

**LICA LONG-TERM SOIL ACIDIFICATION MONITORING – SYNTHESIS OF
THREE SAMPLING EVENTS – 2010 TO 2020**

by

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EXECUTIVE SUMMARY

The Lakeland Industry & Community Association (LICA) was formed in 2000 as a non-for-profit society in response to the expansion of oil and gas production in the Cold Lake oil sands region of Alberta. LICA initiated environmental monitoring of air, water and land resources in 2003.

In 2010, LICA began soil acidification monitoring. Three long-term soil sampling plots were established: one in Moose Lake Provincial Park in 2010, another in Whitney Lakes Provincial Park in 2011, and a third on Crown Land near Tucker Lake in 2012. Soil sampling is carried out at these plots every four years in a staggered manner (one site per year). A fourth site established in the early 1980s is located near the west shore of Cold Lake; this location is operated by Alberta Environment and is complementary to the sites established by LICA.

The location of the three sites established by LICA were informed by a study commissioned by LICA in 2007. This preliminary or screening study of potential soil and water acidification within the LICA Area assembled information about locations and extents of sensitive soils as well as current levels of exposure to acidic deposition. This study was used to identify areas for potential monitoring sites. Major considerations and criteria for selecting sites included the following:

- Soils should be sensitive to acidic deposition, as indicated by low acid buffering capacity;
- Sites should be on similar soils and under similar native vegetation, these being generally sandy soils under jack pine stands as used in other monitoring programs;
- Landscape should be well drained and have gentle slopes; and,
- Since soil chemistry changes are slow, monitoring needs to be long-term; therefore, sites should have a high likelihood of protection from development over a long-term.

Several sites were examined within a region delineated approximately by Whitney Lakes Provincial Park in the southeast, Cold Lake Indian Reserve to the northeast, Wolf Lake to the northwest, and the hamlet of Mallaig to the west. Soils were described and samples for laboratory analysis were taken of the LFH layer (forest floor, or duff layer), the Ae horizon (topsoil), and the top of the B horizon (upper subsoil). Chemistry data for the soils indicated suitability for monitoring based on the selection criteria. Sites were characterized by sand textured materials and were classified as Eluviated Dystric Brunisols of the Liza soil series in the northern LICA area, and Nestow series in the southern part of the area.

Protocols of the Alberta's Long-Term Soil Acidification Monitoring (LTSAM) program were adopted by LICA for sampling plot establishment, soil sampling, and laboratory analysis. Upon selecting the locations for the three LICA monitoring sites, two subsites were located within each site. These were demarcated as 24 m by 24 m squares and were further subdivided into 12 m by 12 m plots, and each plot was subdivided into 2 m by 2 m subplots. The subplots were the basic sampling units for monitoring. One subplot was sampled in each of the 12 plots, thus providing 12 replicates for analysis. Sampling events are planned for four-year intervals, as in the Alberta Environment LTSAM program, allowing for a monitoring period of 44 years.

The soil layers sampled in each sampling cell are: LFH (duff), 0-2, 2-5, 5-10, 10-15, 15-30, 30-45, and 45-60 cm. Soil samples are obtained by digging square pits (about 60 cm x 60 cm) near the centre of each sampling cell. About one litre of sample is obtained from each of the soil layers.

Samples were analyzed in a soil laboratory for the main indicators of soil acidification as follows:

- Soil pH_c – soil acidity is measured as pH; all soils have a certain level of acid buffering capacity, but as acid is added, the pH will begin to decrease. pH measured in soil mixed with calcium chloride solution (pH_c) is commonly used with forest soils.
- Base Saturation (BS) – the term ‘base cations’ refers to a group of soluble elements that consist of calcium, magnesium, potassium and sodium. These elements are also plant nutrients. Exchangeable base cations are attached to surfaces of soil particles but can be displaced by other base cations or acid cations such as hydrogen and aluminum, thus acidifying the soil. Base saturation refers to the amount of exchangeable base cations in a soil as a proportion of all exchangeable cations, including hydrogen and aluminum. Acid additions to soil remove base cations from the surfaces of particles, and they are then washed deeper into the soil, where they are less available for use by plants.
- Base Cation to Aluminum (BC:Al) Ratio – as the pH decreases in a soil, the amount of soluble aluminum can increase. Aluminum can be toxic to plants at elevated levels, but toxicity is counteracted by base cations. The ratio of base cations to aluminum is an indicator of the toxic level of aluminum in the soil.
- Total Sulphur (TS) – the amount of sulphur in soil can increase over time if deposition of SO_2 and other sulphur forms occurs. It is not an acidification indicator but is a useful ancillary parameter.

After completion of analyses, remaining sample materials are archived and stored, currently in facilities of Alberta Environment. Data are presented in table format in reports.

Another feature of this report entails examining the potential acidification of the monitoring sites by application of a computer soil chemistry model that simulates the change in soil acidification parameters under selected acid loadings over time. A model referred to as the ARC soil acidification model has been applied to several studies in Western Canada. It is useful mainly for comparing different types of soils, and for obtaining a general idea of the time frame in which a soil could become more acidic.

The results of monitoring after three sampling events between 2010 and 2020, and of soil acidification simulations, are summarized below.

Acidification Trends

Decreasing trends in pH and base saturation percentage were observed in some of the sites, particularly in the LFH, 0-2 cm and 2-5 cm soil layers. Increasing trends were found in lower layers.

At the Moose Lake site (sampled in 2010, 2014 and 2018), trends of decreasing pH_c were detected only in the LFH layer of the East subsite, and the 2-5 cm, 5-10 cm and 10-15 cm layers of the West subsite. No trends of decreasing BS or BC:Al ratio were found.

At the Whitney Lakes site (sampled in 2011, 2015 and 2019), trends of decreasing pH_c were detected in the LFH layer of both East and West Whitney Lakes subsites, but there were no trends of decreasing pH_c identified for the mineral layers. No trends of decreasing BS or BC:Al ratio were found.

After the three sampling events (2012, 2016, 2020) over an eight year period at the Tucker Lake site, trends of pH_c decrease occurred in the LFH layer and the 2-5 cm layer of the Tucker Lake North subsite, and the 5-10 cm and 10-15 cm layers of both the South and North subsites. No trends of decreasing BS or BC:Al ratio were found.

The LTSAM Cold Lake East subsite was sampled eight times between 1982 and 2017. Decreasing pH_c was found in the 0-2 cm and 2-5 cm layers of this site, and reduction in BS occurred in the 0-2 cm layer. Cold Lake site data were available only for the East subsite.

The Cold Lake East site displayed a trend, with regression analysis showing pH_c decreasing annually by ~ 0.01 - 0.02 pH units/year in the 0-2 cm and 2-5 cm mineral layers; i.e., changes did not occur uniformly, but overall decreased from 4.9 to 4.2 between 1982 and 2017. This is in accordance with previous analysis of this site for the same sampling period by Cho et al. (2019). While trends were observed at the Moose Lake site, they were different between the East and West subsites, and changes indicating uniform acidification therefore do not appear to be occurring. The trend toward acidification is slightly stronger at the Tucker Lake site as compared to the Moose Lake site, as decreasing pH_c occurred in the LFH layer at both subsites, and surface mineral layers showed declining pH_c , but in different layers. At both the Tucker Lake and Moose Lake sites, increasing Total Sulphur in the LFH layer provides further evidence for potential acidification.

The above comments for all LICA monitoring sites are made with caution as there have been only three sampling events to date. The comments regarding the Cold Lake site are made with greater confidence as they are based on eight sampling events since 1982.

Upward Trends in Parameters

Trends of increasing BS and BC:Al ratios were noted in some lower layers in all sites. These increases may be due to loss and transfer of exchangeable cations from the surface 0-2 cm and 2-5 cm layers to the lower layers but may also be attributable to natural variability of the soil properties. Continued monitoring will help assist interpretation of reasons for these observations.

Variability

The pH measurements were least variable among the acidification parameters of LICA sites, with coefficients of variation (CVs) among all layers and sites ranging between 0.03 and 0.06. BS values also had relatively low CVs, ranging from 0.05 to 0.15. BC:Al ratios had the highest variability with CVs between 0.26 and 0.78. Determining CVs is useful in that it helps to indicate relatively more difficulty and need for caution in recognizing differences and trends if they are relatively high.

Statistical Analyses

ANOVA and linear modelling approaches showed significant differences even in instances where there was a 0.1 or 0.2 pH change, or where other parameters showed very small differences. It is therefore important to distinguish between statistically important and biologically important differences. For example, a difference of 0.2 pH units can be statistically significant but is likely within the range of pH values at a site, and moreover is not likely to result in measurable biological effects.

Both ANOVA and regression multivariate statistical approaches are particularly useful tools for analyzing the monitoring data, yet they have limitations. Use of ANOVA identifies significant differences in data but does not identify trends. Regression analysis is needed mainly to support the ANOVA analysis but is useful only if trends are linear. Trends in some soil chemical parameters are not necessarily linear, and caution is thus required in applying these tools.

Paired Subsites

Paired subsites were established to allow for possible loss due to agents such as forest fire; with this approach, there is the possibility that one of the subsites may survive such an event. Pairing subsites has other advantages, principally by adding robustness to statistical analysis by providing additional data representing a site or forest stand. As examples, the Moose Lake subsites did not provide results that were sufficiently similar to conclude that acidification is occurring. By comparison, the results for the Tucker Lake subsites showed greater consistency with each other, and acidification is more evident. Thus, pairing of subsites enables more balanced comparison of results at each site and provides more rigour to the statistical analysis of differences and trends.

Acidification Modelling in Relation to PAI and Trends

The high acidification sensitivity of the monitoring site soils was demonstrated through the response curves and critical loads obtained from acidification simulations. Different critical loads of PAI on the monitoring site soils were calculated on the basis of pH_c , BS and BC:Al critical values. These ranged from 0.15 to 0.6 $\text{kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$ when based on 100 years of PAI, and 0.2 to $>1.0 \text{ kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$ when based on 50 years of PAI. Based on their critical loads and response curves, the order of acidification sensitivity among the sites is: Moose Lake \approx Cold Lake \approx Tucker Lake $>$ Whitney Lakes. All sites respond in their soil chemical parameters according to the level of PAI, but under similar levels, the modelling results suggest that the Whitney Lakes site will be require a longer period to show changes.

Synopsis

The following are the highlights of the analysis of three LICA soil monitoring events that were initiated in 2010, and of the LTSAM Cold Lake site which has had eight monitoring events since 1982.

- Some indications of acidification (pH_c decrease and/or TS increase) among the LICA sites were found mainly for the Tucker Lake and Moose Lake sites. No indications were found for the Whitney Lakes site.
- Overall, interpretations are challenging with results from just three monitoring events to date.
- After eight monitoring events, the LTSAM Cold Lake site showed acidification trends, with pH_c in the top 5 cm declining by about 0.5 units and base saturation percentage declining slightly in the top 0-2 cm layer since initiation of monitoring in 1982.
- Measurements of pH_c provide the strongest evidence for acidification, supported to some extent by total sulphur measures.
- With some indications of acidification occurring, the continuation of soil monitoring of the sites in the LICA area is warranted.
- Modelling indicated that significant short term acidification (to 25 cm depth) is not expected at the LICA sites under the current PAI scenarios. There exists the potential for acidification to occur in the longer term. Acidification in the surface soil layers (e.g., LFH, 0-2 cm and 2-5 cm) has occurred and based on monitoring results, is likely to continue.

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1.0 INTRODUCTION

1.1 LICA MONITORING BACKGROUND AND OBJECTIVES

The Lakeland Industry and Community Association (LICA) was formed in 2000 as a not-for-profit association responding to oil and gas production activities in the region. The LICA region centers on the MD of Bonnyville, with its eastern boundary at the Saskatchewan border, and extends in north, west, and south directions to include portions of several counties as well as the Alberta portion of the Canadian Forces Cold Lake Air Weapons Range. The association consists of three main components: (1) a Synergy Group (Synergy Alberta, 2021) that facilitates all stakeholders' voices when addressing issues concerning the environment in the LICA region; (2) the Watershed Planning and Advisory Council (WPAC) for the Beaver River Watershed, one of eleven WPACs in Alberta, and; (3) an Airshed Zone monitoring the air quality throughout the LICA region. LICA collects, shares and acts upon data, traditional knowledge and information relevant to the environment, through scientific study, community engagement and meaningful partnerships (LICA, 2021).

LICA conducts and/or oversees air and water monitoring, with airshed monitoring consisting of continuous monitoring stations, time-integrated monitoring stations, passive monitoring stations, soil acidification monitoring plots, and Beaver River Valley meteorology monitoring sites (LICA, 2021). Soil acidification monitoring plots have been established in order to reveal possible effects of airborne pollutant deposition.

The overall vision of LICA is that the environment in the LICA region be ecologically healthy and sustainable. LICA's mission is to collect, share and act upon data, traditional knowledge, and information relevant to the environment, and that this be achieved through scientific study, community engagement and meaningful partnerships (LICA, 2017).

The primary role of LICA's airshed program is to operate a regional air quality monitoring network and produce air quality data. Guided by the Air Monitoring Directive (Alberta Government, 2021), LICA's air monitoring program was designed to meet regional data and information needs. Monitoring efforts undertaken by LICA include direct measurement of air quality parameters (e.g. ozone, sulphur dioxide, hydrogen sulphide) and air effects on the environment (e.g. soil acidification, precipitation chemistry) (LICA, 2017). With regard to soil acidification, the objective is to detect changes in key soil acidification attributes that could affect the overall environment, including vegetation cover, surface water quality and groundwater quality.

1.1.1 LICA Soil Monitoring History

Acid deposition and its impacts on the environment have been issues in many areas of the world. In Alberta, the development of sour gas extraction and processing, oil sands development, and expansion of coal-fired power generation facilities through the 1960s and 1970s led to concerns about the potential for acidifying impacts on soils and water bodies in Alberta. Acidifying emissions were already causing environmental problems in eastern Canada. Consequently, in the 1980s Alberta Environment (now Alberta Environment and Parks (AEP)) in conjunction with other agencies implemented the Acid Deposition Research Program (ADRP), and undertook major studies on acidifying emissions in Alberta, including the classification of soil sensitivity to acid deposition (Holowaychuk and Fessenden, 1987). Site-specific studies were conducted to

determine if emissions of sulphur and nitrogen oxides were having impacts on vegetation and soils (e.g., Priezel at al. (2004). The Alberta environment ministry initiated a long-term soil acidification monitoring program (LTSAM) in the early 1980s, and an extensive soil and vegetation monitoring program was initiated by the Wood Buffalo Environmental Association in the 1990s. These monitoring approaches are similar to numerous programs for monitoring acidification effects on ecosystems in various countries, particularly in northern Europe.

In 2006, LICA commissioned a preliminary study of potential soil and water acidification titled *Exploratory Study of Potential Acidification Impacts on Soils and Surface Water within the LICA Area* (AMEC Earth & Environmental 2007). The study included recommendations for monitoring soil chemistry in the LICA region, including:

- Establishment of monitoring sites with the preferred soil types being highly sensitive, sandy Brunisolic soils, as well the extensively occurring Luvisols on glacial till capped by coarse textured materials (the Athabasca soil series). Vegetation types should be uniform across sites. The Brunisols are mostly associated with jack pine/lichen stands, and mixedwood stands would be appropriate for the Luvisolic (Athabasca) soils;
- Establishing monitoring sites in the 'monitoring exceedance zone' for sensitive soils; that is, within areas of $0.17 \text{ kmol}_e \text{ ha}^{-1} \text{ y}^{-1}$ potential acid input (PAI), as well as in a lower PAI area to enable comparing near-source with relatively pristine sites;
- Encouraging Alberta Environment (AENV) to continue periodic monitoring at a site located near the west side of Cold Lake, which was established as part of a provincial monitoring network in 1988; and;
- To the extent possible, co-locating soil monitoring sites with air quality monitoring sites.

The AMEC (2007) report also suggested establishing a monitoring system following either the protocols of AENV in their Long Term Soil Acidification Monitoring Program, or that of the Wood Buffalo Environmental Association (WBEA) in their Terrestrial Effects Monitoring Program (TEEM). The TEEM program monitors potential acidification effects at increasing distances from major point sources or clusters of point sources. The purpose of the AENV program is to track possible changes in soil acidification status in different parts of the province, with eight sites having been established. The establishment of sites began in the early 1980s. The monitoring methodology and the results of the first two monitoring events were reported by AENV (Roberts et al. 1989). The AENV program was recommended by AMEC (2007) in part because of the presence of a monitoring site already located within the LICA study area, which precludes the need for a fourth LICA site within the higher deposition area.

LICA initiated environmental monitoring of air, water and land resources in 2003, and as part of this program, soil acidification monitoring began in 2010 by establishment of long-term soil sampling plots in Moose Lake Provincial Park. Two more plots were established in the LICA region over the next two years in Whitney Lakes Provincial Park and in the Tucker Lake vicinity. Soil sampling is being carried out at these plots every four years in a staggered manner (one site per year). LICA's efforts enhance the existing soil acidification monitoring program carried out by Alberta Environment near the Cold Lake Fish Hatchery (LICA, 2010).

1.2 MONITORING EVALUATION

1.2.1 Acidification attributes

The evaluation herein focuses on soil attributes considered to be the most indicative of acidification effects. Holowaychuk and Fessenden (1987), in assessing the overall sensitivity of Alberta's soils to acidification, recognized that base loss, acidification (pH reduction) and aluminum (Al) solubilization were among the most important soil responses to acidification, these changes possibly leading to secondary impacts such as reduced nutrient availability and altered microbial dynamics. They also recognized that cation exchange capacity and pH were determinants of sensitivity to these changes. Subsequent work in Alberta with respect to assessment of acidification rates (Abboud and Turchenek 1990), and derivation of critical loads (Abboud and Turchenek 1988; Turchenek et al. 1992), followed many aspects of European approaches to assessing acid deposition impacts wherein pH, base saturation percentage, Al concentration (mmol L^{-1}) and base cation to aluminum (BC:Al) ratio were determined to be parameters most closely related to vegetation impacts. Consequently, the examination of the LTSAM sites focused on detecting possible trends in the above three soil chemistry attributes, with additional properties such as total sulphur, carbon and nitrogen measured to track possible accumulation over time.

1.2.1.1 Soil pH

Soil pH is defined as the pH of a solution in equilibrium with soil. It is determined by means of a glass or other suitable electrode, or chemical indicator, usually using distilled water or a salt solution at a specified soil-solution ratio. Various methods can be used to measure soil pH; those particularly relevant in acid deposition impact evaluations are as follows:

- $\text{pH}(\text{H}_2\text{O})$, or pH_H - a soil sample is made into a paste with distilled or de-ionized water, and pH is measured by insertion of a pH electrode into the paste;
- $\text{pH}(\text{CaCl}_2)$, or pH_c - a soil sample is mixed in 0.01M CaCl_2 at a 1:2 soil:solution ratio (w:v), and the pH is measured with an electrode dipped into the solution;
- $\text{pH}(\text{paste})$ - a saturated paste of soil in water is filtered, and the pH of the filtrate is measured with a glass electrode; and,
- $\text{pH}(\text{solution})$ - soil solution is extracted *in situ*, and the pH of the solution is measured with a glass electrode.

Theoretically, the $\text{pH}(\text{solution})$ measure provides the most realistic indication of the pH environment of plant roots. However, $\text{pH}(\text{solution})$ is the most difficult to obtain due to the time and equipment required for in situ extraction of adequate sample for measurement of pH and other parameters.

pH_H is commonly used to estimate pH in the plant root environment. The pH_c method involves measuring pH of soil sample suspended in 0.01 M CaCl_2 solution at a fixed soil:solution ratio. This method has several advantages over pH_H , among them being reproducibility even with dried soil samples. The salt solution generally results in a pH value about 0.5 to 0.7 units lower than that determined in water. Thus, it underestimates the soil solution pH, although it has also been considered to more accurately estimate the pH at the surfaces of soil particles because the weak

salt solution simulates the soil electrolyte concentration adjacent to these surfaces. pH_c expresses a relationship between hydrogen and other cations in the soil solution (Bache 1980). Thus, it is responsive to changes in the concentrations of base cations relative to hydrogen, and as such can be useful in monitoring because it would decrease as base cations are lost from soils. Miewes et al. (1986) also noted that pH_c is the more appropriate pH measure for characterizing the buffer range of a soil. Measurement of pH_c is most commonly applied at a 1:2 soil:solution ratio (Kalra and Maynard 1991).

Both the pH_c and pH_H measures are commonly used in research and reported in the literature. Consequently, it is important to indicate which measure is used.

Low soil pH is typical of Alberta Boreal forest soils. However, very low pH levels can have an effect on plant growth, and a soil pH_H of 4.2 reported in CLRTAP (2017) is applied as a threshold that poses a high risk of damage to forest ecosystems.

1.2.1.1 Base Cation to Aluminum (BC:Al) Ratios

The aluminum ion (Al^{3+}) can be toxic to plants at elevated levels, but clear relationships between Al levels and plant health have been difficult to establish (Cronan and Grigal, 1995). The term 'BC' refers to the sum of the molar concentrations of the cations Ca, Mg and K, and its ratio to aluminum (BC:Al) has been found to correlate strongly with plant root or shoot damage. Sverdrup and Warfvinge (1993) reviewed BC:Al ratios as indicators of stress in forest ecosystems and found that different ratios were specific to different species of forest trees and other plants. A threshold BC:Al molar ratio of 1 is commonly applied in setting critical loads for forest soils in European countries (Starr, 2000), although a threshold as low as 0.2 has been shown to be tolerated by forest species (Blaser et al., 2008). In Alberta, a BC:Al ratio of 2 has been recommended for modelling assessments of acid deposition on soils (Alberta Environment, 2008; Cumulative Environmental Management Association, 2004).

In the absence of research specific to forest species in western Canada, it is difficult to select an appropriate BC:Al ratio that would be protective of all species. The BC:Al ratio of 1 or 2, which is applied to forest soils in Europe, may not be protective of all forest ecosystem types. The Cumulative Environmental Management Association (CEMA 2004) examined critical loads of soils in the Athabasca oil sands region, and suggested limiting model-predicted change in either base saturation or the ratio of base cations to aluminum (BC:Al) in mineral horizons of acid sensitive mineral soils to less than 50% of the difference between pre-industrial values and fixed effects levels (CEMA 2004). This approach is adopted in further discussion within this document.

1.2.1.2 Base Saturation Percentage

Soil percent base saturation was identified by Cronan and Grigal (1995) and by Miewes et al. (1986) as important in evaluating potential acidification stress on forest ecosystems. While there are various methods of measuring base saturation, the method relevant to threshold limits is based on percent of 'effective cation exchange capacity', which is defined as the cation exchange capacity (CEC) that occurs at field pH, as opposed to CEC measured at a specified pH (i.e., using a pH buffered extractant). Effective CEC is measured by extraction of exchangeable cations using a neutral, unbuffered saturating solution such as NaCl, KCl, $BaCl_2$ or NH_4Cl . The effective CEC quantifies the number of negatively charged sites with which cations are associated; the major

cations in most soils are Ca, Mg, K, Na, Al, Fe, Mn and H. Thus;

$$\text{CEC} = \text{Ca} + \text{Mg} + \text{K} + \text{Na} + \text{Al} + \text{Fe} + \text{Mn} + \text{H} \text{ (expressed as cmoles charge per kg)}$$

$$\text{Base Sat} = (\text{Ca} + \text{Mg} + \text{K} + \text{Na}) / (\text{Ca} + \text{Mg} + \text{K} + \text{Na} + \text{Al} + \text{Fe} + \text{Mn} + \text{H})$$

Ca, Mg, K and Na are categorized as basic cations because the reaction between an exchangeable cation and free H^+ derived from dissociation of water results in generation of hydroxyl (OH^-). Al, Fe and Mn, on the other hand are categorized as acidic cations, as they react and tie up OH^- from H_2O , resulting in release of an equivalent amount of H^+ (McBride 1994).

For forest ecosystems, a threshold base saturation reduction to a level of 5% was suggested by Ulrich et al. (1984), while a reduction to 15% was recommended as a threshold by Cronan and Grigal (1995). More recent evidence for this level as a practical threshold is provided from studies of forest soil recovery from acidification, wherein soils with BS < 0.20 (20%) were found to have reduced capacity for recovery (Hazlett et al., 2020). These threshold values refer to base saturation calculations based on 'effective cation exchange capacity' (see above). CEMA proposed an approach similar to that for BC:Al for determining a threshold level for base saturation to protect forest ecosystems.

1.2.2 Acid Deposition Levels in the LICA Area

Levels of potential acid input (PAI) to soils and vegetation were estimated in a 2007 exploratory study of potential acidification impacts on soils and surface water within the LICA area (AMEC Earth & Environmental, 2007). A modelling approach was applied to calculate and map PAI levels in the LICA area, wherein PAI refers to the net acidity considering the deposited acidifying and neutralizing compounds in both wet and dry deposition. The PAI, measured in units of $\text{kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$, is an indicator of acid deposition for surface soil.

Mapping of PAI was conducted by using thresholds applied by Alberta Environment (2008) for initiating management actions. In particular, PAI levels of $0.17 \text{ kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$ to $0.22 \text{ kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$ designate the 'monitoring' load for soils sensitive to acidification, within which monitoring and study of receptor sensitivity are recommended. PAI levels of 0.22 to $0.25 \text{ kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$ designate a 'target' load for sensitive soils, which is the level of maximum acceptable deposition that provides long-term protection from adverse ecological consequences to the most sensitive ecosystem components and is practically achievable (Alberta Environment, 2008). A level of $0.25 \text{ kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$ is the 'critical' load for acid sensitive soils; this level is the highest load that will not lead to long-term, harmful changes to a receptor.

Mapping and modelling of PAI in the AMEC Earth & Environmental (2007) study revealed areas with levels potentially greater than the monitoring load of $0.17 \text{ kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$, along with small areas with PAI greater than $0.22 \text{ kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$. One of the criteria for monitoring site selection entailed location within areas having PAI levels greater than $0.17 \text{ kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$. Two monitoring sites, Whitney Lakes and Tucker Lake, met this criterion. A third site (Moose Lake) was located in a lower PAI area to enable comparison of the above with a relatively pristine site.

Earlier modelling of the Province of Alberta provided estimates of PAI for grid cell subdivisions of the province defined as 1° latitude by 1° longitude, which for the Cold Lake area is 54°00' to 55°00' north latitude and 100°00' to 111°00' west longitude (Cheng et al., 1997). The PAI estimate for this region was 0.10 to 0.15 kmol_c ha⁻¹ y⁻¹. Estimates obtained by WBK and Associates (2004) were 0.10 to 0.17 kmol_c ha⁻¹ y⁻¹ for each of 1995, 2000, and 2010 (projected). A subsequent 2006 estimate resulted in this same level of PAI for the Cold Lake grid cell, while a projected estimate for 2020 was 0.06 to 0.10 kmol_c ha⁻¹ y⁻¹ (Alberta Government, 2014).

More recent modelling conducted by Imperial Oil Limited (2016) indicated zones of PAI that differ from the earlier study of the LICA area. The modelling was conducted as part of an environmental impact assessment of an expansion of Imperial Oil's Cold Lake Operations. Only the more northerly soil monitoring sites, Tucker Lake and Cold Lake, were within the area of investigation, and both of these were located in zones with 0.10 - 0.15 kmol_c ha⁻¹ y⁻¹ PAI. Estimated PAI levels based on both the above studies are presented in Table 1.

Table 1. Estimated Potential Acid Input at Monitoring Sites.

Site Location	PAI (kmol _c H ⁺ ha ⁻¹ y ⁻¹) (AMEC Earth & Environmental, 2007)	PAI (kmol _c H ⁺ ha ⁻¹ y ⁻¹) (Imperial Oil Limited, 2016)
Moose Lake	~0.1	nd ^z
Whitney Lakes	~0.17	nd
Tucker Lake	~0.17	0.10 – 0.15
Cold Lake	~0.17	0.10 – 0.15

^z not determined; these sites were outside the area of investigation in Imperial Oil Limited (2016)

1.3 LICA AREA DESCRIPTION

1.3.1 LICA Area Overview and Map

The LICA area extends from the Fourth Meridian (the Saskatchewan border) to Range 8, inclusive, with varying portions of Range 9. North to south, the study area extends from the middle of Township 73 to Township 55, inclusive, and includes most of Township 54 within Ranges 7 and 8; about a third of Township 53 within Ranges 3, 4 and 5; Township 53, Ranges 1 and 2; and, and the upper part of Township 52 within Ranges 1 and 2 (LICA 2005). Much of the mid and north LICA area is located within the Beaver River drainage basin, while the south part is within the North Saskatchewan River basin. As of late 2021 the LICA extends westward to include all of the Beaver River watershed. The LICA area along with locations of monitoring sites is depicted in Figure 1.

