University of Alberta

Response of Soil Properties and Plant Growth to Sulphur Addition at the Breton Plots

by

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Abstract

The Classical Breton Plots were established in 1929 to help define successful agricultural practices on Gray Luvisols. Long-term results suggested that atmospheric sulphur (S) deposition may have influenced yields on these S-deficient soils. Analyses on archived samples indicated that most soil chemical properties were no longer distinctly altered by management practices following 30 years of liming. A spatial gradient was observed in these properties, which may be due to a natural acidity gradient. A greenhouse experiment was conducted to evaluate the effects of increasing S addition on plant growth and soil properties from plots with soils under different management practices. Previous soil management alone affected wheat yields, while soil management and S addition showed a significant interaction for alfalfa yields. The current level of S deposition, 3.4 kg S ha^{-1}, is unlikely to significantly acidify soils at the Breton Plots, but may have a positive effect on crops by acting as a fertilizer.

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The last three years have not been without challenges. I have learned how strong I can be and that the world is full of wonderful, giving people extending their hands; all you have to do is be open and willing to accept their help. I hope I can offer the same kindness to someone else someday.

Amanda

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List of Abbreviations

ANOVA	Analysis of variance
BS	Base saturation
C	Carbon
CEC_e	Effective cation exchange capacity
CEC	Cation exchange capacity
C:N	Carbon to nitrogen ratio
EC	Electrical conductivity
K	Potassium
L	Lime
LP	Lime plus phosphorous
LNPKS	Lime, nitrogen, phosphorous, potassium, and sulphur
N	Nitrogen
NPK(-S)	Nitrogen, phosphorous, and potassium (minus sulphur)
NPKS	Nitrogen, phosphorous, potassium, and sulphur
P	Phosphorous
S	Sulphur
SAR	Sodium adsorption ratio
SOM	Soil organic matter

1 Introduction and Literature Review

1.1 Introduction

1.1.1 Gray Luvisols in Alberta

Luvisolic soils in Alberta extend over approximately 15 million ha and represent 30% of the provincial land base (Izaurralde et al., 1993). Gray Luvisols are typically low in organic matter and as a result have poor tilth, low water-holding capacity and low nutrient status. They have moderately acidic solums (pH 5.0 to 6.0) under natural conditions despite the fact that they have a high base saturation (Robertson, 1991; Agriculture and Agri-Food Canada Research Branch, 1998; Bentley et al., 1971). When settlers began to farm Luvisolic soils they experienced many new management problems; cultivated Luvisols quickly lose their humus-rich LFH horizon resulting in a poorly structured Ap horizon made up primarily of the low organic matter, Ae horizon. Therefore upon cultivation the upper mineral horizon pulverizes easily and crusts severely after wetting, which leads to water run-off and poor seedling emergence. Problems with fertility were recognized early in the cultivation of Luvisols by farmers and researchers who saw the need to study and develop suitable farming practices for them (Robertson, 1979). Natural acidity levels may not greatly reduce yields of commonly grown crops, however nitrogen (N) and sulphur (S) fertilizers must be applied and may lead to further acidification (Newton, 1936; Wyatt et al., 1939; Nyborg and Bentley, 1971; Bentley et al., 1971).

1.1.2 Soil Acidity and Sulphur Deposition

Soil pH affects nutrient solubility and therefore plant availability of macronutrients (O'Hallorans et al., 1997; Hue and Licudine, 1999). Most macro nutrients are optimally available between pH of 6.5 to 8 with the exception of P that is most available between pH values of 6 to 7. Most micro nutrients are available for plant uptake between pH of 5 to 7 (McCauley et al., 2003). Deficiencies of nutrients such as Ca, Mg, N, S, P, and Mo occur when the pH drops below optimal levels (Nyborg et al., 1977; Sumner and Yamada, 2002).

Near neutral pH the solubility of elements such as Al and Mn is low (O'Hallorans et al., 1997; Hue and Licudine, 1999), however their solubility increases as pH decreases and may result in toxic levels in acid soils (Rice et al., 1977; Nyborg et al., 1977). This increased solubility is a result of dissolution of clay minerals or gibbsite, $Al(OH)_3$ and MnO_2.

Aluminium toxicity begins at concentrations well below 1 mg L^{-1}, but large differences exist between plant species with respect to the Al concentration they can tolerate (Grime and Hodgson, 1969). Extractable Al can be considered toxic in Breton Plot soils at 1.5 ppm or above, and Mn at 20 ppm when extracted by 0.05 M $CaCl_2$ (McCoy and Webster, 1977). Severely acid soils (pH <4.0) may also have high concentrations of heavy metals due to increased solubility (Blake and Goulding, 2002).

Acid soils are less suitable for cropping than neutral or slightly alkaline soils and soil acidity can reduce the yields of certain crops such as alfalfa at pH <6.0 and barley at pH ≤ 5.5 due to toxicity or nutritional problems (Elliott et al., 1973; Hoyt et al., 1974; Rice et al., 1977). While pH between 6.5 to 6.8 is optimum for most crops; crops vary in their tolerance for soil acidity. Oats are very tolerant to acidity and wheat and canola are moderately tolerant (Hoyt et al., 1974). Legumes are particularly sensitive to soil acidity because the Nfixing root nodules are adversely affected, reducing plant growth (Holding and Lowe, 1971). Alfalfa is more sensitive than other legumes, and pH between 6.8 to 7.0 is recommended for optimal growth (Havlin et al., 1999). The growth and persistence of alfalfa on moderately acid soils appears to be limited by the inability of known strains of *Rhizobium meliloti* to colonize these soils (Robson and Loneragan, 1970). The sensitivity of alfalfa and its symbiont to soil acidity was well documented in a review by Robson (1969). Furthermore, alfalfa is known to have a high requirement for K, Ca, and Mg, whose uptake by plants can be limited by soil acidity (Bear and Wallace, 1950; Jones, 1967). Sumner and Yamada (2002) divided acidic soils in two main categories: pH below 5.2 to 5.4 where toxicities of Al and Mn are often the growth limiting factor, and pH above 5.4 where responses to liming are not so much from the elimination of Al and Mn toxicities but are attributed to increases in nutrient availability. There seems to be little economical benefit in liming to pH greater than 5.5 for most crops (Sumner and Yamada, 2002).

With the exception of fertilized agricultural soils, atmospheric deposition is the major cause of acidification in most soils (Van Breemen et al., 1984; Blake et al., 1999). There are many forms of sulphur (S) deposition including: elemental S, SO_x, reduced compounds such as FeS, FeS_2, H_2S, and H_2SO_4, $(NH_4)_2SO_4$, or neutral salts such as $CaSO_4$ (Hunt et al., 1982; Bradford et al., 2001; Mayer et al., 1995; Picard et al., 1987; Turchenek et al., 1987). Wet and dry deposition refers to S deposited by several mechanisms: in rain and snow, rain intercepted by trees, dry particulates and direct adsorption of SO_2 (Legge, 1988). S deposited is retained in both organic and inorganic forms in acid forest soils; in areas where less than 10 kg S ha^{-1} yr^{-1} occurs most atmospheric S is cycled through the organic S pool (Mayer et al., 2001). However, under high deposition (>15 kg ha^{-1} yr^{-1}) the main pool becomes inorganic SO_4 (Alewell, 2001). Sulphur deposition has two main effects on soil: the addition of nutrient S, which is deficient in some soils, and the acidification of soils if S is in a reduced form (Nyborg and Walker, 1977). Reduced forms are acidifying due to the release of H^+ ions during oxidation.

Sulphur deposition is a naturally occurring process; however anthropogenic emissions have increased its occurrence and have had a dramatic effect on global S cycling in the past two centuries, unprecedented in the geological record (Schlesinger, 1997). Global anthropogenic emissions of SO_2 have increased about twenty-fold since 1850 with the most rapid increase in Europe and North America between 1940 and 1970 (Brimblecombe et al., 1989). Using stable isotope analysis at the Rothamsted Plots (UK) it was estimated that anthropogenic S contributed 62 to 78% of the S uptake by wheat at the peak of SO_2 emission and accounted for 28 to 37% of topsoil S in 1965 (Zhao et al., 1999).

In Alberta natural SO_2 emissions have been estimated at 34,000 to 43,000 tonnes $year^{-1}$ and anthropogenic emissions are approximately 300,000 tonnes $year^{-1}$ (Sandhu, 1970; Nyborg et al., 1980). The largest emitter of sulphur oxides is the petroleum industry including natural gas processing and oil sands plants, followed by coal-fired electric generating stations; smaller contributors include pulp and paper, chemical and fertilizer industries, highways and urban centres (Palmer and Trew, 1987; Legge, 1988). The acidity of rainfall is usually not of consequence in central Alberta (Walker et al., 1980; Nyborg and Walker, 1977), however all S compounds may undergo acidifying reactions in the soil (Caiazza et al., 1978). Direct absorption appears to be the most important mechanism of SO_2 deposition to soil surfaces (Nyborg and Walker, 1977).

Sulphur deposition reports in Alberta have varied greatly. In central Alberta, rain and snow contained 2 to 4 kg S ha^{-1} yr^{-1} (Walker, 1969); in more remote areas estimates were 1 to 2 kg S ha^{-1} yr^{-1} (Walker et al., 1980). The provincial average for total S deposition has been measured at 9.3 kg ha^{-1} yr^{-1} (Palmer and Trew, 1987) however total S gain in potted soils downwind from a large emitter was as high as 12 to 53 kg S ha^{-1} in one summer (Nyborg et al., 1977). Dry deposition exceeds wet deposition in Alberta (Nyborg et al., 1991); near Edmonton the ratio of dry to wet S deposition was 4.8 (Caiazza et al., 1978).

It has been speculated that sulphur deposition has played a role in yield trends observed at the Breton Plots. More specifically, it was hypothesized that increased oil activity in the area resulted in S addition to the atmosphere and the soil (Robertson, 1991). The Breton area has been reported to receive on average 7 kg S ha^{-1} yr^{-1} total deposition (Legge, 1988) and more recently ~3.4 kg S ha^{-1} (0.21 k_{eq} H^{+} $ha^{-1}y^{-1}$) total deposition at a monitoring site near the Breton Plots (West Central Airshed Society, 2003).

1.1.3 Effect of Long-term Agricultural Management on Soil Properties

Long-term agricultural experiments have proven to be valuable for assessing the interaction among soils, climate, crops and people (Izaurralde et al., 1995). They have provided reliable information on a wide range of topics, including: climate-induced variability in yields, low-input farming practices, the effects of manure and chemical fertilizers on crop production, cultivation-induced changes in soil organic matter (SOM) and soil quality and weed control efficacy (Haugen-Kozyra et al., 1997). The Breton Plots have been a valuable resource for researchers and farmers throughout Alberta and remain so today, particularly since we can now study long-term effects of farm management practices. The

Breton Plots are the only long-term plots on Luvisolic soil in North America and possibly world-wide.

1.2 Breton Plots

1.2.1 History and Site Description

The Breton Plots, located near the town of Breton, 110 km southwest of Edmonton (53° 05' 9.5" N, 114° 25' 49.4" W), were established by the University of Alberta in 1929 to find "a system of farming suitable for the wooded soil belt" (Robertson, 1979). They are located on 4.5 ha of glaciated landscape with slopes ranging from 1 to 4%. The dominant soil is an Orthic Gray Luvisol (Breton loam), with some inclusions of a Gleyed Gray Luvisol (Warburg loam) and small tongues of a Humic Gleysol developed on alluvial-lacustrine material. The climate is cryoboreal subhumid with annual precipitation of 547 mm and mean annual air temperature of 2.1°C (Izaurralde et al., 1993). The Classical Plots were designed to test two cropping systems: continuous wheat and a four-year rotation consisting of wheat, oats, barley (under-seeded with forage) and forage (Bentley et al., 1971). Initially the experiment consisted of five blocks of land, designated series A to E, each divided into eleven strips for the various soil amendments. Block E contained continuous wheat and blocks A to D each represent one year of the 4-year rotation. Soil amendments included several combinations of nutrients: nitrogen (N), phosphorus (P), potassium (K) and sulphur (S) in addition to lime (L) and farmyard manure (Robertson and McGill, 1983). An additional block of land, series F, was added in 1938 expanding the four-year rotation into a five-year rotation by adding a second year of forage. In 1941 series E, was split in half creating the present day wheat-fallow rotation that alternates from the east to the west half of the series (Figure 1.1).

The forage species have changed over time however they have always contained at least one legume species for N_2 fixation. The rate and method of soil amendment has also changed since the founding of the plots. Originally all fertilizers were broadcast annually, from 1946 to 1964 fertilizers were added every second year, and annual fertilization was resumed in 1965 (Table 1.1). In 1972, the east half of all plots in series A, B, C, D and F, and both sides of the plots in series E were limed to pH 6.5 in response to acidity problems as revealed by low alfalfa yields (Juma et al., 1997). Fertilizer rates were increased in 1980 and brought up to common farm application rates (Table 1.1 and Table 1.2). The N application rate in the five-year rotation is dependant upon the year in the rotation (Table 1.2). In 2001, oats were removed from the five-year rotation and replaced with a second year of barley to allow for better control of wild oats; oats had not been returned to the rotation as of 2005. Grain crops are harvested in the fall and forage crops are cut in early July. First year forage is cut a second time in September while second year forage is clean cultivated for the remainder of the growing season. Prior to 2000, only stubble ~15 cm tall was left on the plots following harvest. Since 2000, straw is left on the plots following wheat and the first year of barley. It is removed from the second year of barely to avoid suppressing the underseeded forage crop. All plots not designated for forage the following season are tilled annually (Juma et al., 1997).

1.2.2 Major Findings at the Breton Plots

There have been many important findings from the research at the Breton Plots including: attribution of increased productivity to addition of manure or chemical fertilizers, including S containing fertilizers; attribution of soil acidification to use of ammonia containing fertilizers; and attribution of SOM increases to extended crop rotations (Bentley et al., 1971; Robertson and McGill, 1983; Juma et al., 1997). Other findings include an increased understanding of: nutrient deficiencies, liming, soil tilth, quality of feeds, carbon sequestration and greenhouse gas evolution (Bentley et al., 1960; Robertson, 1979; Juma et al., 1997; Carcamo, 1997; Janzen et al., 1998; Lemke et al., 1998; Izaurralde et al., 2001; Grant et al., 2001).

Gray Luvisols were identified to be deficient in S after decades of debate between prominent researchers in the University of Alberta's Soil Science department. The need of sulphur as a fertilizer was often overlooked as only legumes were thought to benefit from additional S. The confusion was finally clarified when it was noted that S and N produced large increases in yield when applied together in grasses (non-legumes) (Nyborg and Bentley, 1971). It is now accepted that many Luvisols are deficient in both N and S and that application of both is required for non-legumes but that only S is necessary for inoculated legumes (Robertson, 1979).

Cultivation and disturbance of soil has substantially decreased both SOM concentration and total mass (Jenny, 1941; Jenkinson, 1981 ; McGill et al., 1988). Soil management practices that have caused the greatest decline of SOM are summer-fallowing, intensive tillage and removal of crop residues (McGill et al., 1988; Rasmussen and Collins, 1991). Specific crop and soil management practices such as elimination of summer-fallow, reduced tillage/direct seeding, crop rotations including forage grasses and legumes, the use of fertilizers, and use of green or farmyard manure may return SOM to the soil (McGill et al., 1986; Janzen, 1987; Campbell et al., 1991; Nyborg et al., 1995; Riffaldi et al., 2001), because they either increase carbon inputs and or reduce losses. Legume based systems resulted in the highest SOM increases compared to rotations without legumes (Howieson and Ewing, 1986). After fifty years at the Breton plots the five-year rotation contained approximately 20 percent more SOM than the two-year rotation (McGill et al., 1986). This was attributed to continuous cropping and the inclusion of legumes in the five-year rotation (Robertson, 1991). Also SOM was greater in fertilized plots than control plots because adding nutrients resulted in increased plant growth, which in turn increased organic material in the roots and stubble thus increasing organic inputs to the soil. Finally SOM was greater in the manure-amended plots than in those receiving commercial fertilizer because in addition to crop response to nutrient addition, manure also is an organic input to the soil (Robertson, 1991).

1.2.3 Yield Trends on the Classical Breton Plots

Five-year running averages of wheat yield and first year forage yield are shown in Figure 1.2 and Figure 1.3. These yield trends contradict our understanding of the effects of management practices on crop yields.

