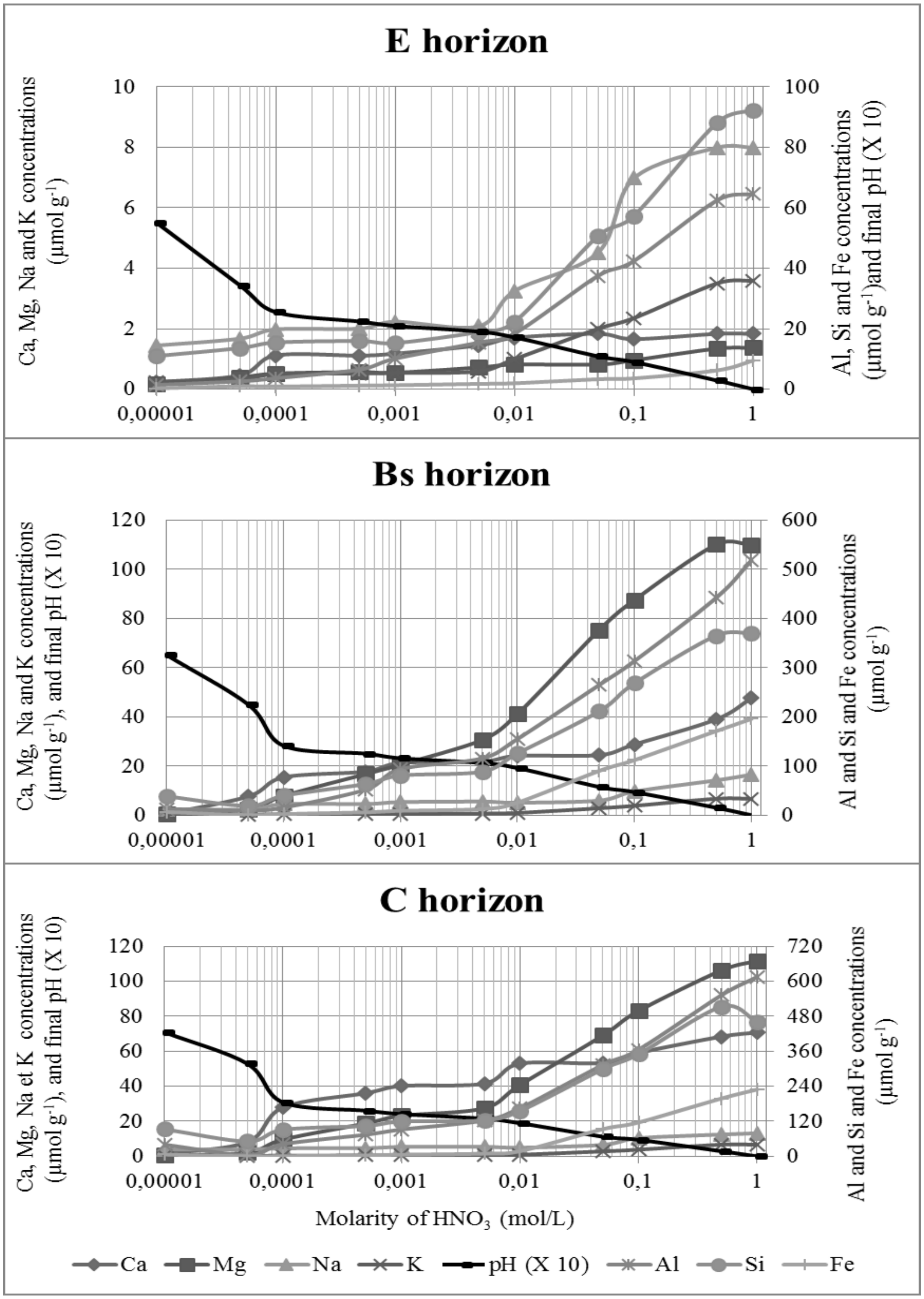

Figure 5.1: Final dissolved cation concentration and solution pH as a function of the molarity of HNO$_3$. Note that pH (X 10) is plotted on the secondary Y-axis for E horizon and on the primary Y-axis for B and C horizons.

Table 5.3: Molar ratios[r] of base cations in incident precipitation, soil extracts (weatherable and exchangeable pools), soil solution at 50 cm depth and in stream water.

BC ratio	Location	Precipitation	Weatherable	Exchangeable	Soil solution	Stream
Ca:Na						
	Zone 1		0.70 (0.09)^{a}	0.67 (0.05)^{a}	1.24 (0.11)^{b}	
	Zone 2		1.94 (0.19)^{c}	0.70 (0.01)^{d}	1.22 (0.11)^{e}	
	Zone 3		2.37 (0.43)^{f}	1.15 (0.07)^{f}	1.55 (0.16)^{f}	
	Watershed[s]	2.98 (0.29)^{g}	1.67 (0.50)^{h}	0.84 (0.16)^{h}	1.34 (0.12)^{i}	1.15 (0.09)^{hi}
Mg:Na						
	Zone 1		0.21 (0.04)^{j}	0.16 (0.02)^{j}	0.26 (0.03)^{k}	
	Zone 2		0.38 (0.02)^{l}	0.19 (0.00)^{m}	0.26 (0.03)^{n}	
	Zone 3		0.68 (0.03)^{o}	0.24 (0.01)^{p}	0.32 (0.04)^{p}	
	Watershed	0.91 (0.08)^{q}	0.42 (0.13)^{r}	0.20 (0.02)^{s}	0.28 (0.03)^{t}	0.28 (0.02)^{t}
K:Na						
	Zone 1		0.068 (0.00)^{u}	0.148 (0.01)^{v}	0.039 (0.01)^{w}	
	Zone 2		0.054 (0.00)^{x}	0.167 (0.00)^{y}	0.029 (0.01)^{z}	
	Zone 3		0.078 (0.02)^{ab}	0.169 (0.01)^{a}	0.042 (0.01)^{b}	
	Watershed	0.224 (0.07)^{c}	0.063 (0.00)^{d}	0.161 (0.01)^{c}	0.037 (0.00)^{e}	0.061 (0.01)^{de}

[r] The values are means (SE) for the period 1995-1997 and 1999-2002. Mean values with same superscripts do not differ significantly ($p < 0.05$)

[s] Whole-watershed, calculated as the mean of the three zones (weatherable, exchangeable and soil solution), or measured at the watershed scale (precipitation) and at the catchment outlet (stream).

