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Key Points:
- Nitrogen budgets were constructed covering the major landscape types of Canada
- Canadian forests are in N balance, while agricultural systems are accumulating N
- Canada is a major exporter of nitrogen as hydrocarbons, fertilizers, and food

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Interactions between reactive nitrogen and the Canadian landscape: A budget approach

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Abstract The movement of excess reactive nitrogen (N_r) from anthropogenic activities to natural ecosystems has been described as one of the most serious environmental threats facing modern society. One of the approaches for tracking this movement is the use of budgets that quantify fluxes. We constructed an N_r budget for Canada using measured and modeled values from the scientific literature, government databases, and data from new agri-environmental indicators, in order to produce information for policy makers and scientists to understand the major flows of nitrogen to allow a better assessment of risks to the Canadian environment. We divided the Canadian territory south of 60°N into areas dominated by natural ecosystems, as well as by agricultural and urban/industrial activities to evaluate N_r flows within, between, and out of these units. We show that Canada is a major exporter of N_r due to the availability of inexpensive commercial fertilizers. The large land area suitable for agriculture makes Canada a significant agricultural N_r exporter of both grain crops and livestock. Finally, Canada exports petroleum N mainly to the United States. Because of its location and prevailing atmospheric transport patterns, Canada is a net receptor of N_r air pollution from the United States, receiving approximately 20% of the N_r leaving the U.S. airshed. We found that overall, terrestrial natural ecosystems as well as the atmosphere are in balance between N_r inputs and outputs when all N reactive and nonreactive fluxes are included. However, when only reactive forms are considered, almost 50% of N entering the Canadian atmosphere cannot be accounted for and is assumed to be lost to the Atlantic and Arctic oceans or to unmeasured dry deposition. However, agricultural and freshwater landscapes are showing large differences between measured inputs and outputs of N as our data suggest that denitrification in soils and aquatic systems is larger than what models predict. Our work also shows that Canada is a major contributor to the global flow of nitrogen through commercial exports.

1. Introduction

The fixation of inert atmospheric N_2 gas into organic and reduced inorganic forms requires considerable energy to occur. In nature, biological nitrogen fixation is carried out by bacteria living in the nodules of legume roots and free-living bacteria in soils, whereas inorganic production results from high-energy pulses in lightning. In preindustrial agricultural societies farmers learned how to harness biological N fixation by growing legumes and cyanobacteria in rice paddies and by recycling animal manure and crop residues. In the early part of the twentieth century, reactive nitrogen (N_r) became much more abundant in both natural and managed ecosystems due to the inputs of manufactured nitrogenous fertilizers (Haber-Bosch process which uses fossil fuels as energy sources), deposition of N_r emitted from combusted fossil fuels (from transportation and energy generation), and from increased agricultural production of N-fixing leguminous crops [*Erisman et al.*, 2008; *Galloway et al.*, 2003]. A number of environmental and human health concerns have resulted from unintended N_r leakages from these new anthropogenic sources.

In a recent review of global environmental threats, *Rockström et al.* [2009] rated excess N_r as one of the most serious current global environmental stressors. N_r leakages from agricultural sources and industrial sources are

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causing the eutrophication of estuaries and marine systems throughout the world [*Diaz and Rosenberg*, 2008; *Seitzinger and Sanders*, 1997], enriching and acidifying terrestrial ecosystems [*Driscoll et al*., 2003; *Nordin et al*., 2005] and altering atmospheric chemistry [*Forster et al*., 2007]. Both reduced and oxidized forms of N_r serve as precursors for a number of chemical reactions that result in formation of fine particulate matter ($PM_{2.5}$) and ozone, which are injurious to human health [*Paulot and Jacob*, 2014; *Mauderly and Wyzga*, 2011; *Sneeringer*, 2009]. Nitrous oxide emitted from soils and water contributes significantly to global climate change and has been described as the dominant ozone-depleting substance emitted in the 21st century by *Ravishankara et al.* [2009].

Reactive nitrogen flows originating from agriculture and fossil fuel combustion have measurably modified the global N cycle since the early 1900s [*Canfield et al*., 2010; *Galloway et al*., 2008]. The term "nitrogen cascade" was coined to describe the series of transformations and exchanges which occur within and between natural and anthropogenic systems as well as between environmental media. The term communicates a critical feature of N_r, which is its tendency to transform from one species to another [*Galloway et al*., 2003], each with distinct impacts. Despite the known deleterious effects of excess N_r to the environment and to human health, the use of synthetic N fertilizers and the combustion of fossil fuels are as unavoidable as it is necessary to feed and sustain a growing global population and economy. It is therefore important to understand how N_r is used and transported around the globe in order to manage and mitigate its many impacts.

Constructing mass balance models is a useful approach for quantifying the fate of important, environmentally active compounds. In the study of environmental N_r, a number of studies have examined the flow of N within a single sector such as agriculture or natural ecosystems, as well as between and within political jurisdictions. Accurate understanding of overall N_r balances, however, requires that flows be quantified comprehensively with reference to geographical, sectorial, and/or ecosystem boundaries. The collection, synthesis, and evaluation of data from multiple sources therefore require interdisciplinary or intersectorial data exchanges in order to better understand the full scope, complexity, and ramifications of N_r flows. Reactive nitrogen budgets have previously been developed at several scales, from the global [*Fowler et al*., 2013; *Galloway et al*., 2008; *United Nation Economic Commission for Europe* (*UN-ECE*), 2013], national [*Houlton et al*., 2013; *Leip et al*., 2011a; *Science Advisory Board*, 2011], to more specialized, regional analyses such as N_r use and loss in river catchments [*Howarth et al*., 1996a], and even at the farm level [*Drury et al*., 2007; *Yang et al*., 2007].

Although it has a small population, Canada is a large country containing abundant natural resources including fossil fuels and a vast amount of agricultural and forested land. The country exports hydrocarbons in raw and manufactured forms, as well as agricultural and wood products, all containing significant amounts of N_r [*StatsCan*, 2013]. Moreover, because of the availability of relatively inexpensive energy sources, Canadian manufacturers also produce and export synthetic N fertilizers [*International Fertilizer Industry Association* (*IFIA*), 2014]. The vast Canadian forests are prone to fires [*Stocks et al*., 2002] so that burning also contributes oxidized N species to the atmosphere. The United States also emits large amounts of N_r into shared air and watersheds; hence, the influence of U.S. N_r emissions on Canada can be very important [*Vet et al*., 2005].

Though national N budgets have been constructed for the United States [*Science Advisory Board*, 2011] as well as for a number of European countries [*Leip et al*., 2011a], none has yet been produced for Canada. As the country's economy, size, and climate are very different from these other jurisdiction, it is important to understand how N_r cycles in areas where resource extraction is important. The information from a budget also can provide an indication of the relative importance of resource-based economies to global N cycling.