The NPKS plots had very high forage yields (4 to 6 t ha^{-1}) until 1955, lower yields (~3 t ha^{-1}) were obtained from 1955 to 1967 and still lower yields (~2 t ha^{-1}) from 1967 to 1979. This decline in forage yield is likely due to the gradual acidification of soil through the application of ammonia-containing fertilizers (21-0-0 and 16-20-0) (Juma et al., 1997). Further evidence for this is revealed by the relative composition of forage species. Legumes species are sensitive to soil acidity; alfalfa is particularly sensitive but red clover is more tolerant. Unpublished comments in the Breton Plots yield ledger noted that the forages were dominantly red clover (although both red clover and alfalfa had been planted) in 1952, 1954 and 1955. In 1967 red clover was removed from the rotation and forage yields dropped dramatically. From ~1967 to 1980 NPKS plot forage yields were about the same as the check plot yields. The application of lime in 1972 increased forage yields somewhat, however yields decreased again in the latter part of the 1970's. In 1980 the rates of N, P, and K fertilizers were increased but the rate of S was decreased. Yields were then higher than the late 1970's however they were still lower than the 4 to 5 t ha^{-1} level they had reached at their peak. It has been speculated that the S rate was limiting forage yields after 1980.

The check plots had low forage yields, near 1.0 t ha^{-1}, from 1935 to 1960. After 1960 check plot yields increased to 2 t ha^{-1}. Robertson (1991) speculated that increased oil drilling in the area increased S in the atmosphere and hence added some S to the soil. Since Luvisols of the Breton area are S deficient (Bentley et al., 1971), the additional S would be beneficial to forage crops that fix N_2. Over time this can lead to increased organic matter in the soil from increased plant biomass and this may be an additional factor in increasing yields. The increases may also be due in part to other positive rotation effects including reduction of diseases (Cook, 1988; Cook et al., 1987), reduced pest species (Olkowski, 1986; Bezdicek and Granatstein, 1989) and improved soil physical properties (Kirschenmann, 1989).

The NPK(-S) plots are complex to interpret due to the varied management they had in their history. Initially, the plot received lime (L) plus P amendment (Table 1.1). The forage yields were fairly high (reaching 4.5 t ha^{-1}) from 1930 to 1935, however they dropped rapidly, and were similar to check plot yields from 1950 to 1960. This was likely due to nutrient deficiencies. After 1964, the plot received LNPKS amendment and the forage yields increased. This plot may also have benefited from S obtained from the atmosphere as previously discussed. The fertilizer amendment was changed again in 1980 to NPK(-S) and yields declined again (Table 1.2).

Forage yields on manure plots ranged between ~ 2 to 3 t ha^{-1} from 1930 to 1950. After 1950 forage yields began to increase and reached ~4.5 t ha^{-1} in 1967. From 1967 onwards, the forage yield fluctuated between 2 and 5 t ha^{-1}. Increases in the manure plots are likely due to increased organic matter and S obtained from the atmosphere. By 1980 the manure plots were found to contain greater SOM in comparison with the check and NPKS plots (Robertson, 1991). Nutrient supply in manure can vary with the source, quality, decomposition level etc. of the manure applied therefore some variation may be due to the manure itself.

Wheat yield was highest on the NPKS plots from 1930 to 1967. After 1967, there was a distinct decrease in the NPKS plot yields until 1980. This decline in wheat yield was in part explained by the N status of the soil (Juma et al., 1997). As previously described, forage yields decreased markedly after 1967. With less legume growth, less N was fixed in the soil therefore N may have been deficient for wheat growth. The application of lime in 1972 increased forage growth and subsequently increased wheat yields. Increased cereal growth within a legume-containing rotation is typical and explained by increased nitrogen from N_2 fixation by legumes (Nambiar et al., 1982; De et al., 1983; Senaratne and Hardarson, 1988; Wani et al., 1994). Wheat yields continued to increase after 1980, when fertilizer rates were increased, and became comparable to the manure plot yields.

Wheat yields on the check plots were low (~1 t ha^{-1}) between 1930 and 1960. Wheat yields increased after 1960 and can likely be attributed to the increase in available N from the legumes in the forage crops.

The NPK(-S) plot had low yields, between 1 to 2 t ha^{-1}, from 1930 to ~1964. This can be attributed to nutrient deficiencies (including S) because these plots received only LP amendment during these years. Yields increased to 2 to 3 t ha^{-1} between 1964 and 1980. During this time period the plots were amended with LNPKS removing much of the nutrient limitations of the plots. After 1980 the plots were amended with NPK(-S) and the rate of application was increased, however S was no longer applied to this plot. Wheat yields peaked around 1985 near 3.5 t ha^{-1} then decreased to remain at 2 to 2.5 t ha^{-1} from ~1985 to 2003. This may be due to decreases in legume growth after the removal of S in 1980.

Wheat yield on manured plots were at least two to three times greater than wheat yield on check plots from 1940 to 2003. The nutrients in manure were likely quite variable, however they were not measured prior to 1980. Yields fluctuated from year to year however the trend has been increasing overall and yields have doubled from 1930 to 2003. This can be attributed to increases in SOM and other positive rotation effects as discussed previously.

1.3 Project Objectives

This project was undertaken because of some anomalies in the long-term yield trends and the speculation that S deposition in combination with soil amendments was affecting crop yields on the Classical Breton Plots. The project was split into two components: 1) analysis of archived soil samples and 2) simulation of S deposition in a greenhouse experiment. Archived soil samples from the Breton Plots were analysed to assess changes in chemical properties including: total C and C:N ratio, pH, exchangeable acidity, exchangeable Al and Mn, effective cation exchange capacity (CEC_e), and base saturation.

Simulation of S addition to soil samples in the greenhouse experiment tested the response of alfalfa *(Medicago sativa)* and wheat *(Triticum aestivum)* to different levels of acidic input while growing on soils from the check, manure, NPKS and NPK(-S) plots and the adjacent natural area. Soil chemical properties were analysed after plants were harvested. The objectives of this experiment were to: 1) measure changes in soil chemical properties including: pH; exchangeable Al and Mn; exchangeable acidity; CEC_e; electrical conductivity (EC); and base saturation and, following varying applications of H_2SO_4 on Breton Plots soil; 2) measure yield response of wheat and alfalfa grown on soils from different long-term management plots (check, manure, NPK(-S), and NPKS) to S amendment; and 3) look for relationships between soil chemical properties and crop yields.

Chapter two will consist of the analysis of the long-term changes in soil chemical properties using the archived soil samples of the Breton Plots. Chapter three consists of the greenhouse experiment and chapter four contains the conclusions and synthesis. Extra data are contained in the appendix section.

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1.5 Tables and Figures

Table 1.1 Approximate fertilizer, manure and lime application rates to the Breton Classical Plots for the period 1930-1979[a]. Adapted from Cannon et al (1984)

Plot	Treatments 1930-1979	Nutrients added (kg ha^{-1} y^{-1}) N	P	K	S[e]
1	Check	0	0	0	0
2	Manure (M)[b]	76	42	91	20
3	NPKS	10	6	16	10
4	NS	11	0	0	11
5	Check	0	0	0	0
6	Lime (L)	0	0	0	0
7	LNPKS[c]	0(11)	10(6)	0(16)	1(9)
8	P	0	9	0	1
9	MNPS	86	48	91	28
10	NPS	10	6	0	8
11	Check	0	0	0	0

[a] In 1944-1963, fertilizer was applied every second year at rates approximating N (9), P (5), K (14) and S (8) kg ha^{-1} each year.

[b] Applied every fifth year, in later years at 44 t ha^{-1}. Nutrient rates are annual equivalents and are estimates based on manure applied from 1976-1986 inclusive.

[c] This treatment was initially a lime (L) plus phosphorus (LP) treatment. In 1964, it became LNPKS. Nutrient application rates after 1964 are shown in parentheses.

[d] Lime was broadcast and tilled onto plot 6 and 7 several times between 1930 and 1948 for a total application of approximately 6.6 t ha^{-1}. No lime was applied to plots 6 and 7 between 1949 and 1971, but Series E and the east half series A, B, C, D and F were limed where necessary to pH 6.5 in 1972.

[e] All S was added as SO_4^-.

Table 1.2 Revised treatments and fertilizer and manure application rates to the Breton Classical Plots from 1980 onwards. Adapted from Cannon et al (1984)

Plot	Treatments 1980-current	Nutrients added ($kg\ ha^{-1}\ y^{-1}$) N	P	K	S[d]
1	Check	0	0	0	0
2	Manure	a	-	-	-
3	NPKS	b	22	46	5.5
4	NKS(-P)	b	0	46	5.5
5	Check	0	0	0	0
6	Lime	0	0	0	0
7	NPK(-S)	b	22	46	0
8	PKS (-N)	0	22	46	5.5
9	NPKS[c]	b	22	46	5.5
10	NPS(-K)	b	22	0	5.5
11	Check	0	0	0	0

[a] N application via manure depends upon the rotation. The 2-yr wheat-fallow rotation receives equivalent of 90 kg N ha^{-1} for each wheat crop. The 5-yr cereal-forage rotation (wheat, oat, barley, forage and forage) receives 176 N ha^{-1} every 5 years. Since 1980, manure is added at the rate of 88 kg N ha^{-1} per application after oat harvest and at the time of second forage plough down.

[b] N amounts depend on the crop and its place in rotation: Wheat after fallow 90 kg ha^{-1}; wheat after forage 50 kg ha^{-1}; oat after wheat 75 kg ha^{-1}; barley after oat 50 kg ha^{-1}; legume-grass forage after barley 0 kg ha^{-1}:forage after forage 0 kg ha^{-1}.

[c] The soil in the NPKS treatment of plot 9 ripped to a depth of 75 cm in 1983.

[d] All S added as elemental S.

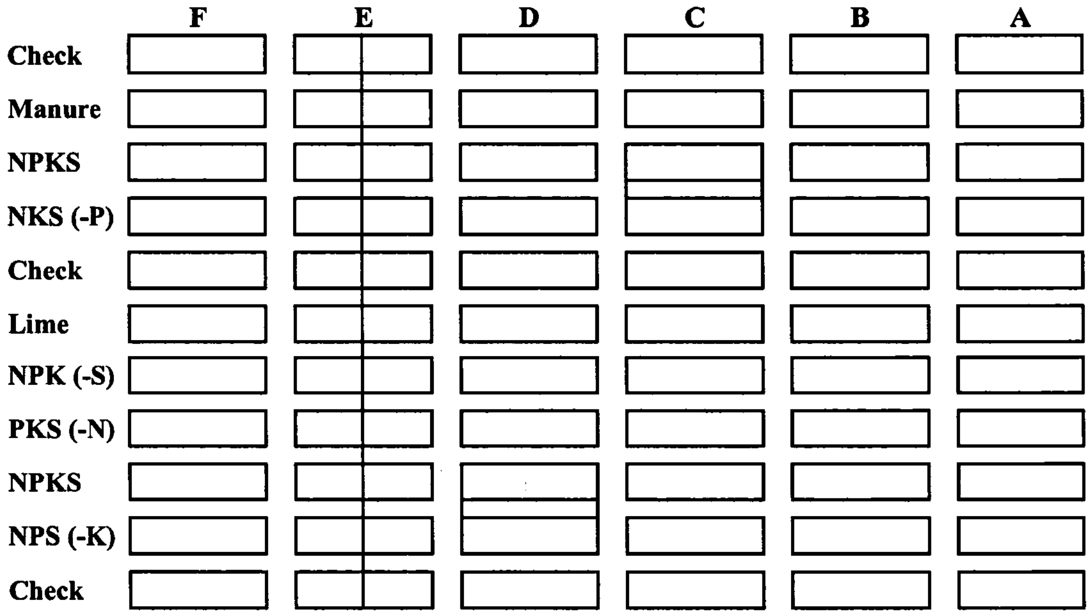

Figure 1.1 Layout of the Classical Breton Plots. The line in series E depicts the separation of the two-year rotation. N ↑

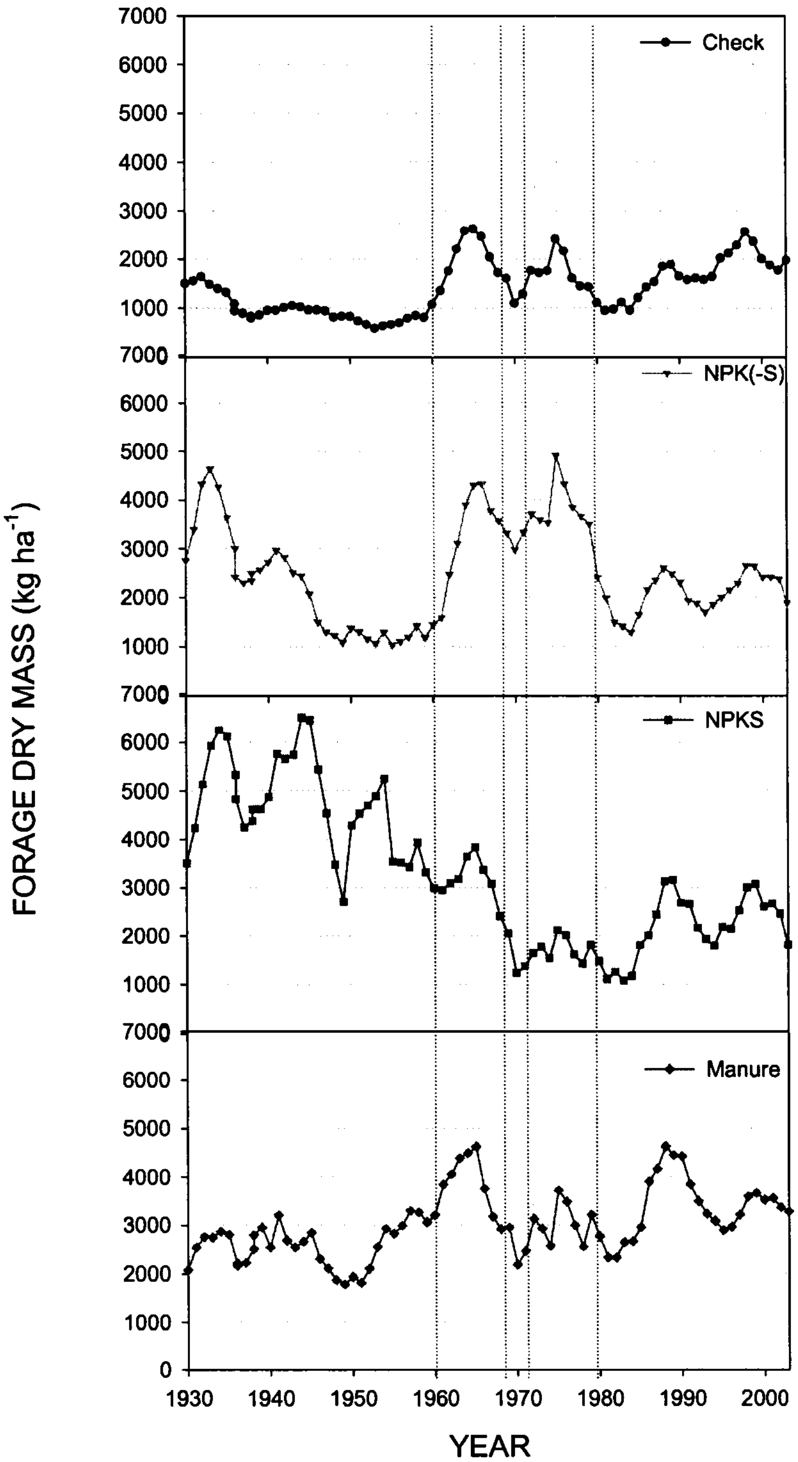

Figure 1.2 Five-year running averages of first year forage yield (first cut) on selected Classical Breton Plots from 1930-2003 (limed half after 1972) in the five year rotation