5.4.4 Base cation weathering flux estimates

The present-day weathering rates estimated using our approach are reported in Table 5.4. At the scale of the watershed, BC weathering estimates averaged about 0.44, 0.11, 0.26 and 0.02 $\text{kmol}_c\ \text{ha}^{-1}\ \text{yr}^{-1}$ for Ca, Mg, Na and K, respectively. The estimated BC weathering rates were tested for temporal trends for the 1995-2006 period and no significant trends were observed (data not shown). However, BC weathering rates were relatively variable from year to year with a coefficient of variation (ratio of the standard deviation to the mean) of 26.9% over the studied period.

5.4.5 Links between variations in BC weathering rates and climatic variables

Descriptive statistics of climatic variables are reported in Table S5.2 and showed relatively important variations. Only the number of frost days (NFD) was retained in the best model for predicting total BC weathering rates. This model had an Akaike weight of 0.268 (Table

5.5). The other plausible model included the number of consecutive days without frost (CDWF). Between 40 and 51% of the variation in BC weathering rates could be explained by these two plausible models.

Table 5.4. Base cation weathering rates ($\text{kmol}_c\ \text{ha}^{-1}\ \text{yr}^{-1}$) estimated for the Hermine watershed.

Year	Ca	Mg	Na	K	Total.BC
1995	0.368	0.093	0.220	0.015	0.696
1996	0.356	0.090	0.213	0.014	0.674
1997	0.269	0.068	0.161	0.011	0.510
1999	0.503	0.127	0.301	0.020	0.952
2000	0.436	0.111	0.261	0.017	0.825
2001	0.604	0.153	0.362	0.024	1.143
2002	0.293	0.074	0.175	0.012	0.554
2003	0.349	0.088	0.209	0.014	0.660
2004	0.593	0.150	0.355	0.024	1.122
2005	0.519	0.132	0.311	0.021	0.982
2006	0.524	0.133	0.314	0.021	0.991
Mean	0.438	0.111	0.262	0.017	0.828
SE	0.036	0.009	0.021	0.001	0.067
Min	0.269	0.068	0.161	0.011	0.510
Max	0.604	0.153	0.362	0.024	1.143

Table 5.5: Multi-model-inference summary statistics of the plausible models describing BC weathering rates as predicted by environmental variables. Statistics include: AICc = Akaike information criterion corrected for small samples (it is an estimator of the information lost when the full reality is represented by a model), ΔAICc = difference between the model AICc and the best model AICc, AICc.w = model AICc weight (it is the relative probability for a particular model to be selected as the best fit one in this set of models and conditional to the dataset used, based on the AICc criterion), R^2adj. = adjusted regression coefficient for the model; NFD = number of frost days; CDWF = consecutive days without frost.

Response variable	Model	AICc	ΔAICc	AICc.w	$R^2_{adj.}$	*p*-value
Total BC weathering rates						
	NFD	-2.454	0.000	0.268	0.51	0.008
	CDWF	-0.249	2.205	0.089	0.40	0.022

The environmental variable with the highest relative impact on weathering rates over the study period was NFD, followed by CDWF (Table S5.3 in Appendix C). However, only NFD had a relative importance higher than 0.3 which is indicative of a good prediction potential (Burnham and Anderson 2002). Moreover, the number of frost days was negatively associated with BC weathering rates whereas the number of consecutive days without frost was positively correlated (Figure 5.2).

5.5 Discussion

5.5.1 Determining the appropriate HNO_3 molarity for extracting the weatherable BC pool

The dissolution experiment aimed at determining the stoichiometric BC to Na ratios of the mineral material from which BC are thought to be released in natural conditions. Resulting cation concentrations were plotted as a function of HNO_3 molarity (Figure 5.1). Cation concentrations were higher for Bs and C horizons, where weathering has been moderate to absent, compared to the highly weathered E horizon of this podzolic soil (except for K where the concentration was similar in the three horizons up to HNO_3 10^{-2} M). Because BC-rich minerals are less abundant in the E than in the Bs and C horizons (Table 5.2), the exception noted for the K concentrations, for HNO_3 molarities comprised between 10^{-5} M and 10^{-2} M, may be due to the greater abundance and accessibility of reactive sites on altered K-bearing minerals resulting from the intense weathering of the E horizon (Critelli et al., 2014). The ratios Ca:Na, Mg:Na and K:Na also differed between the Ae and the other two horizons (Figure S5.1 in Appendix C).

The overall increase in BC concentrations with increasing HNO_3 molarity (Figure 5.1), reflects the characteristic dissolution behaviour of aluminosilicates under increasingly acidic conditions (Gudbrandsson et al., 2011; Sverdrup, 1990; Courchesne et al., 1996; Nezat et al., 2007).

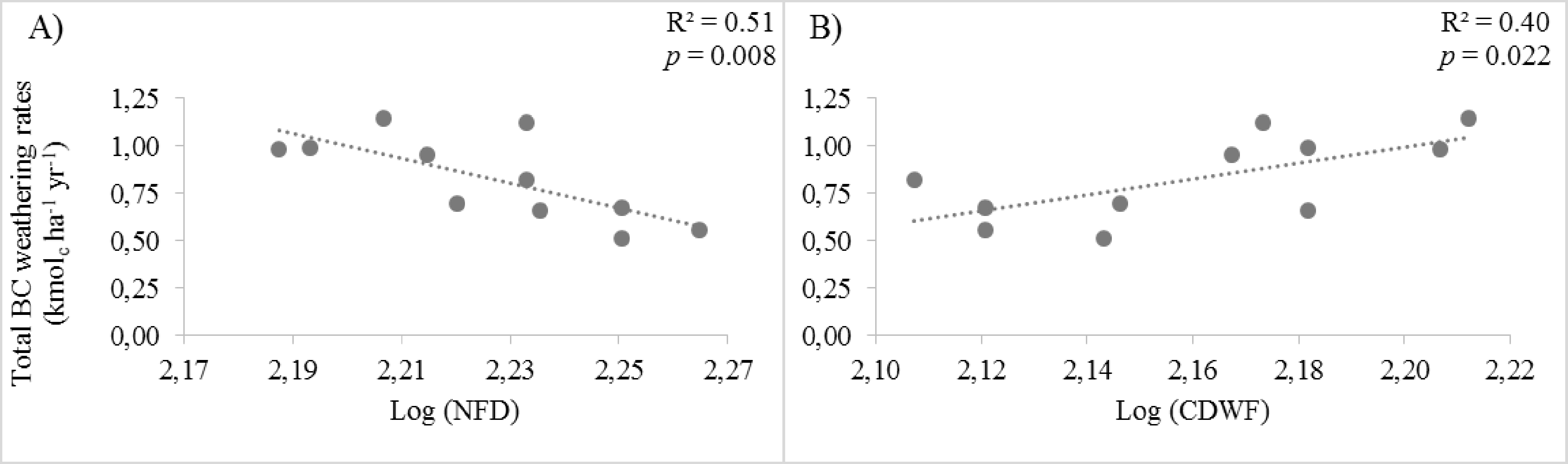

Figure 5.2: Total BC weathering rates at the watershed scale versus significant environmental variables: A) log (number of frost days) and B) log (consecutive days without frost).