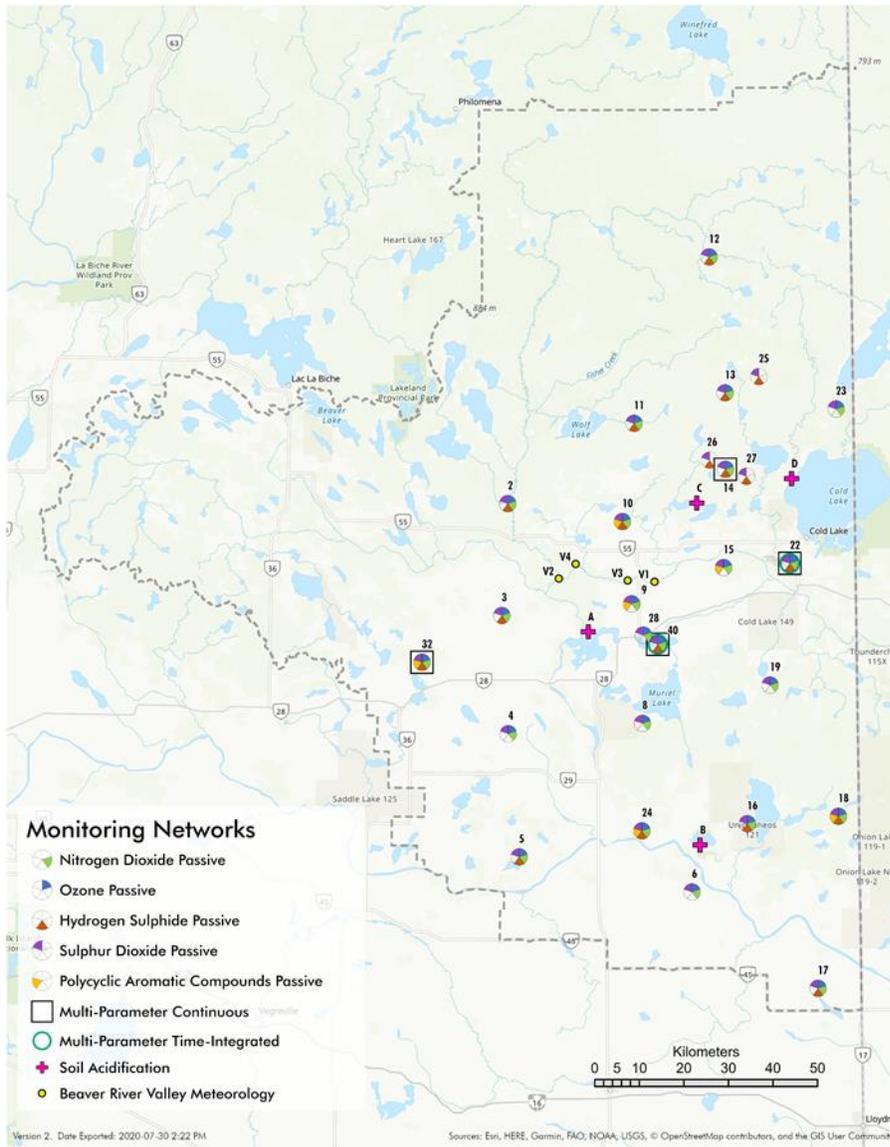
1.3.2 Biophysical Description of the LICA Area

The LICA study area is described in the context of 'ecoregions' as described in National Ecological Framework (Canadian Soil Information Service, 2018) and Agricultural Regions of Alberta Soil Inventory Database (AGRASID) (Alberta Soil Information Centre, 2021). Long-term temperature and precipitation data are indicated below (Table 2) for the ecoregions in general (sourced from Canadian Soil Information Service, 2018) and for specific locales and the soil monitoring sites in the LICA area (sourced from Alberta Climate Records, University of Lethbridge, 2019). The mean temperatures for the ecoregions are lower than those of specific locations within the ecoregions. Reasons for this are (1) the ecoregion temperatures represent large areas that extend across the

prairies, (2) the site-specific temperatures may be affected by local geoclimatic conditions, and (3) the ecoregion descriptions, which were originally prepared in the 1990s, apply 30 year means for the period 1961 to 1990 (Canadian Soil Information Service, 2018), whereas the site-specific means are for the period 1990 to 2017 (University of Lethbridge, 2019).

The southern part of the LICA area, from Township 52 at the Saskatchewan border to about Townships 57 and 58 in Ranges 8 and 9, occurs within the Aspen Parkland Ecoregion, which is considered transitional between the boreal forest to the north and the grasslands to the south. The climate is marked by short, warm summers and long, cold winters with continuous snow cover. Mean temperatures and precipitation for the Aspen Parkland Ecoregion are indicated in Table 2.

The ecoregion is classified as having a transitional grassland ecoclimate. Most of the ecoregion is now farmland but in its native state, the landscape was characterized by trembling aspen and shrubs, with grassland communities occupying drier sites on loamy Black Chernozemic soils. Poorly drained, Gleysolic soils support willow and sedge species. This broad plain region, underlain by Cretaceous shale, is covered by undulating to kettled, calcareous, glacial till with significant areas of level lacustrine and hummocky to ridged fluvioglacial deposits. This ecoregion generally corresponds with the Black Soil Zone in Alberta. There are no soil monitoring sites in this part of the LICA area.



- | | | |
|--------------------|-----------------|-------------------------------------|
| 2 Sand River | 12 Foster Creek | 23 Medley – Martineau |
| 3 Therien | 13 Primrose | 24 Fort George |
| 4 Flat Lake | 14 Maskwa | 25 Burnt Lake |
| 5 Lake Eliza | 15 Ardmore | 26 Mahihkan |
| 6 Telegraph Creek | 16 Frog Lake | 27 Mahkeses |
| 8 Muriel – Kehewin | 17 Clear Range | 28 Bonnyville |
| 9 Dupre | 18 Fishing Lake | 32 St. Lina |
| 10 La Corey | 19 Beaverdam | 40 Bonnyville East – Charlotte Lake |

- | | |
|-------------------------------------|-------------------------------|
| A Moose Lake Soil Plot | V1 Beaver River Valley Site 1 |
| B Whitney Lakes Soil Plot | V2 Beaver River Valley Site 2 |
| C Tucker Lake Soil Plot | V3 Beaver River Valley Site 3 |
| D Cold Lake Fish Hatchery Soil Plot | V4 Beaver River Valley Site 4 |

Source: LICA (2020)

Figure 1. LICA Area with Locations of Soil and Other Environmental Monitoring Sites.

Trends in Soil Acidification in the LICA area – 2010 to 2020

Table 2. Average Temperature and Precipitation from 1991 to 2017 in the LICA Area

Location	Temperature Mean Annual (°C)	Temperature Mean Summer (°C)	Temperature Mean Winter (°C)	Precipitation Mean Annual (mm)
Parkland Ecoregion ^z	1.5	15	-12.5	400
St. Paul	2.2	15	-11.5	384
Vermilion	2.6	15.5	-11.3	366
Boreal Transition Ecoregion ^z	1	14	-13.5	450
Moose Lake site	2.2	15.2	-12.0	390
Whitney Lakes site	2.2	15.2	-12.0	376
Mid-Boreal Uplands Ecoregion ^z	-1 to 1	13 to 15.5	-13.5 to -16	400
Tucker Lake site	2.0	15.1	-12.1	408
Cold Lake LTSAM	2.0	15.2	-12.3	405
Conklin ^y	1.3	14.5	-12.8	424

^z Temperatures and precipitation are indicated for each overall ecoregion, and for specific locations within the LICA area, including the soil monitoring sites.

^y Conklin temperature and precipitation information is included for context, showing the LICA area to be transitional to the cooler climate of the north.

The middle part of the LICA area, to the north of the Aspen Parkland and extending to Townships 63 and part of 64 in the northeast, is within the Boreal Transition Ecoregion. The ecoregion is characterized by warm summers and cold winters. Mean annual temperatures and precipitation amounts are indicated in Table 2. The ecoregion is classified as having a subhumid low boreal ecoclimate. It marks the southern limit of closed deciduous boreal forest and the northern limit of arable agriculture. Closed cover of trembling aspen with lesser areas of balsam poplar and white spruce, tall shrubs, and a thick understory of mixed herbs constitutes the predominant vegetation. Poorly drained sites consist mainly of sedges and willow, with some black spruce and tamarack. Underlain by Cretaceous shale, this hummocky to kettled plain is covered by calcareous, glacial till, significant inclusions of relatively level lacustrine deposits, and some coarse-textured glaciofluvial deposits reworked by wind to eolian deposits in places. Associated with the rougher morainal deposits are many small lakes, ponds, and sloughs occupying shallow depressions. The region drains northeastward via the Saskatchewan River system. Well to imperfectly drained Gray Luvisols and Dark Gray Chernozemic soils are predominant; local areas of Black Chernozemic, peaty Gleysolic, and Mesisolic soils also occur. Over 70% of the ecoregion is farmland, with spring wheat and other cereals, oilseeds, and hay being the dominant crops.

The Moose Lake and Whitney Lakes soil monitoring sites are located within this ecoregion. The Whitney Lakes site is located at the southern edge of this ecoregion, within an ecodistrict (i.e., a subdivision of an ecoregion) designated as the Laurier Upland. This is characterized by landscape that is hummocky with some undulating areas. Soils consist of Black Chernozems developed on medium textured till, with minor Luvisols and Brunisols on coarse textured glaciofluvial and eolian materials. Dominant soils are the Angus Ridge soil series (Eluviated Black Chernozems on glacial till), Uncas (Dark Gray Chernozems on glacial till), and Primula (Eluviated Eutric Brunisol on very coarse textured glaciofluvial deposits). The Whitney Lakes soil monitoring site is characterized by Eluviated Dystric Brunisols of the Nestow series, which are very similar to the Primula soils, but are more acidic.

The Moose Lake site is situated within the Moose Lake Plain ecodistrict, characterized by undulating landscape with numerous water bodies and peatlands. Major soils are Brunisols

developed on coarse textured sediments (glaciofluvial and eolian). Minor soils and land types include Organics and water bodies. The main soil series are Niton (Eluviated Eutric Brunisols) and Nestow (Eluviated Dystric Brunisols), both on very coarse textured materials. The soils at the Moose Lake site are typical of the Nestow soil series.

The northern part of the LICA area, northward from the southern to middle part of Township 63 in Ranges 1-5, and from the middle of Township 64 within Ranges 6-9, is within the Mid-Boreal Uplands Ecoregion. This ecoregion occurs as separate, mostly upland areas of the Alberta Plateau, south of the Canadian Shield. The climate has predominantly short, cool summers and cold winters. Mean temperature and precipitation are indicated in Table 2. The ecoregion is characterized by a predominantly subhumid mid-boreal ecoclimate. Vegetation consists of mixed coniferous and deciduous forest with medium to tall, closed stands of trembling aspen and balsam poplar, with white spruce, black spruce, and balsam fir. Deciduous stands have a diverse understory of shrubs and herbs; coniferous stands tend to promote feathermoss. Cold and poorly drained fens and bogs are covered with tamarack and black spruce. Underlain by Cretaceous shales, these uplands are covered by kettled to dissected, deep, loamy to clayey-textured glacial till, lacustrine deposits, and inclusions of coarse, fluvioglacial deposits. Elevations range from about 400 to over 800 m asl. Numerous small lakes, ponds, and sloughs occupying shallow depressions are associated with the morainal deposits. In most of the ecoregion, drainage is northward toward the Athabasca and Clearwater Rivers, but the portion of the ecoregion within the LICA area lies within the Beaver River drainage basin, wherein the river flows eastward into Saskatchewan and ultimately to Hudson Bay.

Well-drained Gray Luvisolic soils are dominant in the region. Significant inclusions are peaty phase Gleysols and Mesisols that occupy poorly drained depressions. Dystric Brunisols occur on droughty, sandy sites. The Tucker Lake soil monitoring site is located within the Hilda Lake Plain ecodistrict, which is an undulating landscape with some peatlands characterized by Luvisols and Brunisols developed on medium textured till and inclusions of coarse textured glaciofluvial and eolian sediments. Athabasca series (Orthic Gray Luvisol on till) and Spedden series (Dark Gray Luvisol on till) are dominant. Eluviated Dystric Brunisols of the Liza series occur on the coarse textured deposits.

The Long-Term Monitoring site of AEP (Cold Lake site) is located within the Silesia Plain ecodistrict of the Boreal Uplands ecoregion. This ecodistrict has undulating landscape with numerous water bodies and valleys with confined floodplains. Gray Luvisols developed on medium textured till (Athabasca series) are dominant soils. Minor soils include Chernozems, Gleysols, eroded soils, and Brunisols. This ecodistrict is similar to and lies adjacent to the Hilda Lake Plain ecodistrict. Elevations are generally higher in the Silesia Plain (reaching about 610 m) as compared to about 550 to 580 m in the Hilda Lake Plain. The Athabasca soil series is dominant, with Liza soils, which characterize the Cold Lake monitoring site, constituting a minor component of the ecodistrict.

1.4 REPORT OBJECTIVES

The objectives of this report are to review and analyze the soil monitoring data collected since the LICA program was initiated. There have been three soil sampling events completed during the

period 2010 to 2020, as follows: Moose Lake site – 2010, 2014 and 2018; Whitney Lakes site – 2011, 2015 and 2019; Tucker Lake site – 2012, 2016 and 2020. The data are examined to determine if any trends in soil chemistry changes can be detected. Information from the AEP Cold Lake monitoring site is included in this report to enable an assessment of current conditions using all available data for the area. The results of the synthesis of information to date may also assist in review of the program, sites, and monitoring parameters, as well as in possible identification of program changes and need for integration with related monitoring programs.

2.0 METHODS

2.1 FIELD METHODS

2.1.1 Site Selection

Sites were selected according to criteria that included estimated levels of deposition of acidic and acidifying substances, presence of acid sensitive soils, location in undisturbed forest, and long-term secured access and constraints on future development. The soils at each site are described in the reports for site establishment and initial sampling by Abboud and Turchenek (2011, 2012, 2013, for Moose Lake, Whitney Lakes, and Tucker Lake sites, respectively).

2.1.1.1 Acid Deposition Levels

Levels of acid deposition were estimated in a 2007 exploratory study of potential acidification impacts on soils and surface water within the LICA area (AMEC Earth & Environmental, 2007). A modelling approach was applied to calculate and map potential acid input (PAI) levels in the LICA area, wherein PAI refers to the net acidity, which consists of the deposited acidifying and neutralizing compounds in both wet and dry deposition. The PAI is an indicator of acid deposition for surface soil measured in units of $\text{kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$. Mapping of PAI was conducted by using thresholds suggested by Alberta Environment for initiating management actions. In particular, PAI levels of $0.17 \text{ kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$ to $0.22 \text{ kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$ designate the 'monitoring' load for soils sensitive to acidification, within which monitoring and study of receptor sensitivity are recommended. PAI levels of 0.22 to $0.25 \text{ kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$ designate a 'target' load for sensitive soils, which is the level of maximum acceptable deposition that provides long-term protection from adverse ecological consequences to the most sensitive ecosystem components, and is practically achievable (Alberta Environment, 2008). A level of $0.25 \text{ kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$ is the 'critical' load for acid sensitive soils; this level is defined as the highest load that will not lead to long-term, harmful changes to a receptor.

Mapping and modelling of PAI in the 2007 study (AMEC Earth & Environmental, 2007) revealed areas with levels potentially greater than the monitoring load of $0.17 \text{ kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$, along with very small areas with PAI greater than $0.22 \text{ kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$. One of the criteria for monitoring site selection entailed location within areas having PAI levels greater than $0.17 \text{ kmol}_c \text{ha}^{-1} \text{y}^{-1}$. Two monitoring sites, the Whitney Lakes and the Tucker Lake sites, met these criteria. A third site (Moose Lake site) was located in a lower PAI area (i.e., $<0.17 \text{ kmol}_c \text{ha}^{-1} \text{y}^{-1}$) to enable comparison of the above with relatively unaffected soil conditions. However, the more recent modelling by Imperial Oil Limited (2016) shows that two of these sites (Tucker Lake and Cold Lake) are in zones with $0.10 - 0.15 \text{ kmol}_c \text{ha}^{-1} \text{y}^{-1}$ PAI. The Whitney Lake site was outside of the area of modelling in this latter study.

2.1.1.2 Situating Sites on Acid Sensitive Soils

The criteria for acid sensitive soils are based on Holowaychuk and Fessenden (1987) who described sensitive soils as those with cation exchange capacity $\leq 6 \text{ cmol}_c \text{kg}^{-1}$ and with high susceptibility to aluminum solubilization and base cation loss. In northeast Alberta forests, these generally are sandy Brunisolic soils with forest cover of jack pine (*Pinus banksiana*). Such soils are common in the LICA area (Alberta Soil Information Centre, 2016).

2.1.1.3 Location of Sites in Undisturbed Forest

Locating sites was limited to undisturbed forest in order to provide indication of possible effects in natural forest ecosystems in the region. Location on cultivated soils was avoided because agricultural practices such as nitrogen fertilization, which can act as an acidifying agent, would mask the effects of acidifying emissions from atmospheric deposition. Acidification of agricultural soils is indeed an issue in Alberta, but different assessment methods and treatments (e.g., liming) are required to address the issue (Alberta Agriculture and Rural Development, 2003).

2.1.1.4 Long-Term Access

The soil monitoring sites can support monitoring for at least 44 years. Consequently, protection of sites from disturbance and development is desirable. This was accomplished by locating two of the sites within provincial parks (Whitney Lakes and Moose Lake). The Tucker Lake site does not have as robust protection as that afforded by location with a provincial park. However, this site is on Crown Land which has a Protective Notation for an 'Ungulate Habitat Protection Area'; a Protective Notation is granted to areas of land and water systems requiring special management practices to protect their resource values (Alberta Sustainable Resource Development, 2006).

2.1.1.5 Field Program and Features of the Selected Sites

A search for suitable soil monitoring sites was carried out in the LICA area in 2010 (Abboud and Turchenek, 2011). Eleven sites were examined in a region delimited approximately by Whitney Lakes Provincial Park in the southeast, Cold Lake Indian Reserve to the northeast, Wolf Lake to the northwest, and the hamlet of Mallaig to the west. Potential soil monitoring sites were accessed by vehicle on local roads and trails and then by foot in the forest. The jack pine vegetation type was first confirmed, and then the soil was examined by digging a small pit to a depth of approximately 50 cm, followed by hand augering to a one metre depth. The soil was described, and samples (to 30 cm depth) for laboratory analysis were obtained from the LFH layer (forest floor, or duff layer), the Ae horizon (topsoil), and the top of the B horizon (upper subsoil).

The chemistry data for all Brunisolic soils indicated suitability for monitoring based on the selection criteria. Two of the eleven sites were Luvisolic soils. Although Luvisolic soils generally have higher acid buffering capacity than Brunisolic soils, these were also evaluated in terms of possible inclusion in the monitoring program, although they were eventually withdrawn from consideration. Site selection was finalized on the basis of other considerations indicated above.

The Moose Lake site is situated within Moose Lake Provincial Park, near the town of Bonnyville. The Whitney Lakes site is in Whitney Lakes Provincial Park, located south-east of the hamlet of Lyndbergh. The Tucker Site is located about a kilometre south of the west end of Tucker Lake. All sites are in forested areas, on predominately sandy soils classified as Eluviated Dystric Brunisols according to the Canadian System of Soil classification (Soil Classification Working Group, 1998). In the Moose Lake and Whitney Lakes areas these are referred to as the Nestow soil series. The soil at the Tucker Lake site is the same as that at the other two sites, but the Liza soil series is applied to it because it lies within a different ecoregion, or more specifically, in a different soil correlation area as defined by Alberta Soil Information Centre (2016). Details of site and soil profile characteristics of the selected sites are provided in the reports for site establishment and initial sampling by Abboud and Turchenek (2011, 2012, 2013).

The parent material at each site is glaciofluvial or eolian overlying glaciofluvial, and of sand texture with few gravel-size coarse fragments. This material is highly pervious and is very rapidly drained. Vegetation is jack pine with ground cover mainly of bearberry (*Arctostaphylos uva-ursi*) and lichen (*Cladina* and other species), with feather moss species in some places. The vegetation corresponds to the a1 ecosite phase according to '*Field Guide to Ecosites of Northern Alberta*' (Beckingham and Archibald, 1996).

2.1.1.6 LTSAM Monitoring Site

A long-term soil acidification monitoring (LTSAM) program carried out by Alberta Environment includes a site located near the Cold Lake Fish Hatchery (Roberts et al., 1989; Abboud et al., 2012). This site is included in this synthesis of monitoring results due to its location within the LICA area, and to its history of monitoring, having been established in 1982. This site effectively provides a fourth location for the LICA monitoring program. The Cold Lake site is situated near a $0.17 \text{ kmol}_e \text{ H}^+ \text{ ha}^{-1} \text{ y}^{-1}$ isopleth of acid deposition, according to the acidification overview of AMEC Earth & Environmental (2007). However, more recent modelling has indicated that the vicinity of the Cold Lake site lies with a zone with $0.10 - 0.15 \text{ kmol}_e \text{ H}^+ \text{ ha}^{-1} \text{ y}^{-1}$ acid deposition (Imperial Oil Limited, 2016). The soils at this site are classified as Eluviated Dystric Brunisols on sandy glaciofluvial materials, thus falling into the same category as the three LICA sites. The soil series designation is Liza, which is the same as that of the Tucker Lake site.

2.1.2 Monitoring Plot Design

The sampling design for soil monitoring was based on a stratified random sampling procedure as described by Roberts et al. (1989) and Abboud et al. (2012). Each site had two subsites established in order to provide a possible surviving site should one be destroyed (e.g., fire, vandalism). Each subsite (24 m X 24 m) was subdivided into 12 plots (6 m X 8 m) and assigned a letter from A to L. The plots were further subdivided into 12 subplots (2 m X 2 m). The subplots were randomly assigned a number from 1-12, each number reflecting the number of the sampling event. This provides a total of 12 replicates for each sampling event, and 12 sampling events over the course of the program. The detailed layouts for each of the subsites are in the reports for site establishment and initial sampling by Abboud and Turchenek (2011, 2012, 2013).

The Tucker Lake North subsite differs from the above in having dimensions of 18 m by 18 m, with plots 4.5 m by 6 m, and subplots 1.5 by 1.5 m. The site is characterized by choppy topography and fitting the site into a smaller area with gentler slopes required the smaller size.

Corners of the subsites were marked with 10 cm diameter round fence posts; a metal tag was nailed to one of the corner posts and labeled to provide a plot reference point. The corners of the plots were marked with cedar stakes; individual stakes that deteriorated over time were replaced during subsequent site visits.

2.1.3 Soil Sampling Procedure

At each monitoring site, the subplots within each plot were located for each sampling event within each of the subsite layouts (e.g., subplot 1 was sampled during the first sampling event, subplot 2 during the second event, etc.). At or near the centre of each subplot, a pit (50-60 cm square) is laid out; the soil pit site is moved off centre if a tree or plentiful roots occur at the centre. The

vegetative growth, including live moss and lichen, is removed and set aside. The LFH horizon is removed by hand with the aid of a stainless-steel knife or spatula. This material can either be set aside or bagged as an LFH sample with careful removal of mineral soil and live vegetation. Where it is more convenient, the LFH material can be sampled at a separate spot within the subplot. A pit is then dug to a depth of about 60-80 cm. Tree roots encountered are removed with pruning shears or shovel. The soil removed is set aside on a plastic tarp to avoid impacting adjacent subplots with subsurface soils; topsoil material (A horizon) is piled separately from subsoil (B horizon) material.

The walls of the soil pit are squared off and cleared of any foreign material with a knife or spatula. Mineral horizons are then sampled at depths of 0-2, 2-5, 5-10, 10-15, 15-30, 30-45, and 45-60 cm from three sidewalls of the pit with a stainless-steel spatula, scoop and tray. In some cases, an abundance of roots impedes sampling one of the sidewalls and a larger area is sampled on two sidewalls instead, or three areas are selected wherever sampling can be completed without interference by high density of roots. Upon completion of sample removal, the mineral soil removed from the pit is replaced, with tamping by foot, in the order it was removed. The replaced mineral soil is topped off by the LFH material and vegetative growth removed at the beginning of the procedure. Although roots are cut and mosses and lichens are disturbed, rapid regeneration occurs and evidence of the sampling is rarely evident on subsequent sampling trips.

At the time of plot establishment, a separate soil pit was excavated for sampling of soils according to natural pedogenic horizons. The pit was located outside of but near each plot. This was carried out as part of site characterization, particularly the classification of individual horizons and the overall soil profile.

2.2 LONG-TERM SAMPLING SCHEDULE

Sampling of the Moose Lake, Whitney Lakes and Tucker Lake sites was initiated in 2010, 2011, and 2012, respectively. With a consistent four-year sampling pattern, the LICA plots can be sampled until 2054 – 2056 (Table 3). The sampling history and upcoming schedule of the AEP Cold Lake site is also indicated in Table 3. With an initial sampling event in 1982, the final sampling the AEP site is expected to be carried out in 2029.

2.3 SOIL SAMPLE LABORATORY ANALYSIS

Laboratory analyses are completed according to methods applied in the AEP long term monitoring program. Samples are initially dried at about 30°C to constant dry weight, and then passed through a 2 mm sieve or through a rotary grinder with 2 mm openings. The grinder is used to break up any soil clumps and to separate coarse roots from the soil fine earth fraction. The methods used for the various analyses are discussed below and summarized in Table 4.

Analyses were initially carried out at the soil laboratory of Alberta Innovates -Technology Futures (formerly Alberta Research Council). From 2016 to date, the analyses were completed at the laboratories of the Canadian Forest Service, Northern Forestry Centre, in Edmonton, Alberta.

Table 3. Sampling Timelines for Soil Monitoring Sites in the LICA Area

Sampling Year	Site ^z			
	Moose Lake	Whitney Lakes	Tucker Lake	Cold Lake
1982				1 ^y
1986				2
1990				3
1994				4
2001				5
2005				6
2009				7
2010	1			
2011		1		
2012			1	
2013				8
2014	2			
2015		2		
2016			2	
2017				9
2018	3			
2019		3		
2020			3	
2021				10 ^x
2022	4			
2023		4		
2024			4	
2025				11
2026	5			
2027		5		
2028			5	
2029				12

^z Each site consists of two paired subsites

^y Blue cells – sampling years to date

^x Yellow cells – planned near-future sampling years

The same parameters are to be measured by the same methods over the duration of the program. However, in order to keep costs under control, only the LFH, 0-2, 2-5, 5-10, and 10-15 cm depth samples were analyzed for chemical properties. In the case of the AEP Cold Lake site, laboratory analyses have been consistently completed for samples from just one of the two subsites. All samples collected at each sampling event are archived in AEP storage facilities in Edmonton.

2.3.1 Soil pH

Soil pH was measured in CaCl₂ using the same methodology in all sampling years, as outlined in Roberts et al. (1989). A 1:2 mixture (soil:0.01 M CaCl₂) for mineral samples, and a 1:4 mixture for LFH material, was stirred for 30 minutes, left to settle for 30 min, and then measured with a pH meter equipped with a combination pH electrode after equilibrating the electrodes for 1 min.

Table 4. Analytical Methods used for Soils Analysis

Parameter	Method	Notes
pH (CaCl ₂)	Method 3.11 in McKeague (1978)	The soil-to-solution ratio for litter material is 1:4 and for mineral soil is 1:2. Solution is 0.1 M CaCl ₂ . Measurement is with a pH meter and a combination pH electrode.
Electrical Conductivity	Method 4.13 in McKeague (1978)	Measurement occurs in the saturated paste extract of a soil sample.
Soluble Ions	Method 3.21 in McKeague (1978)	By the saturated paste method and ICP-OES analysis of the extract.
Cation Exchange Capacity - Unbuffered	Method 18.2 in Carter and Gregorich (2008)	By 0.1 M BaCl ₂ (barium chloride) extractant, and measurement of Ba by ICP-OES.
Exchangeable Cations	Method 18.2 in Carter and Gregorich (2008)	ICP-OES scan for Ca, Mg, Na, K, Fe, Mn, Al and Si for both the BaCl ₂ extracts.
Total Carbon (C), Nitrogen (N), and Sulphur (S)	Method 3.611 in McKeague (1978) and LECO (2006)	LECO combustion method.

2.3.2 Exchangeable Cations and Cation Exchange Capacity

Exchangeable cations and cation exchange capacity (CEC) were determined using the method of Rhoades (1982), as described in Roberts et al. (1989). Soil samples were extracted with non-buffered BaCl₂ (1:10 soil:solution ratio) after shaking the soil and solution mixture for 2 hours and then filtering through a Whatman #42 filter. The exchangeable cations (Ca²⁺, Mg²⁺, Na⁺, K⁺, Fe³⁺, Mn²⁺ and Al³⁺) were determined by inductively coupled plasma atomic emission spectroscopy. The CEC was calculated as the sum of the exchangeable cations:

$$\text{CEC} = (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^{+} + \text{K}^{+} + \text{Fe}^{3+} + \text{Mn}^{2+} + \text{Al}^{3+})$$

where the exchangeable ions are expressed as cmol_c kg⁻¹ (Hendershot and Duquette, 1986). The base saturation percentage (BS) is calculated as:

$$\text{BS} = ((\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^{+} + \text{K}^{+})/\text{CEC}) \times 100$$

2.3.3 Soluble Ions

Soil saturated pastes were prepared according to the USDA Soil Salinity Laboratory method (USDA, 1954; Rhoades, 1982), were extracted using a vacuum extractor, and then the extracts were analyzed for pH, electrical conductivity and soluble ions. Soluble ions (Ca, Mg, Na, K, Al, Fe, Mn, S) were determined in the extracts by inductively coupled plasma atomic emission spectroscopy. Extract pH was measured using a pH meter with a combination electrode. Extract electrical conductivity was measured using a conductivity meter and saturation percentage was calculated from the weights of the soil and added water.

2.4 STATISTICS

2.4.1 Basic Statistics

Basic statistics (i.e., mean, standard deviation and coefficient of variability) were calculated for the acidification indicators and their input variables using MS Excel[®] functions (AVERAGE and

STDEV respectively). Coefficient of variation (CV) refers to the standard deviation divided by the mean.

2.4.2 Multivariate Statistics

2.4.2.1 Study Design

The design within each location-site combination is a variant of a split-plot design often applied in agricultural field trials. The main plot blocks are the twelve replicate plots established at each location-site. These main-plot blocks are repeatedly measured at multiple years (the main-plot factor). The subplots factor is the depth sampled in each year.

The study design was described in terms of sampling design (Sections 2.1.2 and 2.1.3) and sampling periods in Section 2.2. To reiterate, the monitoring design consists of sites at three locations within the LICA area, two study subsites at each location, twelve plots (labelled A...L) within each subsite, twelve subplots within each plot, and in each sampling year (usually 4 years apart), soil from each subplot was sampled at up to 7 depths (0-2, 2-5, 5-10, 10-15, 15-30, 30-45, and 45-60 cm). Litter (LFH) samples were also taken but were not included in the analysis except for pH, TC, TN and TS. Note that the same depths are sampled in each year, but the actual years when the sites were measured differed.

2.4.2.2 Analysis of Variance

Analysis of variance (ANOVA) was applied in the statistical examination of monitoring results. In the ANOVA analysis, no pattern of changes among years is assumed. The hypothesis of interest is that the mean of the variable under consideration does not change across years.

The key assumptions are:

- a) the variances of the measurements in each year are equal;
- b) measurements taken at different sampling points have the same correlation regardless of how apart the sampling occasions are. For example, measurements within a replicate that are 4 years apart have the same correlation as measurements within a replicate that are 8 years apart (this is known as compound symmetry); and,
- c) the residuals are normal.

The Year effect will measure a common change in the mean across years (for each depth level).

The above analysis was conducted as a two-factor ANOVA (ANOVA: Two Factor with Replication) using MS Excel® Data Analysis Tools.

Analysis of variance (ANOVA) was performed on the main soil acidification variables, namely pH, base saturation, and base cation:aluminum (BC:Al) ratio, as well total sulphur (TS). Differences among the three sampling years for each site and between the two subsites (North and South, or East and West) were examined. Tukey's Honest Significant Difference test (Steel and Torrie, 1980, 1960) was subsequently applied to these attributes to determine whether differences in the data were statistically significant ($\alpha=0.05$ level of confidence). The statistics were based on the 12 replicates from each subsite.

2.4.2.3 Linear Regression

The ANOVA approach is completely general in the sense that there is no *a priori* pattern to the response expected if the hypothesis of equal means is not tenable. For example, the means could increase, then decrease for a few sampling occasions, and then increase again.