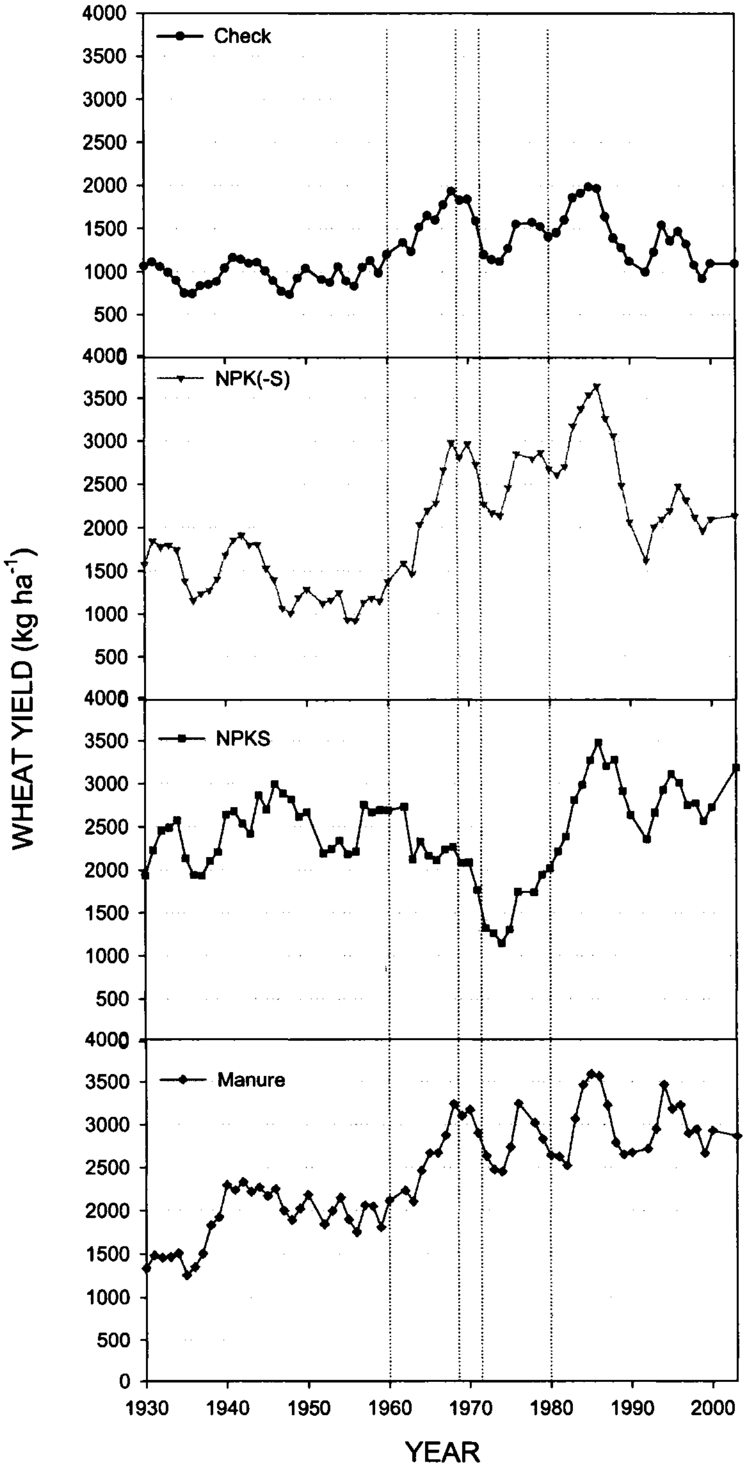

Figure 1.3 Five-year running averages of wheat (grain) yield on selected Classical Breton Plots from 1930-2003 (limed half after 1972) in the five-year rotation

2 Changes in Soil Chemical Properties in the Classical Breton Plots from 1972-2003

2.1 Introduction

It is clear that soil management has the potential to distinctly alter soil quality in the long-term. Sustainability of cropping systems is largely determined by the effects of management practices on soil properties as these relate to the capacity of soil to function (Karlen et al., 1997). Research plots, such as the Breton Plots, provide the opportunity to observe the effects of agricultural practices on soil productivity in the long-term and have proven to be valuable and reliable tools for assessing the interaction between soils, climate, crops and people (Izaurralde et al., 1995). They also assist agriculturists in designing agricultural systems that are environmentally sustainable (Karlen et al., 1994).

The Classical Breton Plots are long-term plots on Luvisolic soil and are currently entering their seventy-sixth year of research and production. They were initiated in 1929 near the town of Breton, approximately 110 km SW of Edmonton, to find "a system of farming suitable for the wooded soil belt" (Robertson, 1979). They consist of six series of land (A-F) with eleven plots each and encompass a two-year rotation and a five-year rotation (Figure 2.1). Soil amendments include manure, lime and several fertilizer combinations.

Yield data has been recorded at each harvest, as shown in Figure 2.2 and Figure 2.3. Overall, the manure, check, and NPK(-S) plots wheat yields have exhibited trends that increase over time; however the NPKS plot had a fluctuating trend. Decreases in wheat and forage yields of the NPKS plots between 1960 and 1979 have been attributed to the gradual acidification of soil by the application of ammonia-containing fertilizers (21-0-0 and

16-20-0) and the N status of the soil (Juma et al., 1997). Legumes, particularly alfalfa, are sensitive to soil acidity. When legume growth decreased, root nodules fixed less N and wheat yields in following years were subsequently reduced. Once the fertilizer rate was increased in 1980, increasing the N supply, wheat yields in the NPKS plots increased and reached levels comparable to the manure plot yields.

Increases in yields of the check, manure and NPK(-S) plots were in part due to increased forage yields. The average of first-year forage yields on the check plots increased to 2 t ha^{-1} after 1960. It was speculated that increased sulphur (S) in the atmosphere from oil and gas activity in the area added S to the soil through deposition. The Luvisols of the Breton area are deficient in S (Bentley et al., 1971). Therefore the addition of S would be beneficial to legume crops (because they fix N_2) and lead to increased yields. Yield trends would also be affected by seasonal variations in precipitation and pest species, however these effects were minimized by using the 5-year running averages.

It was hypothesized that management practices at the Breton Plots have modified soil quality in relation to changes in yield trends. Hence the objective of this study was to evaluate changes in soil properties due to management practices over time. Archived soil samples from the Breton Plots were analysed to assess changes in chemical properties including: total C and C:N ratio, pH, exchangeable acidity, exchangeable Al and Mn, effective cation exchange capacity (CEC_e) and base saturation. It was hypothesized that soil chemical properties would vary distinctly as a function of the amendments applied.

Long-term manure plus lime amendment was hypothesized to have improved soil quality by increasing total C, CEC_e and base saturation while simultaneously reducing exchangeable Al and Mn and exchangeable acidity. Amendment with chemical fertilizers

(NPKS and NPK) plus lime was also expected to have increased total C, CEC_e and base saturation while reducing exchangeable Al and Mn and exchangeable acidity; however the effect was expected to be smaller than with manure amendment because of the acidifying effect of chemical fertilizers. Lime only amendment was hypothesized to have decreased total C and CEC_e and increased base saturation; few changes were anticipated in exchangeable Al and Mn and exchangeable acidity for this treatment.

2.2 Materials and Methods

2.2.1 Soil Analyses

Stored soil was collected from the archives of the Breton Plots for analyses as shown in Table 2.1. The check, manure, NPK(-S) and NPKS plots were selected for the study. The amendment history of the Classical Plots has varied over time and is shown in Table 2.2 and Table 2.3. Soil samples were air dried and sieved (<2 mm) at the time of storage. The pH values of most archived soil samples were determined in suspension with water (usually a 1:5 soil to water ratio) at the time of collection. To conserve samples, pH measurements were not duplicated in this study, and previously recorded data were used instead. While current pH meters have an accuracy of ± 0.002, technology has improved since these data were collected, and the precision of the pH data set is probably lower than can be provided by current instrumentation.

Exchangeable cations were extracted by 0.1 M $BaCl_2$, a neutral salt, to preserve the "field" pH of the soils during the extractions (Hendershot and Duquette, 1986). Concentrations of the cations in the extract solutions were determined by atomic absorption spectrophotometry (AAS). The AAS precision is indicated by the standard deviations for the standards run after every 14 samples for Ca, Na, K, Mg, Mn, and Al respectively: 0.94, 1.19, 1.39, 0.70, 0.16 and 0.49 mg L^{-1}. CEC_e was calculated as the sum of Ca^{2+}, Mg^{2+}, Na^+, Al^{3+}, K^+, and Mn^{2+} (Hendershot et al., 1993b). Base saturation (BS) was calculated from the concentrations ($cmol_c$ kg^{-1}) of exchangeable cations extracted by $BaCl_2$ as:

$$\%BS = \frac{(Na^+ + K^+ + Ca^{2+} + Mg^{2+})}{CEC_e} \times 100$$

Exchangeable acidity was determined by extracting soil samples with 1 M KCl and titrating the filtrate with 0.01 M NaOH to the phenolphthalein endpoint (Thomas, 1982). Samples were run in duplicate and results were averaged to minimize the effect of operator error. The amount of exchangeable acidity (Al^{3+} plus H^+) was calculated based on the amount of NaOH required to reach the endpoint (pH approximately 8.3) (Hendershot et al., 1993a). The precision of this method was ± <5%.

To determine total C and N, sub-samples were ground in a ball grinder to 150 μm and dried overnight at 70°C; approximately 50 μg of ground soil was weighed and encapsulated in tin for combustion analysis. Percentage of C and N were measured with a Carlo-Erba elemental analyser (model NA-1500, Carlo-Erba Inc., Milan, Italy). The precision of this instrument was found to be ± 0.013% for N and ± 0.004% for C.

2.2.2 Statistical Analyses

The Classical Breton Plots do not contain treatment replicates; therefore statistical analyses of the data cannot be conducted. The plots originated before modern statistics were used and their creators did not predict that the University of Alberta would maintain these plots in the long-term. Studies on these plots benefit from accumulated background information including knowledge of soil treatment, cropping history and system performance (Wani et al., 1994) and therefore are valuable despite the statistical limitations of the design.

2.3 Results

The plots were limed periodically to bring the soil to pH 6.5. Liming history of the plots used in the experiment (Table 2.4) was compiled to assist in the interpretation of the results because many of the chemical properties tested are strongly influenced by liming.

Total C showed an increasing trend over time in all soils, although some of the trends exhibited many fluctuations and were not clear (Table 2.5). Total C was generally highest in the manure plots and lowest in the check plots. Overall values were higher in series F than series A and C. The C:N ratios ranged from 10.48 to 12.35 (Table 2.6). They appeared to be lower in series F than series C and lower in series C than series A. Trends due to soil amendment varied among the series and were not well defined.

Soil pH varied over time among series and soil management (Table 2.7). The pH values were higher in series F than series A and C. Generally pH increased over time in the limed check, manure and NPKS soils but remained fairly consistent in the NPK(-S) soil. Soil amendment at the Breton Plots had a more distinct effect on pH values prior to lime application in 1972. The NPK(-S) plots (the only plots that received lime prior to 1972) had the highest pH values in 1972, but there were fewer differences among plots after 1972. The NPKS plots had the lowest pH values on many sampling dates likely because of the acidifying effect of N (NH_4^+) fertilizer application over forty years. Prior to 1980 S was added as SO_4 and would not be acidifying. However after 1980, S was added as elemental S which can also acidify soil upon oxidation.

Exchangeable acidity decreased in all plots over time resulting in very little variation among plots after 1990 (Table 2.8). The exchangeable acidity values in the NPK(-S) and manure plots were low (<0.1 $cmol_c\ kg^{-1}$) in all years. The values for the check and NPKS plots in series A and C, were higher at the earlier sampling dates but decreased over time. In 1972 these two plots had lower exchangeable acidity values in series F than in series A and C. From 1990 to 2003 the values of the NPKS and check plots were similar to those of the NPK(-S) and manure plots.

Exchangeable Al fluctuated in the plots over time and varied among the series (Table 2.9). Exchangeable Al was below its detection limit of 0.03 $mg\ L^{-1}$ in most plots prior to 1990; however after 1990 it was detected in most plots. Exchangeable Al values in series A (with the exception of the NPKS plot) were greater in 1990 than in previous years. In series C and F exchangeable Al was greater in 1998 than in previous years. The NPKS plot in series A and C had the highest amounts of exchangeable Al in 1972 before liming decreased the values.

Values for exchangeable Mn were mostly in the toxic range using the limit of 0.074 $cmol_c\ kg^{-1}$ (20 ppm) as defined by McCoy (1977). All values were below the toxic level in 2003 following recent liming (Table 2.10). Overall exchangeable Mn generally was lowest in series A and highest in series C. Also for series C, fluctuations with time in the amounts of exchangeable Mn were higher than for the other two series.

Soil CEC_e measurements varied with soil management and among series (Table 2.11). In general the CEC_e increased in the check, manure and NPKS soils over time, primarily between 1998 and 2003. CEC_e values in the NPK(-S) plots fluctuated over the years. Overall values were highest in series F and lowest in series A and these differences became more apparent over time. When soil pH was plotted against soil CEC_e values for all plots and series (Figure 2.4), the observed correlation indicated that pH-dependent CEC is a factor in these soils (r=0.79, p=<0.001).

Base saturation was greater than 97% in most samples (Table 2.12). Samples below 97% were mainly in the NPKS plots and had values between 95 and 96%. Base saturation increased over time, especially from 1998 to 2003, i.e. within the time period of the most recent liming. In 1972, base saturation was marginally higher in series F than in series A and C. However the differences were very small and all series became more similar over time.

2.4 Discussion

The usefulness of stored soils from long-term experiments is often questioned because changes may occur during storage (Blake et al., 2000). A study conducted on archived samples from the Rothamsted plots found no significant changes linked to storage in total C and N, and only small changes in exchangeable cations (Blake et al., 2000). They concluded that after two to three months of storage, chemical properties of the samples attained equilibrium, and that any changes in the chemical properties of air-dried archived soils were smaller than those caused by management and atmospheric inputs (Blake et al., 1999; Blake et al., 2000). The archived soils used in my study were also air-dried prior to storage; therefore it is unlikely they have changed much since their sampling date with respect to most of their properties.

In analysing the Classical Breton Plots soils, caution must be exerted when discussing results. As mentioned in the methods section, the plots were not designed with replication in mind, which precludes the use of statistical analyses. While data precision can be defined with regard to laboratory analyses, field spatial variability and potentially statistically significant differences among soil management types cannot be quantified from the soil samples that were archived. However, results from the Classical Breton Plots are valuable for the unique long-term record they provide.

Carbon contents measured in this study (Table 2.5) were comparable to previous SOC results from the Breton plots. Carbon was found to be greater in the manure amended plots than in those receiving chemical fertilizer because, in addition to crop response to nutrients contained in manure or fertilizers, manure also constitutes an organic input to the soil (Robertson, 1991). Previously, carbon was found to be increasing in the check plot soil from 1936 to 1990 and in the manure and NPKS plots from 1972 to 1990 (Izaurralde et al., 2001). The largest changes were observed in the manure plots, and the smallest change in the check plots. Fertilization leading to increased organic C has been shown in many long-term experiments and its effect is dependant on the rate and type of fertilizer applied. Manure application usually increases the organic C content of soils to a greater degree than chemical fertilizer application (Malhi et al., 1991; Robertson, 1991; Schjønning et al., 1994; Malhi et al., 1997). Izaurralde et al. (2001) stated that after fifty-one years the soil still appeared to be gaining C in the five-year rotation. My results confirmed that soil C increased between 1990 and 2003 (Table 2.5). Increases in soil C in the five-year rotation are assumed to be a result of rotation and fertilizer effects. Other factors that may play a role include changes in soil amendment rates in 1980, increases in legume yields due to liming, atmospheric deposition, the decrease in sampling depth in the latter sampling years and/or other unknown factors. The C:N ratios were found to be relatively stable over time (Table 2.6). A previous study at the Breton Plots also showed fairly stable C:N ratios in the NPKS and manure plots from

1972 to 1990 and a small decreasing trend in the check plot from 1938 to 1990 (Izaurralde et al., 2001).

The pH values were lower at the NPKS plots than the others plots prior to liming in 1972 (Table 2.7). Long-term NH_4-based fertilizer application, such as those used at the Breton Plots, tends to result in soil acidification and increases in extractable Al and Mn (McCoy and Webster, 1977; Malhi et al., 1991; Malhi et al., 2000). By 1972 the pH of the NPKS plot had been reduced to 5.2 to 5.4. Soil pH at the Breton Plots was reported to range from 5.2 to 6.7 in 1929 depending on the month of sampling (Newton, 1931) and from 6.0 to 6.4 in 1936 (Odynsky, 1936). Although there may be discrepancy between these two records, it appears that the soil pH was higher when the plots originated than in 1972. This decrease in pH was attributed to the acidifying effect of N fertilizers (McCoy and Webster, 1977). Trends in the archived pH data are difficult to assess, as some of the variability in the results may be due to differences in tillage and sampling depth, differences in sampling dates, as well as difference in laboratory methods. However, some trends were evident in the data. pH values were higher in the NPK(-S) plots than in the other plots in 1972. This may be explained by the varied history of the NPK(-S) plot (Table 2.2). From 1930 to 1963, this plot received lime plus P amendment, and, from 1964 to 1970, lime plus NPKS amendment. It was changed to the current NPK(-S) amendment in 1980. Therefore the NPK(-S) plots did not receive any N fertilizer until 1964, after which time the rate was low at 11 kg ha^{-1}. Therefore lime applied throughout the history of the NPK(-S) plots probably resulted in the higher pH values observed for these plots in 1972.