Yet, the BC concentrations (Figure 5.1) and BC:Na molar ratios (Figure S5.1) reached quasi-stability at HNO_3 molarities comprised between 10^{-4} M and 10^{-3} M. For these molarities, the final pH of the extractions varied from 2.55 to 2.10 in the E, from 2.83 to 2.32 in the Bs and from 3.08 to 2.42 in the C horizons, respectively. These values were as close as we could get to the pH of field soil solutions. Indeed, the pH of soil solutions collected at 50 cm depth averaged 5.4 to 5.5 for zones 1, 2 and 3. We thus concluded that the best acid strength to obtain BC:Na ratios representative of the weathering products was comprised between 10^{-4} M and 10^{-3} M HNO_3. Accordingly, a HNO_3 5 X 10^{-4} M solution was used in the sequential experiment to extract the potentially weatherable BC pools from the seven composite soil samples.

5.5.2 Using BC:Na ratio of the weatherable pool as a tracer at the watershed scale

Based on the conservative behavior of Na in forested ecosystems, it has been used as an indicator of weathering in several geochemical studies (Likens and Bormann, 1995; Bailey et al., 2003; White et al., 2009). For acidic forested soils of granitic lithology such as those of the Hermine watershed, Na input is due to atmospheric deposition and silicate (plagioclase) weathering. Moreover, Na is only weakly involved in ecosystem reactions and pool changes involving biomass, forest floor, secondary clay minerals and the soil exchange complex (Bailey et al., 2003; White et al., 2009). As a result, net changes in Na storage are not considered to contribute significantly to ecosystem losses or gains at the annual scale (Bailey et al., 2003; White et al., 2009).

We compared BC:Na ratios in the HNO_3 5 X 10^{-4} M extract with those of incident precipitation, soil exchangeable pool, soil solution and stream water (Table 5.3). For the weatherable pool, the BC:Na ratios range from 0.054 (K:Na; Zone 2) to 2.37 (Ca:Na (Zone 3) and significant differences appear in these ratios between this pool and other compartment of the Hermine watershed. For a given BC, net losses from the watershed due either to weathering release or mineralization during organic matter decomposition would result in stream water outputs having BC:Na ratios greater than that of the weatherable pool. Conversely, net accumulation or retention of BC within the watershed due to immobilization in the biomass, or secondary mineral formation would result in stream water outputs with BC:Na ratios lower than that of the weatherable pool. The results reported in Table 5.3 show that for the weatherable pool, Ca:Na molar ratio was lower in Zone 1 and higher in Zone 2 compared to the soil solution, suggesting Ca losses (Zone 1) and Accumulation (Zone 2) in some compartments of the Hermine watershed. Minimal or no change in Ca was observed in Zone 3 or at the watershed scale during the study period. As for Mg:Na molar ratios, they were higher in the weatherable pools compared to the soil solutions and stream water, indicating Mg accumulation in some compartments of the Hermine watershed (except for Zone 1 where Mg is depleted). Regarding K/Na, the ratios were higher in the weatherable pools than in soil solutions (Zones 1 and 2), but they remained almost unchanged for Zone 3 and when compared to the stream water, resulting in minimal or no change at the watershed scale. Given that Ca:Na and Mg:Na molar ratios are higher in the weatherable than in the exchangeable pools when accumulation are observed, we hypothezised that Ca and Mg accumulations could potentially occur in biomass or to a lesser extent in secondary mineral formation. To the opposite, K accumulation seem to occur in the soil exchangeable reservoir.

5.5.3 Interannual variability in recent BC weathering rates at the Hermine watershed

Average BC weathering rates estimated with our approach (Table 5.4) are of the same order of magnitude as present-day rates estimated by Bélanger et al. (2002) at the Hermine watershed with the dynamic biogeochemical model SAFE. These values were also well within the range of present-day rates previously calculated for similar forested soils using other methods (Watmough and Dillon, 2003; Ouimet and Duchesne, 2005; Houle et al., 2012; Augustin et al., 2015b, 2016).

Temporal change in BC weathering rates was analyzed in relation to temporal variation in climate for the period 1995–2006. Although weathering rate calculations were carried out for individual BC, multivariate analysis were performed for total BC weathering rates only because the new method developed here yields rates that varied according to the same pattern as Na. According to the Akaike information criteria (AIC and AICc), only two models with one significant climatic variable were obtained for predicting BC weathering rates

(Table 5.5).

The annual variation in BC weathering rates were explained by the number of frost days or the number of consecutive days without frost, with variance explanation of 51 and 40%, respectively. The inverse relationship between the number of frost days and BC weathering rates reflects not only the fact that soil water in its liquid form is a key reagent in mineral weathering reactions and BC leaching (Dorn, 1995; Gordon 2005; Riebe et al. 2004; Velbel 1993; White and Blum 1995), but also the importance of the length of the period during which water circulates freely in the soil (Riebe et al., 2004). Interestingly, the same variable was important for explaining the spatial variability of weathering rates for 72 watersheds in Québec (Augustin et al., 2015b). Indeed, intimate contact between soil water, soluble acidic compounds and exposed fresh mineral surfaces is essential for weathering reactions to proceed (Dorn, 1995; Velbel 1993). The number of consecutive days without frost is also related to temperature and determines the length of the growing season. The longer the growing season, the longer the period during which weathering reactions take place. However, if water becomes a limiting factor (eg. during very dry years), temperature can accelerate the process of evapotranspiration and thus negatively affect the chemical weathering process.