The downside to this generality is that it has reduced power to detect specific trends. For example, if the actual trend over time is a linear reduction in the mean, a regression approach where this linear trend is specifically investigated will have greater power to detect a trend than the ANOVA. However, if the actual trend is not a linear change over time, the regression approach has a reduced power to detect the trend.

The key assumptions are the same as in the ANOVA approach.

The Year effect will measure a common linear change in the mean across years (for each depth level).

The above analysis was conducted using a regression procedure (Regression in MS Excel® Data Analysis Tools). It is possible to obtain tests for linear year effects for each depth separately (called slices) without discarding the gain in information from pooling across depths.

ANOVA results were used to detect changes in acidification parameters, with regression data used as supporting evidence only. The response of soils to acidity inputs is not linear, and regression was therefore not considered to be appropriate for the primary analysis; however, where changes occur along a short segment of the overall response curve, the regression approach was considered to provide useful information, especially when combined with another (i.e., ANOVA) approach. As noted previously, there is no pre-supposed pattern of change in applying ANOVA. The regression analysis is used herein mainly to describe a change determined by ANOVA to be significant, as possibly being a trend in either the positive or negative direction.

3.0 RESULTS OF MONITORING

Data are presented in graphs and tables below. All data are also provided in previous reports (Abboud and Turchenek, 2011, 2012, 2013, 2015, 2016, 2017, 2019, 2020, 2021).

For purposes of statistical analysis, values below the analytical detection limit were set to one-half of the difference between the detection limit and zero.

The BC:Al ratios are very sensitive to small values in the denominator, e.g., a value of 0.01 vs 0.02 for the Al concentration will double the ratio. This leads to large variability (in the order of 100+) in these ratios.

Preliminary plots of the variance of the pH, BS, BC:Al and TS values showed that the standard deviation of pH values was independent of the mean, that the standard deviation of the BC:Al ratio increased with the mean, and the standard deviation of the BS and TS values decreased with the mean. This suggests that no transformation is needed to analyze the pH, BS and TS values, and that a logarithmic transformation is suitable for the analysis of the BC:Al values.

Both the analysis of variance (ANOVA) and regression approaches were applied to the pH, BS, log(BC:Al) and TS values. For each variable, tests for trend from the ANOVA and regression approach are provided. These results are summarized in tables along with the observed p-values for each variable. Graphical presentation of pH_c values, BS, BC:Al ratio and TS% in each of the sampled layers at all plots are included for each site. Results of both descriptive statistics and ANOVA are presented for each of the monitoring sites in the sections that follow. Comments regarding the monitoring parameters in these sections are made below in terms of trends, where significance is indicated in relation to an α level of 0.05. Stated inferences regarding the statistical significance of these trends are supported by a Tukey Honest Significant Difference test done for the means of each of the three indicator variables to compare yearly variations within horizons at each study location.

There is always the danger when many variables are tested in multiple ways that some statistically results will be false positives. For example, if about 100 independent tests were performed when no trend is present with the usual $\alpha=0.05$ level, then about 5 tests could show a statistically significant trend.

3.1 MOOSE LAKE SITE

Soil samples from the East and West Moose Lake subsites were analyzed for soil parameters, as described above. Table 5 shows the data for the main acidification indicators along with simple statistics for each soil attribute according to soil layer and subsite. Table 6 shows the mean values for the acidification indicators and the results (p-values) of the multivariate statistical analyses, the single-factor ANOVA (with Tukey Honest Significant Difference (HSD) extension) and the Linear Regression analysis for each soil layer and subsite. The data are also presented graphically in Figures 2 to 5.

The following examines some aspects of the data.

3.1.1 pH_c

- The data show differences in pH_c (pH of soil mixed with CaCl₂ solution) in soil layers among the years 2010, 2014 and 2018. Variability is low, with CVs being 0.06 or lower for the LFH and mineral layers (Table 5).
- Statistically significant differences (between years) in pH_c (Table 6) were observed in the LFH layer for both the East and West subsites, the 0-2 cm and 2-5 cm layers of the West subsite, and the 5-10 cm and 10-15 cm of both the East and West subsites.
- Regression analysis of pH_c with years (Table 6 and Figure 2) showed a statistically significant trend (with a negative slope) for pH_c in the LFH layer of the East subsite and in the 2-5 cm, 5-10 cm and 10-15 cm layers of the West subsite.
- The statistically significant regression slopes indicated a potential for pH_c to decrease annually by 0.05 pH units/year in the LFH and 0.03-0.04 pH units for the mineral layers.

3.1.2 Base Saturation

- Base saturation is a key acidification indicator defined as the proportion of exchangeable base cations (K, Na, Ca and Mg) to the cation exchange capacity. CVs ranged from 0.05 to 0.15 among the layers and sampling years (Table 5).
- Statistically significant differences (between years) in BS (Table 6) were observed in the 2-5 cm layer of the West subsite, 5-10 cm layer of the East subsite and the 10-15 cm layer of both the East and West subsites.
- Regression analysis of BS with years (Table 6 and Figure 3) showed a statistically significant trend (with a positive slope) for BS only in the 5-10 cm and 10-15 cm layers of the East subsite.
- The statistically significant differences and trends in BS with years can be a result of movement of base cations down the soil profile or of field variability, as only 3 sampling years were available for analysis.

3.1.3 Base Cation:Al Ratios

- The BC:Al ratios showed relatively high variability as indicated by CV values from 0.30 to 0.78 (Table 5).
- The BC:Al ratios were also consistently higher in 2014 as compared to 2010, in all soil layers (Table 5), but values in 2018 show some rebound toward the earlier values.
- Statistically significant differences (between years) in BC:Al ratios (Table 6) were observed in 0-2 cm of the West subsite and the 2-5 cm, 5-10 cm and 10-15 cm layers of both the East and West subsites.
- Regression analysis of BC:Al ratios with years (Table 6 and Figure 4) showed a statistically significant trend for BC:Al ratios (with a positive slope) in all mineral layers of the West subsite.
- The statistically significant differences and trends in BC:Al ratios with years can be a result of movement of base cations down the soil profile or of field variability, as only 3 sampling years were available for analysis.

3.1.4 Total Sulphur

- Total Sulphur (TS %) showed wide variability especially in the lower mineral horizons (values were at or below detection limits). The LFH layer showed the least variability with CV values from 0.17 to 0.32 (Table 5). The mineral horizon variability increased with depth (due to lower TS values) and ranged from 0.21 to 0.66 (Table 4).
- Statistically significant differences (between years) in TS (Table 6) were observed in the LFH and 2-5 cm layers of the East subsite, and the 0-2 cm and 2-5 cm layers of the West subsite. The 5-10 and 10-15 cm layers were not considered for ANOVA (nor regression analysis) due to the large number of TS values at or below the detection limit.
- Regression analysis of TS with years (Table 6 and Figure 5) showed a statistically significant trend (with a negative slope) for TS in the LFH layer of the East subsite, and a statistically significant trend (with a positive slope) in the 0-2 and 2-5 cm layers of the West subsite.
- The statistically significant differences and trends in TS with years can be a result of movement of S down the soil.

Table 5. pH, BS, BC:AI Ratios and TS - Moose Lake Site - 2010, 2014 and 2018

pH_c^z		LFH			0-2 (cm)			2-5 (cm)			5-10 (cm)			10-15 (cm)		
Year	Subsite	Mean	SD ^z	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV
2010	East	4.3	0.2	0.05	4.7	0.2	0.04	4.8	0.1	0.03	4.8	0.2	0.03	4.7	0.2	0.03
2014	East	4.2	0.1	0.03	4.5	0.2	0.05	4.7	0.2	0.04	4.6	0.2	0.04	4.6	0.1	0.03
2018	East	3.9	0.2	0.05	4.6	0.1	0.02	4.8	0.2	0.04	4.8	0.1	0.03	4.8	0.1	0.02
2010	West	4.1	0.2	0.05	4.7	0.2	0.04	4.9	0.2	0.04	4.9	0.2	0.03	4.8	0.2	0.03
2014	West	3.8	0.1	0.03	4.3	0.2	0.05	4.5	0.2	0.04	4.7	0.2	0.04	4.7	0.2	0.04
2018	West	4.2	0.2	0.04	4.6	0.3	0.06	4.7	0.2	0.04	4.6	0.2	0.04	4.6	0.2	0.03
<i>Base Saturation</i>		LFH			0-2 (cm)			2-5 (cm)			5-10 (cm)			10-15 (cm)		
Year	Subsite	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV
2010	East	-	-	-	0.83	0.08	0.10	0.81	0.06	0.08	0.74	0.08	0.11	0.72	0.08	0.11
2014	East	-	-	-	0.84	0.09	0.11	0.85	0.07	0.09	0.79	0.09	0.11	0.74	0.07	0.10
2018	East	-	-	-	0.78	0.06	0.07	0.84	0.05	0.06	0.84	0.06	0.07	0.86	0.04	0.05
2010	West	-	-	-	0.81	0.06	0.08	0.87	0.06	0.07	0.83	0.09	0.11	0.8	0.10	0.12
2014	West	-	-	-	0.74	0.11	0.15	0.77	0.10	0.14	0.78	0.11	0.14	0.79	0.11	0.14
2018	West	-	-	-	0.82	0.09	0.11	0.8	0.08	0.10	0.77	0.07	0.09	0.73	0.07	0.09
<i>BC:AI Ratio</i>		LFH			0-2 (cm)			2-5 (cm)			5-10 (cm)			10-15 (cm)		
Year	Subsite	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV
2010	East	-	-	-	9	6	0.61	5	3	0.56	3	1	0.45	2	1	0.37
2014	East	-	-	-	11	8	0.74	6	2	0.34	5	4	0.73	5	3	0.59
2018	East	-	-	-	6	2	0.31	3	1	0.33	3	1	0.30	2	1	0.27
2010	West	-	-	-	3	1	0.32	3	2	0.63	2	0.4	0.27	2	1	0.38
2014	West	-	-	-	8	4	0.52	5	2	0.39	3	1	0.36	4	2	0.54
2018	West	-	-	-	8	3	0.42	5	4	0.78	3	1	0.26	2	1	0.34
<i>Total Sulphur (%)</i>		LFH			0-2 (cm)			2-5 (cm)			5-10 (cm)			10-15 (cm)		
Year	Subsite	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV
2010	East	0.126	0.022	0.17	0.007	0.002	0.34	0.004	0.001	0.29	0.002	0.001	0.25	0.002	0.000	0.26
2014	East	0.097	0.017	0.17	0.008	0.004	0.45	0.004	0.002	0.56	0.003	0.001	0.52	0.002	0.001	0.53
2018	East	0.097	0.029	0.30	0.005	0.001	0.22	0.002	0.001	0.43	0.002	0.001	0.30	0.002	0.001	0.53
2010	West	0.090	0.028	0.32	0.004	0.001	0.22	0.002	0.000	0.21	0.002	0.001	0.33	0.001	0.001	0.36
2014	West	0.079	0.025	0.32	0.004	0.001	0.35	0.002	0.001	0.51	0.002	0.001	0.45	0.001	0.000	0.27
2018	West	0.097	0.023	0.24	0.007	0.004	0.51	0.004	0.003	0.66	0.002	0.001	0.47	0.002	0.001	0.43

^z pH_c – pH measured using $CaCl_2$ solution; SD – standard deviation; CV – coefficient of variation (SD divided by mean).

Table 6. Multivariate Statistics (ANOVA and Regression) for the Mean Soil pH, BS, BC:Al ratios and TS at the Moose Lake site

Site/ Statistical Results	Depth (cm)	LFH		0-2 (cm)				2-5 (cm)			
	Year ^z	pH	TS (%)	pH	BS	BC:Al	TS (%)	pH	BS	BC:Al	TS (%)
Moose Lake East	2010	4.3 b ^y	0.126 b	4.7 a	0.83 a	9 a	0.007 a	4.8 a	0.81 a	5 ab	0.004 ab
	2014	4.2 b	0.097 a	4.5 a	0.84 a	11 a	0.008 a	4.7 a	0.85 a	6 b	0.004 a
	2018	3.9 a	0.097 a	4.6 a	0.78 a	6 a	0.005 a	4.8 a	0.84 a	3 a	0.002 ab
ANOVA	P value	<0.001	0.005	0.087	0.135	0.247	0.056	0.219	0.278	0.014	0.020
Linear Regression	P value	<0.001	0.005	0.153	0.838	0.206	0.123	0.935	0.318	0.196	0.068
Linear Regression	Slope ^x	-0.054	-0.004	NS	NS	NS	NS	NS	NS	NS	NS
Moose Lake West	2010	4.1 b	0.090 a	4.7 b	0.81 a	3 a	0.004 a	4.9 b	0.87 b	3 a	0.002 ab
	2014	3.8 a	0.079 a	4.3 a	0.74 a	8 b	0.004 a	4.5 a	0.77 a	5 a	0.002 a
	2018	4.2 a	0.097 a	4.6 b	0.82 a	8 b	0.007 b	4.7 b	0.80 ab	5 a	0.004 b
ANOVA	P value	<0.001	0.255	0.001	0.093	<0.001	0.002	<0.001	0.019	0.006	0.025
Linear Regression	P value	0.237	0.532	0.238	0.777	<0.001	0.002	0.017	0.056	0.009	0.028
Linear Regression	Slope ^x	NS	NS	NS	NS	0.043	<0.001	-0.030	NS	0.032	<0.001

Table 6. Concluded

Site/ Statistical Results	Depth (cm)	5-10 (cm)			10-15 (cm)		
	Year ^z	pH	BS	BC:Al	pH	BS	BC:Al
Moose Lake East	2010	4.8 ab	0.74 a	3 a	4.7 b	0.72 a	2 a
	2014	4.6 a	0.79 ab	5 b	4.6 a	0.74 a	5 b
	2018	4.8 b	0.84 b	3 a	4.8 b	0.86 b	2 a
ANOVA	P value	0.024	0.012	0.004	<0.001	0.001	<0.001
Linear Regression	P value	0.552	0.003	0.848	0.318	<0.001	0.808
Linear Regression	Slope ^x	NS	0.012	NS		0.018	NS
Moose Lake West	2010	4.9 b	0.83 a	2 a	4.8 b	0.80 a	1.5 a
	2014	4.6 a	0.78 a	3 b	4.7 ab	0.79 b	4 b
	2018	4.6 a	0.77 a	3 b	4.6 a	0.73 ab	2 ab
ANOVA	P value	0.001	0.175	<0.001	0.002	<0.001	<0.001
Linear Regression	P value	0.004	0.082	<0.001	0.001	0.106	0.017
Linear Regression	Slope ^x	-0.029	NS	0.037	-0.032	NS	0.028

^z Year refers to the sampling year. Data for pH, BS and BC:Al ratios are means calculated from 12 replicates.

^y Letters (a, b, ab, c, bc) indicate statistical significance; means followed by the same letter do not differ significantly from one another at P<0.05 (Tukey's test).

^x Regression slope values are shown when statistically significant at p<0.05, otherwise as NS (not statistically significant (p>0.05))

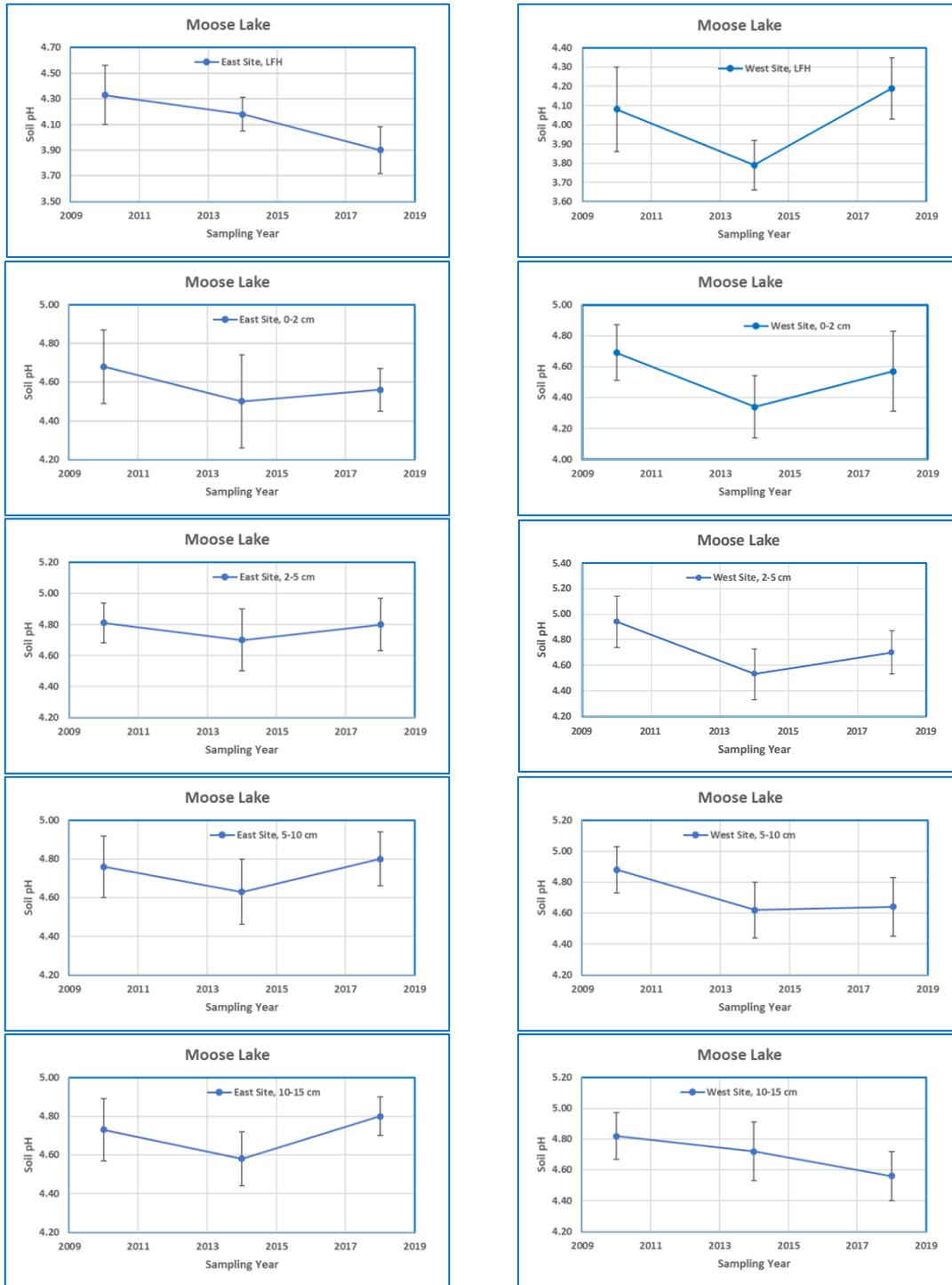


Figure 2. Change in pH at the Moose Lake Site.

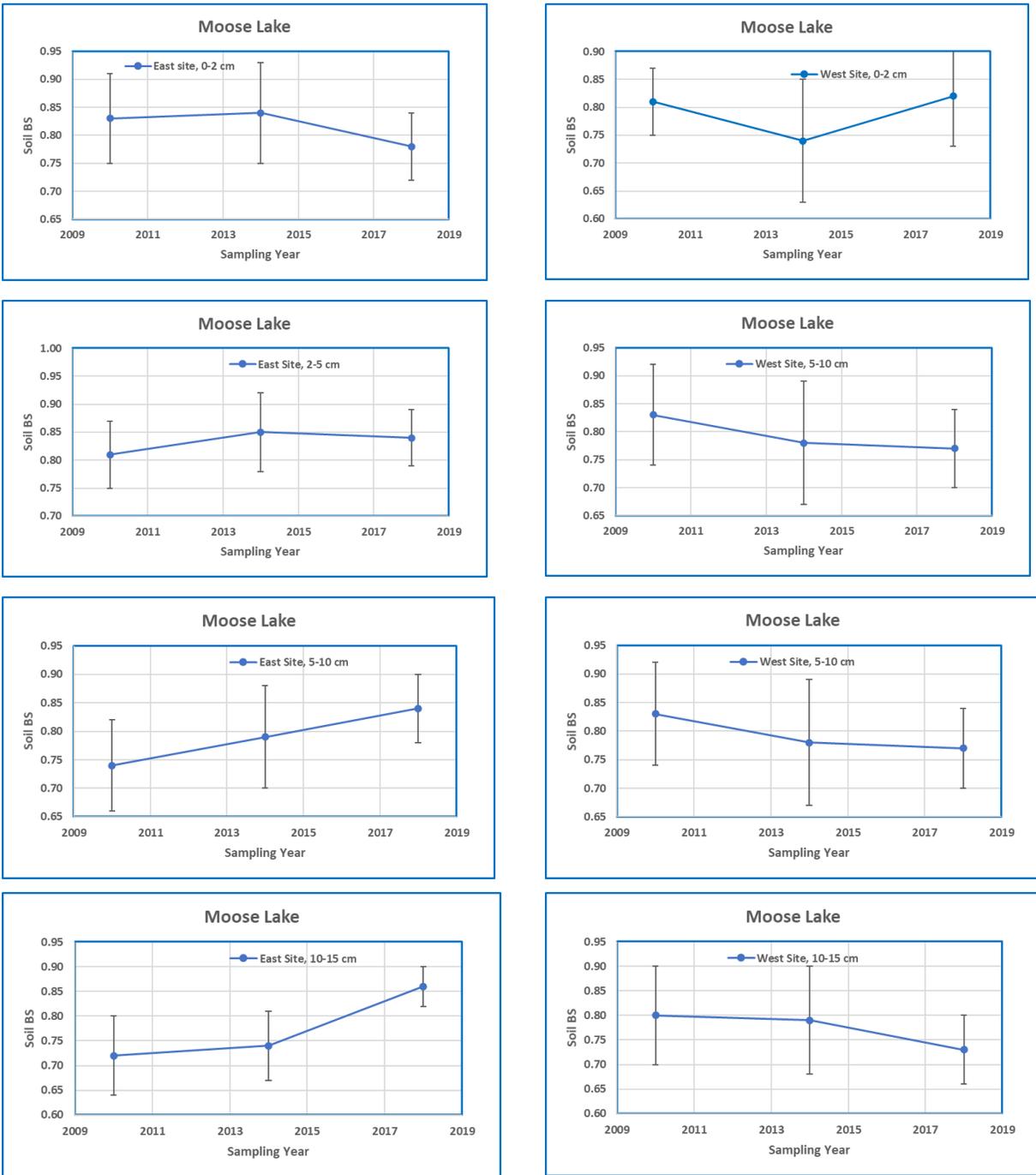


Figure 3. Change in Base Saturation at the Moose Lake Site.

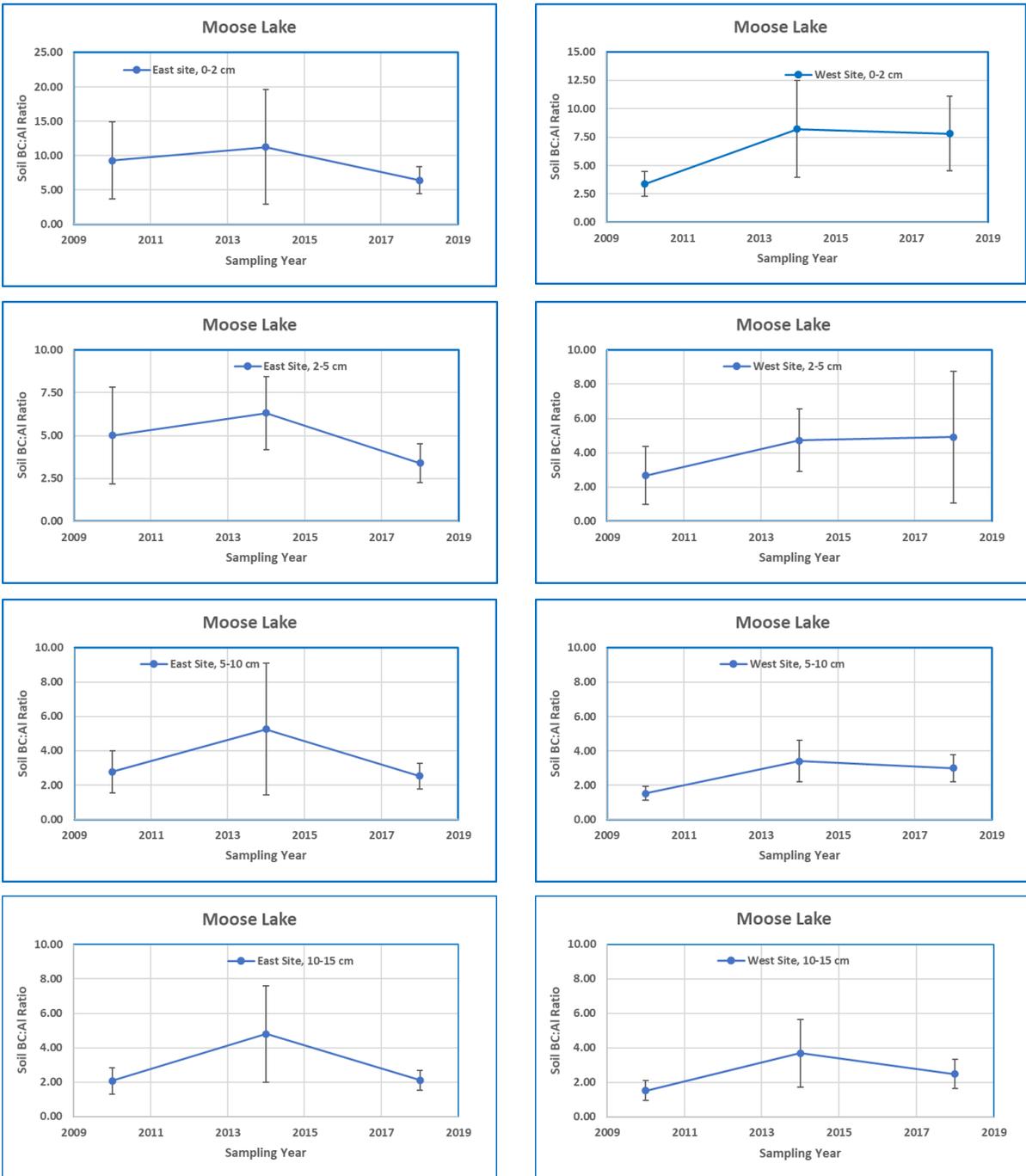


Figure 4. Change in Base cation to Aluminum Ratio at the Moose Lake Site.

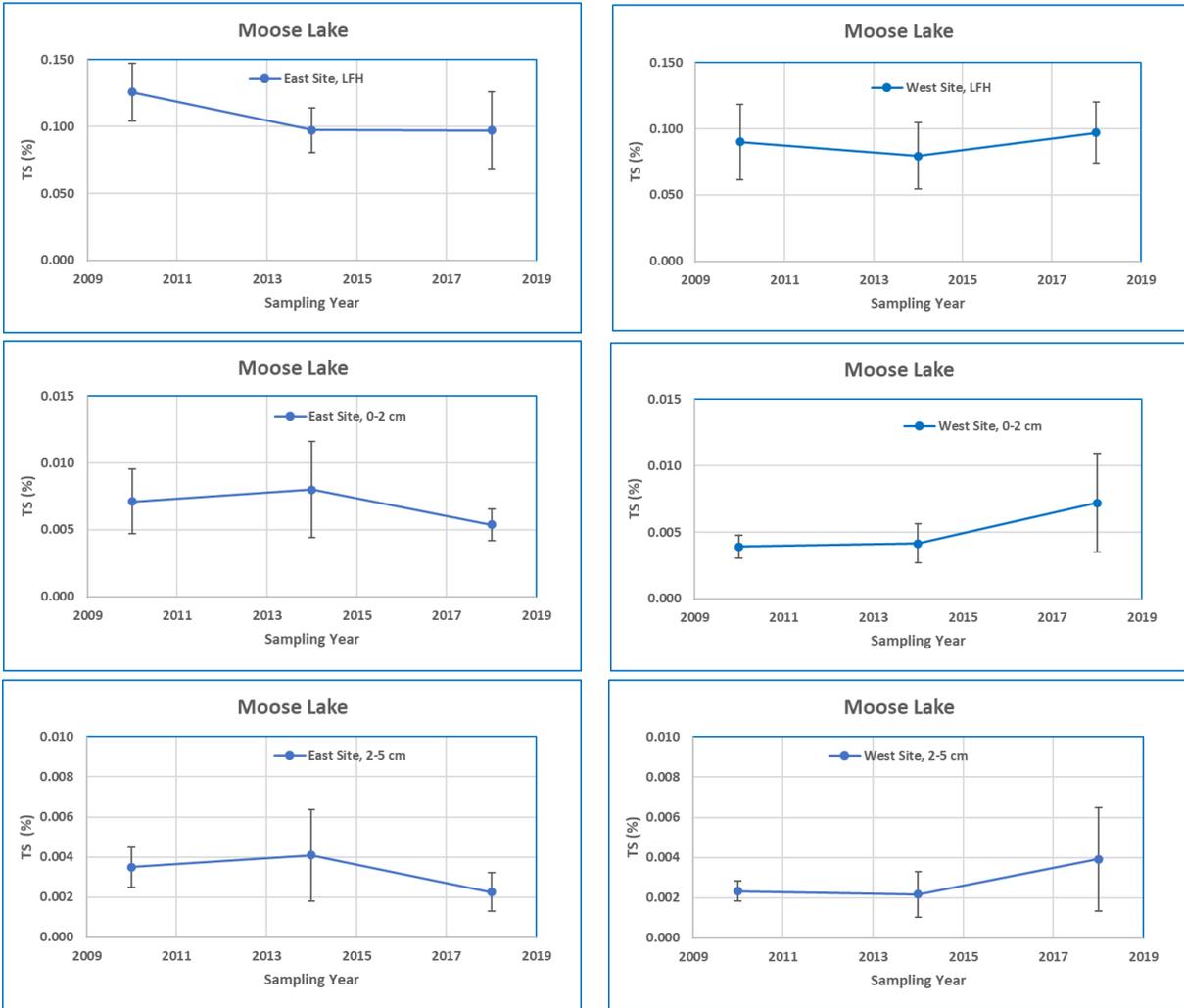


Figure 5. Change in Total Sulphur at the Moose Lake Site.

3.2 WHITNEY LAKES SITE

Soil samples from the East and West Whitney Lakes subsites were analyzed for soil parameters, as described earlier. Table 7 shows the data for the main acidification indicators along with simple statistics for each soil attribute according to soil layer and subsite. Table 8 shows the mean values for the acidification indicators and the results (p-values) of the multivariate statistical analyses, the single-factor ANOVA (with Tukey Honest Significant Difference (HSD) extension) and the Linear Regression analysis for each soil layer and subsite. The data are also presented graphically in Figures 6 to 9.