The main objective of this study is to show the relative importance of domestic and imported N_r sources in relation to the fate and impact of N_r on the Canadian landscape. This will provide information to allow policy makers to initiate mitigation strategies that would have greatest environmental benefits to the country if serious imbalances are seen. It will also provide information to policy makers and scientists involved in assessing global transport of N_r to better understand the importance of nitrogen-rich jurisdictions in modifying global flows.

Because of the size of Canada and of the uneven distribution of N_r modification activities, we decided to divide Canada by landscape units, instead of jurisdictional boundaries. We divided Canada into agricultural,

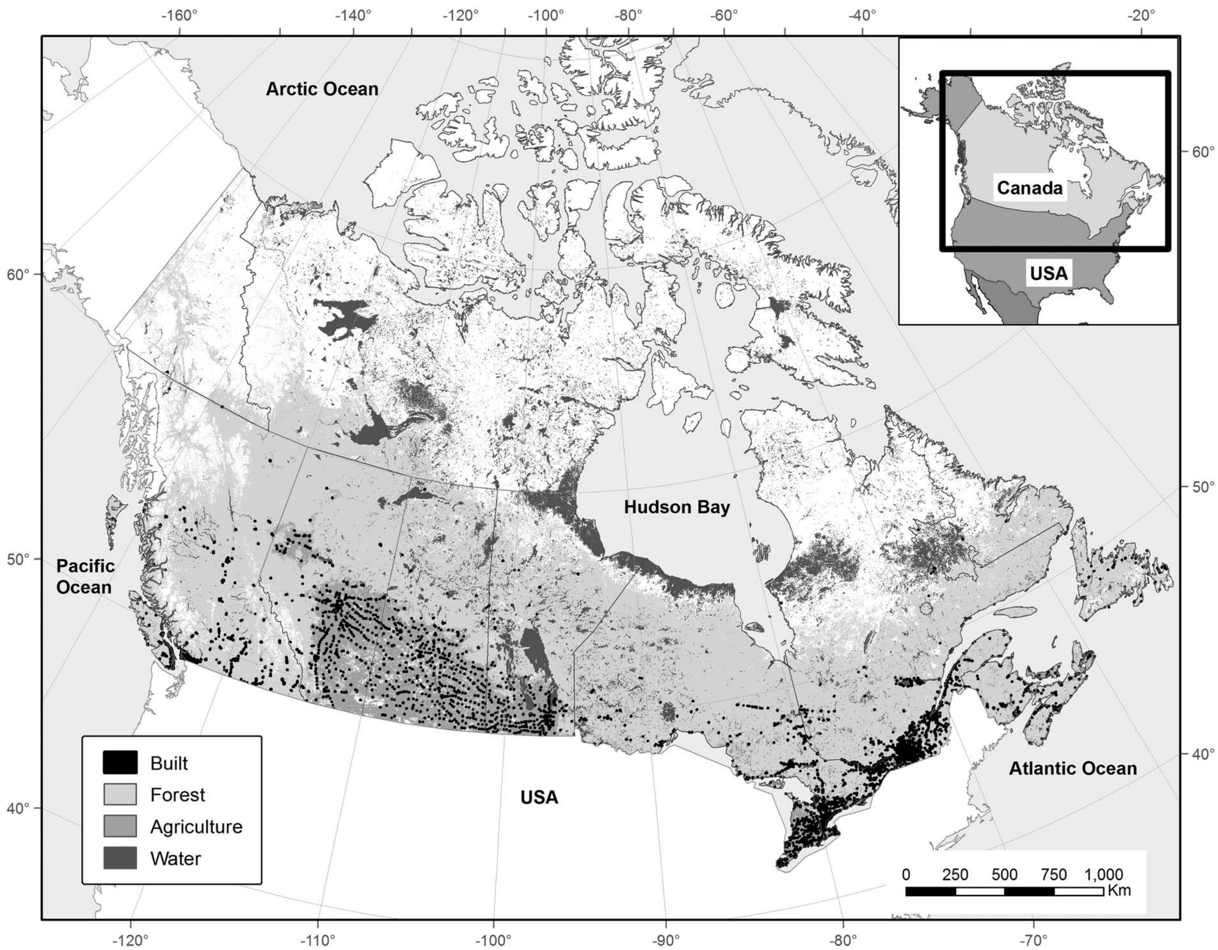

Figure 1. Landscape types of Canada. Only the region south of 60°N was used in this analysis. Natural/forest ecosystems occupy 83% of the surface area (4,874,726 km^2), lakes and open water 5% (313,472 km^2), and agricultural land 12% (682,356 km^2). Built environment occupies < 1% of the land surface (~58,700 km^2), but has been exaggerated in the figure to better identify locations..

forest, urban/industrial, atmospheric, and aquatic components and then identified the major sources, sinks, and pools in each of the components. We then account for N_r movements within and between these pools as well as into and out of Canada by using the atmosphere and freshwaters as integrating media.

2. Study Area

Canada occupies 9,985,000 km^2 of northern North America (Figure 1). In 2006, there were 67.6 × 10^6 ha of agricultural land in Canada which represented about 6.8% of the land area. The country is 4634 km long from Cape Columbia on Ellesmere Island in the north to Lake Erie in Southern Ontario, and its southern boundary with the United States is 8900 km in length [*Natural Resources Canada* (*NRCan*), 2001]. Canada has a large number of ecosystem types including the following: Arctic tundra, wet temperate forests on both Atlantic and Pacific coasts, and semiarid grassland regions mainly in its central portion, though freshwaters and wetlands cover large parts of the country. The area north 60° latitude which includes the Arctic islands occupies 4,055,746 km^2 or 41% of Canada and is not included in this analysis due to low anthropogenic activity and paucity of data for this region.

Canada's population density, agricultural activity, and industry are low in much of the country. The population of ~35 million, agriculture, and industry are spread mostly along its southern border especially along the Great Lakes-St. Lawrence watershed and the lower Fraser Valley in British Columbia and the oil industry center of the Calgary-Edmonton Corridor in Alberta. Canada has the eleventh largest economy in the world, with fossil fuel production, agriculture, and forestry contributing greatly to its economy [*WorldBank*, 2014].

For the purpose of this study, Canada was divided into three broadly defined functional units characterized by the dominant land cover: natural/forest, agriculture, urban/industrial, and two natural integrative media, water, and atmosphere. This subdivision allowed separate N_r budgets to be calculated for each of these units to simplify interpretation of the more complex N_r flows over the whole of the country and indirectly provided more information concerning large-scale processing of nitrogen by natural and anthropogenic sources.

