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TOTAL POTENTIAL ACID INPUT IN ALBERTA

by

Lawrence Cheng¹, Karen McDonald², Dave Fox² and Randy Angle¹

¹ Alberta Environmental Protection 9820-106 Street Edmonton, Alberta T5K 2J6

> ² Environment Canada 4999-98 Avenue Edmonton, Alberta T6B2X3

> > prepared

for

The Target Loading Subgroup SO₂ Management Project Team Alberta Clean Air Strategic Alliance

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For copies of this report, contact:

Air Issues and Monitoring Branch Chemicals Assessment and Management Division Environmental Regulatory Service Alberta Environmental Protection 6th Floor, Oxbridge Place 9820 - 106 Street Edmonton, Alberta T5K 2J6

Telephone: (403) 427-5893

Abstract

The total potential acid input in Alberta was calculated using the Regional Lagrangian Acid Deposition model and precipitation chemistry monitoring data. The total potential acid input is the European method to estimate deposition fluxes of acidifying substances, including wet and dry deposition of SO_x (SO₂ and aerosols of SO₄⁼), NO_y (NO, NO₂, HNO₂, HNO₃ and aerosols of NO₃⁻), NH_x (NH₃ and aerosols of NH₄⁺), and base cations (Na⁺, Mg²⁺, Ca²⁺ and K⁺).

The predicted total sulphur deposition shows two areas of relatively high sulphur deposition $(\ge 0.15 \text{ keq ha}^{-1} \text{ y}^{-1})$ in western Canada: one near Kananaskis at the foothills of southwestern Alberta and one in southern Saskatchewan. The region near Fort McMurray has sulphur deposition of 0.12 keq ha⁻¹ y⁻¹, although it has the highest sulphur emissions. The impacts of ground-level urban sources and long-range transport are evident in nitrogen deposition. Nitrogen deposition is higher in southern Saskatchewan than in northern Alberta and has a higher contribution to the acidification than sulphur. There are several areas of relatively high deposition of acidifying substances in southern Alberta and Saskatchewan. Deposition of base cations shows highest levels in the driest agricultural part in southeastern Alberta. Southern Saskatchewan has a low value, a suspicious result given the frequency of severe dust storms and previous observations showing that base cations dominate the rain chemistry. The predicted total potential acid input near Fort McMurray is as much as in central Alberta. Southern Saskatchewan has relatively high acid inputs, mainly because of the low base cation deposition. The paucity of precipitation chemistry data seems to be responsible for this anomaly.

Total acid input is generally less than 20% of the critical load in Alberta. In the Fort McMurray area, the ratio of total potential acid input to critical load for soil is less than 0.25. Total acid input is about 40% near both Kananaskis and Vauxhall due to the precipitation pattern for the one-year used in the calculation. In southern Saskatchewan, although the predicted total potential acid input is the highest, it is only less than 50% of the critical load because of the low sensitivity of soil in the region.

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1. Introduction

Long-term deposition of acidic and acid-forming substances can alter the structure and function of aquatic and terrestrial ecosystems. Mathematical modelling is the most cost-effective way linking emissions and deposition under complex meteorological and source conditions. Generally, there is insufficient monitoring data to define fully a spatial pattern of acidic loading being experienced by the aquatic and terrestrial ecosystems. Modelling of the transport, chemical transformation and deposition of acidifying constituents allows interpolation or extrapolation of observational data, assists in the design of monitoring networks, and develops quantitative relationships between emission sources and ambient deposition levels. With the source-deposition relationship, the calculated deposition can be compared with the deposition guidelines or objectives to determine whether reductions in the sources may be needed.

The concept of target loads has been applied in eastern Canada as a wet sulphate deposition objective of 20 kg ha⁻¹ y⁻¹ in precipitation to protect moderately sensitive aquatic ecosystems. Target load is defined as the maximum level of acidic atmospheric deposition, that affords long-term protection from adverse ecological consequences, and that is practically and politically achievable. Its value differs from that of the critical load, which is defined as the highest load that will not cause chemical changes leading to long-term harmful effects. Depending upon the social and economic factors, target load can be set at level higher or lower than the critical load. Subsequently refined and broadened to include sulphur and nitrogen deposition from largely anthropogenic sources, the concept of target loads is now used to manage emissions of these and related compounds throughout western Europe.