The following examines some aspects of the data.

3.2.1 pH_c

- The data show little differences in pH_c in mineral soil layers among the years 2011, 2015 and 2019. Variability is low, with CVs being 0.06 or lower for the LFH layer and 0.09 and lower for the mineral layers (Table 7).
- Statistically significant differences (between years) in pH_c (Table 8) were observed only in the LFH layer for both the East and West subsites but not for any of the mineral layers.
- Regression analysis of pH_c with years (Table 8 and Figure 6) showed a statistically significant trend (with a negative slope) for pH_c only in the LFH layer of the East and West subsites.
- The statistically significant regression slopes indicated a potential for pH_c to decrease annually by ~ 0.03 pH units/year in the LFH layers.

3.2.2 Base Saturation

- CVs for base saturation ranged from 0.02 to 0.12 among the layers and sampling years (Table 7).
- Statistically significant differences (between years) in BS (Table 8) were observed in the 5-10 cm layer of the West subsite, and the 10-15 cm layer of both the East and West subsites.
- Regression analysis of BS with years (Table 8 and Figure 7) showed a statistically significant trend (with a positive slope) for BS only in the 5-10 cm layer of the West subsite.
- The statistically significant differences and trends in BS with years can be a result of movement of base cations down the soil profile or of field variability as only 3 sampling years were available for analysis.

3.2.3 Base Cation:Al Ratios

- The BC:Al ratios showed relatively high variability as indicated by CV values from 0.34 to 1.72 (Table 7).
- Statistically significant differences (between years) in BC:Al ratios (Table 8) were observed in 0-2 cm layer of the West subsite and the 2-5 cm, 5-10 cm and 10-15 cm layers of both the East and West subsites.
- Regression analysis of BC:Al ratios with years (Table 8 and Figure 8) showed a statistically significant trend for BC:Al ratios (with a positive slope) in the 5-10 cm layer of the East

subsite and the 10-15 cm of both the East and West subsites.

- The statistically significant differences and trends in BC:Al ratios with years can be a result of movement of base cations down the soil profile, but are more likely due to field variability as only 3 sampling years were available for analysis.

3.2.4 Total Sulphur

- Total sulphur (TS %) showed wide variability especially in the lower mineral horizons (values were at or below detection limits). The LFH layer showed the least variability with CV values from 0.19 to 0.32 (Table 7). The mineral horizon variability increased with depth (due to lower TS values) and ranged from 0.17 to 0.64 (Table 7).
- Statistically significant differences (between years) in TS (Table 8) were observed only in the LFH layer of the East subsite. The 5-10 and 10-15 cm layers were not considered for ANOVA (nor regression analysis) due to the large number of TS values at or below the detection limit.
- Regression analysis of TS with years (Table 8 and Figure 9) showed a statistically significant trend (with a negative slope) for TS only in the LFH layer of the East subsite. The 5-10 and 10-15 cm layers were not considered for regression analysis due to the large number of TS values at or below the detection limit.
- The statistically significant differences and trends in TS with years can be a result of movement of S down the soil profile or of field variability, as only 3 sampling years were available for analysis.

Table 7. pH, Base Saturation, BC: Al Ratios and TS - Whitney Lakes Site - 2011, 2015 and 2019

pH_c^z		LFH			0-2 (cm)			2-5 (cm)			5-10 (cm)			10-15 (cm)		
Year	Subsite	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV
2011	East	4.6	0.3	0.06	5.1	0.4	0.09	5.1	0.4	0.08	5.1	0.5	0.09	5.0	0.4	0.09
2015	East	4.4	0.2	0.05	4.9	0.4	0.08	4.9	0.4	0.07	4.9	0.3	0.07	4.9	0.3	0.06
2019	East	4.3	0.2	0.04	4.9	0.3	0.06	4.9	0.4	0.08	4.8	0.4	0.07	4.8	0.4	0.08
2011	West	4.4	0.1	0.02	4.8	0.3	0.05	4.9	0.2	0.04	4.8	0.2	0.05	4.8	0.2	0.04
2015	West	4.3	0.2	0.03	4.7	0.3	0.06	4.9	0.2	0.04	4.9	0.3	0.05	4.9	0.3	0.05
2019	West	4.2	0.2	0.04	4.7	0.3	0.07	4.8	0.2	0.05	4.8	0.3	0.05	4.0	0.4	0.08
Base Saturation		LFH			0-2 (cm)			2-5 (cm)			5-10 (cm)			10-15 (cm)		
Year	Subsite	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV
2011	East	-	-	-	0.94	0.04	0.04	0.94	0.06	0.07	0.90	0.10	0.12	0.89	0.09	0.10
2015	East	-	-	-	0.93	0.05	0.05	0.95	0.05	0.05	0.96	0.04	0.04	0.97	0.03	0.03
2019	East	-	-	-	0.95	0.04	0.05	0.93	0.06	0.06	0.93	0.06	0.06	0.93	0.07	0.07
2011	West	-	-	-	0.90	0.05	0.05	0.90	0.07	0.07	0.88	0.05	0.06	0.87	0.05	0.06
2015	West	-	-	-	0.91	0.06	0.07	0.94	0.05	0.05	0.94	0.03	0.03	0.95	0.05	0.05
2019	West	-	-	-	0.89	0.07	0.08	0.91	0.06	0.07	0.93	0.05	0.06	0.92	0.10	0.10
BC:Al Ratios		LFH			0-2 (cm)			2-5 (cm)			5-10 (cm)			10-15 (cm)		
Year	Subsite	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV
2011	East	-	-	-	21	18	0.86	25	32	1.30	11	7	0.63	7	4	0.57
2015	East	-	-	-	24	32	1.29	17	17	1.01	7	5	0.66	5	7	1.28
2019	East	-	-	-	15	7	0.49	10	16	1.53	4	7	1.72	1	1	0.61
2011	West	-	-	-	8	3	0.41	7	3	0.45	5	3	0.64	4	1	0.40
2015	West	-	-	-	12	4	0.34	14	9	0.67	12	12	1.03	4	3	0.82
2019	West	-	-	-	6	3	0.40	6	4	0.58	3	2	0.47	1	01	0.44
Total Sulphur (%)		LFH			0-2 (cm)			2-5 (cm)			5-10 (cm)			10-15 (cm)		
Year	Subsite	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV
2010	East	0.095	0.022	0.24	0.012	0.004	0.34	0.007	0.001	0.17	0.004	0.001	0.24	0.003	0.001	0.26
2014	East	0.062	0.017	0.27	0.013	0.004	0.35	0.005	0.003	0.56	0.003	0.002	0.49	0.002	0.001	0.35
2018	East	0.070	0.022	0.32	0.013	0.005	0.43	0.005	0.002	0.33	0.003	0.001	0.27	0.002	0.001	0.30
2010	West	0.100	0.019	0.19	0.009	0.003	0.31	0.006	0.002	0.29	0.004	0.002	0.42	0.003	0.001	0.27
2014	West	0.081	0.022	0.26	0.008	0.002	0.29	0.005	0.002	0.45	0.003	0.002	0.64	0.002	0.001	0.47
2018	West	0.095	0.018	0.19	0.009	0.003	0.36	0.006	0.002	0.43	0.003	0.001	0.38	0.002	0.001	0.41

^z pH_c – pH measured using $CaCl_2$ solution; SD – standard deviation; CV – coefficient of variation (SD divided by mean).

Table 8. Multivariate Statistics (ANOVA and Regression) for the Mean Soil pH, BS, BC:Al ratios and TS at the Whitney Lakes site

Site/ Statistical Results	Depth (cm)	LFH		0-2 (cm)				2-5 (cm)			
	Year ^z	pH	TS (%)	pH	BS	BC:Al	TS (%)	pH	BS	BC:Al	TS (%)
Whitney Lakes East	2010	4.6 b ^y	0.095 b	5.1 a	0.94 a	21 a	0.012 a	5.1 a	0.94 a	25 a	0.007 a
	2014	4.4 ab	0.062 a	4.9 a	0.93 a	24 a	0.013 a	4.9 a	0.95 a	17 a	0.005 a
	2018	4.3 a	0.070 a	4.9 a	0.95 a	15 a	0.013 a	4.9 a	0.93 a	10 a	0.005 a
ANOVA	P value	0.014	0.001	0.264	0.614	0.562	0.946 a	0.158	0.818	0.014	0.225 a
Linear Regression	P value	0.005	0.012	0.174	0.917	0.426	0.791 a	0.070	0.820	0.006	0.172
Linear Regression	Slope ^x	-0.035	-0.003	NS	NS	NS	NS	NS	NS	NS	NS
Whitney Lakes West	2010	4.4 b	0.100 a	4.8 a	0.90 a	8	0.009 a	4.9 a	0.90 a	7 a	0.006 a
	2014	4.3 ab	0.081 a	4.7 a	0.91 a	12 b	0.008 a	4.9 a	0.94 a	14 b	0.005 a
	2018	4.2 a	0.095 a	4.7 a	0.89 a	6 a	0.009 a	4.8 a	0.91 a	6 a	0.006 a
ANOVA	P value	0.002	0.061	0.295	0.605	<0.001	0.804	0.125	0.248	0.003	0.741
Linear Regression	P value	<0.001	0.544	0.124	0.787	0.262	0.769	0.050	0.522	0.687	0.826
Linear Regression	Slope ^x	-0.027	NS	NS	NS	NS	NS	-0.030		0.032	

Table 8. Concluded

Site/ Statistical Results	Depth (cm)	5-10 (cm)			10-15 (cm)		
	Year ^z	pH	BS	BC:Al	pH	BS	BC:Al
Moose Lake East	2010	5.1 ab	0.90 a	11 b	5.0 a	0.89 a	7 b
	2014	4.9 a	0.96 a	7 ab	4.9 a	0.97 b	5 ab
	2018	4.8 b	0.93 a	4 a	4.8 a	0.93 ab	1 a
ANOVA	P value	0.259	0.188	<0.001	0.534	0.042	<0.001
Linear Regression	P value	0.105	0.353	<0.001	0.260	0.162	<0.001
Linear Regression	Slope ^x	NS	NS	-0.080	NS	NS	-0.084
Moose Lake West	2010	4.8 a	0.88 a	5 ab	4.8 a	0.87 a	4 b
	2014	4.9 a	0.94 b	12 b	4.9 a	0.95 b	4 b
	2018	4.8 a	0.93 b	3 a	4.8 a	0.92 ab	1 a
ANOVA	P value	0.800	0.003	0.008	0.629	0.023	<0.001
Linear Regression	P value	0.737	0.009	0.564	0.832	0.081	<0.001
Linear Regression	Slope ^x	NS	0.007	NS	NS	NS	-0.059

^z Year refers to the sampling year. Data for pH, BS and BS:Al ratios are means calculated from 12 replicates.

^y Letters (a, b, ab, c, bc) indicate statistical significance; means followed by the same letter do not differ significantly from one another at P<0.05 (Tukey's test).

^x Regression slope values are shown when statistically significant at p<0.05, otherwise as NS (not statistically significant (p>0.05))

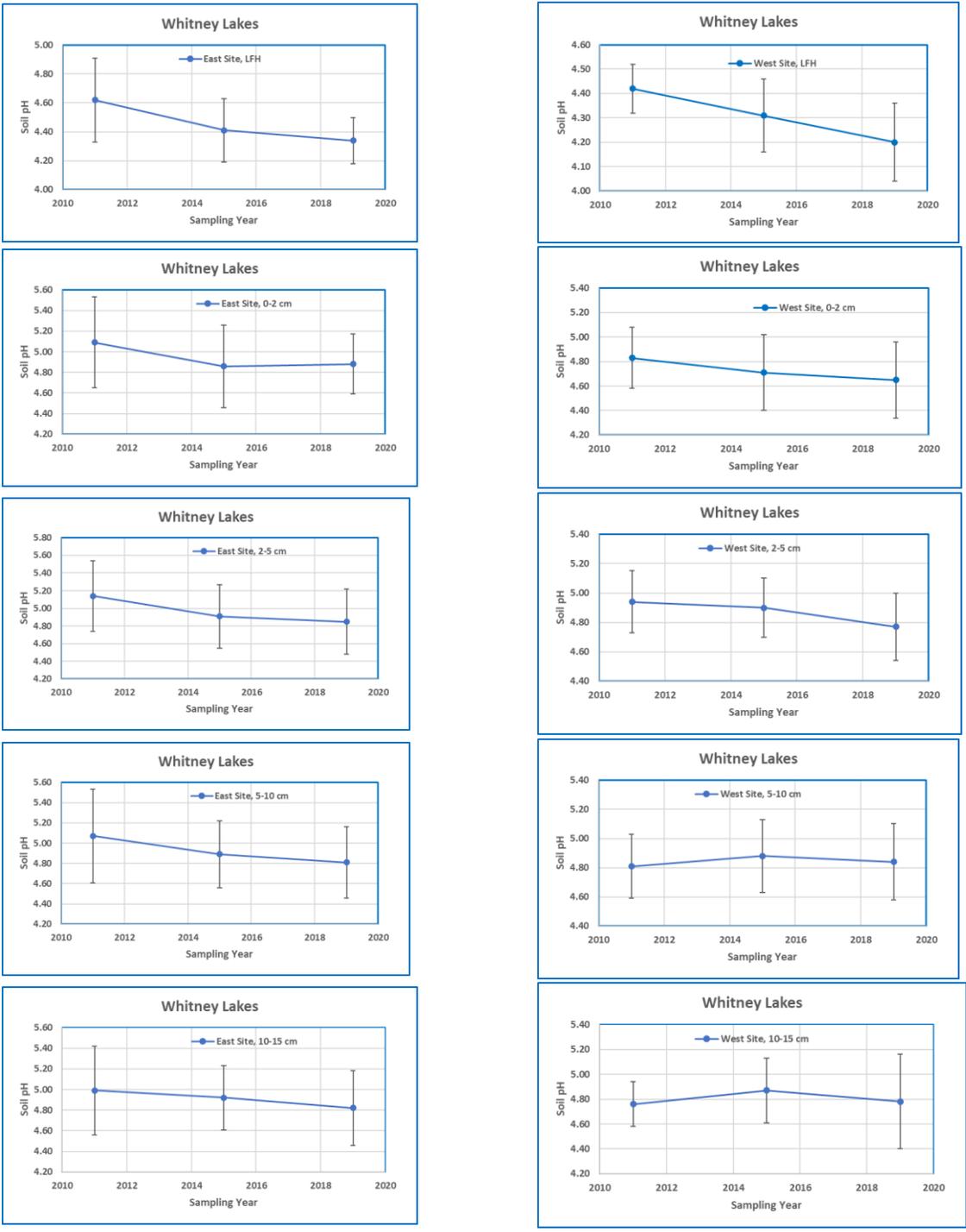


Figure 6. Change in pH at the Whitney Lakes Site.

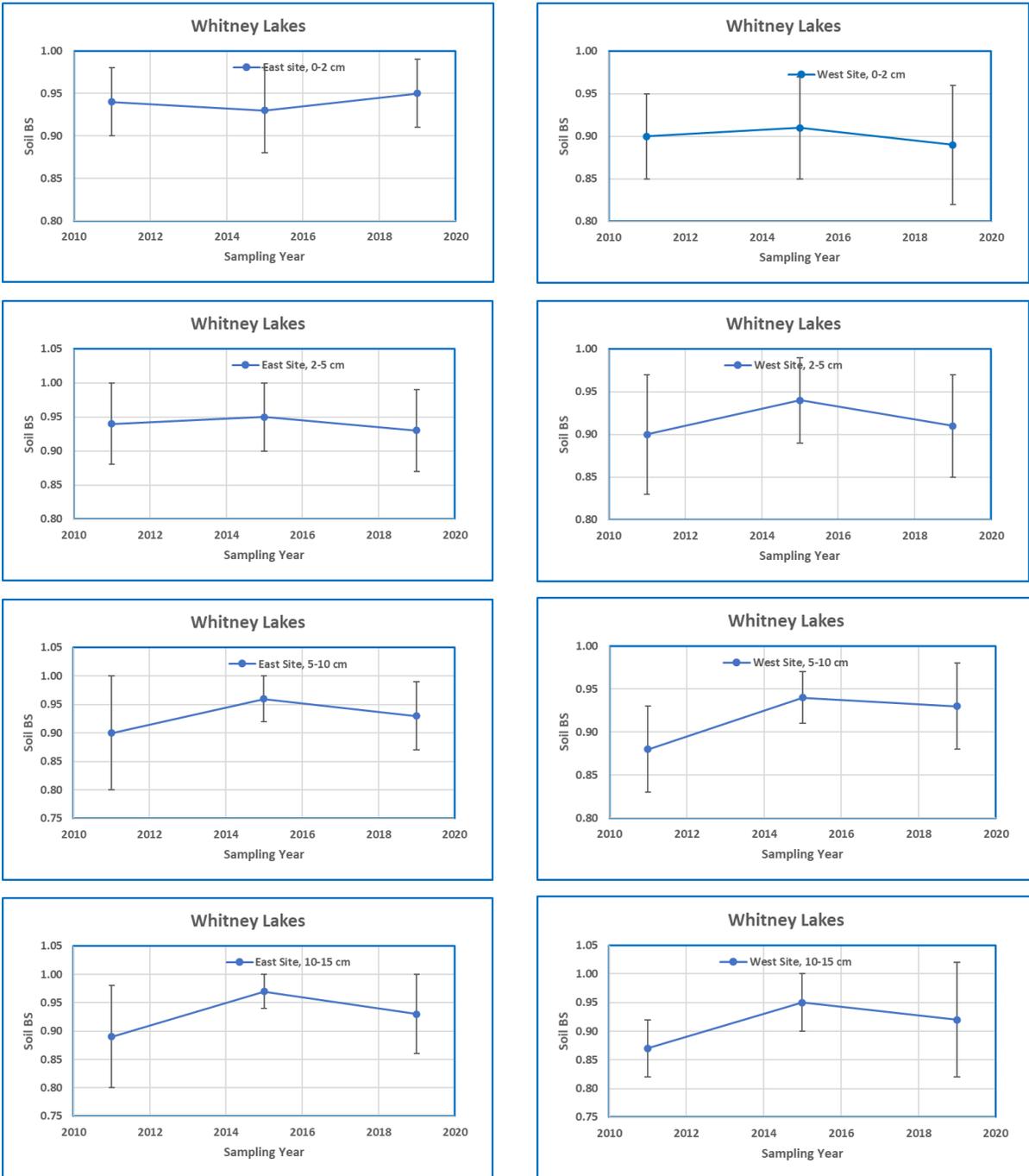


Figure 7. Change in Base Saturation at the Whitney Lakes Site.

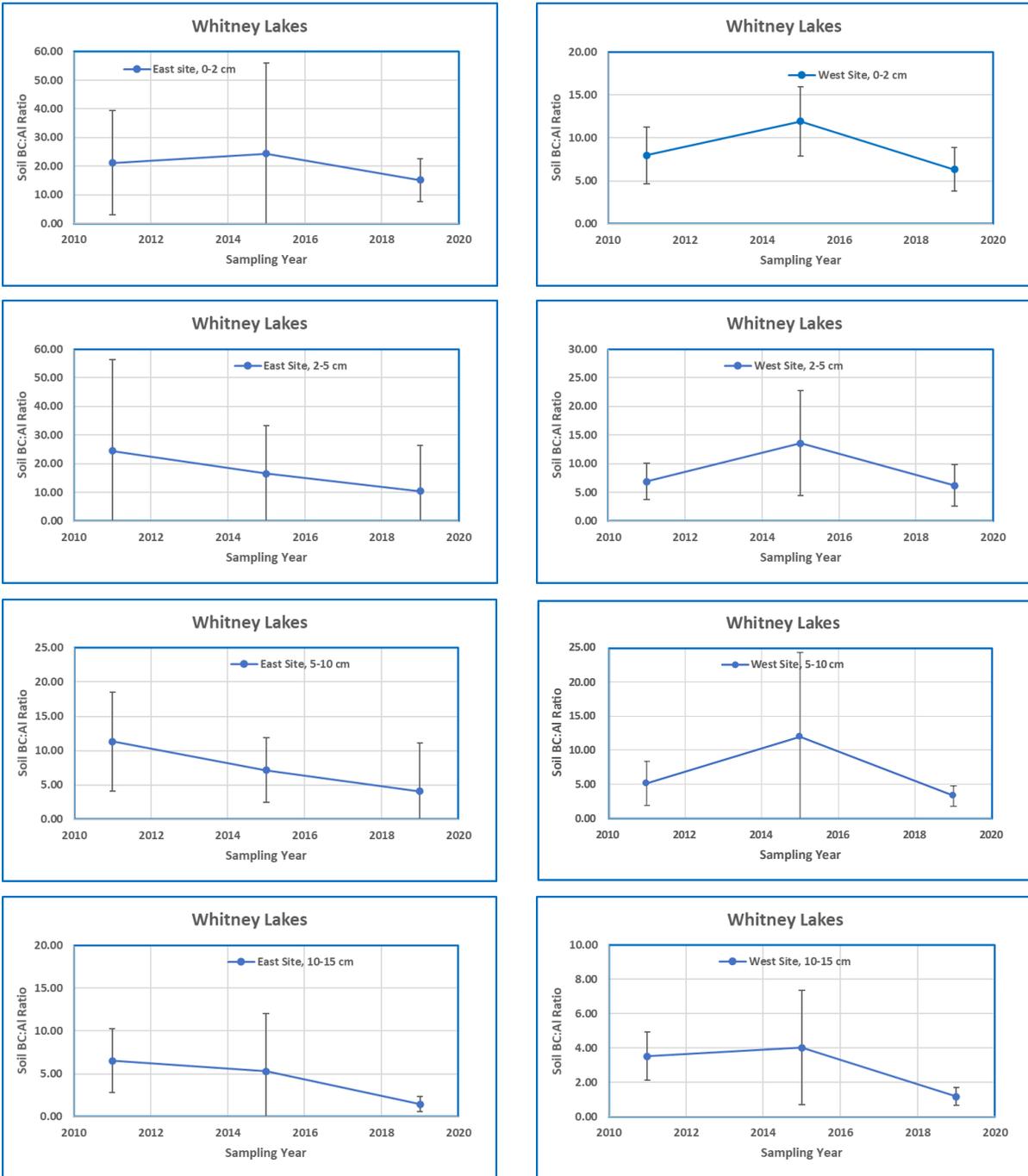


Figure 8. Change in Base cation to Aluminum Ratio at the Whitney Lakes Site.

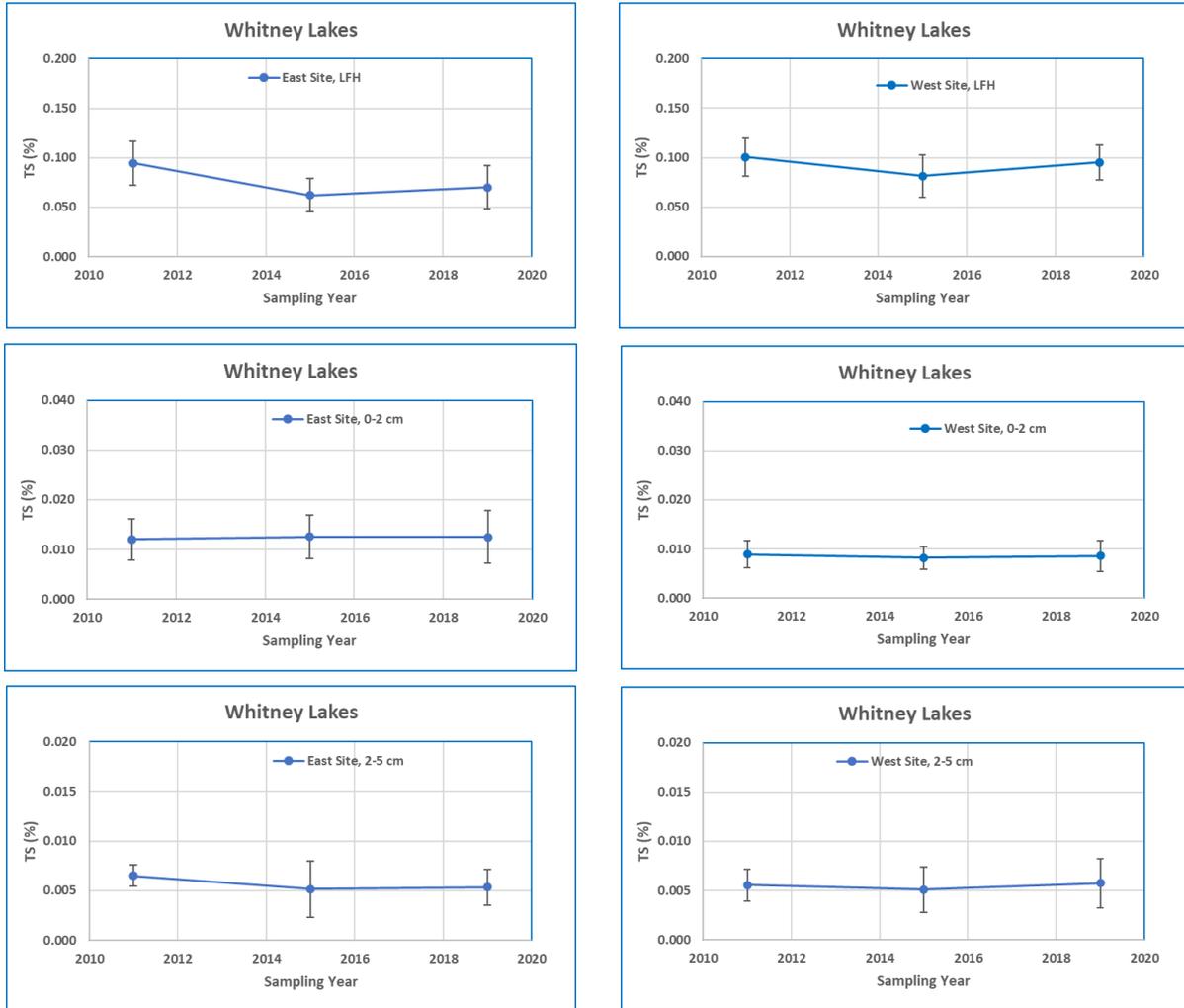


Figure 9. Change in Total Sulphur at the Whitney Lakes Site.

3.3 TUCKER LAKE SITE

Soil samples from the North and South Tucker Lake subsites were analyzed for soil parameters, as described earlier. Table 9 shows the data for the main acidification indicators along with simple statistics for each soil attribute according to soil layer and subsite. Table 10 shows the mean values for the acidification indicators and the results (p-values) of the multivariate statistical analyses, the single-factor ANOVA (with Tukey Honest Significant Difference (HSD) extension) and the Linear Regression analysis for each soil layer and subsite. The data are also presented graphically in Figures 10 to 13.

The following examines some aspects of the data.

3.3.1 pH_c

- The data show differences in pH_c in soil layers among the years 2012, 2016 and 2020. Variability is low, with CVs being 0.07 or lower for the LFH layer and 0.09 and lower for the mineral layers (Table 9).
- Statistically significant differences (between years) in pH_c (Table 10) were observed in the LFH layer and the 5-10 cm and 10-15 cm layers of both the South and North subsites.
- Regression analysis of pH_c with years (Table 10 and Figure 10) showed a statistically significant trend (with a negative slope) for pH_c in the LFH layer, the 2-5 cm of the North subsite and the 5-10 cm and 10-15 cm layers of both the South and North subsites.
- The statistically significant regression slopes indicated a potential for pH_c to decrease annually by ~ 0.03-0.04 pH units/year in the LFH layers and ~ 0.02-0.03 pH units/year in the 5-10 cm and 10-15 cm layers.

3.3.2 Base Saturation

- CVs for base saturation ranged from 0.08 to 0.23 among the layers and sampling years (Table 9).
- Statistically significant differences (between years) in BS (Table 10) were observed in the 0-2 cm and 2-5 cm layers of the North subsite, and the 5-10 cm and 10-15 cm layers of both the South and North subsites.
- Regression analysis of BS with years (Table 10 and Figure 11) did not show any statistically significant trend for BS in both the South and North subsites.
- The statistically significant differences in BS with years can be a result of field variability as only 3 sampling years were available for analysis.

3.3.3 Base Cation:Al Ratios

- The BC:Al ratios showed relatively high variability as indicated by CV values from 0.15 to 1.29 (Table 9).
- Statistically significant differences (between years) in BC:Al ratios (Table 10) were observed in the 2-5 cm layer of the South subsite and the 5-10 cm and 10-15 cm layers of both the South and North subsites.
- Regression analysis of BC:Al ratios with years (Table 10 and Figure 12) showed a statistically significant trend for BC:Al ratios (with a positive slope) in the 2-5 cm, 5-10 cm

and 10-15 cm layers of the South subsite.

- The statistically significant differences and trends in BC:Al ratios with years can be a result of potential movement of base cations down the soil profile but are more likely due to field variability (large CV) as only 3 sampling years were available for analysis.

3.3.4 Total Sulphur

- Total Sulphur (TS%) showed wide variability especially in the lower mineral horizons (values were at or below detection limits). The LFH layer showed the least variability with CV values from 0.18 to 0.38 (Table 9). The mineral horizon variability increased with depth (due to lower TS values) and ranged from 0.22 to 1.04 (Table 9).
- Statistically significant differences (between years) in TS (Table 10) were observed in the LFH and 0-2 cm layers of the South subsite and the LFH layer of the West subsite. The 5-10 and 10-15 cm layers were not considered for ANOVA (or regression analysis) due to the large number of TS values at or below the detection limit.
- Regression analysis of TS with years (Table 10 and Figure 13) showed a statistically significant trend (with a positive slope) for TS in the LFH and 0-2 cm layers of the East subsite and the LFH layer of the West subsite.
- The statistically significant regression slopes indicated a potential for TS to increase annually by ~ 0.0085 to 0.0113 TS(%) y^{-1} in the LFH layers and ~ 0.0009 TS(%) y^{-1} in the 0-2 cm mineral layer. This potential increase is equivalent an increase in TS of 0.11 to 0.17 kmol S ha⁻¹y⁻¹ in the LFH layer and 0.07 kmol S ha⁻¹y⁻¹ in the 0-2 cm mineral layer.
- The statistically significant differences and trends in TS with years can be a result of the accumulation of S from S deposition or due to field variability, as only 3 sampling years were available for analysis.