The pH values of the manure plot were very similar to those of the check plot indicating that manure did not affect pH (Table 2.7). Many studies have found increased pH values in acid soils amended with fresh and composted manure (Iyamuremye and Dick, 1996; Cooper and Warman, 1997; Whalen et al., 2000; Whalen et al., 2002) therefore these results were unexpected. Nonetheless manure amendment has also been shown to have no effect or to decrease soil pH in some cases (Sommerfeldt et al., 1973; Ndayegamiye and Côté, 1989; Chang et al., 1990). pH values in all plots increased in response to lime application (Table 2.7). These changes in pH were accompanied by decreasing trends in exchangeable acidity, and increases in base saturation (Table 2.8 and Table 2.12). Any differences in pH results post-liming cannot be attributed to differences in soil management because of the over-riding influence of lime.

Exchangeable Al can be considered toxic for plants at 0.017 $cmol_c\ kg^{-1}$ (1.5 ppm) according to McCoy (1977). By this standard many of the soil samples tested had toxic amounts of Al (Table 2.9). However, the toxic limit refers to the amount of Al extracted by 0.05 M $CaCl_2$ (McCoy and Webster, 1977) and not to the more concentrated extractant (0.1 M $BaCl_2$) that I used for my analyses. Hence the actual limit for my experiment is likely higher than that expressed by McCoy. For this reason it is unclear if exchangeable Al is toxic, borderline, or at acceptable levels in my samples. Exchangeable Al values still had a tendency to increase in the plots in the later sampling years despite periodic liming and near neutral pH values.

Exchangeable Mn can be considered toxic for plants at 0.074 $cmol_c\ kg^{-1}$ (20 ppm) (McCoy and Webster, 1977). Using this standard, exchangeable Mn has been toxic or borderline toxic in most, if not all, of the soil samples tested (Table 2.10). Exchangeable Mn levels decreased by 1990, and were below toxic level in all samples tested in 2003. Wheat and forage yields did not appear to be suffering from Mn toxicities in the last three decades

(Figure 2.2 and Figure 2.3), therefore this criterion for toxicity may be too strict. As with Al, the toxic limit refers to the amount of Mn extracted by 0.05 M $CaCl_2$ and not 0.1 M $BaCl_2$, therefore the actual limit is likely higher than that reported by McCoy.

McCoy identified a natural acidity gradient in two directions across the plots. Acidity increased from south to north and from west to east as shown by pH, Ca/Σ and H/Σ [where Σ is the sum of exchangeable Ca, Mg, Na, K, and titratable acidity (H^+)] (McCoy and Webster, 1977; McCoy, 1973). They speculated that the gradient was caused by variability in the vegetation cover during soil genesis. Soils of this area supported a mixed deciduous-coniferous forest, and variability in forest cover since the last glaciation could account for differences in soil acidity (McCoy and Webster, 1977). The pH, exchangeable acidity, exchangeable Al and base saturation results in 1972 (i.e.; before lime was applied to all of the plots), all support this pre-existing acidity gradient (Table 2.7, Table 2.8, Table 2.9 and Table 2.12). The pH values and base saturation were higher on average in series F than in series A and C, and the exchangeable acidity and exchangeable Al were found to increase from west to east. Lime applications were calculated based on the amount required to bring the soil pH to 6.5 (Table 2.4). The amount of lime applied to series A and C was greater than in series F, again supporting the east to west pH gradient observed by McCoy (1977). Exchangeable Al appeared to be associated with low pH in the NPKS plots of series A and C in 1972. Exchangeable Mn did not seem as strongly tied to the low pH values, as it was high in a large number of plots that did not show corresponding low pH values. While my results are typical of the dependence of exchangeable Al on pH, they contradict the literature on Mn because low soil pH typically has been shown to increase the solubility of both Al and Mn (O'Hallorans et al., 1997; Hue and Licudine, 1999).

CEC_e values of the manure plots were highest, or among the highest in all series (Table 2.11). All of the plots showed increased CEC_e from 1972 to 2003, which implies that increases are in-part due to the crop rotation while the differences among plots can be attributed to soil amendment. Other long-term studies have found that CEC increased with manure and fertilizer application because of increases in soil organic matter levels (Ndayegamiye and Côté, 1989; Gao and Chang, 1996; Schjønning et al., 2000). At the Breton Plots, it is also possible that with time, continued cultivation and soil sampling for research purposes has brought up materials from the Bt horizons closer to the surface (i.e.; within the sampling depth), which would have resulted in an increase in clay that directly contributes to CEC. It is also possible that sampling depth varied due to compaction of the soil at the time of sampling. pH was plotted against CEC_e for all soil samples (Figure 2.4). The trend shows a pH dependent CEC_e that is similar in all series. pH dependent CEC is typically due to the pH dependent charges of soil organic matter and clay particles. The dominant clays at the Breton Plots are smectites (Crown and Greenlee, 1978), which have high CEC ranging from 60 to 136 $cmol_c\ kg^{-1}$ (Borden and Giese, 2001). Organic matter also has a very high CEC, on average 200 $cmol_c\ kg^{-1}$ or higher (Stevenson, 1994). Although neither clay nor organic matter is typically high in the A horizon of a Gray Luvisol, their high CEC values can explain the range in CEC_e reported in Figure 2.4.

2.5 Conclusions

Soil chemical properties have been changing over the last thirty years of management at the Breton Classical Plots but many properties were not found to be distinctly altered by soil amendments. Although there were some differences among soil management types there were also differences attributed to the series confounding these results. Differences among the series appeared to be more important in some cases than differences in soil management. In particular, pH and base saturation were higher in series F than in series A and C regardless of soil management. CEC_e was higher in series F than in series A, and exchangeable Mn was higher in series C than in series A. Variations among the soil series may be explained by a pre-existing, natural acidity gradient increasing from south to north and west to east. The amount of variation among the series at the Breton Plots indicates that these plots are pseudo replicates of each treatment and must be looked at separately.

Lime amendment has had a considerable effect at the Breton Plots, resulting in increased pH, increased base saturation, decreased exchangeable acidity and possibly decreased exchangeable Al and Mn. Total C has been increasing in all plots, which may be partially due to the five-year rotation; however there are differences among plots indicating that soil amendment has also affected total C by affecting the amount of plant growth and subsequent plant residue inputs to the soils.

The plots receiving manure plus lime amendment seemed to show an improvement in quality as indicated by increases in total C, base saturation, and CEC_e over time, and decreases in exchangeable acidity, exchangeable Al and Mn. The manure plus lime treatment plots had the highest amount of total C, but the lowest amount of exchangeable acidity and among the highest CECe of all plots.

The NPKS and NPK(-S) plots also showed an increase in quality over time as shown by increases in total C and base saturation, and decreases in exchangeable acidity, exchangeable Al and Mn. The pH and CEC_e values increased in the NPKS soils following the addition of lime in 1972. In the NPK(-S) plots, neither pH nor CEC_e appeared to change much after 1972; however this treatment had received additions of lime earlier than the NPKS plots, and did not receive N fertilizer in its earlier years.

Plots receiving only lime (check) also showed improving soil quality over time as indicated by increases in total C, pH, CEC_e, and base saturation and decreases in exchangeable acidity, exchangeable Al and Mn. The check plots had the lowest amount of total C, the highest pH and the among the highest exchangeable acidity values of all plots.

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2.7 Tables and Figures

Table 2.1 Archived Breton Plots soil samples[a] used in analyses

Year	Series A	Series C	Series F	Depth
1972	Manure NPKS Check NPK	Manure NPKS Check NPK	Manure NPKS Check NPK	0-15 cm
1977	Manure NPKS Check NPK	Manure NPKS Check	Manure NPKS Check NPK	0-15 cm
1978			Manure NPKS Check NPK	0-15 cm
1979	Manure NPKS Check NPK	Manure NPKS Check NPK	Manure NPKS Check NPK	0-15 cm
1983		Manure NPKS Check NPK		0-15 cm
1985			Manure NPKS Check NPK	0-15 cm
1990	Manure NPKS Check NPK	Manure NPKS Check NPK	Manure NPKS Check NPK	0-7.5 cm
1998	Manure NPKS Check NPK	Manure NPKS Check NPK	Manure NPKS Check NPK	0-7.5 cm
2003	Manure NPKS Check NPK	Manure NPKS Check NPK	Manure NPKS Check NPK	0-7.5 cm

[a] Samples from the east (limed) half of the plots were used

b Plot #5 was used for check plot analyses

c NPK(-S) plot was initially lime plus phosphorus treatment, in 1964 it became LNPKS, and in 1980 it became NPK(-S) treatment.

Table 2.2 Approximate fertilizer, manure and lime application rates to the Breton Classical Plots for the period 1930-1979[a]. Adapted from Cannon et al (1984)

Plot	Treatments 1930-1979	Nutrients added (kg ha^{-1} y^{-1}) N	P	K	S[e]
1	Check	0	0	0	0
2	Manure (M)[b]	76	42	91	20
3	NPKS	10	6	16	10
4	NS	11	0	0	11
5	Check	0	0	0	0
6	Lime (L)	0	0	0	0
7	LNPKS[c]	0(11)	10(6)	0(16)	1(9)
8	P	0	9	0	1
9	MNPS	86	48	91	28
10	NPS	10	6	0	8
11	Check	0	0	0	0

[a] In 1944-1963, fertilizer was applied every second year at rates approximating N (9), P (5), K (14) and S (8) kg ha^{-1} each year.

[b] Applied every fifth year, in later years at 44 t ha^{-1}. Nutrient rates are annual equivalents and are estimates based on manure applied from 1976-1986 inclusive.

[c] This treatment was initially a lime (L) plus phosphorus (LP) treatment. In 1964, it became LNPKS. Nutrient application rates thereafter are shown in parentheses.

[d] Lime was broadcast and tilled onto plot 6 and 7 several times between 1930 and 1948 for a total application of approximately 6.6 t ha^{-1}. No lime was applied to plots 6 and 7 between 1949 and 1971, but Series E and the east half series A, B, C, D and F were limed where necessary to pH 6.5 in 1972 and thereafter.

[e] All S was added as SO_4^-.

Table 2.3 Revised treatments and fertilizer and manure application rates to the Breton Classical Plots from 1980 onwards. Adapted from Cannon et al (1984)

Plot	Treatments 1980-current	Nutrients added (kg ha^{-1} y^{-1}) N	P	K	S[d]
1	Check	0	0	0	0
2	Manure	a	-	-	-
3	NPKS	b	22	46	5.5
4	NKS(-P)	b	0	46	5.5
5	Check	0	0	0	0
6	Lime	0	0	0	0
7	NPK(-S)	b	22	46	0
8	PKS (-N)	0	22	46	5.5
9	NPKS[c]	b	22	46	5.5
10	NPS(-K)	b	22	0	5.5
11	Check	0	0	0	0

[a] N application via manure depends upon the rotation. The 2-yr wheat-fallow rotation receives equivalent of 90 kg N ha^{-1} for each wheat crop. The 5-yr cereal-forage rotation (wheat, oat, barley, forage and forage) receives 176 N ha^{-1} every 5 years. Since 1980, manure is added at the rate of 88 kg N ha^{-1} per application after oat harvest and at the time of second forage plow down.

[b] N amounts depend on the crop and its place in rotation: Wheat after fallow 90 kg ha^{-1}; wheat after forage 50 kg ha^{-1}; oat after wheat 75 kg ha^{-1}; barley after oat 50 kg ha^{-1}; legume-grass forage after barley 0 kg ha^{-1}; forage after forage 0 kg ha^{-1}.

[c] The soil in the NPKS treatment of plot 9 ripped to a depth of 75 cm in 1983.

[d] All S added as elemental S.

Table 2.4 Liming[a] (kg ha^{-1}) on selected Breton Plots from 1972 to 2003

	Series A				Series C				Series F			
Year	Check	NPK	NPKS	Manure	Check	NPK	NPKS	Manure	Check	NPK	NPKS	Manure
1972	1618	1146	1752	1281	2354	1390	2466	1614	538	0	758	919
1982			4529	3341								
1984							5100					
1986											6622	
2001									3705	4618	4796	3705
2002	2777	3905	3705	1611								
2003					3705	4187	3905	3497				
Total	4395	5051	9985	6233	6059	5577	11471	5111	4243	4618	12176	4624

[a] Lime was applied as required to bring the pH up to 6.5

Table 2.5 Total C (%) of archived Classical Breton Plots soil samples, 5-year rotation, limed half of plots

						Breton Plot						
	Series A				Series C				Series F			
Year	Check	NPK	NPKS	Manure	Check	NPK	NPKS	Manure	Check	NPK	NPKS	Manure
1972	1.36	1.33	1.67	2.15	1.53	1.62	1.59	1.88	1.66	1.73	1.82	1.80
1977	1.33	a	1.59	1.81	1.29		1.88	3.12	1.81		2.02	2.25
1978									1.74	1.80	1.86	1.98
1979	1.15	1.37	2.01	2.04	1.71	1.48	1.43	2.02	1.64	2.06	1.84	2.38
1983					1.43	1.67	1.69	1.71				
1985									1.58	1.72	1.78	2.15
1990	1.25	1.38	1.59	1.99	1.54	1.47	1.54	2.30	1.73	1.86	1.78	2.45
1998	1.37	1.71	1.85	2.58	1.60	1.92	1.92	2.22	1.86	2.02	2.04	3.18
2003	1.43	1.73	2.16	2.47	1.92	1.91	2.02	2.38	2.22	2.20	2.39	3.10

[a] Blank cell indicates no archived sample was available for testing

Table 2.6 Soil C:N ratio of archived Classical Breton Plots soil samples, 5-year rotation, limed half of plots

	Breton Plot											
	Series A				Series C				Series F			
Year	Check	NPK	NPKS	Manure	Check	NPK	NPKS	Manure	Check	NPK	NPKS	Manure
1972	11.60	11.20	11.91	12.35	11.33	11.52	11.13	10.95	10.71	10.62	10.94	10.67
1977	11.47	a	11.68	11.62	11.03		11.26	11.21	10.58		11.44	11.23
1978									10.63	10.53	10.89	10.63
1979	11.31	11.11	12.48	11.91	12.98	10.55	10.59	10.78	10.30	11.01	11.02	11.57
1983					10.91	11.28	11.00	10.12				
1985									10.44	10.46	11.36	11.20
1990	11.17	10.58	11.10	11.25	10.79	10.72	10.62	10.59	10.51	10.51	10.70	10.68
1998	11.06	11.27	11.16	11.89	10.51	11.10	10.79	10.48	10.13	10.29	10.47	10.74
2003	11.62	10.99	11.80	11.30	10.90	11.41	11.14	10.92	10.87	10.77	10.69	10.64

[a] Blank cell indicates no archived sample was available for testing

Table 2.7 pH of Classical Breton Plots archived soil, 0-15cm, limed half of plots

	Breton Plot											
	Series A				Series C				Series F			
Year	Check	NPK	NPKS	Manure	Check	NPK	NPKS	Manure	Check	NPK	NPKS	Manure
1972	6.2	6.7	5.4	6.0	6.0	6.6	5.6	5.9	6.6	7.1	6.2	6.5
1978	a								6.1	6.1	5.5	5.8
1979	6.2	6.2	5.5	5.8	6.0	6.5	5.5	5.9	6.3	6.2	5.9	6.2
1983					6.1	6.5	5.7	6.2				
1985									6.5	6.5	5.9	6.5
1990	6.4	6.3	6.1	6.6	6.4	6.4	6.7	6.4	6.4	6.1	6.6	6.6
1998	6.3	6.0	6.3	6.9	6.0	5.8	5.9	6.3	6.3	6.1	6.0	6.4
2003	6.6	6.5	6.3	6.8	6.4	6.6	6.2	6.3	7.0	6.9	7.1	7.1