Total N_r deposition in Canada is highest in the southeastern part of the country, with values of up to 30 kg ha^{-1} yr^{-1} in parts of Southern Ontario and southern Quebec, most of which is in oxidized form [*Moran et al.*, 2008] . There is also a corridor of higher deposition in the petroleum industry-rich region of Central Alberta and Saskatchewan (~ 10–12 kg ha^{-1} yr^{-1}). The lower Fraser Valley region in southwestern Canada is often subject to high N_r deposition ($>$ 30 kg ha^{-1} yr^{-1}) due to air inversion events associated with trapping by high mountains on three sides. There is also extensive agriculture in southern portions of Ontario, Québec, the Prairie Provinces (Manitoba, Saskatchewan, and Alberta), and in the lower Fraser Valley near Vancouver on the west coast, which contribute to N_r emissions and subsequent local deposition. Moreover, southeastern Canada receives significant N_r deposition which originates in the U.S. Midwest and eastern seaboard [*Vet et al.*, 2005].

3. N Budget Approach and Data Sources

A nitrogen budget quantifies all major N flows (inputs, outputs, and surplus) across all sectors and media within given boundaries and includes movements across these boundaries in a given time frame (typically 1 year). It also can quantify the changes of N stocks within the respective sectors and media [*UN-ECE*, 2013].

We assembled input and output nitrogen data using the standardized spreadsheet approach developed by *Leip et al*. [2011a] for the European Union's Integrated Nitrogen Assessment [*Sutton et al*., 2011]. The spreadsheet model identified all quantifiable N flows within and in and out of each country as defined by political borders and produced a standard graphical display that was used to compare countries to each other. We used data that were mostly collected from the 2007 ± 2 year period, though some values are not specific to a time period but are nevertheless the only published information available. The main data sources are described and listed in the following sections.

3.1. Atmospheric Emissions

Most of the data for N_r emissions to the atmosphere from transportation, industrial, and agricultural industries were extracted from Environment Canada's National Pollution Release Inventory's Air Pollutant Emissions Inventory [*National Pollution Release Inventory* (*NPRI*), 2013]. These data are based on facility-reported data, supplemented with a national database of estimates using statistical information and standard methodologies comparable to those used by the U.S. Environmental Protection Agency (EPA) and the United Nations Economic Commission for Europe. The agricultural ammonia emission calculations were based on the work of *Sheppard and Bittman* [2013], while nonagricultural sources were obtained from *Ayres et al*. [2010]. The N_2O data were obtained from the residual soil nitrogen indicator database as well as the 2000–2005 Canadian N_2O emissions inventory [*Drury et al*., 2007; *Rochette et al*., 2008; *Yang et al*., 2007].

3.2. Atmospheric Deposition and Transport Into and Out of Canada

Deposition of N_r to the Canadian landscape as well as atmospheric transport into and out of the country for the year 2002 was estimated using the AURAMS model (A Unified Regional Air-quality Modelling System) [*Moran et al*., 2008; *Smyth et al*., 2009]. AURAMS is a regional air quality modeling system which consists of three major components: a chemical transport model, a meteorological model with a preprocessor, and an emissions processor. The 2000 Canadian emission inventories for point, area, nonroad mobile, and on-road mobile sources released by Environment Canada in January 2005 were used as inputs. U.S. emissions for point, area, nonroad mobile, and on-road mobile sources, used in AURAMS, were taken from the U.S. EPA 2001 Clean Air Interstate Rule (CAIR) emission inventories released in July 2004 and available from the U.S. EPA (http://www.epa.gov/ttn/chief/emch/index.html). Mexican emissions were taken from the 1999 raw emissions inventories for point, area, and mobile sources released with the 2001 EPA CAIR data.

Biogenic emissions for Canada, the U.S., and Mexico, which included soil NO emissions, were generated using BEISv3.09 algorithms and the Biogenic Emissions Land Cover Database, Version 3 land use data.

The synthesis of NO_2 from lightning was estimated by using the data produced for North America by *Galloway et al.* [2004] and prorating it for Canada based on the maps of *Choi et al.* [2005] which suggest that N production from lightning in Canada is roughly 20% of the total North American value (less Mexico).

3.3. Forest N_r Emissions and Uptakes for Canada

N_r transfers from forested uplands to wet areas, wetlands and streams via runoff, and the resulting N_r losses due to denitrification to the atmosphere, were estimated using the modeling approaches of *Murphy et al.* [2009] and *Nasr et al.* [2011]. Nitrification of NH_4^+ to NO_3^- is an important N cycling process in deciduous forest and agricultural soils which have a moderate pH, and a substantial portion of mineralized N transforms into leachable NO_3^-. Once transferred from the upland areas to lower wet areas, leachable NO_3^- may be reduced into volatile N species products such as N_2O and N_2. In contrast, coniferous forests tend to directly absorb most of the incoming reduced N components from the atmosphere and soil directly into plant or soil organic N because coniferous forest soils are generally too acidic to support nitrifying soil bacteria [*Lupi et al.*, 2013].

The amount of atmospheric N lost by denitrification from deciduous and mixed-wood forests was estimated using

$$N_{\text{denitrification}} = \left(N_{\text{deposition}} + \text{ other } NO_3 - \text{N inputs}\right) x \ \max\left[11.22\ (A_W/A_B)0.22\right] \quad (1)$$

where A_W/A_B is the wet to total area ratio for the forested basins [*Murphy et al.*, 2009]. It is assumed that all incoming N_r deposited dry and wet on coniferous forest uplands is taken up by the vegetation. The NO_3^- portion that falls on wetlands was assumed to be fully denitrified to N_2. Forest (coniferous versus deciduous) and wet areas were estimated, and potential N uptake (from deposition and fixation) and denitrification were calculated on an area basis then summed. N_2 fixation in forests was estimated as the difference between N deposition and modeled forest uptake [*Arp et al.*, 2008; *Murphy et al.*, 2009]. N_r runoff from forested regions was also taken from the *Murphy et al.* [2009] estimate of runoff from forested ecosystems.

3.4. Agricultural N Data Sources

The difference between all estimated inputs and outputs of N_r in about 3000 relatively homogeneous areas covering the agricultural land in Canada was assumed to be surplus and remaining in the soil at the end of the growing season (residual N_r, mainly as soil ammonium and nitrate) [*Drury et al.*, 2007; *Yang et al.*, 2007]. The amount of the residual N_r (primarily nitrate) in each of the defined land areas that was lost from the soil by leaching and runoff, usually after crop harvest in fall, was estimated using precipitation data and a water balance model [*De Jong et al.*, 2009; *Drury et al.*, 2007].