5.6. Conclusion

Dissolution experiments were conducted in the laboratory to characterize the weatherable BC pool of B soil horizons. We developed a new approach for estimating BC fluxes from mineral weathering, based on the determination of BC:Na ratios from the weatherable pool and the use of Na fluxes in surface waters. The method was tested on field data acquired at the Hermine watershed. Comparison of BC:Na molar ratios of the weatherable pool with those from other compartments of the watershed suggests possible accumulation of base cations in some areas of the watershed, while losses or minimal changes are observed in others. The average BC weathering rates estimated are in agreement with contemporary rates reported for a range of forested soils from similar environments. We found that the number of frost days was a prominent factor, having a negative relationship with BC weathering rates, while the association with the number of consecutive days without frost was positive. The best predictive model developed using Akaike's information criterion, including the number of frost days, explained 51% of the variation in BC weathering rates. Studying temporal variability in weathering rates in other watersheds with various characteristics in temperate and other regions of the world would be an important step towards establishing a knowledge base of relationships between hydro-climatic variables and BC weathering rates.

5.7 Acknowledgments

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5.8 Appendix C

Supplementary materials

Table S5.1. Summary of trend analysis results for yearly BC concentrations in incident precipitations (1995-2006), soil solutions (1994-2002) and stream water (1995-2006) using Mann-Kendall test and Sen's Slope Estimator.

Solution	Variable	Mann-Kendall test			Sen's slope estimate	
		Z-score	Kendall's tau	*p*-value	Q_{med}	p-value
Incident precipitations						
	Ca	-17	-0.31	0.213	-0.147	0.210
	Mg	-29	-0.53	**0.029**	-0.063	0.107
	Na	-6	-0.11	0.696	-0.013	0.283
	K	-11	-0.20	0.426	-0.022	1.000
	Total BC	-31	-0.56	**0.020**	-0.222	0.107
Stream water						
	Ca	-22	-0.61	**0.029**	-1.341	0.108
	Mg	-18	-0.50	**0.076**	-0.308	0.108
	Na	6	0.17	0.602	0.732	0.902
	K	12	0.33	0.251	0.194	0.902
	Total BC	-6	-0.17	0.602	-0.773	0.386
Soil solution - Zone 1						
	Ca	-26	-0.93	**0.002**	-1.903	**0.003**
	Mg	-22	-0.79	**0.009**	-0.440	**0.003**
	Na	20	0.71	**0.019**	1.232	**0.016**
	K	12	0.43	0.174	0.159	0.368
	Total BC	-6	-0.21	0.536	-1.053	0.368
Soil solution - Zone 2						
	Ca	-20	-0.71	**0.019**	-1.590	0.133
	Mg	-22	-0.79	**0.009**	-0.328	**0.035**
	Na	18	0.64	**0.035**	1.582	**0.072**
	K	3	0.11	0.799	0.007	0.764
	Total BC	2	0.07	0.902	0.431	0.548
Soil solution - Zone 3						
	Ca	-24	-0.86	**0.004**	-2.259	**0.016**
	Mg	-16	-0.57	**0.063**	-0.533	0.230
	Na	14	0.50	0.108	1.862	**0.035**
	K	10	0.36	0.266	0.185	0.230
	Total BC	2	0.07	0.902	0.288	0.548

Z-score: Mann-Kendall Statistic

Q_{med}: Sen's Slope Estimator

Table S5.2: Descriptive statistics for selected environmental variables at the Hermine watershed (1995-2006)

Variable	Unit	Mean	SD[x]	CV[y]	Min	Max
Average growing season temperature	(°C)	15,4	1,0	6,8	13,8	17,5
Number of degree-days	(°C)	1981	141	7,1	1785	2204
Cooling (October to March) season precipitations	(mm)	467	103	22,0	323	623
Number of consecutive days without frost	(day)	144	12	8,2	127	162
Number of frost days	(day)	168	9	5,6	153	183
Aridity	(cm)	5,4	2,5	47,0	0,0	9,3
Growing season length	(day)	185	18	10,0	157	225
Snowfall proportion	(%)	23	5	23,7	16	37
Mean annual air temperature	(°C)	5,6	0,8	14,7	4,6	7,0
Number of growing season degree-days	(°C)	1984	139	7,0	1756	2147
Total radiation	(MJ/m^2)	4721	115	2,4	4528	4921
Ratio of growing season to total precipitation		0,52	0,07	13,4	0,40	0,60

[x] Standard deviation; [y] Coefficient of variation (%)

Table S5.3: Relative importance of predictor variables (descriptor weight[z]) for base cation weathering rates. NFD = number of frost days; CDWF = consecutive days without frost; TR = total radiation; CSP = cooling season precipitations; ARD = aridity; RGSTP = ratio of growing season to total precipitation; NDD = number of degree-days; GSL = growing season length; MAAT = mean annual air temperature; GDD = growing degree-days; SFP = snowfall proportion; GSMT = growing season mean temperature.

Descriptor	Response variable	
	Total BC weathering rates (Watershed scale)	Total BC weathering rates (Rooting zone)
NFD	**0.634**	**0.290**
CDWF	**0.242**	**0.119**
TR	0.110	0.054
CSP	0.081	0.037
ARD	0.080	0.011
RGSTP	0.070	0.132
NDD	0.067	0.064
GSL	0.060	0.033
MAAT	0.058	0.014
GDD	0.058	0.020
SFP	0.056	0.009
GSMT	0.049	0.016

[z] The descriptor weight is the sum of the weights of the models in which the descriptor is present. It may be interpreted as the probability for the desciptor to be present in the selected model.