[a] Blank cell indicates no archived data found

Table 2.8 Exchangeable acidity ($cmol_c\ kg^{-1}$) of archived Classical Breton Plots soil samples, 5-year rotation, limed half of plots

					Breton Plot							
	Series A				Series C				Series F			
Year	Check	NPK	NPKS	Manure	Check	NPK	NPKS	Manure	Check	NPK	NPKS	Manure
1972	0.37	0.07	0.38	0.07	0.28	0.08	0.28	0.06	0.07	0.05	0.09	0.05
1977	0.31	a	0.33	0.09	0.13		0.14	0.06	0.11		0.10	0.03
1978									0.06	0.05	0.07	0.06
1979	0.14	0.09	0.15	0.04	0.13	0.07	0.13	0.08	0.06	0.05	0.06	0.06
1983					0.18	0.06	0.16	0.06				
1985									0.05	0.04	0.06	0.05
1990	0.07	0.05	0.06	0.06	0.07	0.08	0.05	0.05	0.04	0.04	0.05	0.05
1998	0.06	0.05	0.06	0.05	0.06	0.06	0.06	0.06	0.05	0.04	0.06	0.06
2003	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04

[a] Blank cell indicates no archived sample was available for testing

Table 2.9 Exchangeable Al ($cmol_c\ kg^{-1}$) of archived Classical Breton Plots soil samples, 5-year rotation, limed half of plots

	Breton Plot											
	Series A				Series C				Series F			
Year	Check	NPK	NPKS	Manure	Check	NPK	NPKS	Manure	Check	NPK	NPKS	Manure
1972	0.00	0.00	0.36	0.03	0.00	0.00	0.18	0.00	0.00	0.00	0.00	0.00
1977	0.00	a	0.22	0.00	0.00		0.00	0.00	0.00		0.02	0.04
1978									0.00	0.00	0.00	0.00
1979	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1983					0.00	0.00	0.03	0.00				
1985									0.00	0.00	0.00	0.00
1990	0.01	0.02	0.17	0.15	0.03	0.01	0.01	0.01	0.01	0.01	0.02	0.01
1998	0.00	0.00	0.00	0.00	0.15	0.20	0.18	0.05	0.14	0.16	0.17	0.15
2003	0.01	0.02	0.02	0.01	0.04	0.04	0.03	0.04	0.04	0.04	0.04	0.04

[a] Blank cell indicates no archived sample was available for testing

Table 2.10 Exchangeable Mn ($cmol_c\ kg^{-1}$) of archived Classical Breton Plots soil samples, 5-year rotation, limed half of plots

	Breton Plot											
	Series A				Series C				Series F			
Year	Check	NPK	NPKS	Manure	Check	NPK	NPKS	Manure	Check	NPK	NPKS	Manure
1972	0.12	0.05	0.16	0.10	0.16	0.07	0.29	0.34	0.10	0.09	0.18	0.17
1977	0.13	a	0.17	0.16	0.16		0.22	0.16	0.17		0.22	0.18
1978									0.22	0.20	0.33	0.33
1979	0.14	0.05	0.25	0.20	0.21	0.19	0.23	0.30	0.21	0.07	0.26	0.20
1983					0.27	0.28	0.38	0.27				
1985									0.24	0.16	0.32	0.26
1990	0.14	0.18	0.16	0.13	0.30	0.27	0.19	0.31	0.28	0.29	0.19	0.19
1998	0.07	0.15	0.15	0.09	0.20	0.30	0.25	0.23	0.20	0.19	0.24	0.20
2003	0.01	0.03	0.02	0.03	0.03	0.05	0.03	0.02	0.02	0.02	0.02	0.02

[a] Blank cell indicates no archived sample was available for testing

Table 2.11 Effective cation exchange capacity ($cmol_c\ kg^{-1}$) of archived Classical Breton Plots soil samples, 5-year rotation, limed half of plots

	Breton Plot											
	Series A				Series C				Series F			
Year	Check	NPK	NPKS	Manure	Check	NPK	NPKS	Manure	Check	NPK	NPKS	Manure
1972	10.75	11.75	8.81	11.23	9.85	12.10	9.45	11.90	11.85	14.54	10.45	11.65
1977	10.53	a	8.20	11.03	11.10		10.35	17.23	13.15		11.40	13.79
1978									12.28	13.88	10.80	12.78
1979	10.18	12.14	10.41	13.37	10.85	14.06	10.84	14.87	12.63	13.11	11.69	13.29
1983					9.46	12.44	9.20	12.20				
1985									13.23	14.70	11.01	13.82
1990	11.04	11.61	11.41	14.65	10.55	12.55	12.68	13.77	11.60	13.08	11.92	13.12
1998	10.98	10.50	11.64	16.71	9.84	10.03	11.63	13.92	12.91	14.42	9.48	12.64
2003	12.39	12.23	13.84	15.03	14.94	15.40	15.73	18.69	16.35	18.19	16.72	18.64

[a] Blank cell indicates no archived sample was available for testing

Table 2.12 Base saturation (%) of archived Classical Breton Plots soil samples, 5-year rotation, limed half of plots

	Breton Plot											
	Series A				Series C				Series F			
Year	Check	NPK	NPKS	Manure	Check	NPK	NPKS	Manure	Check	NPK	NPKS	Manure
1972	98.89	99.56	94.15	98.82	98.42	99.41	95.01	97.17	99.17	99.37	98.24	98.52
1977	98.80	a	95.26	98.57	98.59		97.88	99.09	98.72		97.84	98.39
1978									98.22	98.56	96.91	97.42
1979	98.61	99.57	97.64	98.50	98.03	98.63	97.90	97.97	98.37	99.44	97.76	98.52
1983					97.12	97.74	95.58	97.80				
1985									98.19	98.88	97.10	98.12
1990	98.58	98.28	97.11	98.10	96.86	97.76	98.39	97.70	97.55	97.68	98.25	98.50
1998	99.35	98.58	98.74	99.46	96.50	95.02	96.29	97.94	97.33	97.56	95.68	97.29
2003	99.86	99.66	99.69	99.76	99.53	99.39	99.61	99.67	99.64	99.67	99.62	99.66

[a] Blank cell indicates no archived sample was available for testing

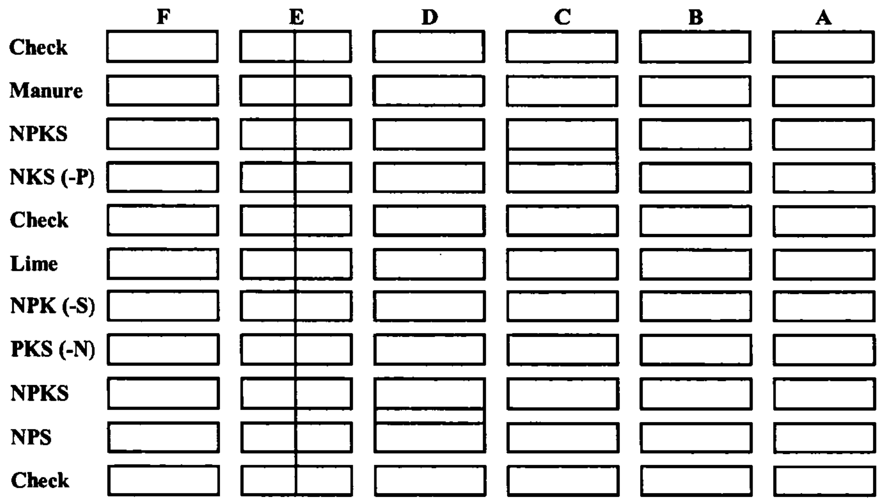

Figure 2.1 Layout of the Classical Breton Plots. The line in series E depicts the separation of the two-year rotation. N ↑

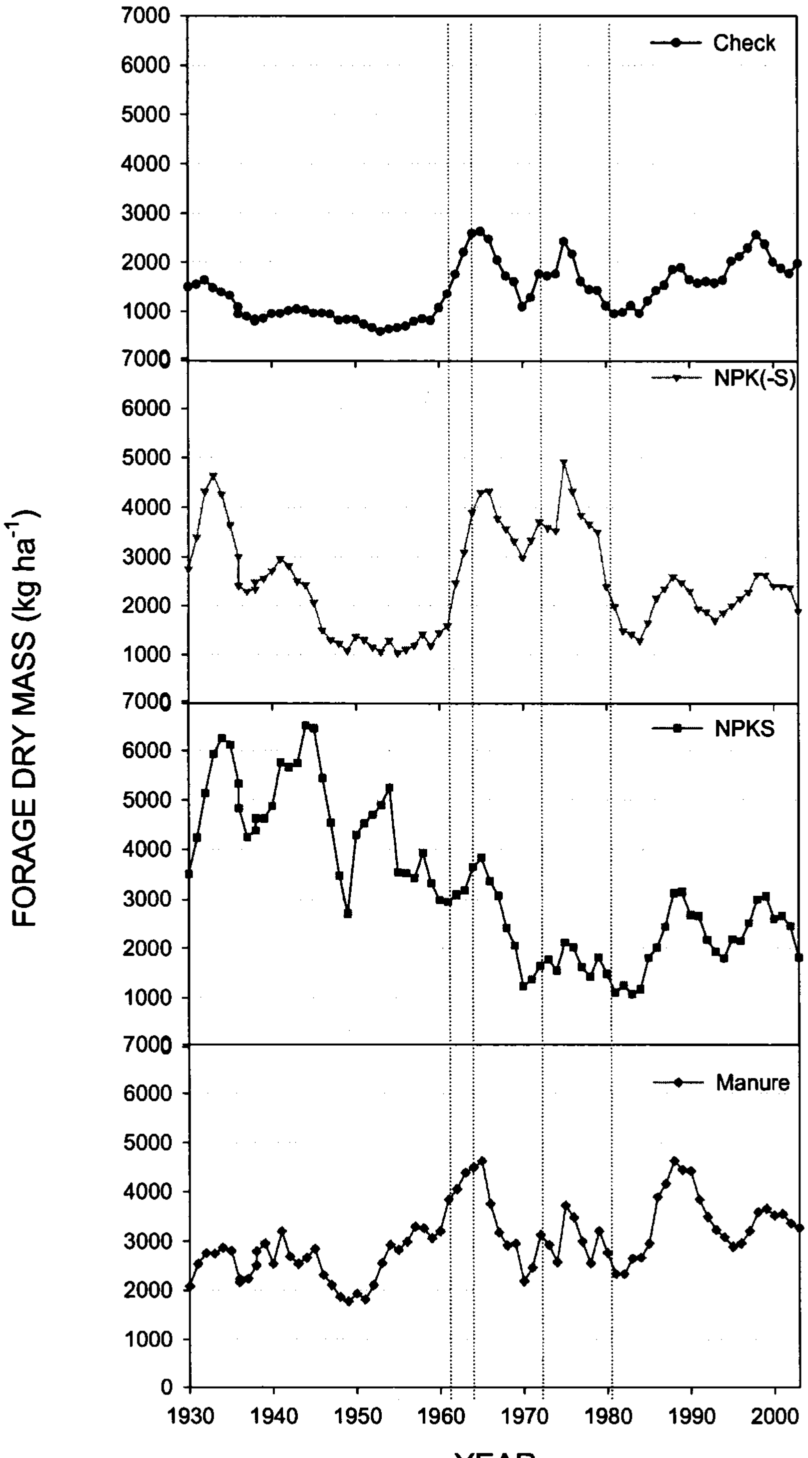

Figure 2.2 Five-year running averages of first year forage yield on the limed half of selected Classical Breton Plots from 1930-2003

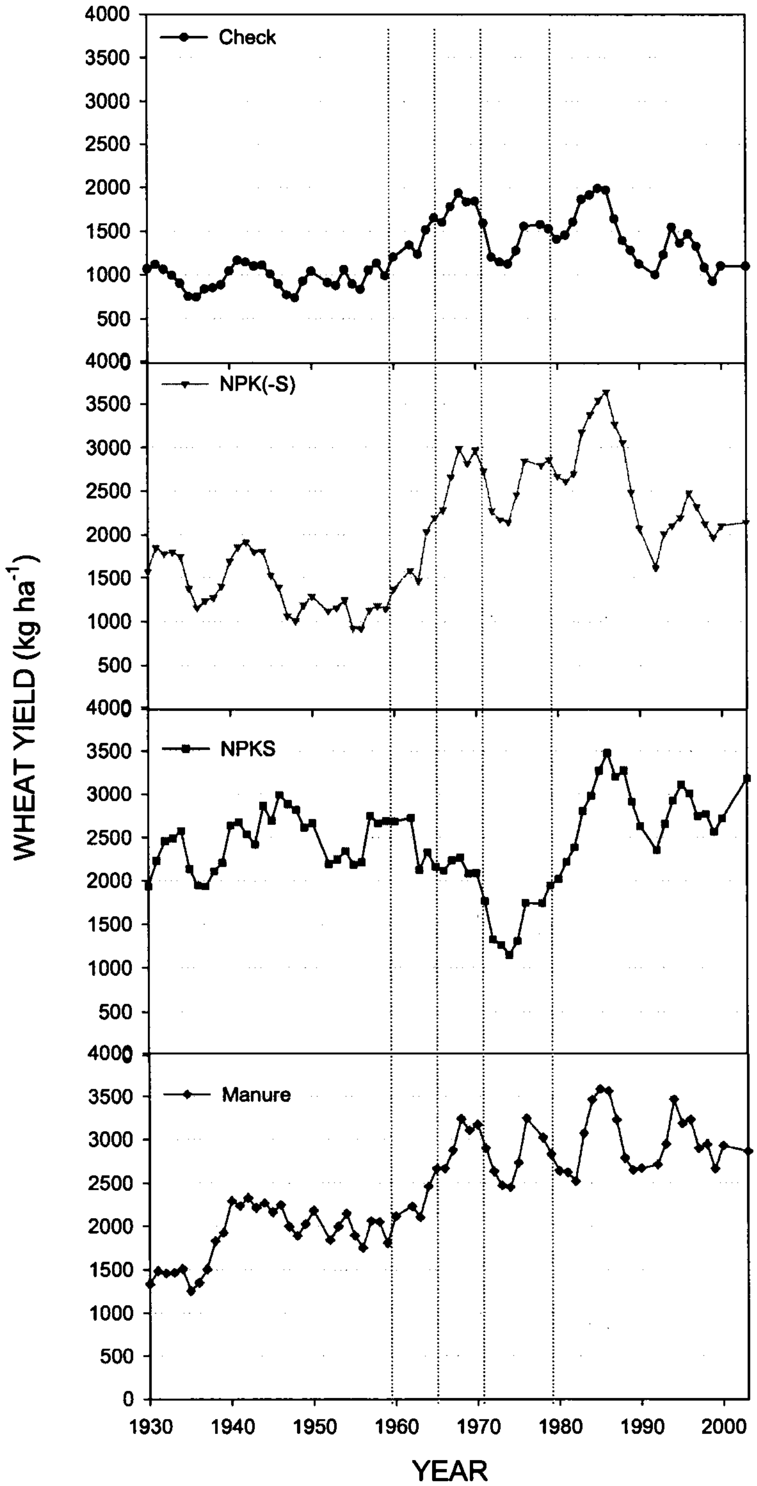

Figure 2.3 Five-year running averages of wheat yield on the limed half of selected Classical Breton Plots from 1930-2003