Western Canada is in an enviable position of being able to establish critical/target loads before adverse environmental effects have been observed; Europe and eastern Canada have had to apply these management methods in response to environmental damage. The natural, physical and chemical characteristics of the aquatic and terrestrial ecosystems define the sensitivity to acid deposition. Total acid deposition includes both wet and dry deposition of sulphur and nitrogen as well as the neutralizing effects of base cations. During the 1980's, Alberta, together with the Western and Northern Canada Acid Deposition/Long Range Transport of Atmospheric Pollutants Technical Committee, completed surveys of soils, waterbodies and vegetation in the settled parts of the province. These were subsequently extended to the more remote northern parts of the province in the late 1980's and early 1990's. The soil sensitivity map to acidic inputs is displayed in Figure 1. The northern half of Saskatchewan and northeastern corner of Alberta contain the most sensitive soils. Two alternative approaches to estimate deposition loads were also considered: the net acidifying potential (Technical Committee Western and Northern Canada Long Range Transport of Atmospheric Pollutants, 1990) and the effective acidity (Alberta Environment, 1990). Recently, under the direction of the SO₂ Management Project Team of the Alberta's Clean Air Strategic Alliance, a multi-stakeholder Target Loading Subgroup was formed to evaluate and make recommendations on the feasibility and desirability of implementing the concept of target and critical loads in the regulatory system for Alberta. After considering the advantages and disadvantages of the two alternatives mentioned above and the advancement in the European approach (CCE, 1995), the subgroup recommended that Alberta adopt the European method for determining and managing critical/target loads.

In Europe, sulphur compounds, as well as reduced and oxidized nitrogen compounds, are considered in the study of acidification of soils and surface waters. (Nitrogen deposition also causes eutrophication (Heij and Schneider, 1991), but this is not addressed here). The components considered in the acidification and eutrophication processes are SO_x (SO_2 and aerosols of $SO_4^=$), NO_y (NO, NO_2 , HNO_2 , HNO_3 and aerosols of NO_3^-); and NH_x (NH_3 and aerosols of NH_4^+). Base cations such as Na^+ , Mg^{2+} , Ca^{2+} and K^+ , play an integral role in the chemical processes of acidic deposition since the acidity of any material is a function of both its acidic and basic compounds. Besides their ability to neutralize acid input, base cations are important nutrient elements for ecosystems. The total potential acid input used in Europe is defined as the difference between the total (wet + dry) potential acid ($SO_x+NO_y+NH_x$) deposition and the total base cations ($Na^+ + Mg^{2+} + Ca^{2+} + K^+$) deposition. In Europe, a critical load of 0.25 keq ha⁻¹ y⁻¹ has been adapted for highly sensitive soils, and 0.5 for moderate and 1.0 for buffered soils (WHO, 1994; Hornung et al., 1995).

This report will present results of the total potential acid input in Alberta calculated using the RELAD (Regional Lagrangian Acid Deposition) model (Cheng et al., 1995; McDonald et al., 1996;



and Cheng and Angle, 1996) and precipitation chemistry monitoring data. The total potential acid input is the European method to estimate deposition fluxes of acidifying substances. The RELAD model will be described. The uncertainty in the results will also be assessed.

2. The Method

The total deposition of potential acid was calculated using the RELAD model. RELAD is a mass-conserving, regional scale Lagrangian model that simulates ground-level ambient concentrations, as well as wet and dry depositions of SO_2 , H_2SO_4 , $(NH_4)_2SO_4$, NO_x ($NO_2 + NO$), HNO₃, and NH_4NO_3 . It is modified from the Regional Lagrangian Model of Air Pollutants (RELMAP) developed by the U. S. Environmental Protection Agency (Eder et al., 1986). Output can be generated by RELAD in two major formats. The first generates arrays of gridded ambient concentrations and wet and dry deposition of pollutants. The second output format produces sourcereceptor matrices where the number of cells or groups of cells can be defined as source or receptor regions. Using this format, the relative contribution of a source region to be the deposition in a receptor region can be determined. Transboundary pollutant transport is also calculated in RELAD by keeping track of the movement of the centre of the pollutant PUF.