The three primary N_r inputs to agricultural soils were from manure, fertilizer, and N fixed by leguminous crops [*Yang et al.*, 2010], while minor inputs were from atmospheric deposition and N fixed by free-living microbes in soil. The quantity of N_r from irrigation water is small and was not considered. Inputs of N_r from manure were estimated from total excreted N in an area, less gaseous N losses (mainly as ammonia) before soil application. Excreted N estimates were based on animal numbers (poultry, cattle, and pigs) obtained from Census of Canada [*Statscan*, 2014] and published excretion factors for each animal class. The life cycles of the various animal types were also taken into consideration, for example, total annual poultry numbers accounted for the lengths of the production cycles as well as the down time between cycles [*Yang et al.*, 2007]. Ammonia losses from manure (barns, pastures, storages including composting, and land application) were taken from *Sheppard and Bittman* [2013], and these estimates were based on total ammonia N in excreta and emission factions determined from published emission factors which were adapted to Canadian farming practices. Farming practices were characterized in 12 ecoregions from an ammonia-focused farm survey of livestock practices carried out in 2006. Emissions from land-applied fertilizer were obtained from *Sheppard and Bittman* [2013]; these values were estimated using industry data for amounts and types of N fertilizers consumed by farmers and emission fractions based on published emission factors adapted to Canadian farming practices which were determined from a 2006 survey of crop producers.

Nitrogen outputs from agricultural soils included N in the harvested portion of the crop (census data and generic N concentrations); ammonia volatilized from manure and fertilizer application (calculated as above); and nitrous oxide emitted from applied fertilizer and manure, and from the mineralized organic N in crop residues of legumes assumed to contain mainly symbiotically fixed N. Emissions of N_2O from nonlegume crops were not included because it was assumed that annual emission factors for manure and fertilizers applied to (mostly nonlegume) crops included emissions from mineralized residues. Although we did not have direct measurements of complete denitrification losses as N_2, the N balance in the budget model assumed a 1:1 ratio of N_2O:N_2 and hence accounted for the complete return of some of the applied N to a nonreactive (N_2) form from farmland [*Yang et al.*, 2007].

3.5. Urban Waste and Runoff

Estimates of total N_r losses from sewage treatment plants to water courses were very difficult to assess using government point source databases due to the large number of jurisdictions which exist and varying reporting approaches between jurisdictions and facility sizes. We therefore used an estimate derived from *Metcalf et al*. [2010]; waste water N losses into rivers and estuaries were calculated using an estimate of 300 L d^{-1} cap.$^{-1}$ for Canada, and assuming that 90% of the population was served by waste water treatment plants [*Chambers et al*., 1997], with a mean N_t value of waste water of 31 mg L^{-1} from *Metcalf et al*. [2010].

N_r losses in urban runoff were made using a five-step process where (a) the total urban area in Canada was estimated by comparing independent published estimates [*NRCan*, 2001] and the Canada Land Inventory [*Agriculture and Agrifood Canada*, 2013]; (b) information for Canada was extracted from a projection of evapotranspiration (ET) values for urban areas across the globe using ET point data from Global evapotranspiration assembly (GETA) 2.0 within a linear model; (c) precipitation estimates for Canada were based on National Climate Center global atmospheric forcing data set [*Ngo-Duc et al*., 2005]; (d) precipitation and ET data sets were converted to the same cell size and location and runoff was then estimated; and (e) summation of runoff by area was computed for each cell. The total value for each cell was calculated in L yr^{-1}, and cells then were summed to obtain total urban runoff per year for Canada in L yr^{-1}. Mean runoff total nitrogen (N_t) value for storm water runoff of 0.73 mg L^{-1} was taken from *Metcalf et al*. [2010] and multiplied by the total urban runoff in L yr^{-1} to obtain N_r losses from urban areas for Canada.

3.6. River N Losses to Estuaries

Exports of total N_r from Canadian rivers to estuaries and the marine ecosystem were taken from *Clair et al*. [2013]. They calculated N exports from rivers which drained 60% of the Canadian landscape to the ocean and derived an algorithm which allowed the estimation of area-normalized values to regions where no data existed. For this study, the N contribution of U.S. states (Minnesota, Wisconsin, Illinois, Indiana, Ohio, Pennsylvania, and New York) to the export from the Great Lakes is attributed to the St. Lawrence River and counted as Canadian exports to the Atlantic, as total N exports for the St. Lawrence were only measured near the river estuary in Québec City.

3.7. Exported Manufactured and Raw Products

Though N in finished and semifinished exported products is not part of the reactive N budget for the country, we include these for completeness to describe the movement of N into and out of Canada. As the production of exported N usually involves the generation of N_r in the manufacturing or growing process, these N costs are included in the figures shown above. Moreover, many Canadian N exports in natural and finished products eventually become part of a reactive N chain elsewhere, so we thought it useful to produce the numbers to identify how Canada might contribute to the "N cascade" elsewhere. N imports also need to be quantified as they eventually will be used and may contribute to the national N cycle so that it is useful to identify how much of "excess N" originates outside the country.

Wood export and import data were taken from the Natural Resources Canada website (http://cfs.nrcan.gc.ca/search?query=wood+exports+2007&cn-search-submit=Search) with data collected by province and summed to provide national estimates. These data were used in conjunction with literature values for the nitrogen content of wood products to calculate a national N balance for wood products for 2006. Average values of 400 kg of wood m^{-3} 0.06% N concentration were used. Statistics for fertilizer production,

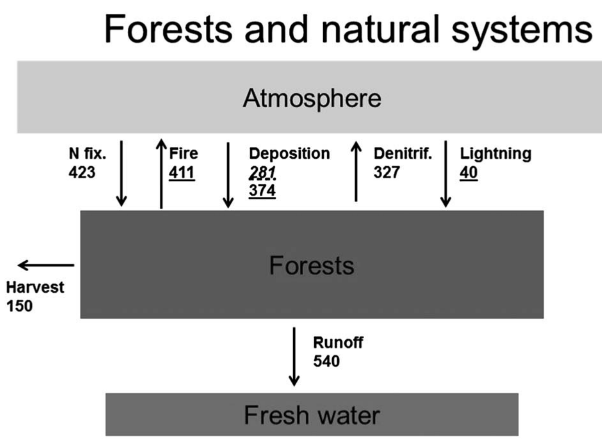

Figure 2. Main components of the forest/natural landscape unit. Inputs into forest total 1118 kt yr^{-1}, while total losses are 1428 kt yr^{-1}. Numbers with solid underlines are oxidized N and in italic with dash underlines are reduced. Numbers not underlined are for total N.

consumption, imports and exports by nutrient, and product were obtained from the International Fertilizer Industry Association database [*IFIA*, 2014].