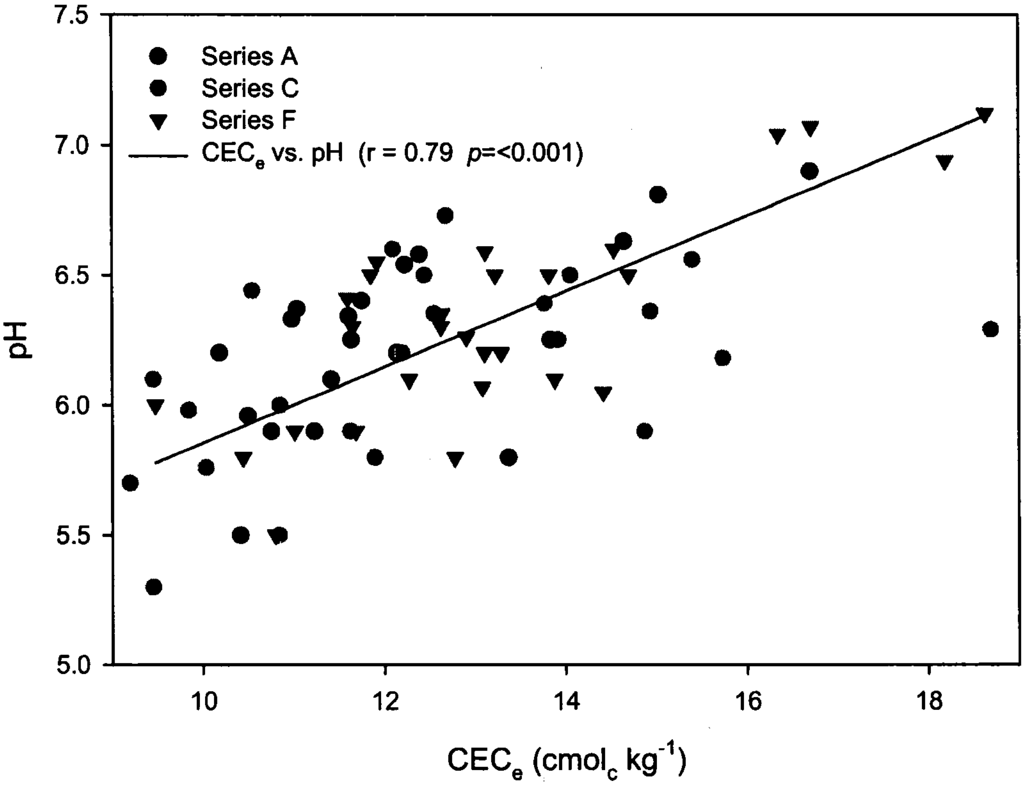

Figure 2.4 pH vs. CEC_e of the Classical Breton Plots soil samples from series A, C, and F, limed half

3 Effects of Sulphur Addition on Plant Growth and Soil Chemical Properties at the Breton Plots

3.1 Introduction

Human activities have had a dramatic effect on global cycling of sulphur (S) in the past two centuries (Schlesinger, 1997). Anthropogenic emissions of SO_2 have increased approximately twenty-fold since 1850 with the most rapid increases occurring in Europe and North America between 1940 and 1970 (Brimblecombe et al., 1989). Stable isotope analysis at the Rothamsted Plots (UK) demonstrated that anthropogenic S accounted for 62 to 78% of the S taken up by wheat at the peak of U.K. SO_2 emissions and contributed to 28 to 37% of topsoil S (Zhao et al., 1999). Increased S deposition has been linked to soil acidification and forest dieback (Ulrich et al., 1980; Reuss et al., 1987). On the other hand, anthropogenic S deposition may be beneficial when S is acting as a fertilizer. Regulated control of SO_2 emissions in Europe resulted in S deficiency in cereal crops due to the corresponding decrease in S deposition (McGrath and Zhao, 1995; Zhao et al., 1999).

Sulphur is a necessary element required by all organisms and is often referred to as the fourth major plant nutrient, following nitrogen (N), phosphorus (P) and potassium (K) (McGrath and Zhao, 1995). Luvisolic soils in Alberta extend over approximately 15 million ha, represent 30% of the provincial land base (Izaurralde et al., 1993) and represent 40% of arable land in Canada. Studies at the University of Alberta's Breton Plots in the 1930's were the first to demonstrate that Gray Luvisols can be deficient in S, and that grasses as well as legumes respond to S fertilization on these soils (Newton, 1936; Bentley et al., 1971; Robertson, 1979). Oil and gas activity in the Breton area intensified in the 1960's, which was speculated to have increased S atmospheric deposition to the Breton Plots (Robertson, 1991). It was further hypothesized that increases in S deposition were partially responsible for the wheat and forage yield increases observed after 1960 (Figure 3.1 and Figure 3.2). Specifically, yields increased in the check (no amendment) plots as well as in plots receiving manure and chemical amendment (NPK). On the other hand, yields in the NPKS plots decreased between 1960 and 1972, which was attributed to the acidifying effect of the ammonia-containing fertilizers applied to these plots (Juma et al., 1997). Gray Luvisols in the Breton area are considered moderately sensitive to acidic inputs due to the low clay and organic matter content in the A horizon (Palmer and Trew, 1987).

The objective of this study was to quantify the influence of S deposition on crop yield and soil properties at the Breton Plots. A greenhouse experiment was designed to evaluate the effects of varying H_2SO_4 amendments on 1) soil chemical properties including: pH; exchangeable Al and Mn; exchangeable acidity; effective cation exchange capacity (CEC_e); electrical conductivity (EC); and base saturation and 2) yields of alfalfa *(Medicago sativa)* and wheat *(Triticum aestivum)* grown on soils from different long-term management plots (check, manure, NPK(-S), and NPKS). Soil from a forested, undisturbed area adjacent to the plots (referred to as native soil) was included as a comparison.

It was hypothesized that S deposition would negatively affect alfalfa growth at lower S deposition levels than wheat because as a legume it is sensitive to soil acidity (Havlin et al., 1999). Past soil management was also hypothesized to have a strong effect on crop yields and soil properties. Soil properties were expected to show a lower response to increasing H_2SO_4 amounts in soils with higher buffering capacities. Plots that had received manure or commercial fertilizer were hypothesized to have higher buffering capacities than the check or native soils because the use of fertilizer increases plant growth, which increases organic inputs to the soil and leads to higher soil organic matter content (Robertson, 1991). Plots that had received manure were further expected to have higher soil organic matter and buffering capacities than the chemically fertilized plots, because in addition to crop response to fertilization, manure also constitutes a direct organic input to the soil.

3.2 Materials and Methods

3.2.1 Site Description

The Classical Breton Plots are the only long-term plots on Gray Luvisols in Canada. They were established in 1929 near the town of Breton, 110 km SW of Edmonton, to find "a system of farming suitable for the wooded soil belt" (Robertson, 1979). They consist of six series of land with eleven plots each and encompass a two-year and a five-year rotation. Adjacent to the north side of the plots is a forested "natural" area that has not been cleared or cropped.

3.2.2 Experimental Design

The greenhouse experiment was designed to test the response of alfalfa and wheat to S addition when grown on soils from four different management plots at the Classical Breton Plots, as well as on soil from the undisturbed area adjacent to the Plots (i.e. native soil). The soil amendment history has varied over time among the plots as indicated in Table 3.1 and Table 3.2.

The Breton area has been reported to receive on average 7 kg S ha^{-1} (Legge, 1988) and more recently ~3.4 kg S ha^{-1} annually at monitoring station near the Breton Plots (West Central Airshed Society, 2003). These levels of S deposition are below average for Alberta and not believed to currently have a negative effect on the Breton Plots crops or soils. Sulphur treatments were chosen at 0, 20, 40 and 175 kg S ha^{-1} for the greenhouse experiment. The highest S level was determined in a pre-experimental trial as the minimum amount of H_2SO_4 required to decrease soil pH to 5.5.

3.2.3 Soil Collection/Preparation

Soil was collected from series F at the Classical Breton Plots post-harvest 2004. Series F was last limed in 2001 and the crop grown in 2004 was wheat. Soil was collected by hand from the top 10 cm of the A horizon in the east half (limed half) of plots 2 (manure), 3 (NPKS), 5 (check), and 7 (NPK(-S)). Approximately 10 randomly distributed points were sampled in each plot and composited. Native soil was also collected and composited from the top 10 cm of the mineral horizons from the adjacent natural area. The forest floor layer was removed prior to soil collection.

Soil samples were passed through a 10 mm sieve, removing rocks and large plant material, then air dried. Air dried soil was potted in 5" square pots and placed on the greenhouse bench. Fertilizer was applied in accordance with the second cereal crop in the five-year rotation (Table 3.2). Native, check, and manure soils were not fertilized; NPKS and NPK(-S) plot soils were fertilized at the rate of 75 kg N ha^{-1}, 22 kg P ha^{-1}, 46 kg K ha^{-1} and 5.5 or 0 kg S ha^{-1}. Sulphuric acid was added to the pots at a rate of 0, 20, 40 or 175 kg S ha^{-1}. Both H_2SO_4 and fertilizer were dissolved in distilled water to a total volume of 150 mL for application. Pots not treated with S or fertilizer received 150 mL of distilled water. Pots were randomly distributed in the greenhouse and rotated weekly. The temperature was approximately 22°C during the day and 18°C at night; the photoperiod was 16 hours.

Seeds were planted approximately 2 cm below the surface after a two week equilibration period. Alfalfa pots received approximately twenty seeds (cultivar AC Nordica) and wheat pots received four seeds (cultivar AC Barrie). Alfalfa seeds were inoculated by Grotech. After establishment, plants were thinned to two plants per pot. Pots were watered every one to three days, on a mass basis to keep them at 80% of their weight at field capacity as calculated prior to the start of the greenhouse experiment.

Wheat was harvested at maturity after 110 days. Grain was threshed and weighed immediately following harvest. Alfalfa was harvested at 141 days when the majority of plants were in flower. Plant materials were oven-dried at 65°C and their dry weights were recorded. Soil was collected at the time of harvest. It was air dried and passed through a 2 mm sieve in preparation for analyses.

3.2.4 Soil Analyses

Soil pH was measured by the saturated paste method (Janzen, 1993). Approximately 200 g of soil was used to make saturated pastes with deionised water. Saturated pastes sat overnight then were vacuum filtered. Exchangeable cations were measured by atomic absorption spectrophotometry (AAS) following an unbuffered extraction with 0.1M $BaCl_2$ (Hendershot and Duquette, 1986). Unbuffered solutions preserve the "field" pH of soil in analyses (Hendershot et al., 1993b). CEC_e was calculated as the sum of exchangeable Ca^{2+}, Mg^{2+}, Na^{+}, Al^{3+}, K^{+}, and Mn^{2+}. Exchangeable Al and Mn were emphasized and reported separately due to their pH dependence and potential toxic effects. Percent base saturation (BS) was calculated from the concentration ($cmol_c\ kg^{-1}$) exchangeable cations extracted by $BaCl_2$ as:

$$\%BS = \frac{(Na^{+} + K^{+} + Ca^{2+} + Mg^{2+})}{CEC_e} \times 100$$

Exchangeable acidity was determined by titration (Thomas, 1982). Soil samples were extracted with 1M KCl and the extract was titrated with ~0.01M NaOH to the phenolphthalein endpoint. The amount of exchangeable acidity (Al^{3+} and H^{+}) was calculated from the amount of NaOH required to reach the endpoint according to Hendershot (1993a). Total C and N were determined by combustion analysis on finely ground (150 μm) soil with a Carlo-Erba elemental analyser (model NA-1500, Carlo-Erba Inc., Milan, Italy).

3.2.5 Statistical Analyses

Data from the wheat and alfalfa experiments were analysed separately. The experiments were designed in complete randomized blocks with 4 replicates. Data were analysed in a 4 x 5 analysis of variance (ANOVA) with four S treatments and five soil management types ($\alpha=0.05$). When there was no interaction between the main effects (S treatment and soil management type), main effects were ranked via a Tukey test. When S treatment * soil management type interaction was significant, further ANOVAs were conducted to test for significant differences within each soil management type and within each S treatment. Linear regressions were conducted to determine potential relationships between 1) pH and other soil properties, and 2) crop yields and soil properties. All statistical analyses were completed using SAS version 9.13 (SAS Institute Inc. NC, USA).

3.3 Results

3.3.1 Soil Chemical Properties

Only total C and C:N ratios for the control treatments (i.e. 0 kg S ha^{-1}) are reported in Table 3.3 and Table 3.4 since these values are not expected to change during the short duration of the greenhouse experiment. The native and manure soils had significantly greater amounts of C than the other soils. The check plots contained the lowest total C, although differences were not statistically significant in the soil samples measured after the alfalfa experiment. The C:N ratios ranged from 15 to 16 in the native soils, and were significantly higher than in the managed soils. Even though some statistical differences were found, all managed soils had similar C:N ratios ranging from 10 to 11. These results are consistent with previously reported C and C:N values at the Breton Plots (Izaurralde et al., 2001).

Soil pH values following wheat growth showed a significant (p=0.015) interaction between soil management type and S treatment (Figure 3.3). pH values in the native and manure soils were significantly lower than in the check soil for all S treatments, and tended to be lower than in the NPK(-S) and NPKS soils. While there was no significant influence of S addition in the check, NPKS and manure soils, both the native and NPK(-S) soils exhibited a significant decrease in pH in the extreme S treatment. Soil pH values after alfalfa growth showed no interaction between soil management type and S treatment (Figure 3.4). Instead, for all soils, there was a highly significant (p<0.001) decrease in pH with increasing S level. Differences among soil types were equally significant (p<0.001), with the native and manure having significantly lower pH than the check and NPK(-S) soils.

Exchangeable Mn values after wheat growth exhibited a significant ($p<0.001$) interaction between soil management type and S treatment (Figure 3.5). Although statistically significant increases were only apparent for the highest (175 kg S ha^{-1}) treatment, exchangeable Mn tended to increase with increasing S treatment in each soil. The native soil had significantly higher exchangeable Mn levels than the managed soils for all S treatments. Exchangeable Mn after alfalfa growth also showed a significant ($p<0.001$) interaction between soil management type and S treatment (Figure 3.6). Values tended to increase with increasing S levels as they did after wheat growth, and the only statistically significant increases were at the highest (175 kg S ha^{-1}) S level. Native soil values following alfalfa growth were notably higher than in the managed soils.

Exchangeable Al following wheat growth showed a significant ($p=0.002$) interaction between soil management type and S treatment (Table 3.3). Values tended to increase with increasing S in the NPK(-S) soil, but decreased with increasing S level in the NPKS soil with significant differences observed only at the highest S treatment in the NPK(-S) soil (data not shown for intermediate treatments). There was no clear pattern in the other soils in response to S level. Also there were no clear trends among soil types within each of the S treatments. Exchangeable Al after alfalfa growth also exhibited a significant ($p=0.001$) interaction between soil management type and S treatment, however exchangeable Al was below the detection limit of 0.03 mg kg^{-1} in the majority of samples (Table 3.4). Detectable values were obtained in the check and NPKS soils only.

Exchangeable acidity following wheat growth exhibited a significant ($p<0.001$) effect of soil management type without an interaction between soil type and S treatment (Table 3.3). There were no statistically significant differences among samples linked to S addition.

The highest values were found in the native soil and the lowest values were found in the check soil. After alfalfa growth exchangeable acidity showed a significant ($p<0.001$) interaction between soil management type and S treatment (Table 3.4). Very few significant differences were found among the different S treatments within each soil management type. Native soil was an exception, and showed a significant increase in exchangeable acidity with S addition. The native soil also had the highest amount of exchangeable acidity of all soils as it did after wheat growth.

CEC_e values following wheat growth showed a significant ($p<0.001$) effect of soil management type without an interaction with S treatment (Table 3.3). There was no significant influence of the S treatments on CEC_e ($p=0.244$). Significantly higher values were found in the native, NPK(-S) and manure soils than in the check and NPKS soils. After alfalfa growth, CEC_e values exhibited a significant ($p=0.02$) interaction between soil management type and S treatment (Table 3.4). Generally the native, NPK(-S) and manure soils had higher CEC_e values and the NPKS and check soils had lower CEC_e values in each S treatment. Some differences were found among the different S treatments within each soil management type, but these did not present any clear trend.

Base saturation was very high in all soils with little variation, ranging from 98.79% to 99.95% (Table 3.3 and Table 3.4). There was a significant ($p<0.001$) interaction between soil management type and S treatment following both wheat and alfalfa growth. Generally base saturation showed a significant decrease in the higher (175 kg S ha^{-1}) S treatment compared to the control. Base saturation was lower in the native and NPKS soils and higher in the NPK(-S) and manure soils within most S treatments (data not shown for intermediate S treatments).

Electrical conductivity following wheat growth showed significant effects of both soil management type ($p<0.001$) and S treatment ($p<0.001$) with no interaction between them (Table 3.3). EC values increased significantly with increasing S level (data not shown for intermediate levels). Values were higher in the native, check and manure soils than in the NPK(-S) and NPKS soils. After alfalfa growth EC values showed a significant ($p=0.03$) interaction between soil management type and S treatment (Table 3.4). In general EC values increased with increasing S level, and were significantly higher in the extreme S (175 kg S ha^{-1}) treatment than in the control for all soil types. At lower S levels there were no differences between soil types however in the extreme S treatment the native and NPK(-S) soils had significantly higher EC values than the check, manure, and NPKS soils.