The north-south and east-west boundaries of the model domain were set in this study from 47° to 62° N latitude and from 100° to 130° W longitude, respectively, with a resolution of $1^{\circ} \times 1^{\circ}$ which is 111 km latitudinally and approximately 60 km longitudinally. The model divides the atmospheric boundary layer into three layers, into which emissions are injected. The model layers, assumed to be constant throughout the model domain, are set below the seasonal mixing height and take into account the plume rise. Discrete puffs of emissions are released every 12 h (default) from each grid cell that contain sources. These puffs are diffused and transported by the wind fields, and subjected to chemical transformation and wet and dry deposition.

For long-term regional-scale models such as RELAD, turbulence-generated dispersion is not as significant as transport and removal processes. A simple parameterization of both horizontal and vertical diffusion is used. During the unstable regimes of midday periods instantaneous, complete mixing is assumed within the three layers. After sunset, all emissions from area sources remain in the first layer and emissions from point sources are allocated into the second layer, in accordance with the typical plume rise. Horizontal diffusion of puffs in RELAD occurs at a constant rate (default value of 339 km² h⁻¹ which is based on the standard deviations of the considerable vector errors associated with calculating long-range trajectories; Clarke et al., 1983). Pollutant mass in the PUF is homogeneous in the horizontal plane at all times. Each PUF is transported in user-defined (3 h default) time steps by using horizontally and temporally interpolated wind fields until the PUF is transported out of the model domain or the mass of the pollutant falls below user-specified minimum value. The transport velocity of the PUF is determined by vertically integrating mass weighted winds of the three layers, which are derived from the preprocessed wind velocities for the grid cell containing the PUF's centroid.

The homogeneous component of the transformation rate of SO_2 to SO_4^{2-} is based upon Altshuller's (1979) midday rate curves for clean troposphere at various latitudinal bands and from Meagher and Olszyna's (1985) algorithm derived from hourly power plants plume measurements from 11 separate studies, while the heterogeneous compound is derived from the work of Scott (1982). It is assumed the SO_4^{2-} generated takes the form of H_2SO_4 , which will react with available NH₃ to become (NH₄)₂SO₄. The NO_x oxidation rate comes from the chemical mechanism of Atkinson et al. (1982). In the presence of NH₃, a chemical equilibrium is established among gaseous HNO₃ and NH₃, and the ammonium nitrate aerosol. The equilibrium constant for this reaction is strongly dependent on relative humidity and temperature (Stelson and Seinfield, 1982). Dry deposition is parameterized in RELAD as a function of predominant land use, stability index and season. The dry deposition velocities are based on the work of Sheih et al. (1979). Wet deposition is parameterized as a function of season and precipitation rate only. The wet deposition rates are expressed as percentage per time step, and are based on the work of Scott (1978).

The base cations include species that tend to neutralize the acidity, especially calcium, magnesium, potassium and sodium. The wet deposition of base cations is obtained from precipitation chemistry monitoring data. The dry deposition flux of base cations is calculated as the product of the dry deposition velocity and ground level air concentration. Concentrations of base

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cations are not measured as extensively as the wet deposition. In this study the ground level air concentrations of base cations were estimated from the precipitation concentrations using scavenging ratio, which were derived from simultaneous measurements of base cation concentrations in precipitation and ground level air performed by Eder and Dennis (1990). This approach to estimate air concentrations is based upon the assumption that cloud droplets and precipitation efficiently scavenge aerosols, resulting in strong correlations within precipitation and air concentrations. This assumption is only valid for well-mixed conditions at a sufficient distance from sources. Factors that influence the magnitude and variability of scavenging ratios include: particle-size distributions and solubilities; precipitation rates and amounts; droplet accretion precesses; air mass trajectories, and the importance of gas-phase scavenging. The variability in the average scavenging ratios increases significantly as the averaging time and hence the amount of data being averaged are reduced. On a monthly basis, they vary over factors of 2-5 and on a daily basis, over an order of magnitude. The scavenging ratios also vary considerably from one species to another. They, however, have been found to be reasonably consistent when averaged over one year or longer (Galloway et al., 1993). Therefore, annual mean precipitation concentrations were used to infer annual mean atmospheric concentrations of Na⁺, Mg²⁺, Ca²⁺ and K⁺, using the results of Eder and Dennis (1990). By interpolating the determined air concentrations and using a typical deposition velocity of 0.001 m s^{-1} . the dry depositions of base cations were also determined.