Data for imports and exports of petroleum products were obtained from the Statistics Canada CANSIM database (http://www40.statcan.ca/l01/ind01/l3_1741_2026-eng.htm?hili_prim72). These data were used in conjunction with estimates of the N content of petroleum products to calculate the resultant N balance. Nitrogen concentration content data were not available for all products, nor for all regions, from a single consistent source. Moreover, meter station and refinery technicians and researchers suggest that values for some products vary widely. For this reason, generic values from published literature sources [*American Petroleum Institute*, 2007; *Wang et al.*, 2007] were adopted. We assumed that the average N content was similar for imported and Canadian products.

The Statistics Canada CANSIM values for food imports and exports were used in conjunction with protein concentration data (N = protein/6.25) for specific foods from the U.S. Department of Agriculture Nutrient Database [*U.S. Department of Agriculture*, 2013] to calculate the food N balance for foods exported and imported into Canada in 2006.

4. Results

4.1. Forest and Terrestrial Natural Ecosystems

Forests dominate natural ecosystems in Canada due to climatic and soil conditions, as well as low population density, which reduces the possibility of large-scale disturbance. The largest input into Canadian natural areas is atmospheric N_r deposition. This is most important in the southern 25% of the country which receives the highest N deposition amounts [*Vet et al.*, 2005] (Figure 2). Biological N fixation is also important and is approximately two thirds of the atmospheric deposition. The potential contribution by lightning is only 3% of total deposition and is a minor contributor to the total. The largest N_r losses from forests are from fire, soil denitrification, and runoff which are responsible for 86% of the total, with the remainder coming from harvesting activities. The overall input-output budget is off by ~ 22%. As most of the values we used in quantifying flows in this landscape were model estimates, this discrepancy is not surprising.

The forests in this analysis included hardwoods in Southern Ontario, receiving ~ 25 kg N ha^{-1} yr^{-1}, rain forests on the Pacific coast (~ 1 kg N ha^{-1} yr^{-1}), as well as northern boreal forests, which are the largest components of the Canadian forest landscape, which can receive between 1 and 3 kg N ha^{-1} yr^{-1} [*Moran et al.*, 2008] depending on location. Because of the large extent of forests in Canada and despite low deposition amounts in most forests, this landscape unit overall still receives 655 kt yr^{-1} N deposition plus 423 kt yr^{-1} through N fixation. However, losses of soil organic N to runoff are also very high (540 kt yr^{-1}), as is denitrification from wet forest soils (327 kt yr^{-1}).

4.2. Agricultural Systems

The largest input of N into the agricultural landscape is from N_2 fixation by leguminous crops (alfalfa, pulse crops, clovers, etc.) and by synthetic fertilizer use (Figure 3). Native legume species in permanent pastures also fix atmospheric N_2, but their contribution is relatively minor. The two other sources of N inputs are free-living microbes in soils (186 kt N) and atmospheric deposition on crops (308 kt N). These combined with N inputs (3615 kt N) sustain current crop production.

Some of the crops are cycled within the agricultural system (1372 kt N) as animal feed (e.g., silage, pasture, forage crops, and grain), whereas some crops and animals leave the agricultural ecosystem (1657 kt N grain

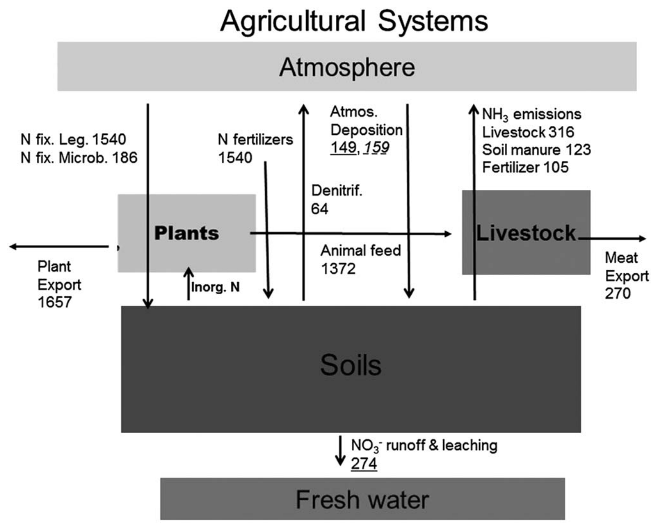

Figure 3. Main components of the agricultural landscape unit. Inputs from deposition, fixation, and fertilizers total 3574 kt yr^{-1}, while losses to crops, the atmosphere, and runoff sum to 2610 kt yr^{-1}. Numbers with solid underlines are oxidized N and in italic with dash underlines are reduced. Numbers not underlined are for total N.

+270 meat) where they are used as food for human consumption or as a source of fuel or fiber domestically or as exported grain and livestock products (Figure 3). There is a direct loss of manure N during excretion, housing, and storage (316 kt N).

The remaining losses of N from the agricultural system include nitrate loss from surface runoff and nitrate leaching through agricultural soils and tile drains to surface waters and ground waters (274 kt N); N_2O losses to the atmosphere through nitrification; NO, N_2O, and N_2 losses of NO_3^- to the atmosphere through denitrification which in total amount to 64 kt N; and ammonia volatilization losses resulting from manure application and fertilizer loss (105 kt yr^{-1}) (Figure 3). Our data thus suggest that the agricultural landscape of Canada is accumulating, on average, 686 kt N yr^{-1}.

4.3. Urban and Industrial Systems

We estimated a budget for the urban/industrial component in Canada, mostly as it affected natural and agricultural systems (Figure 4). Food consumed by the urban population was calculated as the difference between total food N produced, less food N exported, plus food N imported. Fuel N consumed by the built environment was estimated by subtracting all hydrocarbons produced in Canada plus the amounts imported from fuel N amounts which were exported. Atmospheric deposition and amounts from the various emission sources are well quantified, as are the societal waste products from waste treatment [*NPRI*, 2013]. Food products, as estimated by our approach, are by far the greatest inputs into the urban/industrial pool. N losses to the environment were relatively well quantified. Combined transportation, power generation, and industrial N emissions were approximately 81% of all releases from the built environment, while water N releases from sewage treatment plants were also substantial.