Table 9. pH, Base Saturation, BC: Al Ratios and TS - Tucker Lake Site - 2012, 2016 and 2020

pH_c^z		LFH			0-2 (cm)			2-5 (cm)			5-10 (cm)			10-15 (cm)		
Year	Subsite	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV
2012	North	4.4	0.3	0.06	4.6	0.3	0.06	4.6	0.2	0.05	4.6	0.2	0.04	4.6	0.2	0.04
2016	North	4.2	0.3	0.06	4.3	0.4	0.09	4.4	0.3	0.07	4.4	0.2	0.05	4.4	0.2	0.04
2020	North	4.2	0.3	0.07	4.3	0.3	0.06	4.4	0.3	0.06	4.3	0.2	0.04	4.3	0.2	0.04
2012	South	4.1	0.2	0.04	4.4	0.2	0.04	4.5	0.2	0.04	4.5	0.2	0.05	4.6	0.1	0.03
2016	South	4.1	0.2	0.06	4.3	0.3	0.07	4.4	0.2	0.05	4.3	0.1	0.03	4.4	0.2	0.04
2020	South	3.8	0.2	0.06	4.2	0.3	0.06	4.3	0.2	0.05	4.3	0.1	0.03	4.4	0.2	0.03
Base Saturation					0-2 (cm)			2-5 (cm)			5-10 (cm)			10-15 (cm)		
Year	Subsite	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV
2012	North	-	-	-	0.84	0.12	0.15	0.74	0.13	0.18	0.68	0.13	0.19	0.63	0.13	0.20
2016	North	-	-	-	0.84	0.10	0.12	0.82	0.14	0.18	0.82	0.15	0.18	0.80	0.11	0.13
2020	North	-	-	-	0.85	0.10	0.12	0.80	0.13	0.16	0.74	0.10	0.13	0.66	0.15	0.23
2012	South	-	-	-	0.74	0.10	0.14	0.70	0.12	0.17	0.62	0.12	0.19	0.54	0.11	0.20
2016	South	-	-	-	0.84	0.07	0.08	0.83	0.07	0.08	0.80	0.07	0.08	0.75	0.08	0.11
2020	South	-	-	-	0.70	0.11	0.15	0.71	0.16	0.22	0.66	0.13	0.19	0.64	0.13	0.21
BC:Al Ratio					0-2 (cm)			2-5 (cm)			5-10 (cm)			10-15 (cm)		
Year	Subsite	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV
2012	North	-	-	-	8	7	0.79	3	1	0.35	2	0.5	0.23	2	1	0.45
2016	North	-	-	-	8	4	0.52	5	2	0.44	3	1	0.34	3	1	0.39
2020	North	-	-	-	12	7	0.54	7	5	0.60	4	1	0.20	4	1	0.27
2012	South	-	-	-	7	3	0.38	3	2	0.50	2	1	0.35	3	1	0.38
2016	South	-	-	-	11	9	0.84	5	6	1.29	6	7	1.08	8	4	0.53
2020	South	-	-	-	6	3	0.43	4	1	0.33	3	0.5	0.15	3	1	0.24
Total Sulphur (%)		LFH			0-2 (cm)			2-5 (cm)			5-10 (cm)			10-15 (cm)		
Year	Subsite	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV
2012	North	0.1121	0.0293	0.26	0.0068	0.0049	0.72	0.0021	0.0012	0.56	0.0013	0.0005	0.37	0.0012	0.0004	0.33
2016	North	0.0853	0.0215	0.25	0.0069	0.0035	0.50	0.0034	0.0015	0.44	0.0019	0.0008	0.41	0.0016	0.0007	0.42
2020	North	0.1798	0.0679	0.38	0.0139	0.0108	0.78	0.0033	0.0034	1.04	0.0010	0.0000	0.00	0.0013	0.0006	0.50
2012	South	0.1013	0.0240	0.24	0.0069	0.0038	0.54	0.0023	0.0009	0.38	0.0012	0.0004	0.33	0.0010	0.0000	0.00
2016	South	0.0816	0.0303	0.37	0.0057	0.0019	0.33	0.0031	0.0007	0.22	0.0022	0.0006	0.27	0.0020	0.0006	0.30
2020	South	0.2079	0.0365	0.18	0.0083	0.0044	0.53	0.0029	0.0014	0.47	0.0015	0.0007	0.45	0.0013	0.0007	0.49

^z pH_c – pH measured using $CaCl_2$ solution; SD – standard deviation; CV – coefficient of variation (SD divided by mean).

Table 10. Multivariate Statistics (ANOVA and Regression) for the Mean Soil pH, BS, BC:AI ratios and TS at the Tucker Lake site

Site/ Statistical Results	Depth	LFH		0-2 (cm)				2-5 (cm)			
	Year ^z	pH	TS (%)	pH	BS	BC:AI	TS (%)	pH	BS	BC:AI	TS (%)
Tucker Lake North	2010	4.4 a ^y	0.112 a	4.6 a	0.84 a	8 a	0.007 a	4.6 a	0.74 a	3 a	0.002 a
	2014	4.2 a	0.085 a	4.3 a	0.84 a	8 a	0.007 a	4.4 a	0.82 a	5 ab	0.003 a
	2018	4.2 a	0.180 b	4.3 a	0.85 a	12 a	0.014 a	4.4 a	0.80 a	7 b	0.003 a
ANOVA	P value	0.042	<0.001	0.058	0.977	0.142	0.030	0.225	0.365	0.002	0.297
Linear Regression	P value	0.027	0.003	0.092	0.855	0.124	0.021	0.134	0.287	<0.001	0.211
Linear Regression	Slope ^x	-0.032	0.0085	-	-	-	0.0009	-	-	0.568	-
Tucker Lake South	2010	4.1 b	0.101 a	4.4 a	0.74 ab	7 ab	0.007 a	4.5 a	0.70 a	3 a	0.002 a
	2014	4.1 b	0.082 a	4.3 a	0.84 b	11 b	0.006 a	4.4 a	0.83 b	5 a	0.003 a
	2018	3.8 a	0.208 b	4.2 a	0.70 a	6 a	0.008 a	4.3 a	0.71 ab	4 a	0.003 a
ANOVA	P value	<0.001	<0.001	0.160	0.003	0.090	0.195	0.112	0.017	0.594	0.120
Linear Regression	P value	0.003	<0.001	0.076	0.397	0.885	0.342	0.036	0.830	0.532	0.122
Linear Regression	Slope ^x	-0.039	0.0133	-	-	-	-	-0.023	-	-	-

Table 10. Concluded

Site/ Statistical Results	Depth	5-10 (cm)			10-15 (cm)		
	Year ^z	pH	BS	BC:AI	pH	BS	BC:AI
Tucker Lake North	2010	4.6 b	0.68 a	2 a	4.6 b	0.63 a	2 a
	2014	4.4 ab	0.82 b	3 a	4.4 ab	0.80 b	3 ab
	2018	4.3 a	0.74 ab	4 b	4.3 a	0.66 a	4 b
ANOVA	P value	0.004	0.032	<0.001	0.001	0.005	0.011
Linear Regression	P value	0.001	0.266	<0.001	<0.001	0.632	0.003
Linear Regression	Slope ^x	-0.034	-	0.185	-0.034	-	0.174
Tucker Lake South	2010	4.5 b	0.62 a	2 a	4.6 b	0.54 a	3 a
	2014	4.3 ab	0.80 b	6 a	4.4 a	0.75 b	8 b
	2018	4.3 a	0.66 a	3 a	4.4 ab	0.64 ab	3 a
ANOVA	P value	0.018	<0.001	0.050	0.025	<0.001	<0.001
Linear Regression	P value	0.008	0.483	0.791	0.046	0.056	0.878
Linear Regression	Slope ^x	-0.023	-	-	-0.017	-	-

^z Year refers to the sampling year. Data for pH, BS and BS:AI ratios are means calculated from 12 replicates.

^y Letters (a, b, ab, c, bc) indicate statistical significance; means followed by the same letter do not differ significantly from one another at P<0.05 (Tukey's test).

^x Regression slope values are shown when statistically significant at p<0.05, otherwise as NS (not statistically significant (p>0.05))

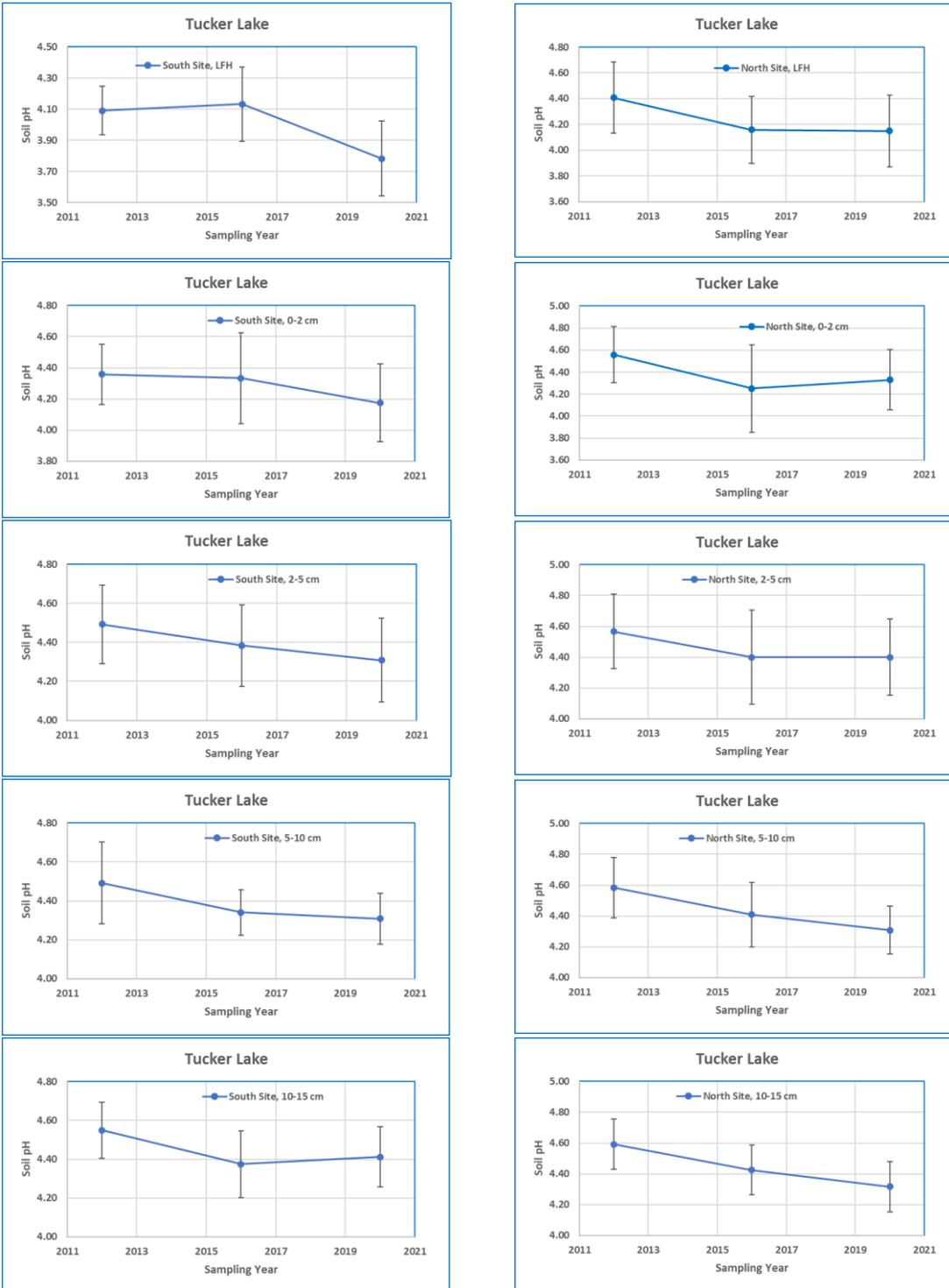


Figure 10. Change in pH at the Tucker Lake Site.

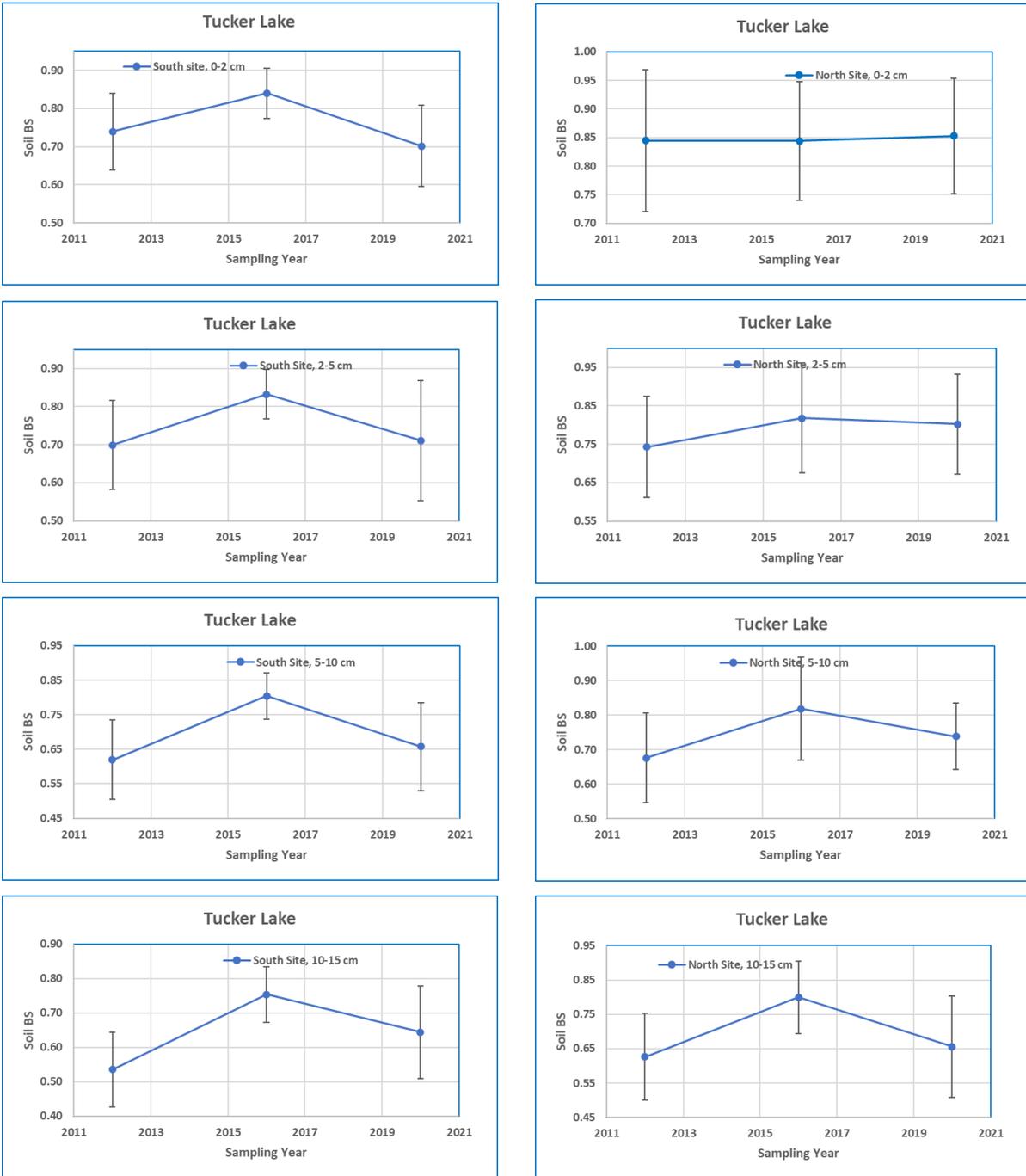


Figure 11. Change in Base Saturation at the Tucker Lake Site.

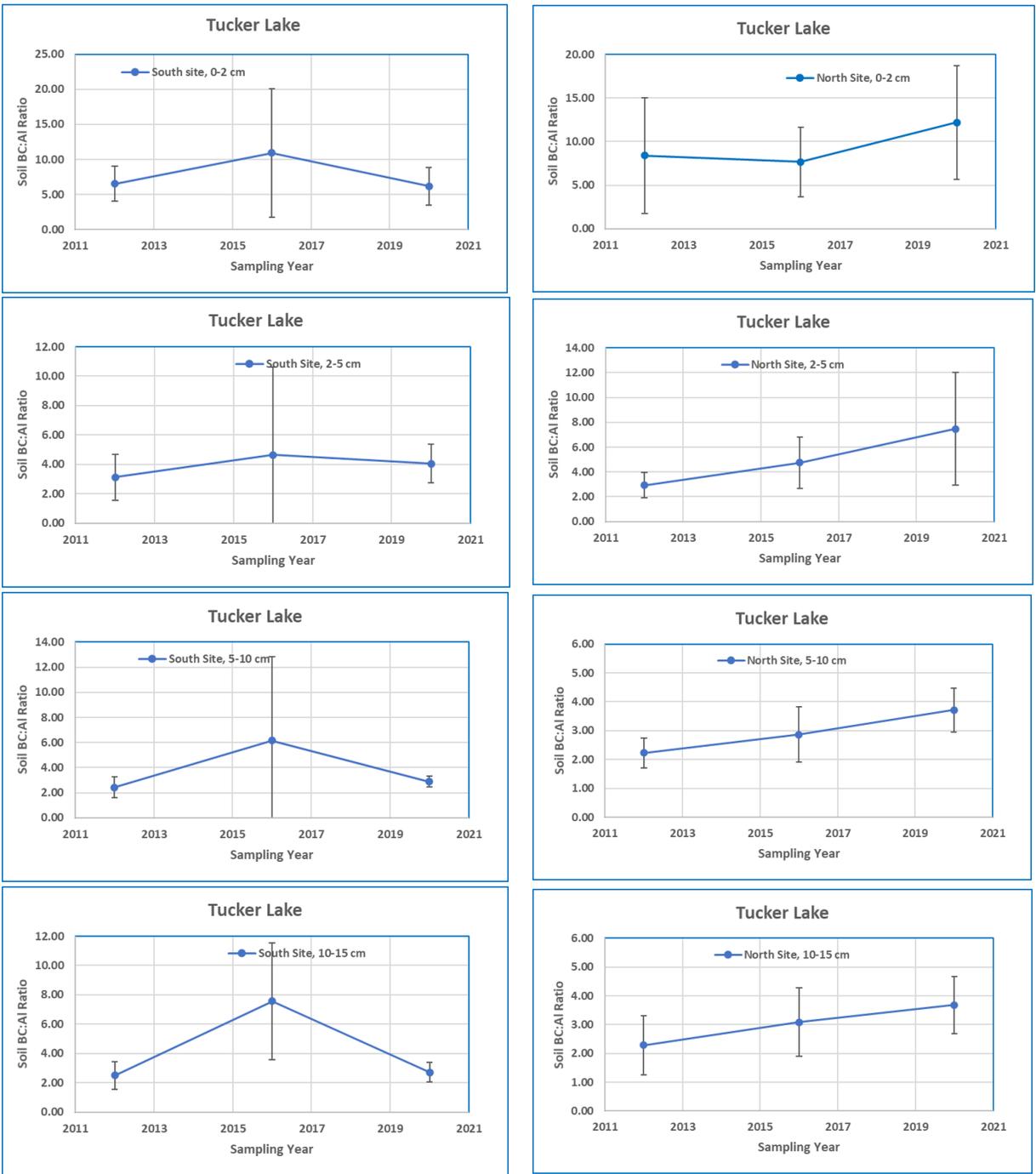


Figure 12. Change in Base cation to Aluminum Ratio at the Tucker Lake Site.

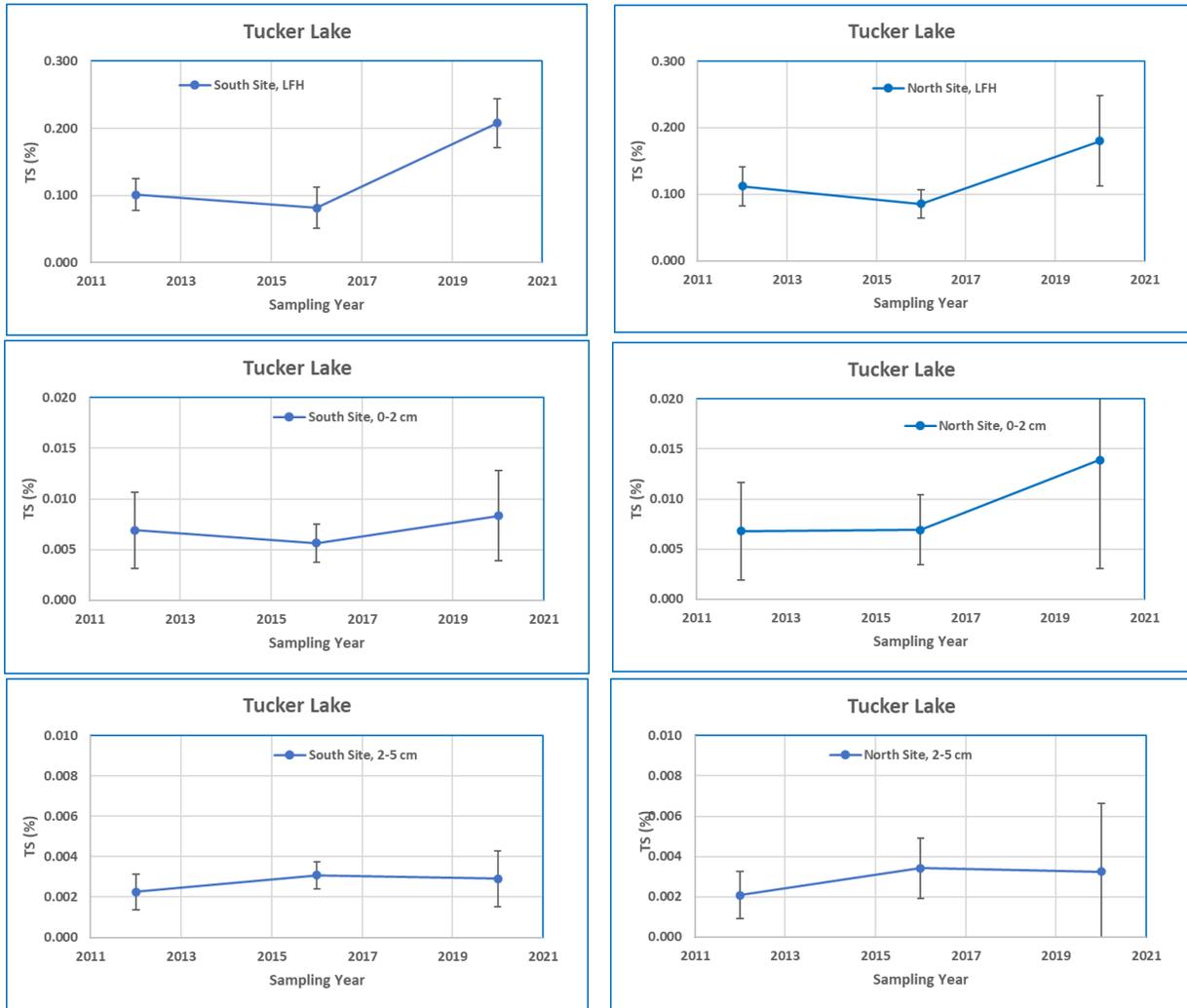


Figure 13. Change in Total Sulphur at the Tucker Lake Site.

3.4 COLD LAKE SITE

Soil samples (only for 0-2 cm, 2-5 cm and 5-10 cm mineral layers) from the Cold Lake East subsite of the LTSAM program were analyzed by Alberta Environment and Parks for soil parameters, similar to the procedures used in the LICA program (Cho et al., 1029). Table 11 shows the data for the main acidification indicators along with simple statistics for each soil attribute according to soil layer and subsite. Table 12 shows the mean values for the acidification indicators and the results (p-values) of the multivariate statistical analyses, the single-factor ANOVA (with Tukey Honest Significant Difference (HSD) extension) and the Linear Regression analysis for each soil layer and subsite. The data are also presented graphically in Figure 14.

The following examines some aspects of the data.

3.4.1 pH_c

- The data show differences in pH_c in soil layers among the years 1982 to 2017. CVs varied from 0.04 to 0.17 for the mineral layers (Table 11).
- Statistically significant differences (between years) in pH_c (Table 12) were observed in the the 0-2 cm layer.
- Regression analysis of pH_c with years (Table 12 and Figure 14) showed a statistically significant trend (with a negative slope) for pH_c in the 0-2 cm and 2-5 cm.
- The statistically significant regression slopes indicated a potential for pH_c to decrease annually by ~ 0.01-0.02 pH units/year in the mineral layers.

3.4.2 Base Saturation

- CVs for base saturation ranged from 0.03 to 0.20 among the layers and sampling years (Table 11).
- Statistically significant differences (between years) in BS (Table 12) were observed in the 0-2 cm and 10-15 cm layers.
- Regression analysis of BS with years (Table 12 and Figure 14) showed a statistically significant trend for BS in both 0-2 cm (negative slope) and 10-15 cm (positive slope) layers.
- The statistically significant difference in BS with years in the 0-2 cm layer can be due to loss of exchangeable cations, while the 5-10 cm increase in BS can be due to movement of cations down the profile or to field variability.

3.4.3 Base Cation:Al Ratios

- The BC:Al ratios showed relatively high variability as indicated by CV values from 0.29 to 1.19 (Table 11).
- Statistically significant differences (between years) in BC:Al ratios (Table 12) were observed in the 0-2 cm, 2-5 cm and 5-10 cm layers.
- Regression analysis of BC:Al ratios with years (Table 12 and Figure 14) showed a statistically significant trend for BC:Al ratios (with a positive slope) in the 0-2 cm, 2-5 cm and 5-10 cm layers.

- The statistically significant differences and trends in BC:Al ratios with years can be a result of movement of base cations down the soil profile but are more likely due to field variability (large CV).

Table 11. pH, Base Saturation, and Base Cation:Al Ratios - Cold Lake Site - 1982 to 2009

pH_c^z		0-2 (cm)			2-5 (cm)			5-10 (cm)			10-15 (cm)		
Year	Subsite	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV
1982	East	4.9	0.4	0.08	4.8	0.4	0.08	4.7	0.3	0.07	4.7	0.3	0.07
1986	East	4.9	0.3	0.07	4.8	0.3	0.06	4.7	0.2	0.05	4.7	0.2	0.04
1990	East	4.7	0.2	0.05	4.6	0.3	0.06	4.5	0.2	0.05	4.7	0.2	0.05
1994	East	4.7	0.3	0.05	4.6	0.2	0.05	4.6	0.2	0.05	4.7	0.2	0.04
2001	East	4.5	0.2	0.05	4.6	0.2	0.04	4.6	0.2	0.04	- ^Y	-	-
2005	East	4.6	0.4	0.09	4.6	0.4	0.08	4.6	0.2	0.04	-	-	-
2009	East	4.4	0.3	0.08	4.5	0.3	0.06	4.6	0.2	0.04	-	-	-
2013	East	4.5	0.3	0.07	4.6	0.8	0.13	4.6	0.2	0.05	-	-	-
2017	East	4.4	0.4	0.09	4.5	0.9	0.17	4.6	0.3	0.06	-	-	-
Base Saturation		0-2 (cm)			2-5 (cm)			5-10 (cm)			10-15 (cm)		
Year	Subsite	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV
1982	East	0.94	0.04	0.04	0.90	0.06	0.06	0.82	0.11	0.14	0.74	0.15	0.20
1986	East	0.93	0.03	0.03	0.85	0.08	0.09	0.74	0.10	0.13	0.70	0.14	0.19
1990	East	0.89	0.08	0.09	0.81	0.10	0.13	0.69	0.14	0.20	0.68	0.13	0.20
1994	East	0.92	0.05	0.06	0.85	0.08	0.09	0.79	0.09	0.12	0.74	0.08	0.10
2001	East	0.87	0.05	0.06	0.85	0.06	0.07	0.84	0.07	0.08	.	.	-
2005	East	0.89	0.07	0.08	0.89	0.06	0.07	0.88	0.05	0.06	.	.	-
2009	East	0.84	0.12	0.14	0.83	0.11	0.13	0.83	0.08	0.10	.	.	-
2103	East	0.89	0.06	0.07	0.84	0.11	0.14	0.82	0.08	0.13	.	.	-
2017	East	0.91	0.07	0.08	0.86	0.12	0.13	0.88	0.09	0.10	.	.	-
Base Cation:Al Ratio		0-2 (cm)			2-5 (cm)			5-10 (cm)			10-15 (cm)		
Year	Subsite	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV
1982	East	38	46	1.19	13	13	1.05	7	7	0.94	6	3	0.53
1986	East	11	5	0.46	5	3	0.49	4	2	0.42	4	2	0.40
1990	East	8	2	0.29	5	2	0.31	4	1	0.23	5	2	0.30
2001 ^Y	East	24	8	0.32	21	7	0.34	15	8	0.54	-	-	-
2005	East	48	52	1.08	17	12	0.71	7	4	0.54	-	-	-
2009	East	12	5	0.47	8	3	0.40	4	3	0.78	-	-	-
2103	East	21	8	0.37	12	4	0.30	7	2	0.33	-	-	-
2017	East	25	15	0.58	17	8	0.46	12	6	0.52	-	-	-

^z pH_c – pH measured using $CaCl_2$ solution; SD – standard deviation; CV – coefficient of variation (SD divided by mean).

^Y Data not available for 1994; data not available in other years are indicated with dashes.

Table 12. Multivariate Statistics (ANOVA and Regression) for the Mean Soil pH, BS and BC:Al ratios at the LTSAM Cold Lake East site.

Site/ Statistical Results	Depth (cm)	0-2 (cm)			2-5 (cm)			5-10 (cm)		
	Year ^z	pH	BS	BC:Al	pH	BS	BC:Al	pH	BS	BC:Al
LTSAM Cold Lake East	1982	4.8 b ^y	0.94 a	28 ab	4.8 a	0.90 a	13 abc	4.7 a	0.82 a	7 a
	1986	4.9 b	0.93 a	11 a	4.8 a	0.85 a	5 a	4.7 a	0.74 a	4 a
	1990	4.7 ab	0.89 a	8 a	4.6 a	0.81 a	5 a	4.5 a	0.69 a	4 a
	1994	4.7 ab	0.92 a	na ^w	4.6 a	0.85 a	na	4.6 a	0.79 a	na
	2001	4.5 ab	0.87 a	24 ab	4.6 a	0.85 a	21 c	4.6 a	0.84 a	14 a
	2005	4.6 ab	0.89 a	48 b	4.6 a	0.89 a	17 bc	4.6 a	0.88 a	7 a
	2009	4.4 a	0.84 a	12 a	4.5 a	0.83 a	8 ab	4.6 a	0.83 a	4 a
	2013	4.5 a	0.89 a	21 ab	4.6 a	0.84 a	13 abc	4.6 a	0.82 a	7 a
	2017	4.4 a	0.91 a	25 ab	4.5 a	0.86 a	17 bc	4.6 a	0.88 a	12 a
ANOVA	P value	<0.001	0.019	<0.001	0.244	0.343	<0.001	0.918	<0.001	<0.001
Linear Regression	P value	<0.001	0.017	0.008	0.006	0.663	<0.001	0.493	<0.001	0.001
Linear Regression	Slope ^x	-0.014	-0.001	0.007	-0.007	NS	0.011	NS	0.003	0.007

^z Year refers to the sampling year. Data for pH, BS and BS:Al ratios are means calculated from 12 replicates.