There were a number of significant relationships between pH and other measured soil properties (Table 3.5). A negative correlation was found between pH and exchangeable Mn, exchangeable acidity, CEC_e, and EC following growth of both alfalfa and wheat, although the correlation with exchangeable Mn and exchangeable acidity was stronger for wheat ($p<0.001$) than for alfalfa. Base saturation was positively correlated to pH, with again a stronger relationship for wheat ($p<0.001$) than for alfalfa ($p=0.018$).

3.3.2 Crop Yields

Soil management type significantly ($p<0.001$) affected grain (wheat) yield results (Figure 3.7). Specifically the NPKS and manure soils exhibited significantly higher yields than the check and native soils. The NPK(-S) soils also showed significantly higher yields than the check soils, but did not differ from other soils. Sulphur addition did not result in any significant changes in grain yields. Alfalfa dry weight results exhibited a significant ($p=0.005$) interaction between soil management type and S treatment (Figure 3.8). In general, the lowest yields were obtained on the check soils within each S level. There were no significant differences among the manure, NPK, NPKS and native soils at the lower S treatments. However, at the extreme (175 kg S ha^{-1}) application the manure soils showed significantly higher yields than the NPK(-S), check, and native soils. Within soil management types, the effect of S addition was variable and there were few significant differences.

There were few significant relationships between grain (wheat) yield and measured soil properties (Table 3.6). Wheat yield was positively correlated to total soil N and CEC_e, and negatively correlated to EC, although only in the case of CEC_e was the relationship strongly (p <0.001) significant. Alfalfa yield showed significant relationships with a greater number of soil properties than wheat. In particular, alfalfa yield was strongly (p< 0.001) and negatively correlated to pH and exchangeable Al, and positively correlated to total C and N, exchangeable Mn, exchangeable acidity, and CEC_e.

3.4 Discussion

Soil pH following the wheat experiment ranged from 5.7 to 7.1 with the majority of values within the optimum range of 6.5 to 6.8 for most crops (Havlin et al., 1999). Following alfalfa growth, the soil pH values ranged from 5.6 to 6.7 and were below optimal levels of 6.8 to 7.0 for this acid sensitive crop (Havlin et al., 1999). However, they remained above 5.5, which is considered to be the cut-off value for alfalfa suitability; the symbiont *Rhizobium meliloti* does not colonize sufficiently when the pH is below 5.5, leaving the plants N deficient and reducing plant growth (Robson and Loneragan, 1970; Robson, 1969).

The pH values showed a significant soil effect following both wheat and alfalfa growth (Figure 3.3 and Figure 3.4). Although the soils received the same amounts of H_2SO_4 in both the alfalfa and wheat components of the experiment, soil pH values following alfalfa growth were more clearly related to S treatment than pH values following wheat growth. The decrease in pH with increasing S was quite distinct after alfalfa growth but more variable after wheat with a significant interaction between soil type and S treatment.

There is evidence in the literature that roots can substantially change rhizosphere pH by releasing H^+ or OH^- to maintain electro-neutrality during nutrient uptake (Riley and Barber, 1971; Nye, 1981; Haynes, 1990; Hinsinger et al., 2002). Legume plants that obtain N from N_2 fixation require high amounts of many cations including K, Ca and Mg (Bear and Wallace, 1950; Jones, 1967). To counterbalance the excess of cations taken up they extrude H^+ from their roots (Tang et al., 1998). On the other hand cereal plants that obtain N as NO_3^- release OH^- or HCO_3^- to counterbalance the excess of negative charges in their roots (Riley and Barber, 1971; Jarvis and Robson, 1983; Weinberger and Yee, 1984). Although the rhizosphere likely accounts for a small volume of total soil, it is possible that alfalfa released H^+ into the soil contributing to the decrease in pH values observed during the greenhouse experiment (Figure 3.4), while wheat may have decreased the acidifying effect of S addition to the soils (Figure 3.3).

It was hypothesized that pH would show smaller decreases with increasing S addition in the more buffered soils that had received manure or chemical fertilization than in the check soils. In particular, manure amended soils typically show increases in soil carbon, and are usually well buffered (Gao and Chang, 1996; Ndayegamiye and Côté, 1989; Sommerfeldt et al., 1988). The pH values in the manure and NPKS soils following wheat growth did not show any response to S addition, which supports the hypothesis. However, the check soil (hypothesized to have the lower buffering capacity) did not show any decrease in pH with increasing S either. Furthermore, following alfalfa growth, there was a significant decrease in pH with increasing S treatment in all soils regardless of past management (Figure 3.4). Despite the higher amount of C in the manure soils (Table 3.4), pH decreased with increasing S level in these soils (Figure 3.4). The lowest pH values were found in the manure soils at 175 kg S ha^{-1}, which directly contradicts our hypothesis. Results may be partially explained based on the acidifying effect of alfalfa on soils as previously discussed. It is interesting to note that alfalfa yields increased from the 20 to the 175 kg S ha^{-1} treatments (Figure 3.8) in conjunction with the decreases in pH in the manure and NPKS soils (Figure 3.4).

Exchangeable Mn and Al usually increase when pH decreases below 5.0, especially in soils experiencing low redox potential conditions (Hoyt and Nyborg, 1971; Sumner and Yamada, 2002). Results from the greenhouse experiment indeed indicated that exchangeable Mn was negatively correlated to pH following both alfalfa and wheat growth (Table 3.5). Exchangeable Al was below detection limit in most of the samples following alfalfa growth, but was negatively correlated to pH following wheat growth.

In the Breton Plots soils, exchangeable Mn has been considered toxic at levels 20 ppm (0.074 $cmol_c$ kg^{-1}) or higher when extracted with 0.05 M $CaCl_2$ (McCoy and Webster, 1977). In this study, exchangeable Mn was found to increase with increasing S level in all soils, and was found to be at toxic concentrations in many soils according to this standard, including the native soil (20, 40 and 175 kg S ha^{-1}) and the NPKS soil at 175 kg S ha^{-1} following alfalfa growth. After wheat growth, toxic levels were also found in the native soil at 20, 40 and 175 kg S ha^{-1} and in the NPKS soil at 175 kg S ha^{-1}. Because the toxic limit defined by McCoy and Webster (1977) refers to the amount of Mn extracted by 0.05 M $CaCl_2$, and not to the more concentrated solution (0.1 M $BaCl_2$) that I used for my analyses, it is difficult to assess if exchangeable Mn was at toxic, borderline or at acceptable levels in my samples. Visible symptoms of toxicity were not observed in any of the wheat and alfalfa plants. However, increases in exchangeable Mn with increasing S addition in the native soil following alfalfa growth reached levels as high as 0.323 $cmol_c\ kg^{-1}$, which are likely above toxicity levels regardless of the type of extractant that was used. Furthermore, for the native soil, the increase in exchangeable Mn (Figure 3.6) was accompanied by a decrease in alfalfa yield (Figure 3.8). Lower values of exchangeable Mn in the managed soils than the native soil may be due to removals by crops.

The exchangeable acidity was low in all cultivated soils (0.012 to 0.042 $cmol_c\ kg^{-1}$), while base saturation was high (>98.8%). This is likely a result of periodic liming over the last thirty years. The most recent liming in series F was in 2001; three years before the soil was collected for this experiment. After alfalfa growth, the native soil exchangeable acidity values were as high as 0.200 $cmol_c\ kg^{-1}$ in the 175 kg S ha^{-1} treatment. The native soils also had an increasing exchangeable acidity trend with increasing S level. The higher levels of exchangeable acidity and increasing trend are likely because this soil has not received any lime amendments. With the exception of the manure soils following alfalfa growth, in all of the soils the only significant decrease in base saturation was in the 175 kg S ha^{-1} treatment. The extreme acid treatment is many times higher that the normal provincial range of 1 to 53 kg S ha^{-1}(Walker, 1969; Nyborg et al., 1977; Palmer and Trew, 1987) indicating that annual levels of S deposition would take many years to have an effect on base saturation if S deposition was the only factor considered.

Wheat yield was affected by soil management treatment only and not S addition (Figure 3.7). Specifically, highest wheat yields were obtained on the manure and NPKS soils and lowest yields were obtained on the check plot soil. These results are in agreement with the long-term trends reported at the Breton Plots (Juma et al., 1997).

It was hypothesized that the acid sensitive alfalfa yield would decrease and show retarded growth at a lower level of H_2SO_4 than wheat. Results, however, did not support this hypothesis. Instead, when all data were included in the analysis, alfalfa yield was found to be negatively correlated to pH (Table 3.6). Alfalfa yields did not show any significant decrease with S addition in the native, check or NPKS soils (Figure 3.8). Only the NPK(-S) soil showed a significant decrease in yield at the extreme S amendment although the alfalfa yield trend on the NPK(-S) soil also seemed to support the two roles S amendment can have as a fertilizer and an acidifier. Yields increased when 20 kg S ha^{-1} was applied illustrating the fertilizer effect of S. Yields then decreased at 175 kg S ha^{-1} showing a negative response to H_2SO_4 amendment.

3.5 Conclusions

The objective of this study was to quantify the influence of S deposition on crop yield and soil properties at the Breton Plots. It was hypothesized that S deposition would negatively effect alfalfa growth at lower S deposition levels than wheat. Past soil management was also hypothesized to have a strong effect on crop yields and soil properties. Soil properties were expected to show a lower response to increasing S addition in soils with higher organic matter and buffering capacities.

Wheat yield was significantly affected by soil management, with the highest yields observed on the manure and NPKS soils, and the lowest yields on the check and native soils. S addition and soil management type showed a significant interaction for alfalfa yield. Alfalfa yields did not show a significant decrease with increasing S addition in most soils, with the exception of the NPK(-S) soil at the extreme S amendment (175 kg S ha^{-1}). Alfalfa yields were significantly lower for the check soil than the other soil types in all S treatments.

Following alfalfa growth, there was a significant decrease in pH with increasing S addition for all soil management types. On the other hand, following wheat, the native and NPK(-S) soils were the only ones showing a decrease in pH in response to S addition.

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3.7 Tables and Figures

Table 3.1 Approximate fertilizer, manure and lime application rates to the Breton Classical Plots for the period 1930-1979[a]. Adapted from Cannon et al (1984)

Plot	Treatments 1930-1979	Nutrients added (kg ha^{-1} y^{-1}) N	P	K	S[e]
2	Manure (M)[b]	76	42	91	20
3	NPKS	10	6	16	10
5	Check	0	0	0	0
7	LNPKS[c]	0(11)	10(6)	0(16)	1(9)

[a] In 1944-1963, fertilizer was applied every second year at rates approximating N (9), P (5), K (14) and S (8) kg ha^{-1} each year.

[b] Applied every fifth year, in later years at 44 t ha^{-1}. Nutrient rates are annual equivalents and are estimates based on manure applied from 1976-1986 inclusive.

[c] This treatment was initially a lime (L) plus phosphorus (LP) treatment. In 1964, it became LNPKS. Nutrient application rates thereafter are shown in parentheses.

[d] Lime was broadcast and tilled onto 7 several times between 1930 and 1948 for a total application of approximately 6.6 t ha^{-1}. No lime was applied to plot 7 between 1949 and 1979, but the east half of the other plots limed where necessary to pH 6.5 in 1972

[e] All S was added as SO_4^-.

Table 3.2 Revised treatments and fertilizer and manure application rates to the Breton Classical Plots from 1980 onwards and soil total C. Adapted from Cannon et al (1984)

Plot	Treatments 1980-current	Nutrients added (kg ha^{-1} y^{-1}) N	P	K	S[c]
2	Manure	a	-	-	-
3	NPKS	b	22	46	5.5
5	Check	0	0	0	0
7	NPK(-S)	b	22	46	0

[a] N application via manure depends upon the rotation. The 2-yr wheat-fallow rotation receives equivalent of 90 kg N ha^{-1} for each wheat crop. The 5-yr cereal-forage rotation (wheat, oat, barley, forage and forage) receives 176 N ha^{-1} every 5 years. Since 1980, manure is added at the rate of 88 kg N ha^{-1} per application after oat harvest and at the time of second forage plow down.

[b] N amounts depend on the crop and its place in rotation: Wheat after fallow 90 kg ha^{-1}; wheat after forage 50 kg ha^{-1}; oat after wheat 75 kg ha^{-1}; barley after oat 50 kg ha^{-1}; legume-grass forage after barley a kg ha^{-1}:forage after forage a kg ha^{-1}.

[c] All S added as elemental S.

Table 3.3 Selected mean soil properties measured after wheat growth

Soil	Exchangeable Al[a] ($cmol_c\ kg^{-1}$)		Base Saturation[a] (%)		Exchangeable Acidity[a] ($cmol_c\ kg^{-1}$)		CEC_e[a] ($cmol_c\ kg^{-1}$)		EC[a] ($dS\ m^{-1}$)		Total C[b] (%)	C:N[b] (C:N)
	0 kg S ha^{-1}	175 kg S ha^{-1}	0 kg S ha^{-1}	175 kg S ha^{-1}	0 kg S ha^{-1}	175 kg S ha^{-1}	0 kg S ha^{-1}	175 kg S ha^{-1}	0 kg S ha^{-1}	175 kg S ha^{-1}	0 kg S ha^{-1}	0 kg S ha^{-1}
Native	0.027 a* A**	0.024 a AB	99.55 a B	98.87 b C	0.047 A	0.055 A	17.66 A	17.08 A	2.15 d A	3.76 a A	3.35 A	15.83 A
	[c] [0.002]	[0.010]	[0.05]	[0.2]	[0.002]	[0.024]	[1.23]	[1.19]	[0.29]	[0.43]	[0.16]	[0.12]
Check	0.031 a A	0.014 b B	99.64 ab B	99.54 b AB	0.012 D	0.021 D	15.32 B	14.45 B	2.03 A	3.52 A	1.93 C	10.06 C
	[0.003]	[0.013]	[0.03]	[0.1]	[0.004]	[0.013]	[1.31]	[0.29]	[0.21]	[0.07]	[0.04]	[0.07]
NPK	0.014 b A	0.057 a A	99.85 a A	99.51 b AB	0.041 BC	0.038 BC	17.71 A	16.92 A	1.71 B	3.11 B	1.97 BC	10.21 C
	[0.021]	[0.027]	[0.12]	[0.15]	[0.007]	[0.003]	[0.17]	[0.38]	[0.20]	[0.33]	[0.04]	[0.11]
NPKS	0.014 a A	0.008 a B	99.65 a B	99.19 b B	0.028 C	0.041 C	14.78 B	15.11 B	1.66 B	2.94 B	2.14 B	10.99 B
	[0.005]	[0.009]	[0.03]	[0.03]	[0.002]	[0.009]	[0.14]	[0.37]	[0.08]	[0.04]	[0.08]	[0.47]
Manure	0.013 a A	0.033 a AB	99.82 a A	99.50 b AB	0.041 B	0.042 B	18.39 A	17.64 A	2.33 A	3.43 A	3.24 A	10.52 BC
	[0.017]	[0.004]	[0.09]	[0.06]	[0.010]	[0.004]	[0.54]	[0.40]	[0.15]	[0.07]	[0.08]	[0.13]

* Lowercase letters indicate significant differences among S treatments within a particular soil type ($\alpha=0.05$)

** Uppercase letters within a column indicate significant differences among soil types within the corresponding S treatment ($\alpha=0.05$)

[a] Values are shown for the control (0 kg S ha^{-1}) and extreme (175 kg S ha^{-1}), omitting the intermediate treatments