3. The Data

The 1990 data were used as the input meteorological and emission data for the RELAD model. Eight upper-air stations, five in western Canada and three in the United States, were used: The Pas, Man.; Stony Plain, Alta.; Fort Smith, NWT; Vernon and Port Hardy, B.C.; Glasgow and Great Falls, Mon., and Spokane, Wash. The number of hourly surface meteorological stations varied from hour to hour, depending upon the availability of data. On the average, 85 or more surface stations were used, with a maximum of 94 stations at particular times in the summer. The hourly surface and the 12-hourly upper-air meteorological data for 1990 were interpolated to 3-hour time step intervals.

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The ambient ozone and ammonia concentrations used in the nitrogen chemistry calculation and the ammonium sulphate conversion were extracted and extrapolated from sporadic monitoring data collected by Alberta Environmental Protection and British Columbia Ministry of Environment, Lands and Parks. The land use data used in the dry deposition calculation were obtained from the land use data bank provided by Environment Canada, with grid cells each of 10,000 km². The land classification scheme specifies nine categories of forest, four of grassland, and seven for the remaining possibilities (fresh water, sea water, tundra, bog, rock, ice and urban). Only twelve land use categories, defined by surface characteristics and vegetation type, were used in the RELAD model. Thus, the percentage frequency of occurrence of the land use types in each model cell was interpolated from the supplied data and the surface characteristics and vegetation types were adjusted to those used in the model.

The NO_x and SO₂ emissions from Alberta and British Columbia were obtained from the 1990 national criteria pollutant inventory managed by Environment Canada. Gridded emissions, including industrial point sources and area sources, in $25\times25 \text{ km}^2$ were supplied. NO_x emissions from area sources are appreciable, accounting for more than one-third of the total emissions. The data received were gridded into the $1^{\circ}\times1^{\circ}$ blocks for incorporating into the RELAD model. The $1^{\circ}\times1^{\circ}$ gridded SO₂ and NO_x emissions are shown in Figures 2 and 3. Each grid square is colour-coded to represent an emission level. It should be noted that the scale is logarithmic. The SO₂ emissions show the familiar pattern in Alberta, of high values in the Fort McMurray oilsands area and in the central region. The NO_x emissions show similar maxima but moderate values (1 to 10 kilotonnes per year) are mode widespread. The 1990 emissions from Saskatchewan were not received in time to be incorporated in the study. Since the predominant transport direction in the model domain is from west to east, the 1985 emissions data were used. It was believed that using the 1985 emission data in Saskatchewan would not cause significant differences to estimates in Alberta.

The 1990 precipitation concentration data for the base cations Na^+ , Mg^{2+} , Ca^{2+} and K^+ , were taken from the National Atmospheric Chemistry (NAtChem) Data Base compiled by the Atmospheric Environment Service of Environment Canada. The system was set up as a central data base and analysis facility to determine the chemistry of regional-scale air and precipitation.



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Precipitation stations in western Canada that base cations were analyzed are shown in Figure 4. There is a reasonable coverage throughout Alberta, in southern British Columbia and in the United States along the Canada-U.S. border. In other regions precipitation monitoring data are not available.

4. The Results

Predicted sulphur loading (wet and dry deposition of SO₂ and aerosols of SO₄²⁻) for western Canada is shown in Figure 5. The map is grey-scaled with a resolution of one model grid cell $(1^{\circ} \times 1^{\circ})$ and increasing deposition intervals of 0.05 keq ha⁻¹ y⁻¹ or kmol H⁺ ha⁻¹ y⁻¹ from 0 to 0.25 keq ha⁻¹ y⁻¹. Note that the scale above 0.25 keq ha⁻¹ y⁻¹ is not linear. There are two areas of relatively high sulphur deposition (> 0.15 keq ha⁻¹ y⁻¹); one is near Kananaskis at the foothills of southwestern Alberta and the other is in southern Saskatchewan. Both high values are caused by the wet deposition of sulphur, resulted from high precipitation amounts in the grid cells. The exact position of these apparent hot spots will vary annually depending on a given year's precipitation pattern, and therefore, will smooth the deposition accumulation spatially over time. The region near Fort McMurray has sulphur deposition of 0.12 keq ha⁻¹ y⁻¹, although it has the highest sulphur emissions in Alberta.