^y Letters (a, b, ab, c, bc) indicate statistical significance; means followed by the same letter do not differ significantly from one another at P<0.05 (Tukey's test).

^x Regression slope values are shown when statistically significant at p<0.05, otherwise as NS (not statistically significant (p>0.05))

^w na - not available.

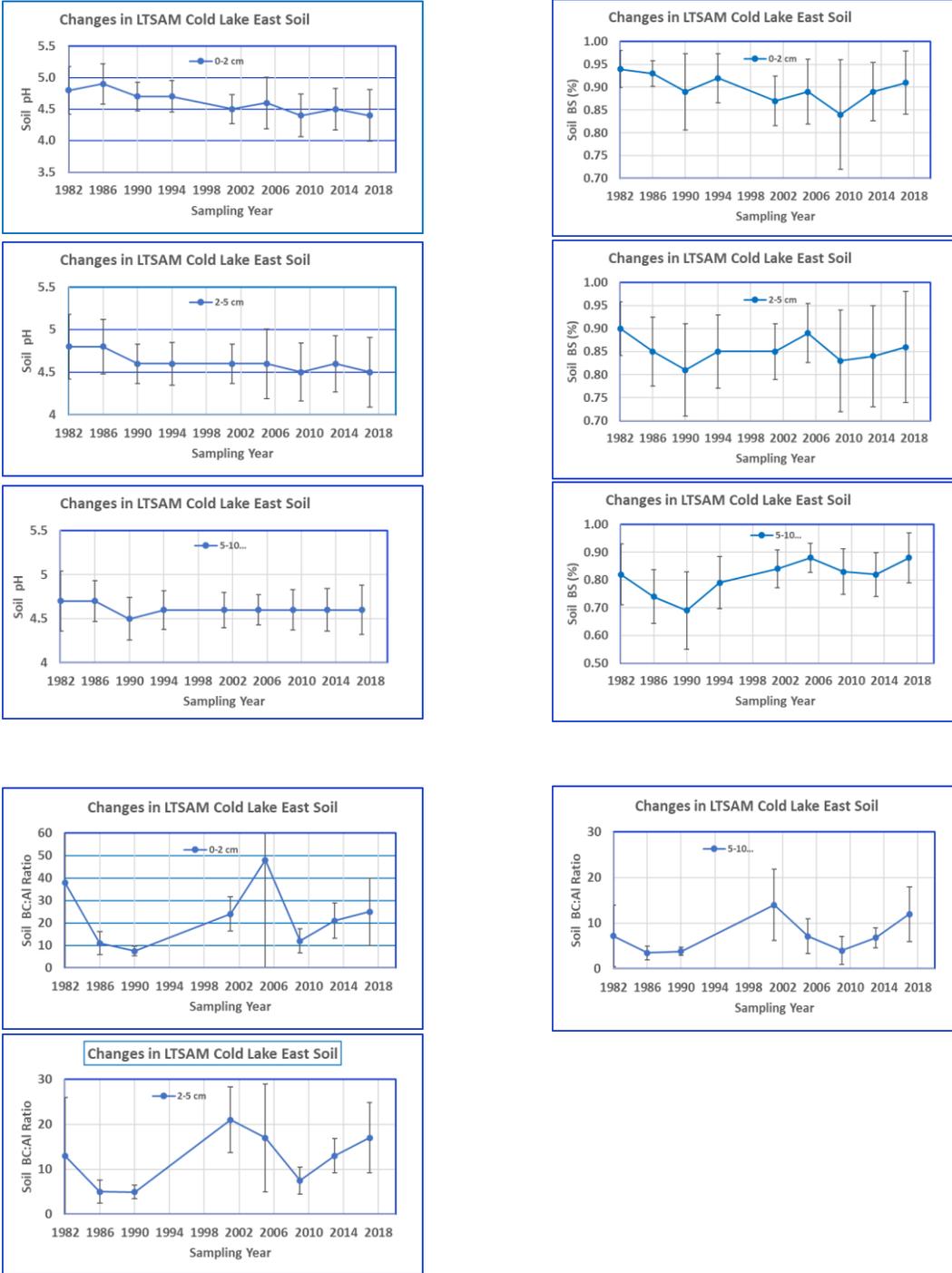


Figure 14. Changes in pH, BS and BC:AI Ratio at the Cold Lake Site.

3.5 STATISTICAL ANALYSIS SUMMARY

Soil acidification parameters were examined using descriptive and multivariate statistics to determine variability in the data, to identify statistically significant differences among the means of the measured chemical parameters, and to determine possible trends over time of decrease or increase of the parameters.

The LICA pH measurements were least variable among the acidification parameters, with CVs among all layers and sites ranging between 0.03 and 0.06. BS values also had relatively low CVs, ranging from 0.05 to 0.15. BC:Al ratios had the highest variability with CVs between 0.26 and 1.72. Determining CVs is useful in that it helps to indicate relatively more difficulty and need for caution in recognizing differences and trends if they are relatively high.

For pH_c, statistically significant differences among years within soil layers were identified as follows:

- in the LFH layer of both subsites at each of the three LICA sites (the LTSAM Cold Lake site does not have data for the LFH layer);
- in mineral 0-2 and 2-5 cm layers of the Moose Lake West subsite, and the 5-10 and 10-15 cm layers of both East and West subsites;
- in no mineral layers of the Whitney Lakes subsites;
- in the mineral 5-10 and 10-15 cm layers at both Tucker Lake North and South subsites;
- in the 0-2 cm mineral layer of the Cold Lake site (data available only for the East subsite).

For BS, statistically significant differences among years were found in mineral soil layers as follows:

- in the 2-5 cm layer of the Moose Lake West subsite, 5-10 cm layer of the East subsite, and 10-15 cm layers of both subsites;
- in the 5-10 cm layer of the Whitney Lakes West subsite and 10-15 cm layers of both the East and West subsites;
- in the 0-2 and 2-5 cm layers of the Tucker Lake North subsite and the 5-10 and 10-15 cm layers of both the North and South subsites;
- in the 0-2 and 10-15 layers of the Cold Lake East site.

For BC:Al ratio, statistically significant differences among years were found in mineral soil layers as follows:

- at both the Moose Lake and Whitney Lakes sites, in the 0-2 cm layers of the West subsite, and the 2-5, 5-10 and 10-15 cm layers of both East and West subsites;
- in the 2-5 cm layer of the Tucker Lake North subsite and the 5-10 and 10-15 cm layers of both North and South subsites;
- in the 0-2, 2-5 and 10-15 cm layers of the Cold Lake East site.

For TS, statistically significant differences among years were found as follows:

- in the LFH and 2-5 cm layer of the Moose Lake East subsite and both 0-2 cm and 2-5 mineral layers in the West subsite;
- only in the LFH of one subsite (Whitney Lakes East);
- in the LFH layer at both Tucker Lake subsites, and the 0-2 cm layer of the South subsite.

The above differences are based on ANOVA and the Tukey test for statistically significant differences. These statistical procedures do not provide information about trends in monitoring data over time, and therefore, regression analysis was performed for this purpose.

For pH_c, regression analysis revealed trends as follows:

- trends (with negative slopes) in the LFH layer of the Moose Lake East subsite, and the 2-5 cm, 5-10 cm and 10-15 cm layers of the West subsite;
- trends (with negative slopes) in the LFH layer of both East and West Whitney Lakes subsites; there were no trends detected for the mineral layers;
- trends (with negative slopes) in the LFH layer, the 2-5 cm layer of the Tucker Lake North subsite, and the 5-10 cm and 10-15 cm layers of both the South and North subsites;
- trends (with negative slopes) for pH in the Cold Lake 0-2 cm and 2-5 cm layers.

Trends for BS were as follows:

- trends (with positive slopes) in the Moose Lake 5-10 cm and 10-15 cm layers of the East subsite;
- trend (with positive slope) in the 5-10 cm layer of the Whitney Lakes West subsite.
- no statistically significant trend for BS in both the Tucker Lake South and North subsites;
- trends for BS in the Cold Lake 0-2 cm (negative slope) and 10-15 cm (positive slope) layers.

Trends indicated for BC:Al ratio were as follows:

- statistically significant trends (with positive slopes) in all mineral layers of the Moose Lake West subsite;
- trends (with positive slopes) in the 5-10 cm layer of the Whitney Lakes East subsite and the 10-15 cm of both the East and West subsites;
- trends (with positive slopes) in the Tucker Lake 2-5 cm, 5-10 cm and 10-15 cm layers of the South subsite;
- trends (with positive slopes) in the Cold Lake 0-2 cm, 2-5 cm and 5-10 cm layers.

Trends indicated for TS were as follows:

- statistically significant trend (with a negative slope) for TS in the LFH layer of the Moose Lake East subsite, and a statistically significant trend (with a positive slope) in the 0-2 and 2-5 cm layers of the West subsite;

- trends (with negative slopes) in the Whitney Lakes LFH, only in the East subsite;
- trends (with positive slopes) in the Tucker Lake LFH and 0-2 cm layers of the North subsite and the LFH layer of the South subsite.

The statistically significant regression slopes at each of the LICA sites indicated potential for pH_e to decrease annually by ~ 0.03 - 0.05 pH units/year in the LFH layers. The slopes also show potential decrease in Moose Lake mineral soil layers of ~ 0.02 - 0.04 pH units, and for ~ 0.02 - 0.03 pH units/year in the 5-10 cm and 10-15 cm layers of the Tucker Lake site. No decreases are shown for the Whitney Lakes site. At the Cold Lake site, the potential decrease is ~ 0.01 - 0.02 pH units/year in the mineral layers.

Increases of TS over time, indicating accumulation of S, were displayed in the LFH layers at both the Tucker Lake subsites. The Whitney Lakes site had no indications of TS increase over time, while the combination of some increases and some decreases at the Moose Lake site are difficult to decipher. TS data were not available for the Cold Lake site.

The statistically significant differences and trends of increased BS with years at the three LICA sites can be a result of movement of base cations down the soil profile. The data may also reflect field variability, as only 3 sampling years were available for analysis. The statistically significant difference in BS with years in the Cold Lake 0-2 cm layer can be due to loss of exchangeable cations, while the 5-10 cm increase in BS can be due to movement of cations down the profile or to field variability. Similar to BS, the statistically significant differences and trends in BC:Al ratios with years can be a result of movement of base cations down the soil profile but could also reflect field variability.

4.0 SOIL ACIDIFICATION MODELLING OF LICA SITES

4.1 PREDICTIVE ACIDIFICATION MODELING

Numerous models have been developed to examine soil acidification, to predict changes in acidification parameters over time and to derive critical loads. Modeling approaches comprise two main categories referred to as 'steady-state methods' and 'dynamic modeling'. Within each category, there are varying degrees of sophistication ranging from simple calculations to complex mathematical constructs.

Steady-state models calculate deposition levels that avoid harmful effects in ecosystems in steady-state. They are mainly used for calculation of critical loads into the distant future, but they do not calculate the rate of change over time. Two types of steady-state models have been developed for soils. One-layer models consider the soil as a single layer, whereas the multi-layer models consider chemical conditions in different soil layers or horizons. The one-layer Steady State Mass Balance (SSMB) model has been the most applied tool for derivation of critical loads of soils in Europe (CLRTAP, 2017).

Dynamic models are a family of more complex models that use various calculations to simulate changes in soil solution or water chemistry due to acid deposition over time. Most dynamic models require somewhat more input data than steady-state models. They have been applied in derivation of critical loads, and are useful in scenario analysis, e.g., for assessing effects of given deposition levels over a selected period of time, and for determining the effects of different emission abatement strategies. The most complex dynamic models are integrated forest-soil models that link soil processes to other processes such as vegetation growth, hydrology, and nutrient cycling.

The ARC model (developed at the Alberta Research Council), applied herein to examine future trends at the LICA and Cold Lake LTSAM sites, is a relatively simple, semi-empirical dynamic model, wherein acidification trends are in part based on soil chemistry relationships determined from readily available data which can be found in soil survey reports and other soil databases.

4.2 ARC MODEL DESCRIPTION

The ARC model simulates LFH and mineral soil chemical processes directly related to acidity and acidification of soils, and predicts the associated soil properties of pH, base saturation, solution Al^{3+} concentration and base cation to aluminum (BC:Al) ratio. The initial one-layer ARC model (mineral layer) is described in detail in Turchenek and Abboud (1988), Abboud and Turchenek (1990) and the two layer model (LFH and mineral) in Abboud et al (2002). The model was initially adapted from the Bloom and Grigal (1985) model, with modifications for calculations of acid inputs and acidification processes, method of output of model results, and inclusion of calculations for base cation to aluminum (BC:Al) ratio. These are described in greater detail in the following sections.

4.2.1 MODEL INPUTS

The model requires climatic, soil and acid input data with a provision for varying time period for exposure and a varying time increment reporting simulation results.

Climate and Water Balance Data

Simulation of soil chemistry changes with the ARC model was carried out for the litter (LFH) horizon and the surface 25 cm layer of mineral soil, this being the depth within which the majority of plant roots occur (Bloom and Grigal, 1985; van Rees, 1995). After accounting for aerial evaporation, precipitation and forest throughfall were considered to first react with the LFH horizon. If any water passed through the LFH horizon, the reaction products would in turn react with the solids and soil solution in the mineral layer. Any excess water would then pass through the 25 cm mineral horizon and into lower layers. The amounts of water passing through the two soil layers were estimated through a series of calculations of the daily soil water balance with inputs including daily precipitation, daily evapotranspiration, and soil water holding capacity. The process is a simplified 'cascading water bucket' approach for soil water balance calculations as described, for example, by Romano et al. (2011), Poporato et al. (2004), and Paul et al. (2003). This approach assumes that water in excess of field capacity moves down to the next soil compartment, provided that compartment is not saturated; if the LFH is saturated, the water passes into the 25 cm mineral layer to the point of saturation, after which it passes into layers below. Calculations using MS Excel® are carried out on a daily timescale. Each soil compartment is intermittently filled or partially filled by precipitation events. The soil water storage capacity is depleted by surface runoff, drainage, and evapotranspiration processes. For the ARC model, surface runoff is not considered, and it thus approximates water movement on a more or less level surface. Due to higher evapotranspiration relative to precipitation, penetration of soil water below the root zone can occur only with relatively high precipitation events as well as spring thaw of accumulated snow. Further description of the process can be found in Abboud et al. (2002).

Daily precipitation values for Cold Lake for the 2004 year were applied in the water balance calculations; this year was selected as being climatically representative because its total precipitation was similar to that of the long-term climate normals for 1981 to 2010 (Government of Canada, 2020). Evapotranspiration rates were from Bothe and Abraham (1993). Data for water holding capacity and bulk density were obtained from Tajek et al. (1989).

Soil Data

Soil data inputs for the ARC model were as follows:

pH – by the CaCl₂ solution (1:2) method. Where the pH_c data were determined in a CaCl₂ solution (1:2), then the following equation (Bloom and Grigal, 1985) was used to transform into a water paste pH_w:

$$\text{pH}(\text{H}_2\text{O}) = \text{pH}(\text{CaCl}_2) + 0.7$$

Cation exchange capacity and exchangeable bases – by the neutral salt (barium chloride) extraction method.

The input data for soil pH, CEC, and sum of bases were weighted mean values for the whole LFH layer (usually less than 25 cm) and the top 25 cm of air-dried mineral soil. The thickness of the soil horizons and the bulk density were considered in computing the means. The calculations were made as previously documented by Turchenek and Abboud (1988) and Abboud and Turchenek (1990).

Partial pressure of CO₂ – Assumed to be 0.005 atmosphere.

Activity coefficients of monovalent, divalent and trivalent ions – Activity coefficients for each modelled soil horizon were calculated from the mean values for individual members of that series.

The activity coefficients (γ_i) were calculated using the Davies equation (Lindsay, 1979).

$$\text{Log } \gamma_i = -AZ_i^2 \left[\frac{I}{1+I^{0.5}} \right] - 0.3 I$$

Where A = 0.509 for water, Z is ion valence and I is ionic strength in moles L⁻¹

The ionic strengths (I) were calculated from the electrical conductivities of the saturated paste extracts (Lindsay, 1979).

$$I = 0.013 \text{ EC}$$

where I is in moles L⁻¹ and electrical conductivity (EC) of the saturated paste extracts in dS m⁻¹, and,

Initial weathering rates (kmol_c ha⁻¹ y⁻¹) for mineral soils – The weathering rate (r) of soil minerals is estimated in the model by the function,

$$r = r_0 10^{-0.5(\text{pH}-\text{pH}_0)}$$

where r_0 and pH_0 are the initial conditions. The r_0 value is based on soil texture (Sand) and was estimated as 0.07 kmol_c ha⁻¹ y⁻¹ (Abboud et al., 2002) and a pH of 5.0 was applied in the equation.

Acid Deposition Data – Application of the model using a range of PAI values is carried out in order to determine critical loads. The loads used in this modelling exercise were 0.1, 0.2, 0.3, 0.5, 0.7 and 1.0 kmol_c ha⁻¹ y⁻¹. These values were recommended for model application by the Alberta Environment staff and cover existing PAI values and potential extreme future values encountered in the province. The PAI values account for both wet and dry forms of acid deposition.

Time – The model can be executed for any specified length of time, and simulation results can be reported for any specified increment of time within the total simulation period. Predictive soil effects data are especially of interest in terms of the immediate and near future; i.e., the period during which pollutant emissions can be forecast. It is also of interest, from a soil development point of view, to determine soil responses to acid deposition over very long periods of time since

changes in soils occur slowly. Three hundred years was selected for the simulation period. This time frame would not obscure the data for interpretation of short-term effects yet would provide a longer term view of soil changes.

A one year increment of time between reported values in the simulations was selected. This increment assured that sufficient data points were obtained for determining the trends of pH, base saturation, Al^{3+} levels and BC:Al over time.

4.2.2 Model Execution and Data Output

4.2.2.1 Computations

The loss of bases is calculated on an annual basis from,

$$S = I - A - C - W$$

where S is the sum of bases lost, I is the effective acidity in the precipitation plus dryfall (the PAI), A is the acid leached out of the top 25 cm of soil, C is the decrease in bicarbonate weathering due to the decrease in soil solution pH, and W is the base contribution due to weathering. At the end of each year of simulation, a new sum of bases is calculated from the sum for the previous year. New values for pH, Al^{3+} concentration and BC:Al ratio are also calculated from equations relating pH with base saturation, pH with solution Al^{3+} concentration, and pH with BC:Al ratio. A linear function describes the relationship between pH and base saturation of the soil.

4.2.2.2 Base Saturation and pH relationships

The pH-BS relationships for mineral soils were previously developed as linear equations for each soil order in Alberta (Abboud and Turchenek, 1990). Using the data in the Oil Sands area, Abboud et al. (2002) developed a similar relationship for organic soil horizons (LFH and peat layers). The above equations were developed using data where the soil pH was measured in water saturated pastes (pH_w) and the BS was measured from buffered ammonium acetate extractions. We adjusted the model to use pH_c (measured in 1:2 $CaCl_2$ solution) data and BS measured from a neutral salt barium chloride extraction. Thus, the current model used the following pH – BS relationships for the mineral and LFH soil layers:

LFH $pH_c = 3.57 BS + 2.04 \quad R^2 = 0.88$ (using data from CEMA (Abboud et al., 2002))

Mineral $pH_c = 1.48 BS + 3.54 \quad R^2 = 0.26$ (using data from LTSAM Cold Lake plot)

Where pH_c is pH measured in 1:2 $CaCl_2$ solution, and

BS is base saturation measured in a neutral salt barium chloride extraction

4.2.2.3 Application as a Two-Layer Model

The current ARC model accounts for acid interaction with the LFH and mineral layers. This necessitates the calculation of evapotranspiration and precipitation values for both LFH and mineral layers. The precipitation number for the mineral layer was assumed to be equivalent to the quantity of percolation water value passing through the LFH layer. The acid input is assumed

to react with the LFH layers thereby acidifying their soil solutions and contributing the acidity to the mineral layer. Buffering in the LFH layers was assumed to arise from surface reactions (exchange, adsorption and complexation) and solution carbonate reactions. It was considered that there was no weathering in LFH layers.

4.2.2.4 Al Solubility

The solubility of Al in the original ARC model was assumed to follow the empirical model of Bloom and Grigal (1985), derived from Minnesota soils data. Changes to the ARC model, based on data from southeastern Alberta soils, resulted in the use of a more soluble form of gibbsite as an Al controlling mineral (Turchenek and Abboud, 2001).

During our modeling of soils in the Oil Sands area, the solubility of Al in organic (LFH and peat) horizons was determined using the data reported in Abboud et al. (2002), and in mineral horizons using archived data from a joint Syncrude-ARC project (Pauls et al., 1996).

The following equations were used in the model where linear relationships were observed between $\text{Log}(\text{Al}^{3+})$ and pHw.

LFH $\text{Log}(\text{Al}^{3+}) = -2.72 \text{ pHw} + 8.03 \text{ R}^2 = 0.92$ (using data from Abboud et al., (2002))

Mineral $\text{Log}(\text{Al}^{3+}) = -2.66 \text{ pHw} + 8.10 \text{ R}^2 = 0.96$ (using data from Pauls et al., (1996))

Where (Al^{3+}) and pHw are the activities of free Al^{3+} and pH in saturated paste extracts.

4.2.2.5 BC:Al Ratios

In LFH and mineral soils the relationship between BC:Al ratio and pHw shows an exponential relationship. The following equations were used in the model:

LFH $\text{BC:Al} = 0.037 e^{1.78\text{pHw}} \text{ R}^2 = 0.87$ (using data from CEMA (Abboud et al., 2002))

Mineral $\text{BC:Al} = 0.043 e^{1.14\text{pHw}} \text{ R}^2 = 0.64$ (using data from Pauls et al., (1996))

Where BC:Al ratios and pHw values are calculated from measurements of Al, cations and pH in saturated paste extracts.

4.2.2.6 Model Execution and Data Outputs

Computations were made for changes in soil properties on an annual basis. Output data for each time interval included: (1) year; (2) pH of soil; (3) acid input; (4) acid output; (5) protonation; (6) change in pH; (7) base saturation; (8) sum of base cations; (9) base cations lost; (10) Al^{3+} concentration in soil solution, and (11) BC:Al ratio. Elements of model output are indicated in Table 13.

The outputs of major interest are the changing values of soil pH, base saturation, and BC:Al during the time period selected. Model data were transferred to EXCEL spreadsheets to facilitate data analysis in terms of critical loads. Simulations were conducted using the program RS1.

Table 13. Example of Output from the ARC Model Simulating Processes in a Mineral Soil.

LFH											
Time	pH	Sol. Al	Base	BC:Al	Acid In	Acid Out	Protonat.	Bases Lost	Exch. Bases		
(years)	(H ₂ O)	(M)	Saturation	Ratio	(kmol _c ha ⁻¹ y ⁻¹)						
Mineral											
Time	pH	Sol. Al	Base	BC:Al	Acid In	Acid Out	Weathering	Protonat.	Bases Lost	Exch. Bases	Soil Series
(years)	(H ₂ O)	(M)	Saturation	Ratio	(kmol _c ha ⁻¹ y ⁻¹)						

4.3 CRITICAL CHEMICAL CRITERIA AND CRITICAL CHEMICAL VALUES

4.3.1 Overview and Definitions

Soil acidification simulation modelling is used herein to assist explanation of trends seen in monitoring. In doing this, it is helpful to explore and define soil chemical properties in terms of the limits, or thresholds, at which they can be harmful to vegetation and/or other components of ecosystems.

Critical chemical criteria in relation to soil acidification are soil properties that can be directly affected by acidic inputs, which in turn could affect other components of the ecosystem. These criteria are chemical parameters such as pH, exchangeable base saturation (BS), aluminum (Al) concentration in soil solution, base cation (BC) concentration in soil solution, and the ratio of BC to Al concentrations (BC:Al). The chemical criterion is chosen to reflect a change in the ecosystem which would lead to damage. Any or all of these can be selected, and critical loads based upon the inputs chosen can be derived. The parameters chosen to reflect possible effects on ecosystems are based on research mainly in Europe and North America, and consist of pH_c, BS and BC:Al ratio. These are acidification attributes measured in monitoring and are explained in Section 1.2.1 of this report. The ARC model (Turchenek and Abboud 1988) simulates soil chemical processes directly related to acidity and acidification of soils, and predicts the associated soil properties of pH, base saturation and solution Al³⁺ concentration. Critical chemical criteria such as base cation to aluminum ratio (BC:Al ratio) are calculated from the soil solution Ca, Mg, K and Al values.

A threshold for a specific soil chemical parameter is referred to as a critical chemical value (CCV), which is a quantitative value attached to a critical chemical criterion and is defined as the highest (or lowest) value of a critical chemical criterion or combination of criteria that does not cause a significant harmful response in an ecological component. For each critical chemical criterion, critical chemical values must be established (Sverdrup et al. 1990).

The criteria applied to soils, the rationale for each selection, and the critical chemical values (thresholds) assigned to each criterion have been discussed in previous acidification modeling

studies, including a study of forest soils in the oil sands region (Abboud et al. (2002). For pH, the CCV suggested for forest soils is pH_w 4.2 (pH in water), a value adopted from research in Europe (Ulrich et al., 1984; CLRTAP, 2017); this value is equivalent to pH_c 3.5. pH_c 25% or 50% are other pH CCVs derived by calculating a reduced pH_c upon adding an amount of acidity (PAI) equal to 25% or 50%, respectively, of that between the initial pH_c (pH_{ci}) and the minimum recommended pH_c (pH_{cmin}) of 3.5. These CCVs have been applied in Alberta studies to enable recognition of deteriorating soil conditions early in the process, and to be highly protective of ecosystems, as opposed to deterioration toward the brink of damage to an ecosystem. The recommended CL for sensitive soils in Alberta is 0.25 kmol_c H⁺ ha⁻¹ y⁻¹ (Alberta Environment, 2008). This CL was based on research in Europe; low CLs such as this have been derived using an approach involving 50% increase in acidity for sensitive sandy Brunisolic soils in the oil sands area (Abboud et al., 2002). Using the relatively more protective approach of increase in acidity by the smaller amount of 25% is applied herein and follows the approach used in assessing the LTSAM monitoring sites (Abboud et al. 2012)

Two CCVs are calculated for each of BS and BC:Al ratio, namely the minimum value that will cause limited or no damage to an ecosystem, and the value equivalent to 75% of the difference between the initial and minimum recommended values. In other words, a possible critical load is calculated by allowing for a decrease by 25% of the base saturation and the base cation to aluminum ratio. A change of 25% allows for change to occur, but it is limited to a relatively small value. Other percentages could be selected (e.g., 50% or 75%), while a lower level such as 25% implies a greater level of protection for soil-vegetation systems. The minimum suggested CCVs are 0.1 (or 10%) BS and a value of 2 for BC:Al ratio. Critical chemical values specific to the long term monitoring sites are presented later (section 4.6).

The CL is a tool for assessing the risk of acidic and acidifying deposition impacts to ecosystems. The term 'critical load' has been defined in Alberta as 'the highest load that will not cause chemical changes leading to long-term harmful effects on the most sensitive ecological systems' (Alberta Environment, 2008). The CL concept is distinguished from the concept of 'target load', which is defined in Alberta as 'the maximum level of acidic atmospheric deposition that affords long-term protection from adverse ecological consequences, and that is politically and practically achievable' (Alberta Environment, 2008). Critical and target loads are used to examine how pollution can affect natural resources, and consequently what is needed to protect resources. It is not the objective in this report to recommend critical and target loads for soil in the LICA area, but to apply them into the discussion for purposes of comparing with possible soil acidification as revealed by monitoring, with PAI levels in the LICA area, and with provincial guidance on acidifying emissions. The CLs are based only on the mineral layer where abundant roots take up water and nutrients for plant growth.

The derivation of CLs is based on CCVs, but requires consideration of the time frame in which soil chemistry changes occur. Decisions are required as to whether CCVs of soil chemical parameters may be reached in a few years or over a longer period. Fifty and one hundred year time periods were selected for these decisions (Abboud et al., 2002). Fifty years is a relatively short period, and its selection is based on supposition that it is of sufficient length to enable definite detection of an acidification trend and to initiate measures to counteract the trend. One hundred

years is a longer time frame that results in a lower critical load, and it therefore provides a greater measure of protection. Identifying CCVs in the model output tables for the 50 and 100 year periods provides CLs presented later (section 4.6).

4.4 DATA INPUTS

The starting parameters for soils used in simulation modelling are given in Table 14. The soil types and some general descriptive features are indicated along with input data described previously (Section 4.2.1). The total acid input is also provided in Table 14 in terms of H⁺, or potential acid input (PAI).

Table 14. Input Data for Soil Acidification Simulations with the ARC Model

Soil types: All site soils are Eluviated Dystric Brunisols, sand texture; soil series – Nestow and Liza							
Years of iteration – 100; Increment of years in modelling – 1							
Potential acid input (PAI) levels: 0.1, 0.2, 0.3, 0.5, 0.7, 1.0 (kmol _c H ⁺ ha ⁻¹ y ⁻¹)							
Site	Moose Lake East	Moose Lake West	Whitney Lakes East	Whitney Lakes West	Tucker Lake North	Tucker Lake South	Cold Lake LTSAM East
Precipitation (cm y ⁻¹)	46	46	46	46	46	46	46
Litter ET (cm y ⁻¹) ^z	14	14	14	14	14	14	14
Perc into Mineral (cm r ⁻¹)	32	32	32	32	32	32	32
ET from Mineral (cm y ⁻¹)	13	13	13	13	13	13	13
Perc below 25 cm (cm y ⁻¹)	19	19	19	19	19	19	19
LFH							
LFH (cm)	2	2	3	3	4	4	2
LFH pH (CaCl ₂)	4.3	4.0	4.6	4.4	4.4	4.1	4.4
LFH Bases (kmol _c ha ⁻¹)	9.1	6.5	17.5	14.9	19.9	14.8	10.0
LFH CEC (kmol _c ha ⁻¹)	10.1	7.6	18.8	16.4	21.8	16.9	10.9
Activity Coefficient of Al ¹⁺	0.935	0.943	0.928	0.932	0.932	0.940	0.932
Activity Coefficient of Al ²⁺	0.764	0.791	0.741	0.756	0.756	0.782	0.756
Activity Coefficient of Al ³⁺	0.546	0.591	0.510	0.533	0.533	0.574	0.533
Slope of pH-BS Equation	3.57	3.57	3.57	3.57	3.57	3.57	3.57
Mineral 0-25 cm							
Mineral Soil pH (CaCl ₂)	4.7	4.7	4.8	5.0	4.7	4.5	4.7
Mineral Bases (kmol _c ha ⁻¹)	46	42	97	75	35	27	33
Mineral CEC (kmol _c ha ⁻¹)	60	51	105	85	47	44	38
Activity Coefficient of Al ¹⁺	0.955	0.955	0.955	0.960	0.967	0.962	0.982
Activity Coefficient of Al ²⁺	0.833	0.833	0.833	0.851	0.873	0.858	0.929
Activity Coefficient of Al ³⁺	0.663	0.663	0.663	0.696	0.736	0.708	0.847
Slope of pH-BS Equation	1.48	1.48	1.48	1.48	1.48	1.48	1.48
CO ₂ Partial Pressure (atm)	0.005	0.005	0.005	0.005	0.005	0.005	0.005
Weathering (kmol _c ha ⁻¹ y ⁻¹)	0.07	0.07	0.07	0.07	0.07	0.07	0.07

^z Abbreviations: ET – evapotranspiration; Perc – percolation; CEC – cation exchange capacity; atm – atmosphere kmol_c ha⁻¹ – kilomoles of ionic charge per hectare; y⁻¹ – per year

4.5 ACIDIFICATION SIMULATION RESULTS

Data for Years 0, 50 and 100 were extracted from tabulated model output data and are presented in Table 15 for all sites. The simulation results are presented graphically in Figures 15 to 21 below.