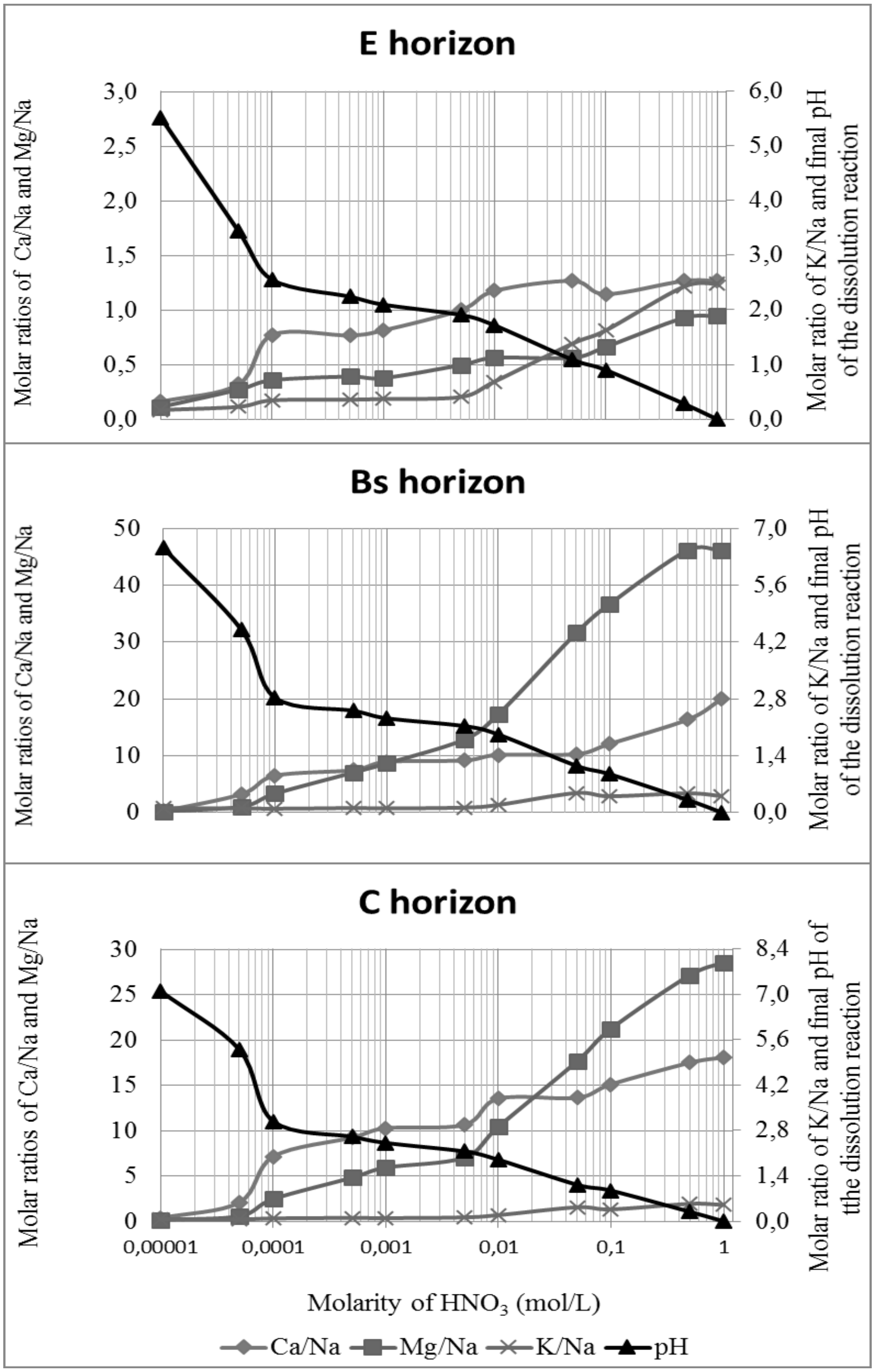

Figure S5.1: Molar ratios of Ca, Mg and K to Na, as a function of the molarity of HNO_3

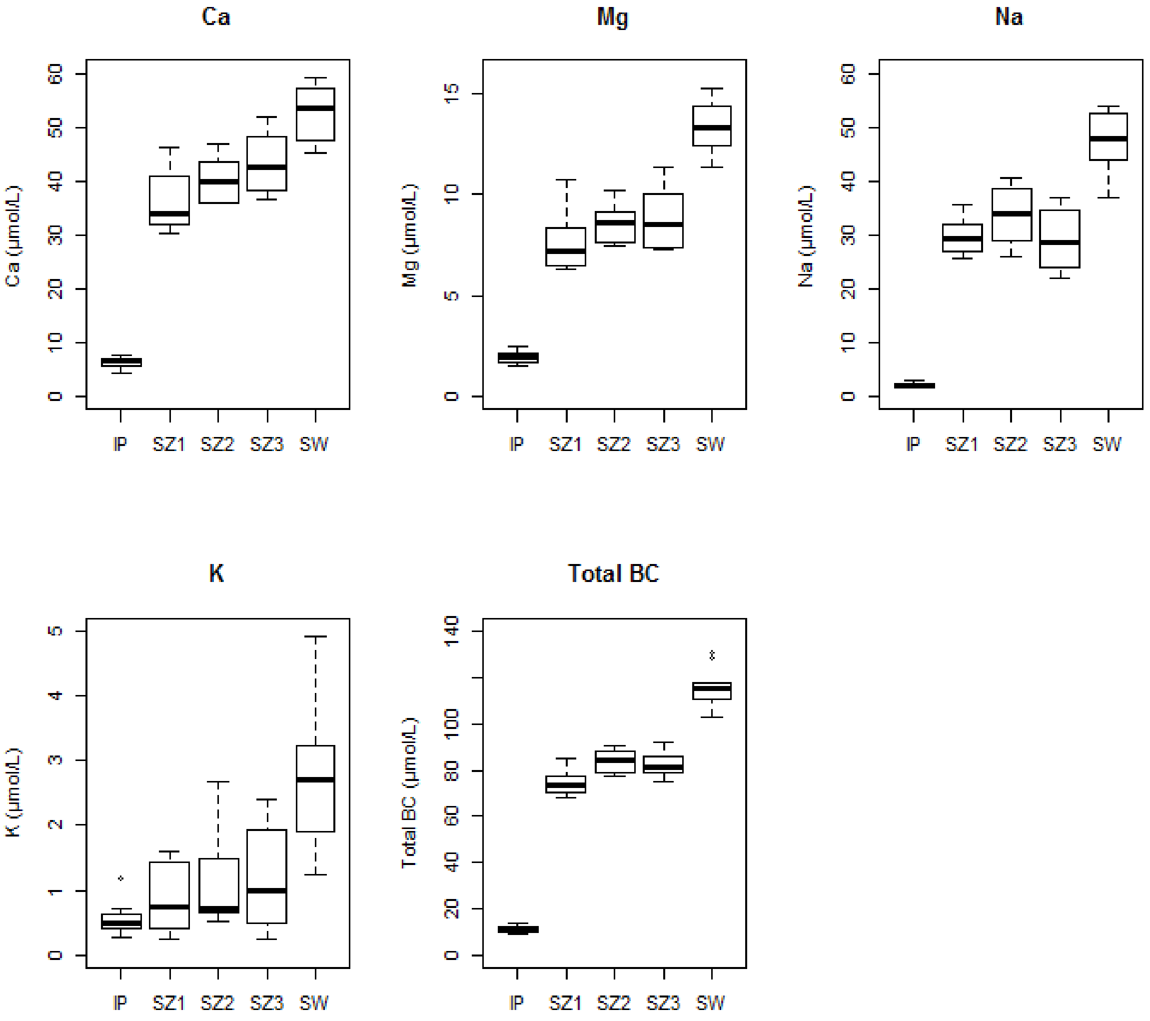

Figure S5.2. Box and whisker plots presenting a summary of BC concentrations in incident precipitations, soil solutions and stream water at the Hermine Watershed (1994-2006). IP: incident precipitation; SZ1: soil solution in Zone 1; SZ2: soil solution in Zone 2; SZ3: soil solution in Zone 3; SW: stream water.