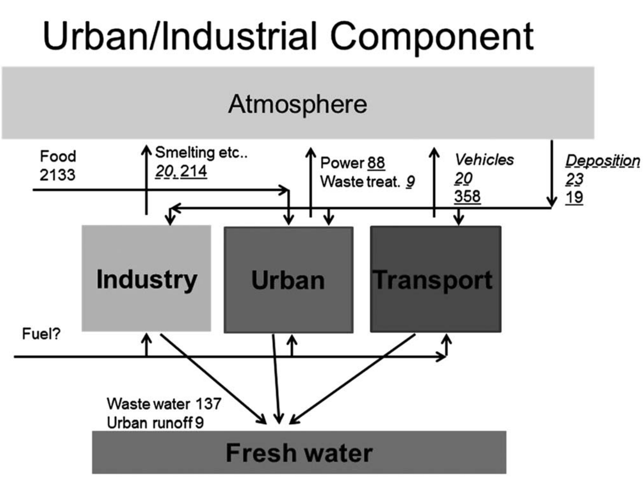

Figure 4. Main components of the urban/industrial landscape unit. Partial inputs add up to 1459 kt yr^{-1}, while losses are 856 kt yr^{-1}. Numbers with solid underlines are oxidized N and in italic with dash underlines are reduced. Numbers not underlined are for total N.

4.4. Water and Atmosphere as Integrators

As one of the main objectives of our work was to understand the overall gains and losses of N_r from the total Canadian landscape, we therefore estimated N_r movement in and out of the Canadian atmosphere and freshwaters to integrate the landscape types and sectors described above. When summed, atmospheric deposition directly into freshwaters, forest and agricultural runoff as well as urban/industrial components and direct deposition contributed an

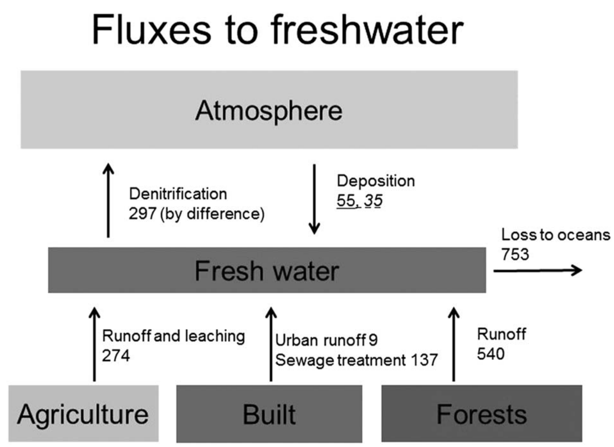

Figure 5. Main components of the freshwater landscape unit. Inputs from deposition, sewage, and runoff from agriculture, urban, and forest systems equal to 1050 kt yr^{-1} while exports from rivers to estuaries are 753 kt yr^{-1}.

estimated 1050 kt N yr^{-1} into southern Canadian fresh waters (Figure 5). Total losses measured at estuaries or leaving the Canadian land mass totaled 753 kt yr^{-1}, which leaves 297 kt yr^{-1} unaccounted for and assumed lost from waters to the atmosphere by denitrification.

The largest estimated N_r input into the Canadian atmosphere (1290 kt yr^{-1}) is advected from the United States and accounts for 20% of the 4600 kt yr^{-1} lost from the U.S. atmosphere to areas outside its borders (Figure 6) [*Science Advisory Board*, 2011]. This is followed by industrial/urban emissions (710 kt yr^{-1}) and forests (738 kt yr^{-1}). The largest nitrogen contribution from the atmosphere to the landscape is N fixation by agricultural and forest systems (2149 kt yr^{-1}), though the greatest anthropogenic contributor was atmospheric deposition (1095 kt yr^{-1}).

When all estimated N inputs (3404 kt yr^{-1}) and losses (3414 kt yr^{-1}) are tallied, our data suggest that the atmosphere over Canada is in N balance. This result is driven in large part because of the great importance of denitrification and N fixation in the overall budget which involve the conversion of inorganic N species to inert N gas and vice versa. However, if we exclude biologically mediated fixation and denitrification from the balance, much of which is natural, and only include N_r inputs and exports which are mostly the result of anthropogenic activities, a different picture emerges. NO_x and NH_3 inputs into the Canadian atmosphere from the U.S. and from Canadian emissions total 2624 kt yr^{-1}, while deposition plus advection to the U.S. total 1258, leaving 1366 kt yr^{-1} of reactive N unaccounted for in this assessment (Figure 6).

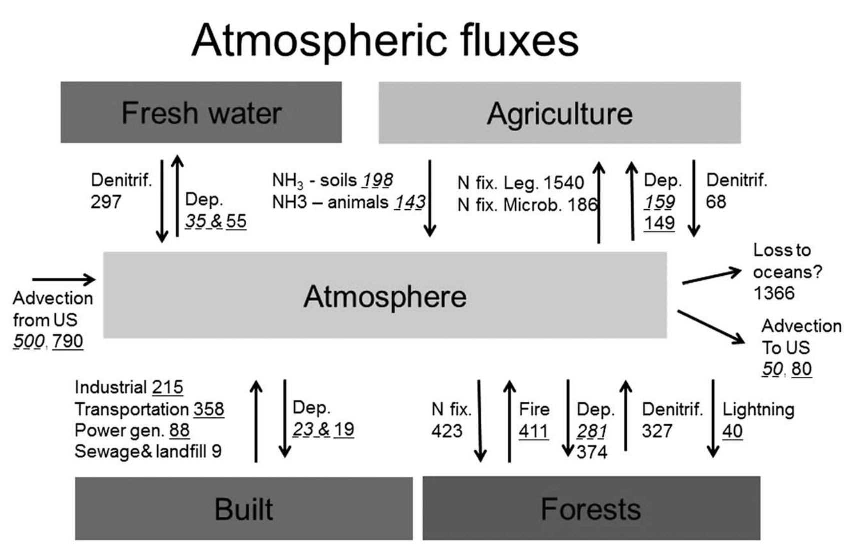

Figure 6. Main components of the atmospheric landscape unit. Total inputs from transboundary transport, natural processes, and urban/industrial/transportation add up to 3404 kt yr^{-1}, losses from transboundary, transport, fixation, and deposition are 3414 kt yr^{-1}. Losses to oceans are calculated by subtracting only N_r losses to deposition (where we include deposition in the Canadian north) and advection to the U.S., from N_r inputs from advection from the U.S., and Canadian emissions. Numbers with solid underlines are oxidized N and in italic with dash underlines are reduced. Numbers not underlined are for total N.

Table 1. Imports and Exports of N for Canada Attributable to Flows of Traded Commodities in 2007[a]

	Import	Export	Difference
Food	503	1303	−800
Hydrocarbons	871	2136	−1265
Fertilizer	342	2025	−1683
Wood	105	125	−20
Totals	1821	5589	−3768

[a]All values are in kt yr^{-1}.

4.5. Commercial Imports and Exports

Canada is a net exporter of N in manufactured products, petroleum, fertilizers, and agricultural products (Table 1) with the United States being the destination of 77% of Canadian exports (by economic value), with the remainder being distributed roughly equally between Europe and the Far East (Statistics Canada http://www.statcan.gc.ca/tables-tableaux/sum-som/l01/cst01/gblec02a-eng.htm).