Figure 6 gives the nitrogen loading $(NO_x, HNO_3, aerosols of NO_3^- and NH_4^+)$ predicted by the RELAD model. Deposition of NH₃ is not simulated in the model. Nitrogen deposition is greatest in Saskatchewan with the highest value being 0.26 keq ha⁻¹ y⁻¹. The impacts of ground-level urban sources and long-range transport are evident. Nitrogen deposition is higher in southern Alberta than in northern Alberta, reflecting the distribution of urban source emissions and prevailing flow pattern. Highest nitrogen deposition in Alberta is 0.2 keq ha⁻¹ y⁻¹, located near Lethbridge and near Medicine Hat in Southern Alberta.

Estimates of total deposition of acidifying substances $(SO_x + NO_y + NH_x)$ was obtained by summing the sulphur and nitrogen depositions. The results are shown in Figure 7. There are several areas of relatively high deposition of acidifying substances (> 0.25 keq ha⁻¹ y⁻¹) in the southern



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regions of Alberta and Saskatchewan. Fort McMurray lies between 0.15 to 0.20 keq ha⁻¹ y⁻¹. Nitrogen deposition has a higher contribution to acidification than sulphur in southern Alberta.

Total deposition (wet and dry) of base cations were calculated at the precipitation monitoring station and the results were interpolated to generate the spatial distribution of base cation deposition in western Canada, which is given in Figure 8. It shows a high level of base cation deposition in the dry agricultural area of southeastern Alberta, consistent with common knowledge about the dustiness of this region. However, the interpolated base cation deposition in southern Saskatchewan is low. This is contrary to the expectation that base cation deposition would be very high in southern Saskatchewan, where the frequency of severe dust storms is highest and base cations dominate the rain chemistry (Shewchuk et al., 1992). The discrepancy is probably due to the paucity of data in the region.

The total potential acid input is determined by subtracting the base cation deposition from the deposition of acidifying substances. Figure 9 gives the distribution of the total potential acid input. It shows that the base cations have the effect of neutralizing much of the acidity in Alberta. These results are very similar to that predicted by Cheng et al., (1995) using effective acidity. The Fort McMurray area receives as much load as in central Alberta. It should be noted, however, that these results are on a regional basis and cannot be used to infer impacts on a local or facility-byfacility basis. Also shown in the figure is that southern Saskatchewan has total potential acid inputs of values between 0.25 to 0.50 keq ha⁻¹ y⁻¹, mainly because of the low base cation deposition calculated for the data sparse area. The soils of most of southern Saskatchewan are of low sensitivity (Interim Acid Deposition Critical Loading Task Group, 1990). It has been recommended that critical loads for soils of low sensitivity be greater than 1.0 keq ha⁻¹ y⁻¹ (WHO, 1994; Maynard, 1996). Thus, the potential atmospheric acid input is less than 50% of the critical load even at the highest deposition area. No harmful effects on the soils would be expected, even based on this likely overestimated total potential acid input in southern Saskatchewan.

Combining the predicted total potential acid input with the soil and water sensitivity information provides the status of the loading conditions and the environmental limits. The fraction



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of potential acid input to critical load for soil in Alberta was calculated using the critical end-points estimated from the soil sensitivity map as suggested by Maynard (1996). The results are shown in Figure 10. Acid input is generally less than 20% of the critical load in Alberta. In the Fort McMurray area, total potential acid input is less than 25% of the critical load for soil. Near Kananaskis and Vauxhall the total potential acid input is 40% of the soil critical load, due to the precipitation pattern for the one-year used in the calculation. This would change with each years changing precipitation.