Both the tables and charts indicate that at the lowest PAI level, change is very slow, with pH_c decreasing in 100 years by only about 0.1 unit, and BS and BC:Al decreasing by 5-10%. Larger decreases occur at 0.2 and 0.3 $\text{kmol}_c \text{ha}^{-1}\text{y}^{-1}$ and are markedly larger at the higher PAI levels of 0.5, 0.7 and 1 $\text{kmol}_c \text{ha}^{-1}\text{y}^{-1}$. At most sites, the decrease in acidification indicators is more rapid in the LFH layers as compared to the mineral soil layers. These are the broad characteristics of the modeling results, but to examine changes in more detail the concepts of critical chemical value (CCV) and critical load (CL) are applied.

An aspect of the ARC model requiring caution in interpretation concerns inadequate handling of extreme cases of low buffering. This is particularly the case with very low pH values, which can be seen in the parts of the response curves where they flatten. At very low pH values, other acid buffering mechanisms that are not included in the model come into play. Changes may in fact continue to occur when the curves flatten, but these are not of concern as these soil chemical levels are at extreme values which would be detrimental to vegetation and general ecosystem health. In other words, soil chemical levels typical of ecosystems are of most interest, and the goal of modelling is to detect potential changes that can begin to lead to deterioration in soil conditions.

Another aspect of the ARC soil acidification model needs to be considered when comparing monitoring results with modelling results. The ARC model predicts acidification parameters for the bulk 25 cm topsoil layer, but monitoring results thus far show changes in the surface 0-2 and 2-5 cm layers, but there have been inconsistent changes in the lower layers (to 15 cm). Results of modelling with monitoring data are thus not directly comparable, except to indicate that some acidification has possibly begun.

Table 15. Changes in Chemistry of LICA and LTSAM Soils (top 25 cm Mineral Layer) Under Different Acid Loadings.**Moose Lake East**

LFH	pH _c				Base Sat				BC:Al Ratio				Mineral	pH _c				Base Sat				BC:Al Ratio			
	Years				Years				Years					Years				Years							
Acid Input (kmol _c ha ⁻¹ y ⁻¹)	0	20	50	100	0	20	50	100	0	20	50	100	Acid Input (kmol _c ha ⁻¹ y ⁻¹)	0	20	50	100	0	20	50	100	0	20	50	100
0.1	4.3	3.9	3.8	3.8	0.90	0.78	0.76	0.76	61	32	30	30	0.1	4.7	4.7	4.7	4.6	0.77	0.76	0.74	0.70	20	20	19	18
0.2	4.3	3.7	3.7	3.7	0.90	0.73	0.73	0.73	61	24	24	24	0.2	4.7	4.7	4.6	4.4	0.77	0.74	0.67	0.57	20	20	17	15
0.3	4.3	3.6	3.6	3.6	0.90	0.71	0.71	0.71	61	22	22	22	0.3	4.7	4.6	4.5	4.2	0.77	0.71	0.60	0.46	20	19	15	12
0.5	4.3	3.5	3.5	3.5	0.90	0.68	0.68	0.68	61	19	19	19	0.5	4.7	4.5	4.2	4.0	0.77	0.65	0.46	0.30	20	17	12	9
0.7	4.3	3.5	3.5	3.5	0.90	0.66	0.66	0.66	61	17	17	17	0.7	4.7	4.4	4.1	3.9	0.77	0.59	0.33	0.22	20	15	10	8
1.0	4.3	3.4	3.4	3.4	0.90	0.64	0.64	0.64	61	15	15	15	1.0	4.7	4.2	3.8	3.8	0.77	0.44	0.15	0.14	20	12	7	7

Moose Lake West

LFH	pH _c				Base Sat				BC:Al Ratio				Mineral	pH _c				Base Sat				BC:Al Ratio			
	Years				Years				Years					Years				Years							
Acid Input (kmol _c ha ⁻¹ y ⁻¹)	0	20	50	100	0	20	50	100	0	20	50	100	Acid Input (kmol _c ha ⁻¹ y ⁻¹)	0	20	50	100	0	20	50	100	0	20	50	100
0.1	4.0	3.8	3.8	3.8	0.86	0.80	0.80	0.80	39	29	29	29	0.1	4.7	4.7	4.6	4.6	0.82	0.81	0.78	0.73	20	20	19	17
0.2	4.0	3.7	3.7	3.7	0.86	0.76	0.76	0.76	39	24	24	24	0.2	4.7	4.6	4.5	4.4	0.82	0.78	0.70	0.59	20	19	16	14
0.3	4.0	3.6	3.6	3.6	0.86	0.74	0.74	0.74	39	22	22	22	0.3	4.7	4.6	4.4	4.2	0.82	0.74	0.61	0.48	20	18	14	11
0.5	4.0	3.5	3.5	3.5	0.86	0.72	0.72	0.72	39	19	19	19	0.5	4.7	4.5	4.2	4.0	0.82	0.67	0.45	0.33	20	16	11	9
0.7	4.0	3.4	3.4	3.4	0.86	0.70	0.70	0.70	39	17	17	17	0.7	4.7	4.4	4.0	3.9	0.82	0.59	0.33	0.27	20	14	9	8
1.0	4.0	3.3	3.3	3.3	0.86	0.65	0.65	0.65	39	13	13	13	1.0	4.7	3.8	3.7	3.7	0.82	0.19	0.13	0.13	20	7	6	6

Table 15. Changes in Chemistry of LICA and LTSAM Soils (top 25 cm Mineral Layer) Under Different Acid Loadings (continued).

Whitney Lakes East

LFH	pH _c				Base Sat				BC:Al Ratio				Mineral	pH _c				Base Sat				BC:Al Ratio			
	Years				Years				Years					Years				Years							
Acid Input (kmol _c ha ⁻¹ y ⁻¹)	0	20	50	100	0	20	50	100	0	20	50	100	Acid Input (kmol _c ha ⁻¹ y ⁻¹)	0	20	50	100	0	20	50	100	0	20	50	100
0.1	4.6	4.3	3.9	3.8	0.93	0.84	0.74	0.71	95	59	34	30	0.1	4.8	4.8	4.8	4.8	0.92	0.92	0.92	0.90	23	23	23	22
0.2	4.6	3.9	3.7	3.7	0.93	0.74	0.67	0.67	95	36	24	24	0.2	4.8	4.8	4.7	4.6	0.92	0.92	0.89	0.82	23	23	21	19
0.3	4.6	3.7	3.6	3.6	0.93	0.67	0.65	0.65	95	25	22	22	0.3	4.8	4.8	4.7	4.5	0.92	0.92	0.85	0.74	23	23	20	17
0.5	4.6	3.5	3.5	3.5	0.93	0.63	0.63	0.63	95	19	19	19	0.5	4.8	4.7	4.6	4.3	0.92	0.89	0.76	0.58	23	22	17	13
0.7	4.6	3.5	3.5	3.5	0.93	0.61	0.61	0.61	95	18	18	18	0.7	4.8	4.7	4.4	4.1	0.92	0.85	0.68	0.44	23	20	15	10
1.0	4.6	3.4	3.4	3.4	0.93	0.59	0.59	0.59	95	16	16	16	1.0	4.8	4.6	4.2	3.9	0.92	0.80	0.55	0.29	23	19	12	8

Whitney Lakes West

LFH	pH _c				Base Sat				BC:Al Ratio				Mineral	pH _c				Base Sat				BC:Al Ratio			
	Years				Years				Years					Years				Years							
Acid Input (kmol _c ha ⁻¹ y ⁻¹)	0	20	50	100	0	20	50	100	0	20	50	100	Acid Input (kmol _c ha ⁻¹ y ⁻¹)	0	20	50	100	0	20	50	100	0	20	50	100
0.1	4.4	4.0	3.8	3.8	0.91	0.81	0.75	0.74	71	43	30	30	0.1	5.0	5.0	5.0	4.9	0.88	0.88	0.87	0.83	29	29	28	26
0.2	4.4	3.7	3.7	3.7	0.91	0.73	0.71	0.71	71	28	24	24	0.2	5.0	5.0	4.9	4.8	0.88	0.88	0.82	0.73	29	28	26	22
0.3	4.4	3.6	3.6	3.6	0.91	0.69	0.69	0.69	71	22	22	22	0.3	5.0	5.0	4.8	4.6	0.88	0.86	0.77	0.63	29	28	24	19
0.5	4.4	3.5	3.5	3.5	0.91	0.66	0.66	0.66	71	19	19	19	0.5	5.0	4.9	4.7	4.3	0.88	0.82	0.66	0.44	29	26	20	14
0.7	4.4	3.5	3.5	3.5	0.91	0.64	0.64	0.64	71	18	18	18	0.7	5.0	4.8	4.5	4.1	0.88	0.78	0.56	0.27	29	24	17	10
1.0	4.4	3.4	3.4	3.4	0.91	0.63	0.63	0.63	71	16	16	16	1.0	5.0	4.7	4.3	3.8	0.88	0.71	0.38	0.10	29	22	13	8

Table 15. Changes in Chemistry of LICA and LTSAM Soils (top 25 cm Mineral Layer) Under Different Acid Loadings (continued).

Tucker Lake North

LFH	pH _c				Base Sat				BC:Al Ratio				Mineral	pH _c				Base Sat				BC:Al Ratio			
	Years				Years				Years					Years				Years							
Acid Input (kmol _c ha ⁻¹ y ⁻¹)	0	20	50	100	0	20	50	100	0	20	50	100	Acid Input (kmol _c ha ⁻¹ y ⁻¹)	0	20	50	100	0	20	50	100	0	20	50	100
0.1	4.4	4.1	3.9	3.8	0.91	0.84	0.76	0.75	71	48	32	30	0.1	4.7	4.7	4.7	4.6	0.74	0.74	0.74	0.69	20	20	20	19
0.2	4.4	3.8	3.7	3.7	0.91	0.76	0.71	0.71	71	32	24	24	0.2	4.7	4.7	4.6	4.4	0.74	0.74	0.67	0.55	20	20	18	15
0.3	4.4	3.7	3.6	3.6	0.91	0.70	0.69	0.69	71	24	22	22	0.3	4.7	4.7	4.5	4.2	0.74	0.73	0.58	0.41	20	20	16	12
0.5	4.4	3.5	3.5	3.5	0.91	0.66	0.66	0.66	71	19	19	19	0.5	4.7	4.6	4.2	4.0	0.74	0.66	0.42	0.26	20	18	12	9
0.7	4.4	3.5	3.5	3.5	0.91	0.65	0.65	0.65	71	18	18	18	0.7	4.7	4.5	4.0	3.9	0.74	0.59	0.28	0.20	20	16	9	8
1.0	4.4	3.4	3.4	3.4	0.91	0.63	0.63	0.63	71	16	16	16	1.0	4.7	4.3	3.8	3.8	0.74	0.48	0.16	0.15	20	13	8	7

Tucker Lake South

LFH	pH _c				Base Sat				BC:Al Ratio				Mineral	pH _c				Base Sat				BC:Al Ratio			
	Years				Years				Years					Years				Years							
Acid Input (kmol _c ha ⁻¹ y ⁻¹)	0	20	50	100	0	20	50	100	0	20	50	100	Acid Input (kmol _c ha ⁻¹ y ⁻¹)	0	20	50	100	0	20	50	100	0	20	50	100
0.1	4.1	3.9	3.8	3.8	0.88	0.81	0.79	0.79	45	33	30	29	0.1	4.5	4.5	4.5	4.4	0.61	0.61	0.60	0.57	16	16	16	15
0.2	4.1	3.7	3.7	3.7	0.88	0.76	0.76	0.76	45	25	24	24	0.2	4.5	4.5	4.4	4.2	0.61	0.59	0.52	0.44	16	16	14	12
0.3	4.1	3.6	3.6	3.6	0.88	0.74	0.74	0.74	45	22	22	22	0.3	4.5	4.4	4.2	4.1	0.61	0.56	0.44	0.35	16	15	12	10
0.5	4.1	3.5	3.5	3.5	0.88	0.71	0.71	0.71	45	19	19	19	0.5	4.5	4.3	4.0	4.0	0.61	0.49	0.30	0.25	16	13	10	9
0.7	4.1	3.5	3.5	3.5	0.88	0.70	0.70	0.70	45	17	17	17	0.7	4.5	4.2	3.9	3.9	0.61	0.41	0.22	0.20	16	12	8	8
1.0	4.1	3.4	3.4	3.4	0.88	0.68	0.68	0.68	45	16	16	16	1.0	4.5	4.0	3.8	3.8	0.61	0.30	0.15	0.15	16	10	7	7

Table 15. Changes in Chemistry of LICA and LTSAM Soils (top 25 cm Mineral Layer) Under Different Acid Loadings (concluded).

Cold Lake East

LFH	pH _c				Base Sat				BC:Al Ratio				Mineral	pH _c				Base Sat				BC:Al Ratio			
	Years				Years				Years					Years				Years							
Acid Input (kmol _c ha ⁻¹ y ⁻¹)	0	20	50	100	0	20	50	100	0	20	50	100	Acid Input (kmol _c ha ⁻¹ y ⁻¹)	0	20	50	100	0	20	50	100	0	20	50	100
0.1	4.4	3.9	3.8	3.8	0.92	0.78	0.75	0.75	71	36	30	30	0.1	4.7	4.7	4.6	4.6	0.87	0.87	0.83	0.78	20	20	19	17
0.2	4.4	3.7	3.7	3.7	0.92	0.72	0.72	0.72	71	25	24	24	0.2	4.7	4.7	4.5	4.3	0.87	0.84	0.73	0.61	20	19	16	13
0.3	4.4	3.6	3.6	3.6	0.92	0.69	0.69	0.69	71	22	22	22	0.3	4.7	4.6	4.3	4.1	0.87	0.80	0.63	0.49	20	18	14	11
0.5	4.4	3.5	3.5	3.5	0.92	0.67	0.67	0.67	71	19	19	19	0.5	4.7	4.5	4.1	4.0	0.87	0.70	0.45	0.38	20	16	10	9
0.7	4.4	3.5	3.5	3.5	0.92	0.65	0.65	0.65	71	18	18	18	0.7	4.7	4.3	3.9	3.9	0.87	0.61	0.34	0.32	20	13	8	8
1.0	4.4	3.4	3.4	3.4	0.92	0.62	0.62	0.62	71	15	15	15	1.0	4.7	4.0	3.8	3.8	0.87	0.38	0.24	0.24	20	9	7	7