Thirty eight percent of the exported N is attributable to hydrocarbons which are abundant in Canadian geological formations. Agricultural commodities (grain and livestock) are also important due to the availability of suitable land and climate, especially in the sparsely populated central part of the country. Canada therefore has a large N surplus that is shared with consumers from other countries. A surprising outcome of these estimates was the small difference between N exports and imports in wood products. Canadians see themselves as a major source of wood for construction in the United States, but the data show that the country also imports a large amount of finished wood products from its trading partners.

5. Discussion

The forest/natural landscape unit (Figure 2) showed a close balance between inputs and outputs as estimated N losses exceeded inputs by only ~22%. Considering that the N cycle in forests is very complex, involving not only growing plants but also soils and soil biota [*Aber et al*., 1998], estimating whether or not a forest is or is not in N balance can be difficult. We are relatively certain about atmospheric deposition amounts as well as exports through loss in rivers, as these originate from measured values. The more difficult inputs and exports to estimate are from the soil gaseous exchanges [*Science Advisory Board*, 2011].

Currently, no individual Canadian forest type seems to be N saturated as *Watmough* [2010] showed no evidence of saturation in Southern Ontario woodlands which receive the highest amount of anthropogenic N in the country. Moreover, as boreal forests are generally N depleted [*Lupi et al*., 2013] and receive low N deposition due to their location far from emission sources, we feel that the difference between estimated N inputs and losses for the overall Canadian forest system is not outside the realm of expectation. This conclusion contrasts with the situation in northeastern U.S., where N saturation is evident in a number of watersheds, with excess N leakage occurring in streams and rivers [*Howarth et al*., 1996b; *Lovett et al*., 2000].

Agricultural systems had the highest N inputs and exports of the landscape units we studied. When all of the 2006 agricultural inputs (3574 kt N) and outputs (2888 kt yr^{-1}) are considered, we estimate a retention of 686 kt N for Canadian agricultural soils in that year. With 61,430,840 ha of total agricultural land in Canada, this balance represents an annual average retention of 11.2 kg N ha^{-1}, approximately 19% of total input from all sources, including N fixation. Our retention number is similar to the value of ~16 kg N ha^{-1} that is implied from the European Nitrogen Budget [*Leip et al*., 2011b] and the United States estimate of 17% of applied N being retained in agricultural lands [*Science Advisory Board*, 2011], though these authors emphasize that total N budgets within all terrestrial systems are highly uncertain. Caution must then be exercised in the use of these numbers, but indications from both the European and U.S. literature cited above, as well as our data, suggest that developed economy agricultural soils seem to be accumulating N.

Our main purpose for constructing an N budget for the urban/industrial component of the landscape (Figure 4) was to assess the effect of transfers from this component to the environment, as was done by *Svirejeva-Hopkins and Reis* [2011] for parts of Europe and *Gu et al*. [2012] for Shanghai, China. Our data show that even with an incomplete assumption of inputs, losses from the urban/industrial/transport sectors are considerably less than what is input into this system. This suggests that the missing N is being taken up by manufactured goods.

Losses from the urban/industrial landscape to the environment which was our main concern are well described, as a number of databases such as *NPRI* [2013] and tabulated standards, i.e., *Metcalf et al*. [2010] provide information suitable for calculating anthropogenic N releases to air and water. Atmospheric emissions from transportation, industry, and power generation (378, 235, and 88 kt N yr^{-1}) show the relative importance of these sources and identify where reductions in N emissions would provide the greatest overall improvements.

Atmospheric NH_3 releases from sewage treatment and landfills (5 and 9 kt N yr^{-1}) are low, with N released into water from treatment plants at 137 kt yr^{-1}. Our data therefore show that of N losses from the urban/industrial landscape, 83% are discharged into the atmosphere and 17% into water. Though Canada occupies a large space, these emissions and discharges were concentrated mostly in heavily populated regions in the southern portion of the country where they would have the greatest ecosystem impacts.

In estimating a nitrogen budget for the Canadian freshwater landscape (Figure 5) we found that unlike Europe and the United States, the largest N input into freshwaters comes from forest soil leachates which are mostly in the form of dissolved organic nitrogen (DON) [*Clair et al*., 2013]. The next largest is from agriculture, where inorganic N forms dominate, and then sewage treatment plants. When all Canadian N inputs into freshwaters were compared to exports from rivers to estuaries, the data showed a loss of 24% of total N either to algal precipitation into lake sediments or to denitrification. This estimated loss is considerably lower than literature values for the U.S. and Europe which ranged between 50 and 60% [*Sebilo et al*., 2003; *Seitzinger et al*., 2006; *Van Breeman et al*., 2002].

The main cause of this loss from freshwaters is thought to be denitrification which is controlled by nitrate concentration, oxygen availability (or its lack), organic C availability, and temperature [*Sjodin et al*., 1997]. Assessing our data, we suspect that there are two scenarios in play which affect the overall loss. The first is that most Canadian rivers drain mainly forested systems where the N_r is mostly in the form of large molecule, refractory soil leachates in the form of dissolved organic nitrogen (DON). DON is less bioavailable and more difficult to break down than N from agricultural fields and waste water systems [*Inamdar et al*., 2012; *Leenheer and Croué*, 2003]. In order for DON to be denitrified, it must first be mineralized to ammonium and then into oxidized forms which may then be denitrified, a process which is chemically complex and is controlled by thermodynamic factors, especially temperature which is very important in Canada. The nature of the DON and the seasonal thermodynamic effect ensure that mineralization of these natural compounds is slower, leading to lower loss from water bodies thus explaining the lower 24% denitrification loss for the whole of Canada, as opposed to the 50–60% estimated in Europe and the United States where temperatures are higher. So in Canada generally, DON is a greater component to freshwater N than in Europe and the U.S. and this affects rates of biogeochemical degradation.

Despite the "national" tendency for more refractory N_r in rivers, the situation is different for the Great Lakes-St. Lawrence (GL/SL) system. *Clair et al*. [2013] measured all N exports from the Great Lakes (GL) basin, a highly populated catchment with intense agriculture and industry at the outlet of the St. Lawrence River which is quite different from the other rivers in Canada. In order to get a better estimate of % N_r loss from this catchment, we had to estimate the contribution from the U.S. portion of the GL catchment. To do this, we assumed that GL Americans generated the same amount of N_r per capita as Canadians, assuming similar climate and agricultural types for that region. The total N loss to freshwaters from agriculture and urban environment of 35 million Canadians was prorated to the U.S. GL population of 25 million [*United States Environmental Protection Agency*, 2004]. This approach estimated that the U.S. GL contribution was approximately 71% of the total Canadian national value for agricultural, sewage, and urban exports (324 kt yr^{-1}). Added to the N input from the Canadian GL population of 101 kt yr^{-1}, we estimated a total aquatic N input of 425 kt N yr^{-1} for the whole GL/SL catchment. Compared to the annual St. Lawrence export into its estuary of 236 kt N yr^{-1}, this showed that 56% of N input into the GL catchment disappeared, most likely to denitrification and loss to sediments, a figure within the range reported in the literature for more developed catchments.