6. Conclusion générale

Cette thèse a étudié l'impact des conditions hydro-climatiques, des propriétés des sols et du matériel parental ainsi que des caractéristiques des bassins versants sur les taux d'altération des minéraux dans la portion québécoise du Bouclier canadien. Plus spécifiquement, en utilisant des données collectées à partir des trois stratégies expérimentales et d'échantillonnage et en appliquant une variété de méthodes d'analyses statistiques, nous avons : 1) quantifié les taux d'altération historiques et contemporains des minéraux dans un large éventail de bassins versants; 2) comparé la performance relative de trois méthodes d'estimation des taux d'altération des minéraux; 3) développé une nouvelle approche pour obtenir des taux d'altération fiables sur des échelles de temps de l'ordre de l'année afin d'analyser la variabilité temporelle des taux d'altération des minéraux; et 4) examiné l'impact de certaines caractéristiques des bassins versants et de facteurs environnementaux sur la variabilité des taux d'altération. Bien que la thèse soit organisée de manière à ce que chaque chapitre ait des objectifs spécifiques, l'ensemble de la recherche forme un bloc cohérent donnant une vue intégrée du sujet abordé.

Dans ce dernier chapitre, nous proposons une synthèse des principaux résultats de la thèse pour mettre en évidence son importance et sa contribution à la recherche sur la biogéochimie en général et l'altération des minéraux en particulier. Nous discutons également des implications associées aux résultats les plus pertinents et nous proposons des pistes de recherche pour des études futures.

6.1 Principales contributions et avancées scientifiques

Ce projet s'inscrit dans un programme de recherche visant à comprendre la réponse des écosystèmes forestiers aux perturbations d'origines naturelle et anthropique. La réalisation de cette recherche a nécessité une masse importante de données collectées via des programmes d'étude à long terme. Ainsi, le projet a donné lieu à des collaborations avec d'autres équipes de recherche, notamment au ministère des Forêts, de la Faune et des Parcs du Québec, à Environnement et Changement Climatique Canada et au consortium Ouranos.

Chapitre 2. Dans le deuxième chapitre de la thèse, nous avons quantifié la fraction de la variation totale des taux d'altération contemporains et des concentrations de cations basiques expliquée par trois groupes de variables (bioclimatiques, sources d'ions et géographiques). La composante bioclimatique expliquait la plus forte proportion de la variation totale des taux d'altération (51.6%) et des concentrations de cations basiques (52.7%). L'interaction entre les groupes de variables, notamment l'interaction entre les variables bioclimatiques et les sources d'ions, expliquait également une proportion substantielle (17.8%) de la variation totale. Les analyses canoniques de redondance (RDA) montrent que les taux d'altération contemporains ainsi que les concentrations des cations basiques dans les lacs ont été positivement influencés par la température, les précipitations sous forme de pluie et les dépôts de sulfate, alors qu'ils étaient affectés négativement par les précipitations sous forme de neige et le nombre de jours de gel.

Chapitre 3. Dans le troisième chapitre, nous avons poursuivi l'analyse de la variabilité spatiale des taux d'altération des cations basiques en nous intéressant cette fois aux taux d'altération historiques estimés par la méthode du bilan de masse en profil qui prend en compte l'ensemble des transformations qui se sont produites dans le sol depuis le début de la pédogénèse. Ici, des analyses multivariées montrent que les variables reliées aux propriétés physico-chimiques des sols avaient un potentiel d'explication de la variance des taux d'altérations historiques des cations basiques qui était beaucoup plus élevé que les variables bioclimatiques pour le jeu de données considéré. Plus spécifiquement, la surface spécifique des sols ainsi que la proportion de feuillus dans la canopée influençaient positivement les taux d'altération à long terme de l'ensemble des cations basiques, alors que l'altitude des bassins versants avait un impact négatif sur ces derniers. L'abondance d'albite dans les sols avait également une influence positive sur les taux d'altération à long terme du Na.

Chapitre 4. Dans le quatrième chapitre de la thèse, c'est la performance relative de trois méthodes d'estimation des taux d'altération des minéraux (PEDON, WATERSHED et MODEL) qui a été évaluée en lien avec des conditions des sites. En effet, en examinant les taux d'altération historiques et contemporains, nous avons observé que la méthode PEDON avait tendance à produire des taux d'altération faibles ou moyens dans les sites contenant un matériel parental et une minéralogie facilement altérable comme la calcite alors que les méthodes WATERSHED et MODEL estimaient des taux d'altération élevés pour les sites contenant la calcite. Ces observations ont été corroborées par les résultats obtenus en appliquant des techniques statistiques non paramétriques pour évaluer la concordance entre les trois méthodes d'estimation. Les tests mis en œuvre ont montré une bonne concordance entres les méthodes WATERSHED et MODEL, alors que la méthode PEDON présentait un degré de concordance plutôt faible avec ces deux méthodes. En analysant différentes causes possibles de la faible concordance entre la méthode PEDON et les autres, nous avons émis l'hypothèse que dans les bassins versants contenant de la calcite, la performance de la méthode PEDON était négativement affectée par des conditions environnementales favorisant la dissolution partielle et le lessivage de la calcite contenue dans le matériel parental initial, y compris dans le matériel situé à la base du profil de sol (horizon C).