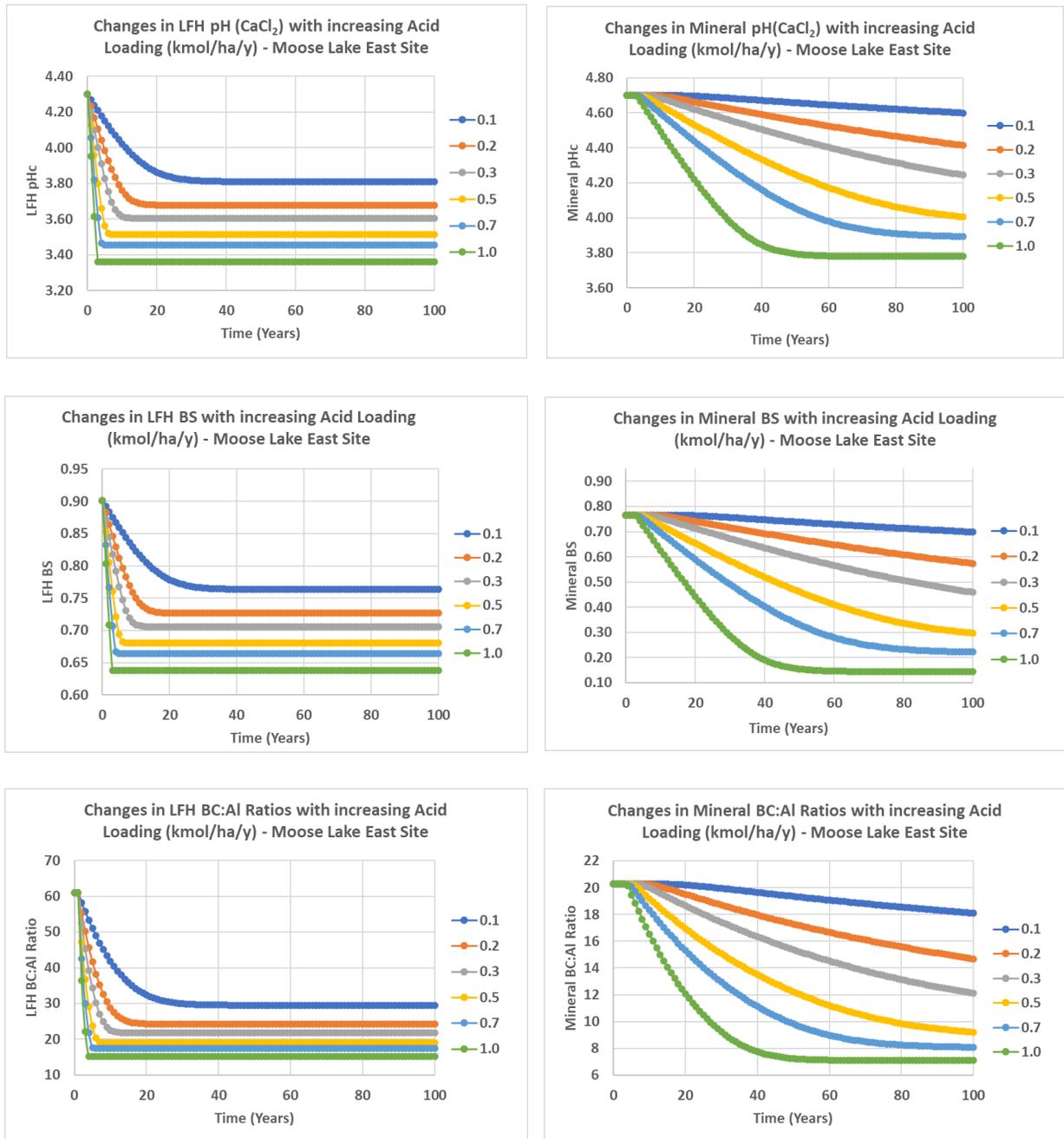


Figure 15. Changes with Acid Loadings in the Moose Lake East Site

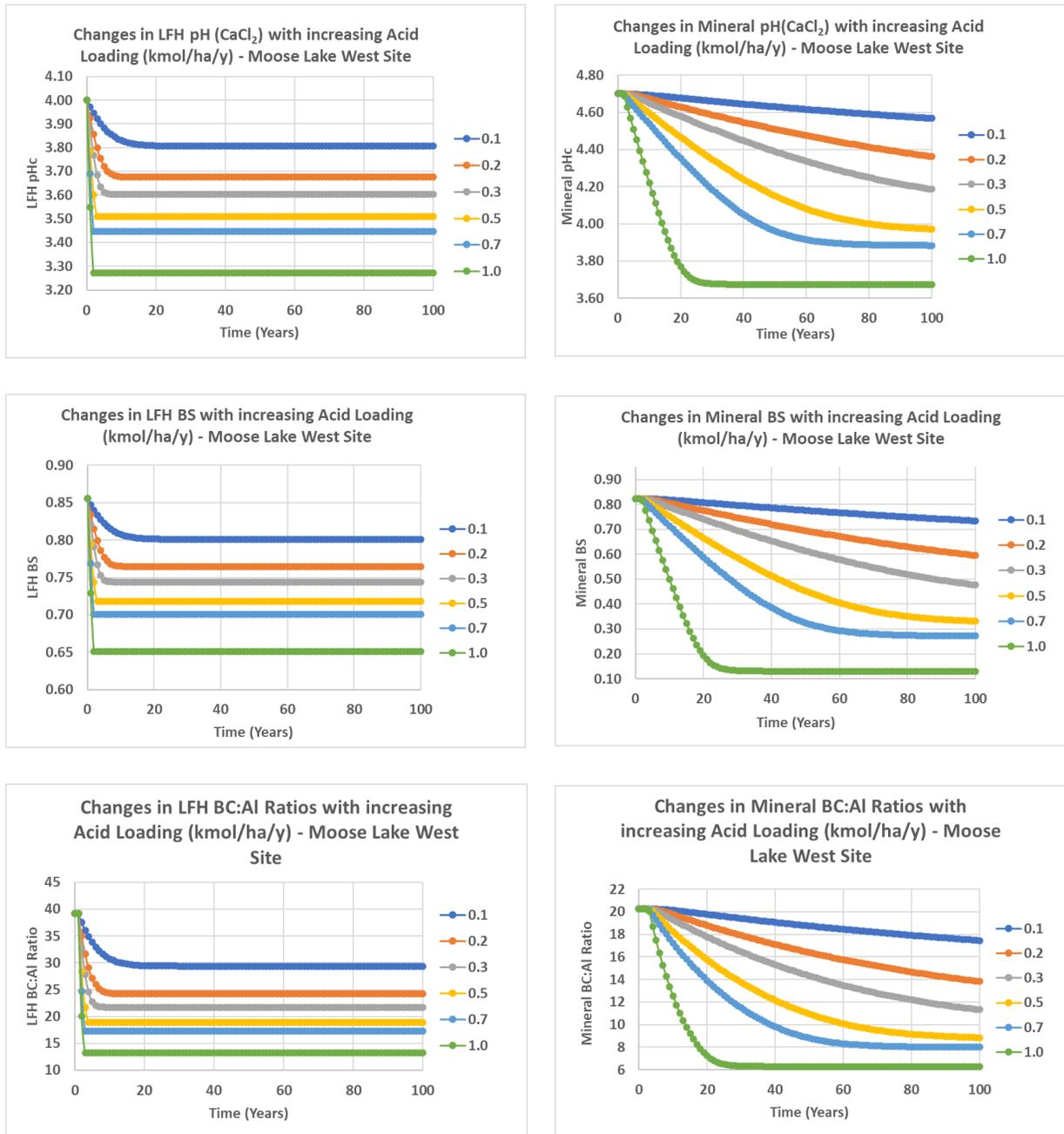


Figure 16. Changes with Acid Loadings in the Moose Lake West Site

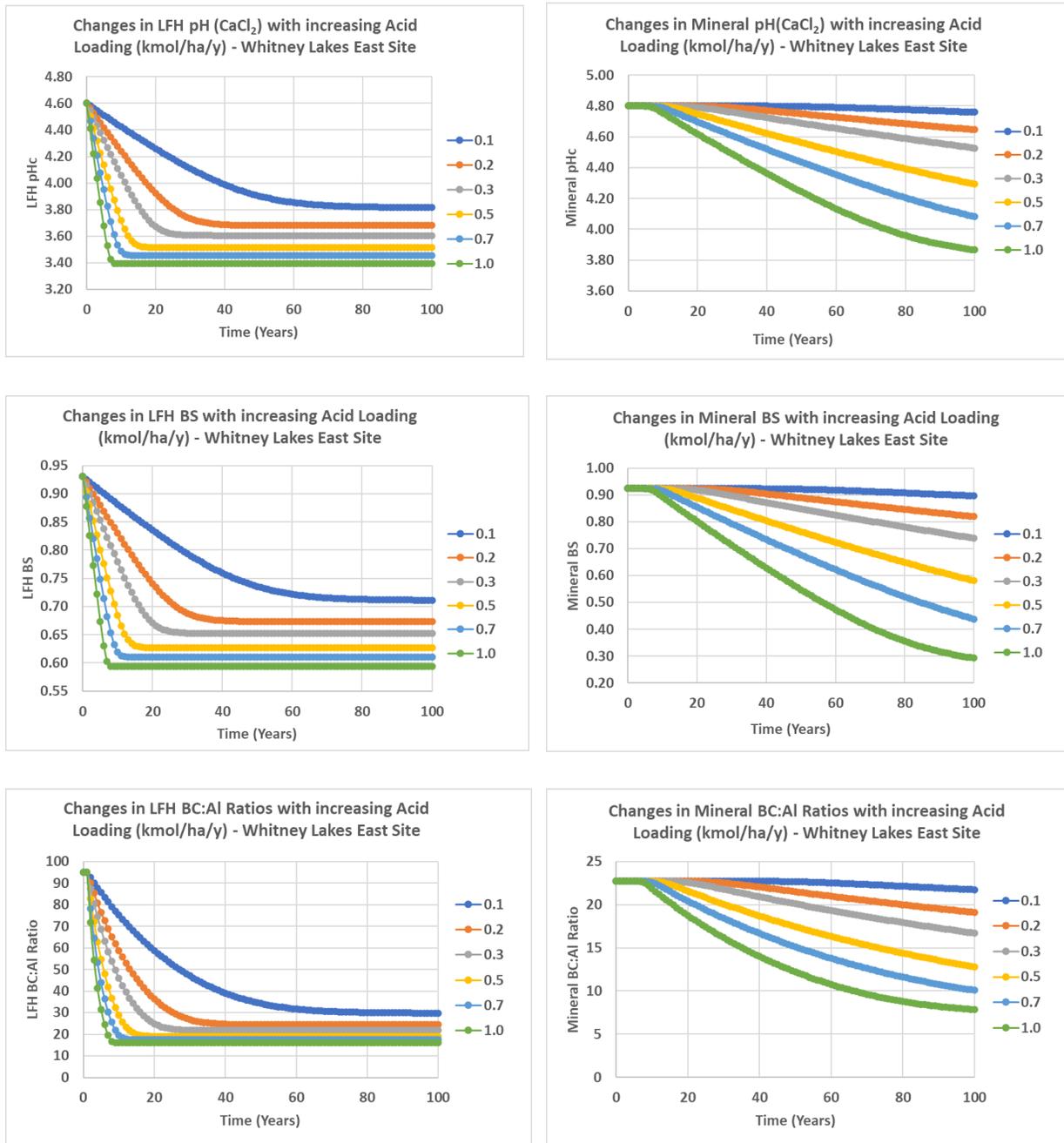


Figure 17. Changes with Acid Loadings in the Whitney Lakes East Site

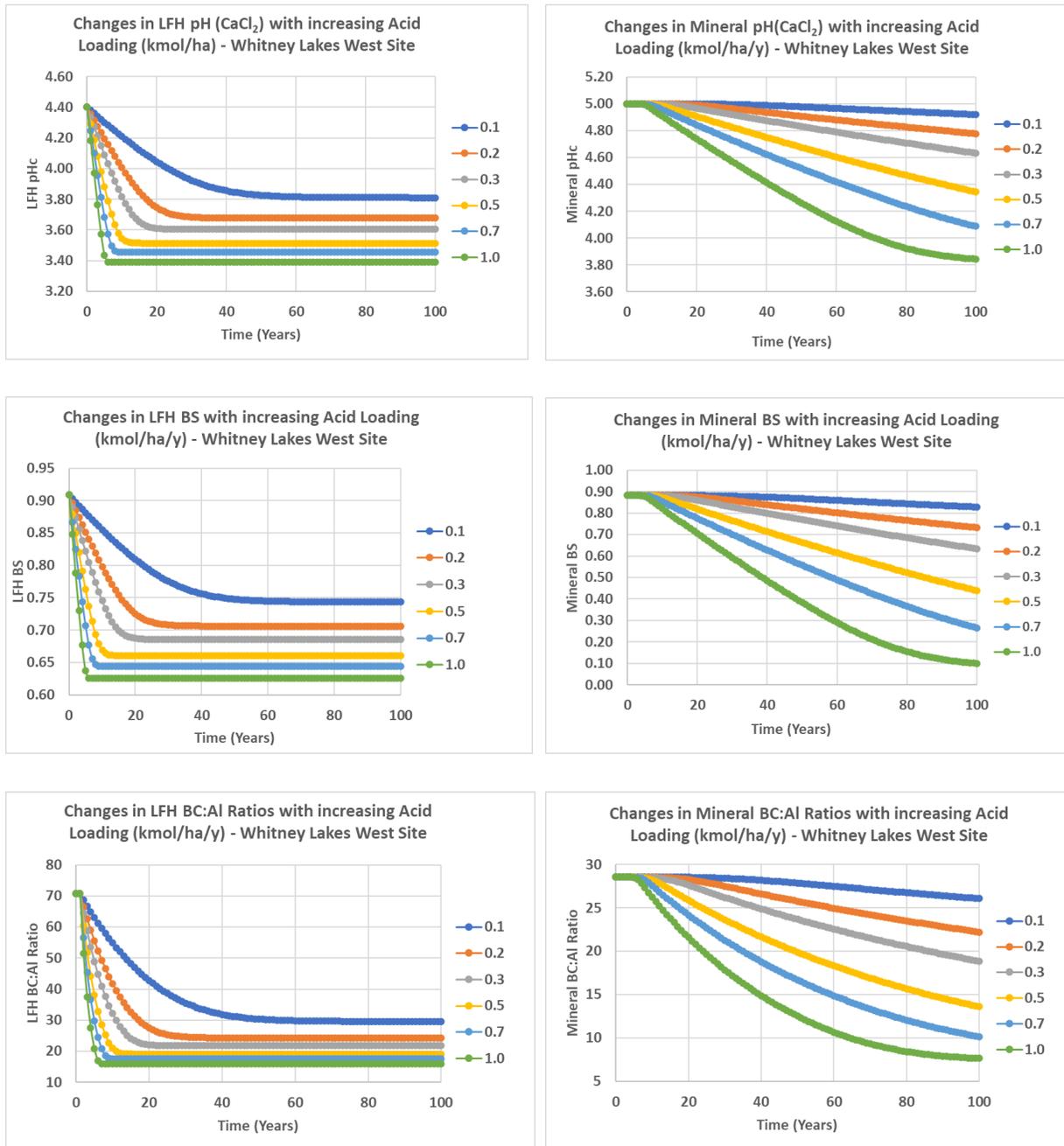


Figure 18. Changes with Acid Loadings in the Whitney Lakes West Site

Trends in Soil Acidification in the LICA area – 2010 to 2020

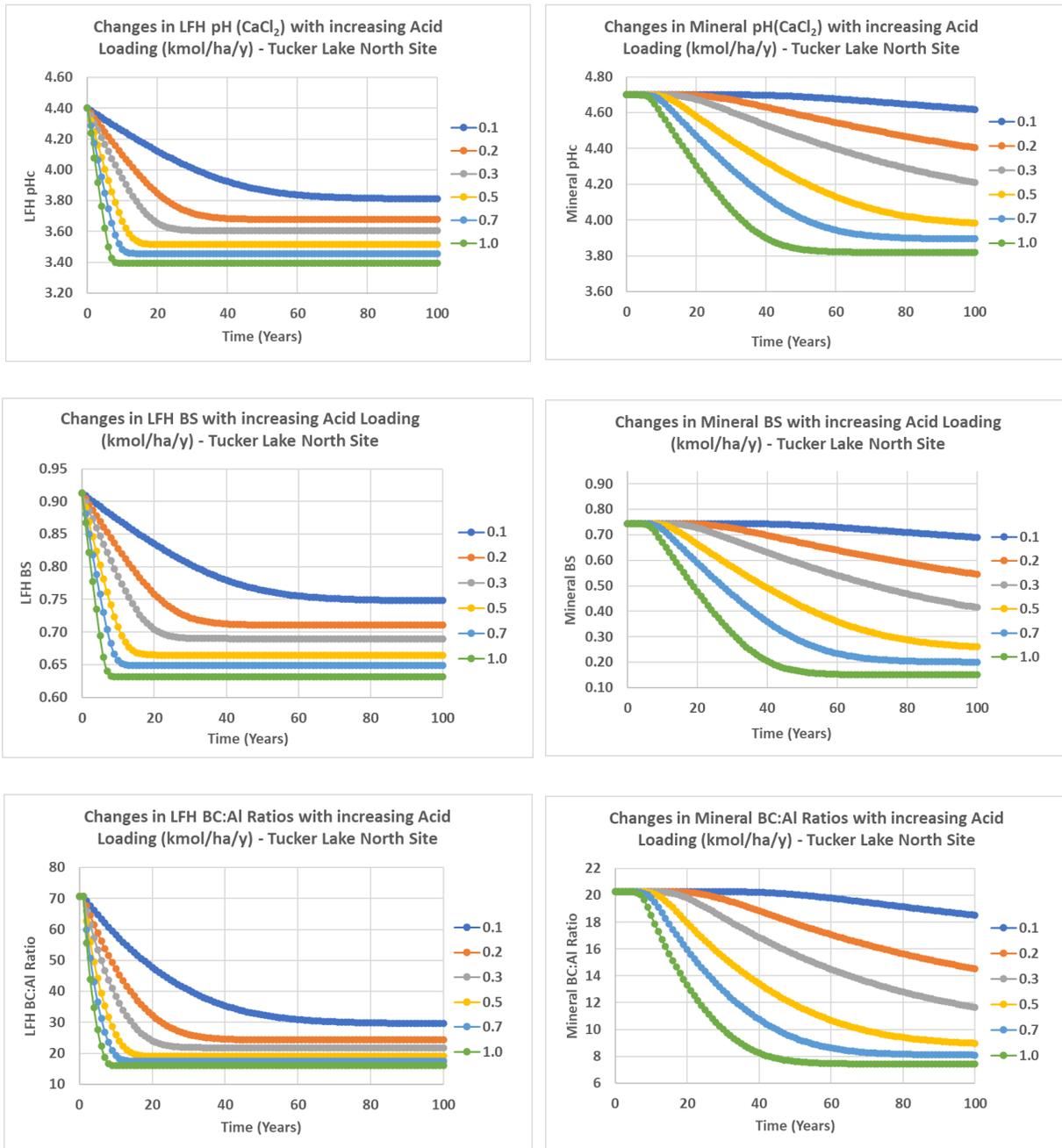


Figure 19. Changes with Acid Loadings in the Tucker Lake North Site

Trends in Soil Acidification in the LICA area – 2010 to 2020

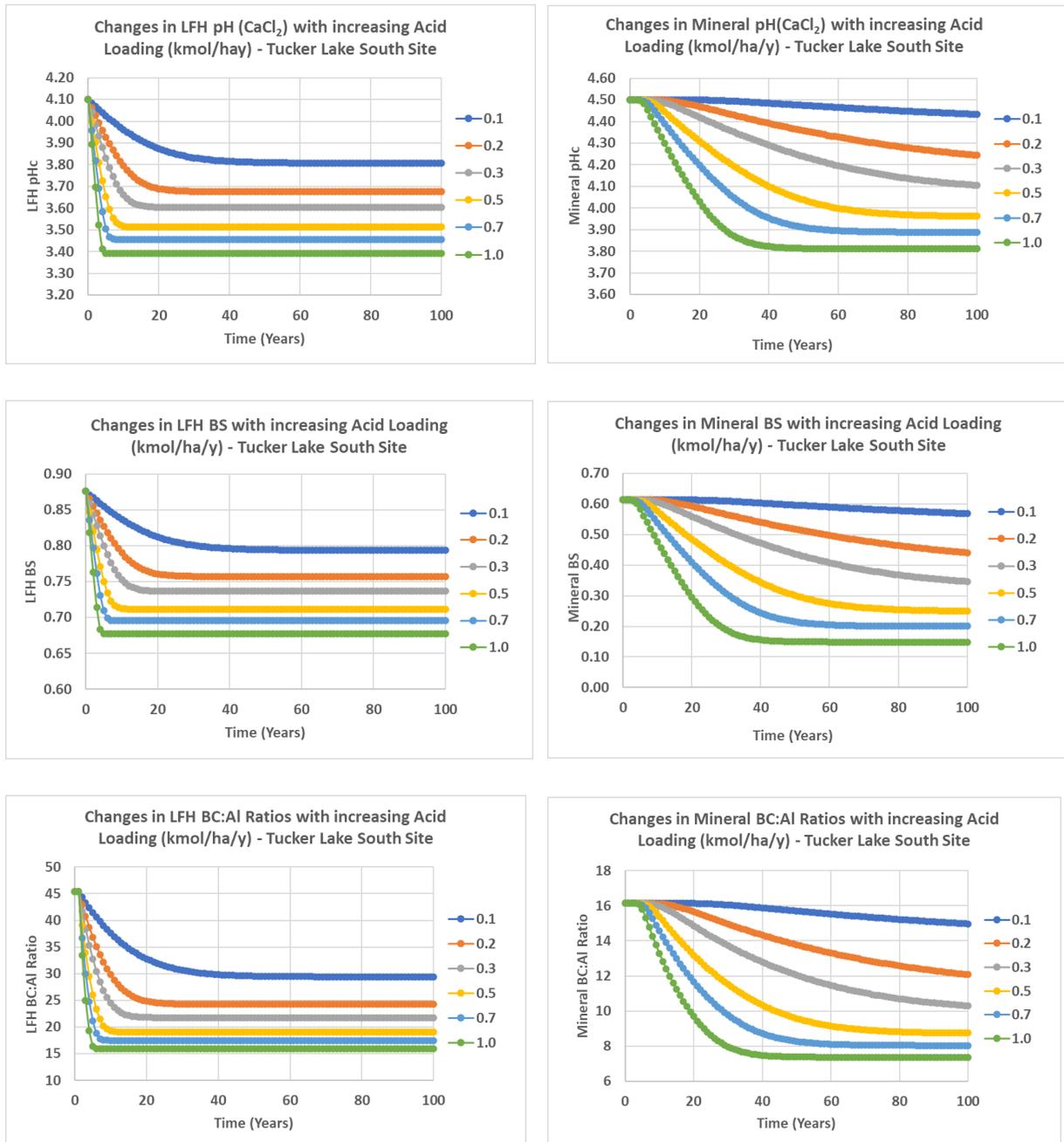


Figure 20. Changes with Acid Loadings in the Tucker Lake South Site

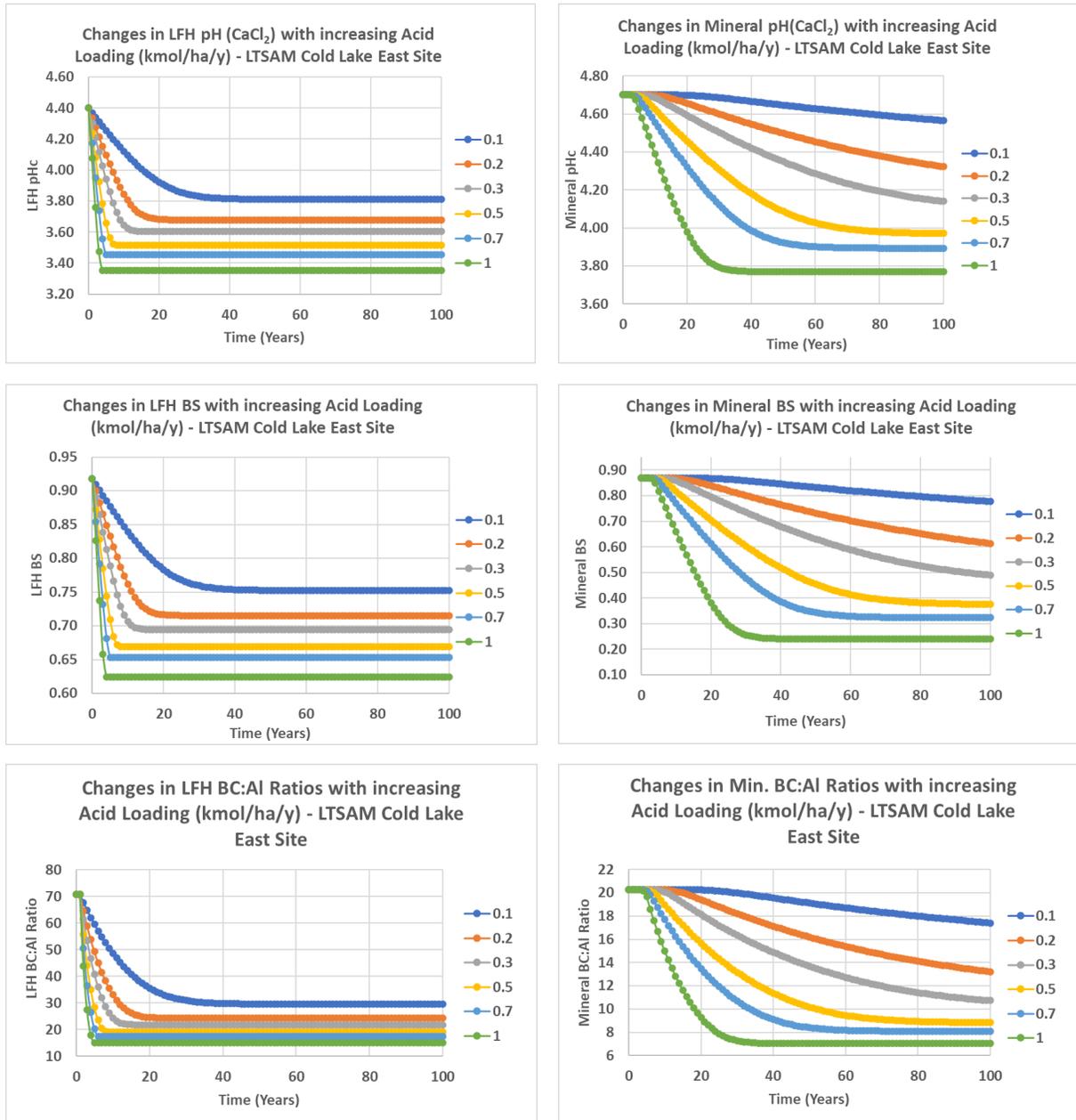


Figure 21. Changes with Acid Loadings in the LTSAM Cold Lake East Site

4.6 CCVs AND CLs OF LICA MONITORING SITES

Critical chemical values and critical loads specific to the long term monitoring sites, derived as indicated in Section 4.3.1, are presented in Tables 16 and 17.

Table 16. Critical Chemical Values of LICA and LTSAM Soils (top 25 cm Mineral Layer)

Site	Critical Chemical Value ^z								
	pH _{ci}	CCV pH _c 25%	CCV pH _{cmin}	BS _i	CCV BS 75%	CCV BS _{min}	BC:Al _i	CCV BC:Al 75%	CCV BC:Al _{min}
Moose Lake E	4.7	4.2	3.5	0.77	0.60	0.1	20	15	2
Moose Lake W	4.7	4.2	3.5	0.82	0.64	0.1	20	15	2
Whitney Lakes E	4.8	4.2	3.5	0.92	0.72	0.1	23	18	2
Whitney Lakes W	5.0	4.2	3.5	0.88	0.69	0.1	29	22	2
Tucker Lake N	4.7	4.2	3.5	0.74	0.58	0.1	20	15	2
Tucker Lake S	4.5	4.1	3.5	0.61	0.48	0.1	16	12	2
Cold Lake	4.7	4.2	3.5	0.87	0.68	0.1	20	15	2

^z Symbols and abbreviations: BS - base saturation; BC:Al - base cation to Al ratio; pH_c - pH in CaCl₂; i - the initial value, used as initial model input; min - minimum; 50% - percentage of the difference between the initial and minimum value; pH_c 25% - 25% additional acidity between pH_{ci} and pH_{cmin}.

Table 17. Critical Loads of LICA and LTSAM Soils (top 25 cm Mineral Layer)

Site	Soil Series	Time (years)	Critical Load (kmol _c ha ⁻¹ y ⁻¹) ^z					
			pH _c 25%	pH _{cmin}	BS 75%	BS _{min}	BC:Al 75%	BC:Al _{min}
Moose Lake E	Nestow	50	0.5	>1	0.3	>1	0.25	>1
		100	0.3	>1	0.2	>1	0.15	>1
Moose Lake W	Nestow	50	0.5	>1	0.3	>1	0.3	>1
		100	0.3	>1	0.15	>1	0.2	>1
Whitney Lakes E	Nestow	50	1	>1	0.6	>1	0.4	>1
		100	0.6	>1	0.3	>1	0.25	>1
Whitney Lakes W	Nestow	50	>1	>1	0.4	>1	0.4	>1
		100	0.6	>1	0.25	1	0.2	>1
Tucker Lake N	Liza	50	0.5	>1	0.3	>1	0.5	>1
		100	0.3	>1	0.2	>1	0.2	>1
Tucker Lake S	Liza	50	0.35	>1	0.25	>1	0.3	>1
		100	0.3	>1	0.2	>1	0.25	>1
Cold Lake	Liza	50	0.4	>1	0.25	>1	0.25	>1
		100	0.25	>1	0.15	>1	0.15	>1

^z Symbols: BS - base saturation; BC:Al - base cation to Al ratio; pH_H - pH in water; i - the initial, or model input value; 75% - percentage of the initial value; pH_H25% - 25% additional acidity between pH_{Hi} and pH_{Hmin}.

Observations regarding the critical loads are as follows:

- CLs calculated for pH_c are higher than those for BS and BC:Al ratio, and those based on BS values correspond to BC:Al values only in some instances.
- The 50 year CLs for pH_c range from 0.35 to >1 kmol_c ha⁻¹y⁻¹, while 100 year loads range from 0.25 to 0.6 kmol_c ha⁻¹y⁻¹.

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- The 50 year critical loads for BS 75% range from 0.2 to >1.0 $\text{kmol}_c \text{ ha}^{-1} \text{ y}^{-1}$, and 100 year loads range from 0.15 to 0.6 $\text{kmol}_c \text{ ha}^{-1} \text{ y}^{-1}$.
- The 100 year CLs based on 'BC:Al 75%' are in the 0.15 to 0.25 $\text{kmol}_c \text{ ha}^{-1} \text{ y}^{-1}$ range, which are lower than those for 'BS 75%'. 50 year CLs are 0.25 to 0.5 $\text{kmol}_c \text{ ha}^{-1} \text{ y}^{-1}$.
- The Whitney Lakes sites have the highest critical load (100 year load of 0.6 $\text{kmol}_c \text{ ha}^{-1} \text{ y}^{-1}$), which indicates that they have the lowest sensitivity of this group of soils. 100 year CLs at the other sites are 0.25 or 0.3 $\text{kmol}_c \text{ ha}^{-1} \text{ y}^{-1}$.
- Minimum critical chemical values will not be reached in these soils unless PAI levels of 1 or >1 $\text{kmol}_c \text{ ha}^{-1} \text{ y}^{-1}$ are reached.

The critical load values suggest that if the most sensitive soils are to be protected from acidification (at a relatively high level of protection), then PAI should not be greater than 0.15 to 0.25 $\text{kmol}_c \text{ ha}^{-1} \text{ y}^{-1}$. This accords with the critical load (0.25 $\text{kmol}_c \text{ ha}^{-1} \text{ y}^{-1}$) for sensitive soils recommended by Alberta Environment's (2008) *Acid Deposition Management Framework*. It is also the critical load determined by modelling of sandy Brunisolic soils in northeastern Alberta (Abboud et al., 2002). Provincial guidelines indicate implementation of management actions (such as monitoring soils) when, after a 5-year evaluation, modelled or monitored PAI exceeds 0.17 to 0.22 $\text{kmol}_c \text{ ha}^{-1} \text{ y}^{-1}$ (Alberta Environment, 2008). Further actions are suggested when the load exceeds 0.22 $\text{kmol}_c \text{ ha}^{-1} \text{ y}^{-1}$. The tendency of soils in the LICA monitoring sites to show some acidification, along with model application verifying the sensitivity of soils in the region, provides validation for the monitoring program and its continuance.

4.7 COMPARISON OF CRITICAL LOADS AND MONITORING DATA

The following discusses the modelling results at each monitoring site and compares them with the monitoring data. Critical loads indicated are only for the relatively more protective BS 75% and BC:Al 75% calculations.

4.7.1 Moose Lake Site

The critical loads for the Nestow soil at the Moose Lake sites are 0.15 - 0.2 $\text{kmol}_c \text{ H}^+ \text{ ha}^{-1} \text{ y}^{-1}$ for the 100 year basis, and 0.25 - 0.3 $\text{kmol}_c \text{ H}^+ \text{ ha}^{-1} \text{ y}^{-1}$ for the 50 year period. Acid deposition (i.e., PAI) modelling in 2007 (AMEC, 2007) indicated that this site is in a low deposition area of <0.17 $\text{kmol}_c \text{ H}^+ \text{ ha}^{-1} \text{ y}^{-1}$, and the level may be <0.1 $\text{kmol}_c \text{ H}^+ \text{ ha}^{-1} \text{ y}^{-1}$ (see Section 1.2.2). The potential acid input is thus in the area of the 100-year critical load, and it is expected that any soil chemistry changes at this site would be minimal.

4.7.2 Whitney Lakes Site

The critical loads calculated for the Nestow soil at the Whitney Lakes site are 0.2 - 0.3 $\text{kmol}_c \text{ H}^+ \text{ ha}^{-1} \text{ y}^{-1}$ for the 100 year period, and 0.4 - 0.6 $\text{kmol}_c \text{ H}^+ \text{ ha}^{-1} \text{ y}^{-1}$ for the 50 year period. The 50 year critical load indicates that soils at this site have more pH buffering as compared to the other three sites. The regional acid deposition estimates for the Whitney Lakes area, based on the study by AMEC (2007), is near 0.17 $\text{kmol}_c \text{ H}^+ \text{ ha}^{-1} \text{ y}^{-1}$. The potential acid input is near the lower part of the range of the 100-year critical load for this site (indicated above) but is lower than the 50 year

critical load. It is thus inferred that the Whitney Lakes soils would not change markedly in the relatively short term (50 years) but are susceptible in the longer term under continued acid deposition at current levels.

4.7.3 Tucker Lake Site

The critical loads for the Liza soil at the Tucker lake site are 0.2 - 0.3 $\text{kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$ for the 100 year period, and 0.3 - 0.5 $\text{kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$ for the 50 year period. The regional acid deposition estimate for the Tucker Lake area is close to 0.17 $\text{kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$, based on relatively recent data from Imperial Oil Limited (2016), as well as from the earlier data of AMEC (2007). The potential acid input is thus near the 50 year critical load for this site. Similar to the Whitney Lakes site, the Tucker Lake 50-year critical load suggested that soils would not change markedly in the relatively short term (50 years) but are susceptible in the longer term under continued acid deposition at current levels.

4.7.4 Cold Lake Site

The critical load derived for BS 75% and BC:Al 75% of the Liza soil at the Cold Lake site is 0.15 $\text{kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$ for the 100 year period, and 0.25 $\text{kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$ for the 50 year period. The monitoring results showed some significant changes in acidification parameters since the start of monitoring in 1982 (Abboud et al, 2012). The regional acid deposition estimate for the Cold Lake area is <0.1 $\text{kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$. This level is lower than the 0.17 $\text{kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$ estimated in the AMEC (2007) study. The level was estimated to be 0.11 $\text{kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$ in the assessment of trends of LTSAM sites in 2012 (Abboud et al., 2012). It is possible that the levels over the years since the early 1980s have fluctuated. The potential acid input is near the 100 year critical load, and less than the 50 year critical load. The gradual changes seen at this site appear to be more or less in accordance with model and critical load predictions for this site.

4.7.5 Modelling Summary

It is helpful to examine the overall trends predicted by the model as shown in the output tables and charts. (Table 15 and Figures 15 to 21). In the Moose Lake mineral soil, little change is predicted within a 50 year period in each of the three parameters (pH_c , BS and BC:Al ratio) at the current PAI level of about 0.1 $\text{kmol}_c \text{ha}^{-1} \text{y}^{-1}$. In the Tucker Lake North example, where the current PAI is closer to 0.2 $\text{kmol}_c \text{ha}^{-1} \text{y}^{-1}$, changes are slow at the beginning of the modelling period but accelerate at about 20 to 30 years. By 50 years, there is a pH_c drop of 0.2 units, and each of BS and BC:Al ratio decrease by about 10%. The actual time of initiation of potential acidification is a consideration as well. Oil extraction activity in the area began in the mid 1970s (e.g., Imperial Oil operations began in 1975 (Imperial Oil Ltd., 2021)). Although other acidic deposition sources may have been present prior to this time, it seems reasonable to consider that any accelerated soil acidification began approximately 40 years ago. Thus, the start of monitoring in 2010 represents a time when some changes may already have occurred in the most sensitive monitoring sites.

The monitoring results for the Cold Lake LTSAM site are informative in this regard, as the initiation of monitoring in 1982 is near the time of potential accelerated acidification. This site has shown a

decreasing trend in the acidification parameters (Cho et al., 2019), but only in the uppermost layers (0-2 cm, and 2-5 cm). To a certain extent, this is in accordance with model simulations that show slow response to acidification at the beginning of the modelling period. As indicated previously, the model applies to the 25 cm surface soil layer. The changes seen thus far, being in the top 5 cm of soil, suggest that actual acidification is progressing more slowly than predicted by modelling. But as noted above, beginning of acidification tends to be slow, and then increases, and it is possible that lower soil layers (between 5 and 25 cm) will change relatively rapidly.

Model predictions were also made for the LFH soil layers at the LICA monitoring sites. The model charts for most of the sites (Figures 15 to 21) show a pH_c response that is somewhat more rapid than that for the mineral soil. The monitoring results also showed decreases in pH_c of 0.2 to 0.4 units, these being statistically significant in all sites except Moose Like West. The charts also show that the responses flatten within about 40 years. This suggests that the monitoring results are still somewhere on the downward slopes of the response curves and have not yet reached the flattened parts of the curves. However, there is the possibility that little change in pH_c will be seen in LFH layers with continued monitoring, but the mineral soil would continue to show changes. Examining the results of the Cold Lake monitoring site, having been initiated nearer the time of time of possible accelerated acidification, would be informative in this regard; unfortunately, LFH monitoring was not included in the LTSAM monitoring protocols.

5.0 DISCUSSION AND CONCLUSIONS

Acidification Trends

Decreasing trends in pH and base saturation percentage were observed in some of the sites, particularly in the LFH, 0-2 cm and 2-5 cm soil layers. Increasing trends were found in lower layers.

At the Moose Lake site (sampled in 2010, 2014 and 2018), trends of decreasing pH_c were detected only in the LFH layer of the East subsite, and the 2-5 cm, 5-10 cm and 10-15 cm layers of the West subsite. No trends of decreasing BS or BC:Al ratio were found.

At the Whitney Lakes site (sampled in 2011, 2015 and 2019), trends of decreasing pH_c were detected in the LFH layer of both East and West Whitney Lakes subsites, but there were no trends of decreasing pH_c identified for the mineral layers. No trends of decreasing BS or BC:Al ratio were found.

After the three sampling events (2012, 2016, 2020) over an eight year period at the Tucker Lake site, trends of pH_c decrease occurred in the LFH layer and the 2-5 cm layer of the Tucker Lake North subsite, and the 5-10 cm and 10-15 cm layers of both the South and North subsites. No trends of decreasing BS or BC:Al ratio were found.

The LTSAM Cold Lake East subsite was sampled eight times between 1982 and 2017. Decreasing pH_c was found in the 0-2 cm and 2-5 cm layers of this site, and reduction in BS occurred in the 0-2 cm layer (data available only for the East subsite).

The Cold Lake East site had the most definite observed trend, where regression analysis showed pH_c decreasing annually by ~ 0.01-0.02 pH units/year in the 0-2 cm and 2-5 cm mineral layers; i.e., changes did not occur uniformly, but overall decreased from 4.9 to 4.2 between 1982 and 2017. This is in accordance with previous analysis of this site for the same sampling period by Cho et al. (2019). While trends were observed at the Moose Lake site, they were different between the East and West subsites, and changes that are spatially consistent therefore do not appear to be occurring. The trend toward acidification is slightly stronger at the Tucker Lake site as compared to the Moose Lake site, as decreasing pH_c occurred in the LFH layer at both subsites, and surface mineral layers showed declining pH_c , but in different layers. At both the Tucker Lake and Moose Lake sites, increasing Total Sulphur in the LFH layer provides further evidence for potential acidification.

The above comments for all LICA monitoring sites are made with caution as there have been only three sampling events to date. The comments regarding the Cold Lake site are made with greater confidence as they are based on eight sampling events since 1982.

Upward Trends in Parameters

Trends of increasing BS and BC:Al ratios were noted in some lower layers in all sites. These

increases may be due to loss and transfer of exchangeable cations from the surface 0-2 cm and 2-5 cm layers to the lower layers but may also be attributable to natural variability of the soil properties. Continued monitoring will help assist interpretation of reasons for these observations.

Variability

The LICA pH measurements were least variable among the acidification parameters, with CVs among all layers and sites ranging between 0.03 and 0.06. BS values also had relatively low CVs, ranging from 0.05 to 0.15. BC:Al ratios had the highest variability with CVs between 0.26 and 0.78. Determining CVs is useful in that it helps to indicate relatively more difficulty and need for caution in recognizing differences and trends if they are relatively high.

Statistical Analyses

ANOVA and linear modelling approaches showed significant differences even in instances where there was a 0.1 or 0.2 pH change, or where other parameters showed very small differences. It is therefore important to distinguish between statistically important and biologically important differences. For example, a difference of 0.2 pH units can be statistically significant but is likely within the range of pH values at a site, and moreover is not likely to result in measurable biological effects.

Both ANOVA and regression multivariate statistical approaches are particularly useful tools for analyzing the monitoring data, yet they have limitations. Use of ANOVA identifies significant differences in data but does not identify trends. Regression analysis is needed mainly to support the ANOVA analysis but is useful only if trends are linear. Trends in some soil chemical parameters are not necessarily linear, and caution is thus required in applying these tools.

Paired Subsites

Sites were established to allow for possible loss due to agents such as forest fire, but with possibility of survival of one of the subsites. Pairing subsites has other advantages, principally by adding robustness to statistical analysis by providing additional data representing a site or forest stand. As examples, the Moose Lake subsites did not provide results that were sufficiently similar to conclude that acidification may be occurring. By comparison, the results for the Tucker Lake subsites showed greater consistency with each other, and acidification is more evident. Thus, pairing of subsites enables more balanced comparison of results at each site and provides more rigour to the statistical analysis of differences and trends.

Acidification Modelling in Relation to PAI and Trends

The high acidification sensitivity of the monitoring site soils was demonstrated through the response curves and critical loads obtained from acidification simulations. Different critical loads of PAI on the monitoring site soils were calculated on the basis of pH_c , BS and BC:Al critical values. These ranged from 0.15 to 0.6 $\text{kmol}_c \text{H}^+ \text{ha}^{-1} \text{y}^{-1}$ when based on 100 years of PAI, and 0.2

to $>1.0 \text{ kmol}_c \text{ H}^+ \text{ ha}^{-1} \text{ y}^{-1}$ when based on 50 years of PAI. Based on their critical loads and response curves, the order of acidification sensitivity among the sites is: Moose Lake \approx Cold Lake \approx Tucker Lake $>$ Whitney Lakes. All sites respond in soil chemical parameters according to the level of PAI, but under similar levels, the modelling results suggest that the Whitney Lakes site will require a longer period to show changes.

Synopsis

The following are the highlights of the analysis of three LICA soil monitoring events that were initiated in 2010, and of the LTSAM Cold Lake site which has had eight monitoring events since 1982.

- Some indications of acidification (pH_c decrease and/or TS increase) among the LICA sites were found mainly for the Tucker Lake and Moose Lake sites. No indications were found for the Whitney Lakes site.
- Overall, interpretations are challenging with results from just three monitoring events to date.
- After eight monitoring events, the LTSAM Cold Lake site showed acidification trends, with pH_c in the top 5 cm declining by about 0.5 units and base saturation percentage declining slightly in the top 0-2 cm layer since initiation of monitoring in 1982.
- Measurements of pH_c provide the strongest evidence for acidification, supported to some extent by total sulphur measures.
- With some indications of acidification occurring, the continuation of soil monitoring of the sites in the LICA area is warranted.
- Modelling indicated that significant short term acidification (to 25 cm depth) is not expected at the LICA sites under the current PAI scenarios. There exists the potential for acidification to occur in the longer term. Acidification in the surface soil layers (e.g. LFH, 0-2 cm and 2-5 cm) has occurred and based on monitoring results, is likely to continue.

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