Nitrogen inputs into the Canadian atmosphere are dominated by the transboundary movement of oxidized N from the United States (Figure 6), most of which originates in the U.S. Midwest and is deposited in the southeastern portion of Canada [*Vet et al*., 2005]. Reductions or modification to this input are dealt with in binational agreements [*Canada-U.S*., 2008] though the scale of the inputs suggests that reductions in that sector will be difficult to achieve in the near to medium term. Industry, transport, and power generation are the main Canadian anthropogenic N inputs into the atmosphere, and changes to these are subject to technological advances as well as legislation.

When we only include reactive N species in budget calculations, mass balance calculations suggest that more than 50% of known reactive species inputs are unaccounted by this budget. The magnitude of the discrepancy is significant and can only be due to inadequately measured dry deposition on the Canadian land mass, and/or to advection to the Atlantic and Arctic Oceans and beyond, most likely to Eurasia [*Sanderson et al*., 2008; *Vet and Ro*, 2008]. A similar measurement shortcoming was identified for the U.S. national budget [*Science Advisory Board*, 2011] which raises an important problem for interpreting mass balance studies and which needs to be dealt with in transnational studies.

The other point the data make is that Canada is unlike other industrialized western countries, in that natural processes are very important in overall N cycling due to the large-scale influence of its forests and agriculture. Natural forest processes emit almost as much N into the Canadian atmosphere in the form of denitrification products and NO_2 from forest fires as the transport/industrial/urban sector, unlike the situation in Europe [*Leip et al*., 2011a] or the United States [*Howarth et al*., 2011] where natural systems produce only a small portion of emissions. Agriculture in Canada produces less than 12% of overall N emissions to the atmosphere, though locally this value can be much higher especially in the agricultural, southern portions of the country [*Ayres et al*., 2008]. N transfers from the atmosphere to the agricultural landscape are dominated by N fixation and deposition which are important due to the large extent of natural areas, as well as managed agricultural lands.

To round out the N flux in and out of Canada, we also estimated N commodity exports and imports to provide a magnitude of the relative importance of exported nitrogen locked into food (mostly grain), fossil fuels, fertilizer, and wood products (Table 1). Overall, Canada exported 3768 kt N more than it imported in 2006 and is therefore one of the larger N exporters in the world based on *Galloway et al*.'s [2008] analysis of global trade.

In all aspects of N flow in Canada, an important determinant is the country's climate. Our annual budget approach used integrated data for all the landscape units, though seasonal climate changes have consequences to overall N cycling. Unlike much of Western Europe and the United States, all of Canada which is under consideration in this work, except for southwestern British Columbia, experiences 4 to 6 months of weather cold enough to freeze soils [*Phillips*, 1990], which reduces soil and water biogeochemical reaction rates and atmospheric exchange processes.

There is evidence that the freeze-thaw cycle is changing due to greater climate variability [*Joseph and Henry*, 2008] and is influencing N leaching and other geochemical reactions in agricultural and forest soils of North America. Moreover, there is also evidence that soils are now frozen for shorter periods of time than in the past due to climate change [*Smith et al*., 2004] so that assumptions now being made about soil denitrification rates and amounts will have to be modified taking climate change into account. The same issues will apply to DON fluxes from soils to rivers if we assume that greater soil organic matter processing will occur under warming conditions.

An important question which needs to be asked is how these N_r exchanges will change in the future. Our data provide a "snap shot" of current conditions and show the relative importance of the various N_r flows in a country where natural resource and agricultural extraction and processing are very important. Some of the more obvious questions which will be asked are the following: (a) how will a changing climate affect forest and agricultural soil processing; (b) how will forest fire frequency and intensity change NO_x emissions to the atmosphere; (c) will there be N emissions reductions from heating; and (d) will there be changes in the production, import and export of food? The issues and details needed to answer these questions can be exceedingly complex [e.g., *Houlton et al*., 2013], and the only way to answer them will be to develop specialized dynamic models of N flows for each major landscape component which will take into account detailed analyses of sectorial changes. *Winiwarter and Hettelingh* [2011] describe the approach needed to develop suitable predictive models of N changes in systems, and these models follow approaches currently used for climate, pollution, and ecosystem predictions. The models will also require specialized process information, as well as clear questions such as provided by *Smit and Skinner* [2002] for agricultural systems. The data we produce in this report are a first step in this process of understanding long-term changes in N_r dynamics.

6. Conclusions

Our data show that N flows in Canada are very different from those seen in Europe [*Leip et al*., 2011a] or the United States [*Science Advisory Board*, 2011], due to the unique combination of large surface area, low population, climate, and the importance of natural resource exploitation. Though Canada produces significant agricultural, industrial, and urban N_r emissions as befits the world's eleventh largest economy, our data show that Canada's large geographical scale ensures that overall, the natural ecosystems in its temperate and boreal zones do not receive N_r at levels that will cause ecosystem changes.

Though our approach provides an overview of nitrogen flows into and out of landscape units, it must also be understood that we provide an "average" picture from across a very large country as our national landscape-based budget shows balances that belie important regional differences. Forest ecosystems located in the southern part of the country near industrialized, urban, or agricultural areas receive N loads that are sometimes greater than critical levels for forests. Though there is currently no published information suggesting that these levels are having impacts, we expect that long-term continuous high deposition levels should eventually cause changes in these terrestrial ecosystems. Northern natural systems, on the other hand, receive very little N in deposition but collectively are important denitrification loci for deposited N_r originating in southern regions. The same geographical issue applies to Canada's freshwater systems.

Canada's agricultural lands receive more N than is exported from agriculture as crop and livestock products. The amount of inorganic N that is transported to the atmosphere and surface waters from agricultural activities (crop and livestock production) is a particular concern as it represents over 550 kt N or about 16.7% of the N inputs into the system from fertilizer addition and the N_2 fixation processes. The estimate of N_r flows into and out of the atmosphere also provided some information which supported the importance of freshwater denitrification in the national N budget.

Our study shows that in terms of total nitrogen flows, Canada is a net N exporter due to fossil fuel exports and Haber-Bosch ammonia synthesis, which allows for both nitrogen fertilizer export and the production/export of agricultural products. However, because of its location, Canada as a whole is not an important direct air and water pollution source for other countries.

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