5. The Uncertainties

The greatest uncertainty in the results of the present study lies in the base cation deposition. There are three major sources of error in these estimates. Firstly, precipitation concentrations of base cations are not available in southern Saskatchewan. Estimates of base cation deposition from interpolation seem too low in that region, which is well known for dustiness. Secondly, the precipitation monitoring data near Fort McMurray may not be representative due to the proximity of precipitation collectors to dusty roads. Both calcium concentrations and pH decreased markedly during the summer of 1988 when the station was moved to a location farther from (but still quite near) gravel roads (Bronaugh 1993).

Thirdly, the inference calculation of base cation dry deposition uses many assumptions. Precipitation concentration measurements are used as a basis for inferring ground-level air concentrations and subsequently the dry deposition of base cations. Conceptually this technique is based on the observation that precipitation efficiently scavenges these aerosols, resulting in a strong correlation between the precipitation concentrations and air concentrations measured at the surface. To comply with the assumption inherent to the concept of scavenging ratios, this technique is best suited for long-term averages (on the order of a year or longer) at sites far from large sources of alkaline aerosols, so that sufficient mixing has occurred. The scavenging ratios adopted in this study were derived from Ontario measurements. The precipitation climatology in Alberta may greatly differ from that of Ontario. Furthermore, deposition velocities of base cations have not been studied



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extensively; the few experimental values reported in the literature vary tremendously. The deposition velocity employed in this study may be in error by as much as 50% or more.

The model used in this study (RELAD) has not been fully validated, although its performance has been evaluated in a number of occasions (Cheng, 1994; Cheng et al., 1995; McDonald et al., 1996). RELAD is a long-term regional scale model that simulates the transport, dispersion, dry deposition, wet deposition and chemical transformation on that scale. Model simulations contribute to the following goals: (1) a better understanding of the effects of meteorological variability, (2) an identification of source regions significantly contributing to regional environmental problem, (3) an estimation of the contribution of source regions to one or more receptor regions. The model parameters are chosen to represent the processes on the regional scale. However, the extent of the sensitivity and applicability of these parameters in western Canada have not been fully examined and validated. Bearing this in mind, uncertainty due to errors in model parameters may also be present.

6. Discussion and Further Work Required

The base cation deposition was calculated using the 1990 precipitation chemistry data. Although this is consistent with the meteorological and emission data, the 1990 precipitation chemistry data may not provide regional and climatological representativeness. A long period-ofrecord (10 y) of monitoring data should be applied to examine variability.

The wet deposition fields generated by the RELAD model are very patchy because the precipitation input data reflect the convective storms that provide amounts of rainfall for this region. It is recommended that the wet deposition be determined by averaging over several years meteorology to smooth the pattern.

The present study shows some unexpected low values for the base cation deposition in southern Saskatchewan. This unexpected result is likely an artifact due to lack of data in the region. Any of the existing information on precipitation chemistry at southern Saskatchewan needs to be gathered and incorporated into the calculation of the total potential acid input of the region.

Qualitative soil and water sensitivity maps are available for all of western Canada. To identify the status of the loading conditions relative to environmental limits more efficiently, more precisely digitized maps should be used in conjunction with the model output.

7. Conclusion

Estimates of total potential acid inputs were calculated. The regional-scale RELAD model was run on a $1^{\circ} \times 1^{\circ}$ grid to determine ground-level ambient concentrations, wet deposition and dry deposition of SO₂, H₂SO₄, (NH₄)₂SO₄, NO_x (NO₂ + NO), HNO₃, and NH₄NO₃. There are only two areas showing sulphur deposition greater than 0.15 keq ha⁻¹ y⁻¹: one near Kananaskis in the foothills of southwestern Alberta and the other in southern Saskatchewan. The region near Fort McMurray has sulphur deposition between 0.10 to 0.15 keq ha⁻¹ y⁻¹. Nitrogen deposition is greatest in southern Saskatchewan with some areas greater than 0.25 keq ha⁻¹ y⁻¹. There are several areas in the southern regions of Alberta and Saskatchewan with deposition of potential acidifying substances greater than 0.25 keq ha⁻¹ y⁻¹. Fort McMurray lies between 0.15 and 0.20 keq ha⁻¹ y⁻¹. The base cations have the effect of neutralizing more than 60% of the acidity in Alberta but by as little as 20% in southwestern Saskatchewan, where the acid input is 25 to 50% the critical load. Generally, the atmospheric potential acid input in Alberta is less than 20% of the critical load for soils.

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