Chapitre 5. Le cinquième chapitre comporte un aspect expérimental novateur où nous avons réalisé des essais de dissolution en laboratoire par extraction séquentielle afin d'obtenir le pool de cations basiques altérables nécessaire pour estimer les flux de ces cations issus de l'altération des minéraux. Il représente ainsi une contribution originale au plan de la quantification des taux annuels actuels d'altération des minéraux. Cette approche a ensuite été utilisée dans le cadre d'un banc d'essai destiné à estimer les taux d'altération annuels au bassin versant de l'Hermine pour la période de 1995 à 2006. Les résultats montrent que les taux estimés étaient du même ordre de grandeur que ceux rapportés pour des sols forestiers provenant d'environnements similaires. Nous y avons également établi les relations entre la variabilité temporelle à court terme des taux d'altération et les variations hydro-climatiques inter-annuelles. Au cours de cette période, les taux d'altération des minéraux étaient négativement affectés par le nombre de jours de gel, alors que le nombre de jours consécutifs sans gel les influençait positivement. Ces relations mettent en évidence l'importance de l'eau sous sa forme liquide pour les réactions de dissolution des minéraux et le lessivage des produits d'altération, mais également l'impact positif de la longueur de la saison de croissance sur l'altération des minéraux.

Bien que nous ayons mis en œuvre des approches différentes pour quantifier les taux d'altération des minéraux, nous avons néanmoins noté une convergence des valeurs estimées qui sont du même ordre de grandeur (Table 6.1).

Tableau 6.1: Taux d'altération estimés [moyenne (erreur-type)] selon différentes approches.

Échelle	Chapitre	Échantillon	Méthode	Ca	Mg	Na	K
				----------------- (kmol ha^{-1} an^{-1}) --------------------			
Spatiale							
	2	n=72 bassins	WATERSHED	0.83 (0.10)	0.25 (0.03)	0.14 (0.02)	0.04 (0.01)
	3	n=21 bassins	PEDON	0.16 (0.04)	0.10 (0.04)	0.09 (0.01)	0.06 (0.01)
Temporelle							
	5	n=11 ans	Bassin Hermine	0.44 (0.04)	0.11 (0.01)	0.26 (0.02)	0.02 (0.00)

La Figure 6.1 synthétise les principaux résultats de cette recherche en lien avec la question centrale et les différents objectifs spécifiques de la thèse. Parmi les avancées scientifiques déterminantes de cette thèse, notons par exemple la mise en relief du rôle prépondérant des variables bioclimatiques sur la variabilité spatiale des taux d'altération contemporains des minéraux dans la région étudiée (chapitre 2). L'influence des facteurs climatiques sur les taux d'altération historiques des minéraux a également été démontrée au chapitre 3. De plus, l'absence de méthode standard pour mesurer les taux d'altération des minéraux entraine une démultiplication des méthodes pour quantifier ces réactions. Les résultats présentés au chapitre 4 invitent donc à la prudence quand vient le temps de choisir une méthode dans le cadre d'un projet de recherche. Entre autres, ce choix doit se faire en lien avec les objectifs de l'étude et les conditions de site.

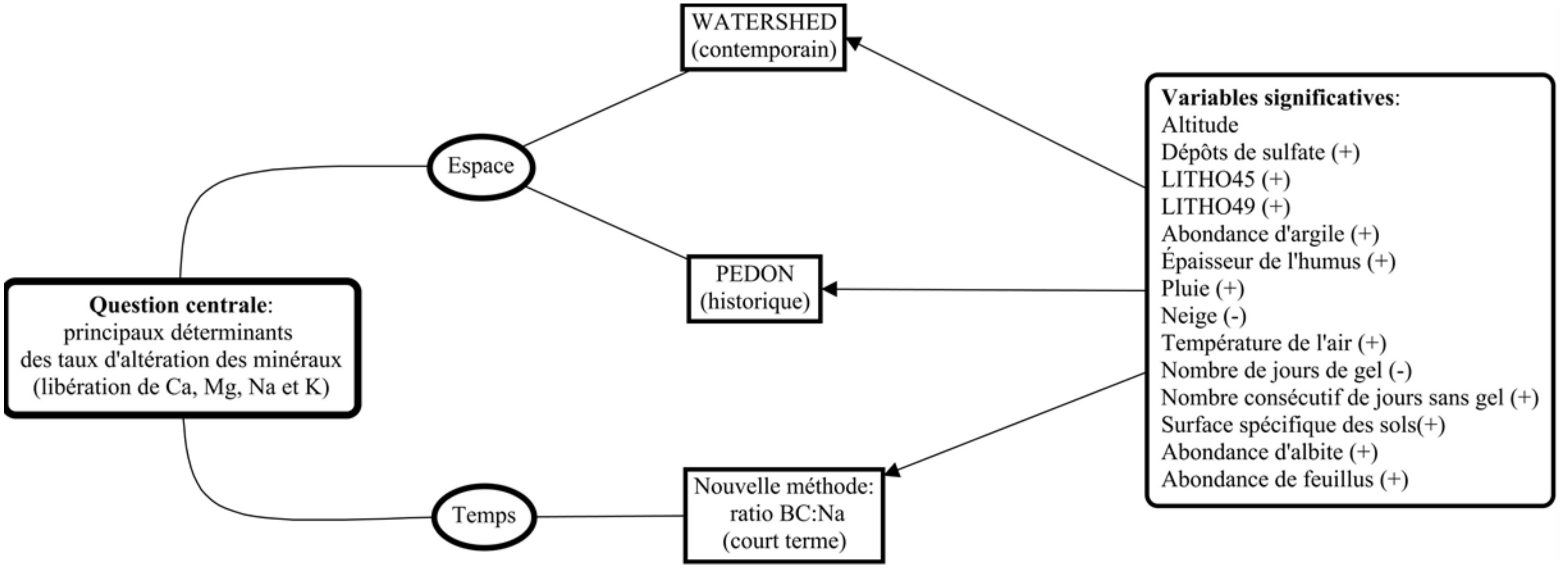

Figure 6.1 : Schéma présentant les principaux résultats de la thèse.

Cette recherche a aussi révélé que la méthode du bilan de masse en profil, qui prend en compte les transformations survenues dans les sols depuis le début de la pédogenèse, a tendance à sous-estimer les taux d'altération des minéraux dans les sols dont le matériel parental contient des minéraux facilement altérables comme la calcite. Dans le chapitre 5, nous avons développé une nouvelle approche méthodologique pour estimer des taux d'altération actuels des minéraux. Nous l'avons testée avec succès au bassin versant de l'Hermine, où nous avons mis en évidence l'influence de facteurs hydro-climatiques sur la variabilité temporelle des taux d'altération des minéraux. C'est l'association de tous ces aspects qui contribue à définir l'étendue des retombées scientifiques de cette thèse.

6.2 Originalité de la thèse

L'originalité de cette recherche se situe tant au niveau des nouvelles connaissances produites qu'au plan des approches méthodologiques appliquées et développées :

Les nouvelles connaissances. L'intégration dans un même projet des axes temps et espace pour expliquer la variabilité des taux d'altération constitue un élément d'originalité. Il en ressort que, sur les deux axes, des variables reliées au climat expliquent une importante proportion de la variation des taux d'altération. L'évaluation de la performance relative des méthodes en relation avec des conditions de site a également permis de produire de nouvelles connaissances, relativement au caractère déterminant du type de matériel parental et de la composition minéralogique des sols (i-e présence de calcite) sur le choix et la performance des méthodes d'estimation des taux d'altération des minéraux. Ces nouvelles connaissances ont pu être obtenues grâce à l'utilisation d'un nombre élevé et d'une diversité de sites qui nous ont permis d'avoir accès à de grands ensembles de données.

Le nombre et la gamme de sites. Le nombre élevé de sites retenus ainsi que les gradients environnementaux (température, précipitations, type de végétation, etc.) qu'ils couvrent constituent un autre élément d'originalité de la recherche. C'est l'une des premières études sur l'altération des minéraux dans les sols qui repose sur un tel nombre de sites, d'autant que l'étendue de l'aire géographique étudiée a favorisé la présence d'une diversité des conditions dans les bassins versants. Tout cela a permi de déployer des stratégies expérimentales et d'échantillonnage et d'appliquer des techniques statistiques appropriées afin de répondre aux objectifs spécifiques de la recherche. Le recours à de telles techniques statistiques est assez rare dans les études sur l'altération des minéraux sachant qu'un grand nombre de site est requis pour leur application.

La diversité et la complémentarité des méthodes. Nous avons mis en œuvre plusieurs méthodes pour estimer les taux d'altération des minéraux. Le fait que ces méthodes utilisent souvent des données d'intrant différentes pour calculer les taux d'altération a ainsi permis de tester l'impact d'un plus grand nombre de variables environnementales dans nos analyses. La comparaison des méthodes d'estimation des taux d'altération des minéraux a également contribué à l'originalité de cette recherche. D'autant que cela a abouti à l'une des découvertes de la thèse, à savoir que la méthode du bilan de masse en profil de sol sous-estime les taux d'altération de cations basiques dans les sols dont le matériel parental contient des minéraux facilement altérables comme la calcite.

Le développement d'une nouvelle méthode. Cette thèse a également une composante expérimentale qui visait au développement d'une nouvelle méthode de quantification de l'altération des minéraux sur des échelles de temps de l'ordre de l'année. Bien qu'elle soit inspirée d'études antérieures, la démarche suivie est originale dans la mesure où elle a mis en œuvre des techniques d'extraction séquentielle dans le but d'extraire la fraction de cations basiques libérable à partir de l'altération des minéraux dans des échantillons de sol. Nous avons appliqué cette nouvelle méthode pour estimer des taux d'altération au bassin versant de l'Hermine entre 1995 et 2006. Grâce à l'utilisation de la nouvelle méthode, ce travail compte parmi les rares études qui ont analysé la variabilité temporelle (inter-annuelle) des taux d'altération des minéraux en lien avec des facteurs hydro-climatiques en milieu naturel.

6.3 Perspectives de recherche

Les avancées scientifiques de ce travail ont un fort potentiel pour améliorer notre compréhension des facteurs environnementaux qui contrôlent les mécanismes impliqués dans les processus d’altération des minéraux. Dans un contexte de changement des conditions environnementales, les résultats ouvrent de nouvelles perspectives de recherche pour faire avancer les connaissances sur la façon dont les changements climatiques pourraient affecter la disponibilité des nutriments dans les écosystèmes forestiers.

Dans ce contexte de changements environnementaux, l'effet exclusif des variables hydroclimatiques sur l'altération des minéraux dans les sols doit être étudié plus en profondeur pour mieux isoler et quantifier leur contribution. Cela est nécessaire pour une meilleure compréhension des impacts potentiels des changements climatiques sur le taux d’altération des minéraux et sur leur capacité à fournir des cations basiques aux réservoirs échangeables des sols.

Dans le chapitre 5, une nouvelle approche méthodologique a été proposée pour estimer les taux d’altération des minéraux. La méthode a été testée au bassin versant de l’Hermine. Ce dernier a également été considéré pour l’analyse de la variabilité temporelle des taux d’altération des minérauix. Sachant que notre démarche vise à proposer une méthode innovante ainsi que des résultats probants sur les processus d’altération, nous ne considérons pas l’utilisation de données provenant d’un site unique comme un problème. En effet, le dispositif expérimental établi à l’Hermine nous a donné accès à un jeu de données sur l’hydrochimie du bassin pour la période de 1995 à 2006. De plus, pour la caractérisation des sols ainsi que l’expérience de dissolution et les analyses d’extraction séquentielles, nous avons eu la possibilité d’utiliser des échantillons de sols prélevés directement dans les fosses pédologiques où les lysimètres ont été installés pour l’échantillonnage de la solution du sol en 1993. Nous avons comparé les ratios molaires de BC:Na obtenus pour la fraction altérable avec des ratios provenant de différents compartiments du bassin versant de l'Hermine au cours de la période d'étude. Les résultats présentés dans le chapitre 5 sont assez révélateurs à ce sujet, montrant un bon niveau de cohérence entre les ratios. Considérant le dispositif établi à l’Hermine, le protocole d’échantillonnage, les méthodes de mesures, les techniques d’analyses ainsi que les approches statistiques mises en œuvre, la plupart des avancées scientifiques issues de cette recherche ont un bon potentiel de généralisation à des sols d’environnements granitiques similaires. Il est toutefois essentiel de confirmer ce potentiel en mettant à l’essai la nouvelle méthode d’estimation des taux d’altération des minéraux dans des contextes pédologiques variés et de comparer sa performance avec celles d’autres méthodes sous différentes conditions de site. De plus, l'étude de la variabilité temporelle des taux d'altération des minéraux dans d'autres bassins versants de régions tempérées et d'autres régions du monde constituerait une étape importante vers l'établissement d'une base plus importante de connaissances sur l’impact de facteurs bioclimatiques sur ces processus, ce qui pourrait servir à tester des scénarios climatiques.

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