[b] Values are shown for the control (0 kg S ha^{-1}) treatment only

[c] Square brackets indicate one standard deviation from the mean

Table 3.4 Selected mean soil properties measured after alfalfa growth

Soil	Exchangeable Al[a] (cmol$_c$ kg^{-1})		Base Saturation[a] (%)		Exchangeable Acidity[a] (cmol$_c$ kg^{-1})		CEC$_e$[a] (cmol$_c$ kg^{-1})		EC[a] (dS m^{-1})		Total C[b] (%)	C:N[b] C:N
	0 kg S ha^{-1}	175 kg S ha^{-1}	0 kg S ha^{-1}	175 kg S ha^{-1}	0 kg S ha^{-1}	175 kg S ha^{-1}	0 kg S ha^{-1}	175 kg S ha^{-1}	0 kg S ha^{-1}	175 kg S ha^{-1}	0 kg S ha^{-1}	0 kg S ha^{-1}
Native	0.000 a* B**	0.000 a B	98.95 a D	98.79 b C	0.141 c A	0.200 a A	17.38 a AB	18.31 a A	2.41 b A	4.07 a A	3.69 A	15.33 A
	[c][0.000]	[0.000]	[0.04]	[0.01]	[0.009]	[0.021]	[0.47]	[0.50]	[0.16]	[0.24]	[0.33]	[0.73]
Check	0.028 a A	0.015 ab AB	99.75 ab BC	99.69 b A	0.027 a B	0.028 a B	15.20 a C	14.39 b B	2.04 b A	2.93 a C	1.90 B	10.08 C
	[0.004]	[0.013]	[0.03]	[0.12]	[0.005]	[0.036]	[0.16]	[0.22]	[0.18]	[0.14]	[0.04]	[0.26]
NPK	0.000 a B	0.000 a B	99.95 a A	99.80 b A	0.032 ab B	0.033 ab B	17.06 bc B	17.42 ab A	2.18 b A	4.18 a A	1.98 B	10.08 C
	[0.000]	[0.000]	[0.01]	[0.02]	[0.004]	[0.002]	[0.15]	[0.29]	[0.22]	[0.09]	[0.09]	[0.26]
NPKS	0.017 a AB	0.025 a A	99.74 a C	99.42 b B	0.034 a B	0.042 a B	15.61 a C	14.63 b B	2.17 b A	3.56 a B	2.10 B	10.58 B
	[0.021]	[0.019]	[0.13]	[0.08]	[0.004]	[0.008]	[0.24]	[0.21]	[0.4]	[0.12]	[0.06]	[0.15]
Manure	0.000 a B	0.000 a B	99.87 a AB	99.79 a A	0.038 a B	0.037 a B	18.01 a A	18.31 a A	2.16 c A	3.51 a B	3.30 A	10.69 B
	[0.000]	[0.000]	[0.01]	[0.03]	[0.001]	[0.004]	[0.45]	[0.36]	[0.19]	[0.35]	[0.02]	[0.16]

* Lowercase letters indicate significant differences among S treatments within a particular soil type α=0.05

** Uppercase letters within a column indicate significant differences among soil types within the corresponding S treatment α=0.05

[a] Values are shown for the control (0 kg S ha^{-1}) and extreme (175 kg S ha^{-1}), omitting the intermediate treatments

[b] Values are shown for the control (0 kg S ha^{-1}) treatment only

[c] Square brackets indicate one standard deviation from the mean

Table 3.5 Correlation coefficients (Pearson's r) describing the relationships between pH and other soil properties including exchangeable Al and Mn ($cmol_c\ kg^{-1}$); exchangeable acidity ($cmol_c\ kg^{-1}$); CEC_e ($cmol_c\ kg^{-1}$); EC ($dS\ m^{-1}$); and base saturation (%). Bold-faced type indicates a significant relationship at p<0.05 (n = 80)

	WHEAT		ALFALFA	
Variable	*r*	*p*	*r*	*p*
Exchangeable Al	**-0.26**	0.02	0.09	0.44
Exchangeable Mn	**-0.52**	0.00	**-0.29**	0.01
Exchangeable Acidity	**-0.53**	0.00	**-0.24**	0.03
CEC_e	**-0.46**	0.00	**-0.46**	0.00
EC	**-0.49**	0.00	**-0.53**	0.00
Base Saturation	**0.53**	0.00	**0.26**	0.02

Table 3.6 Correlation coefficients (Pearson's r) describing the relationships between yield and soil properties including pH; total C and N(%); exchangeable Al and Mn (cmolc kg^{-1}); exchangeable acidity (cmolc kg^{-1}); CECe (cmolc kg^{-1}); EC (dS m^{-1}); and base saturation (%). Bold-faced type indicates a significant relationship at $p<0.05$ (n = 80)

	WHEAT		ALFALFA	
Variable	*r*	*p*	*r*	*p*
pH	-0.10	0.39	**-0.41**	0.00
C	0.13	0.24	**0.41**	0.00
N	**0.27**	0.01	**0.31**	0.00
Exchangeable Al	-0.06	0.63	**-0.29**	0.01
Exchangeable Mn	-0.06	0.58	**0.31**	0.01
Exchangeable Acidity	0.21	0.07	**0.33**	0.00
CEC_e	**0.29**	0.01	**0.40**	0.00
EC	**-0.24**	0.03	0.09	0.42
Base Saturation	0.10	0.40	**-0.27**	0.02

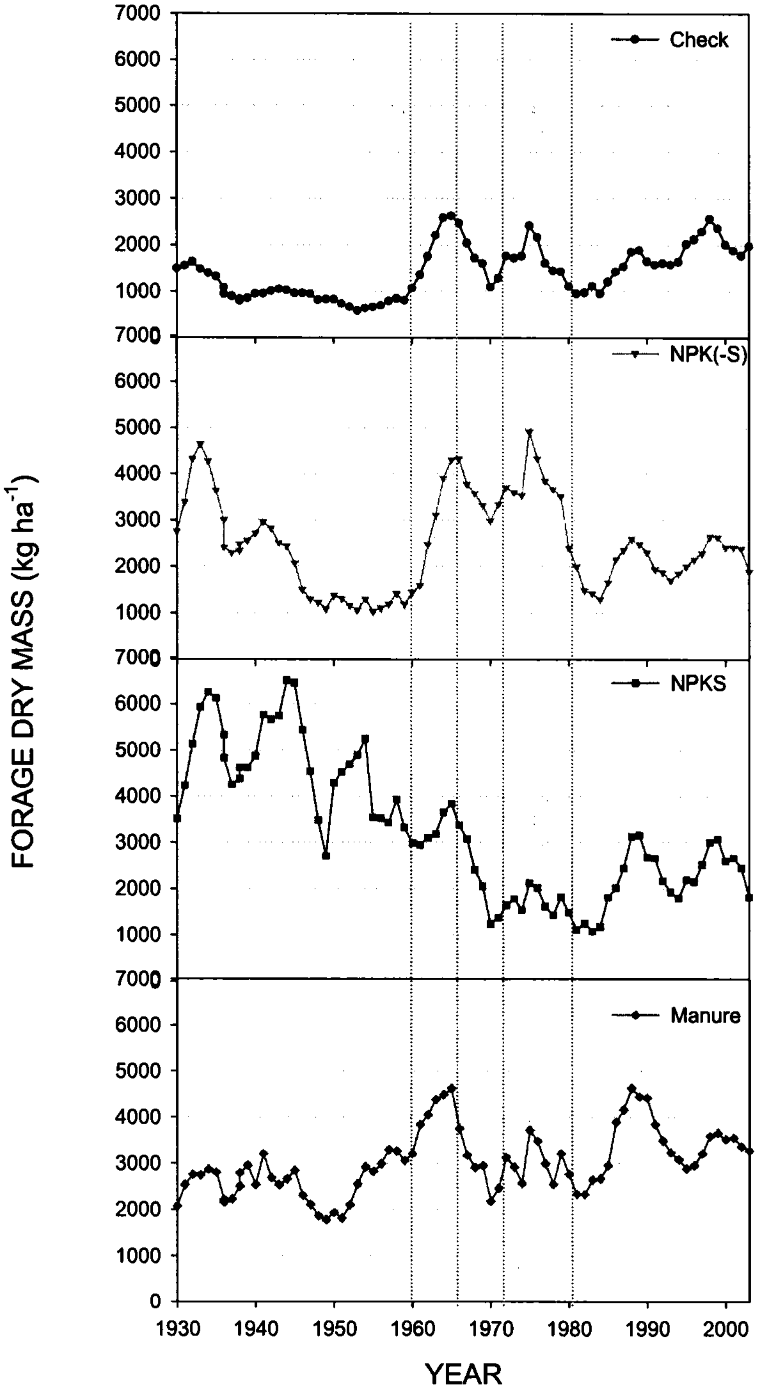

Figure 3.1 Five-year running averages of first year forage yield (first cut) on selected Classical Breton Plots from 1930-2003 (limed half after 1972)

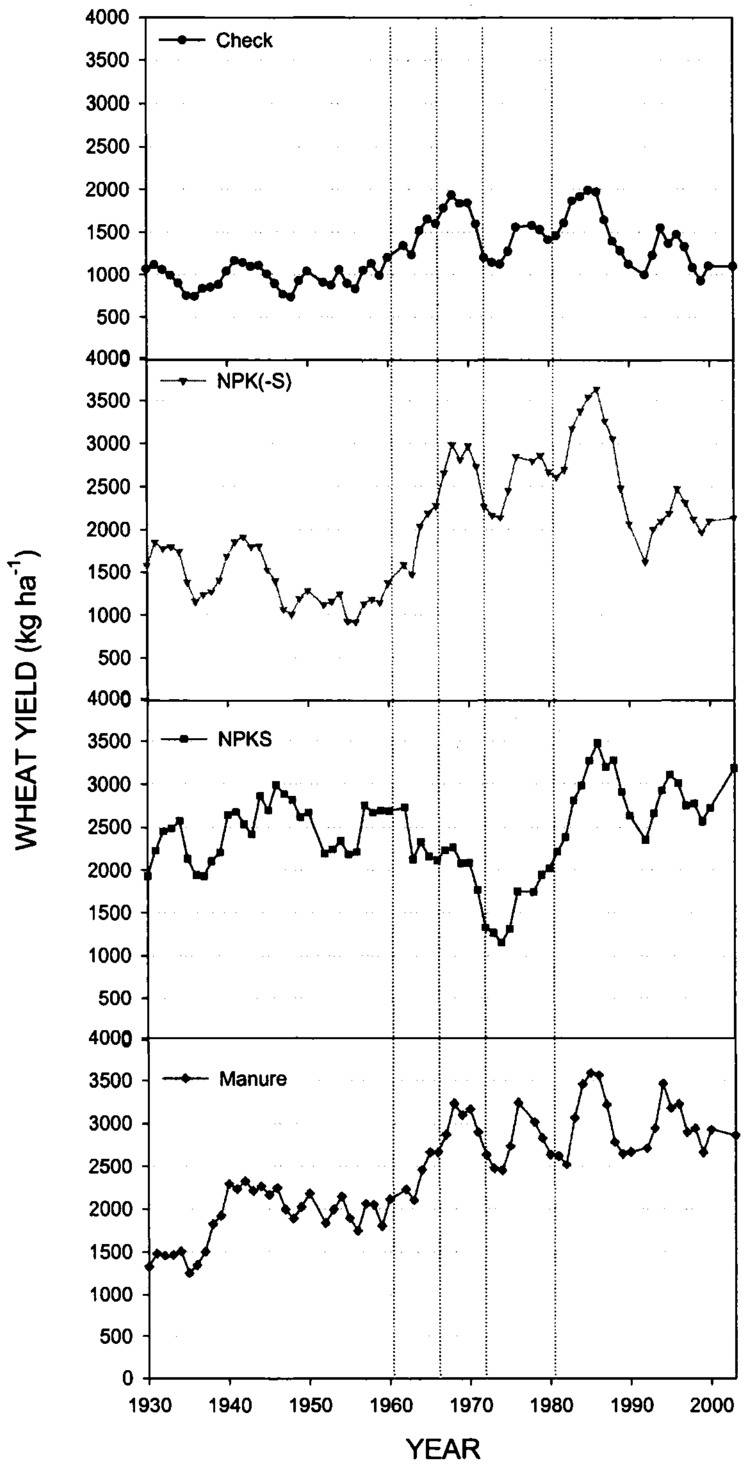

Figure 3.2 Five-year running averages of wheat (grain) yield on selected Classical Breton Plots from 1930-2003 (limed half after 1972)

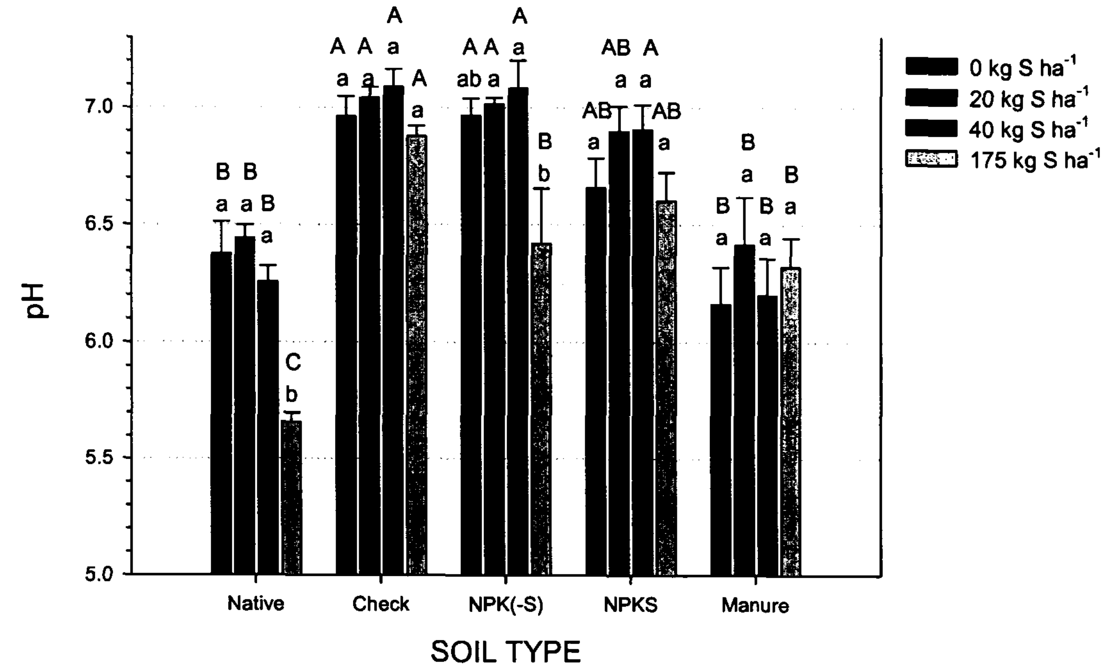

Figure 3.3 Soil pH in five Breton Plot soils with four S treatments after wheat growth. Uppercase letters indicate significant differences among soil types within the corresponding S treatment and lowercase letters indicate significant differences among S treatments within a particular soil type (α=0.05)

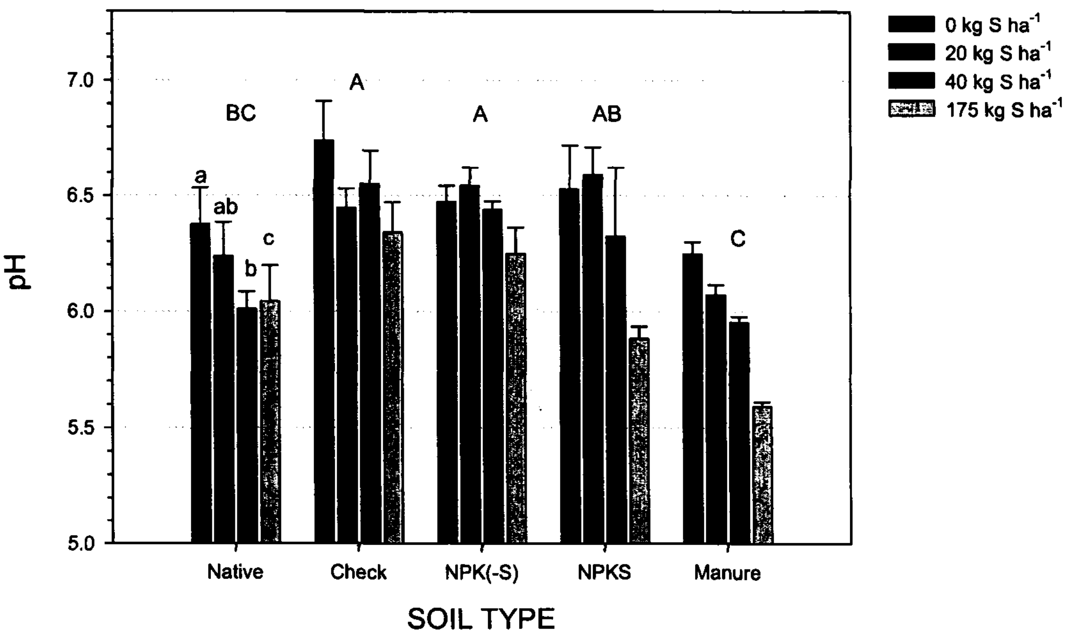

Figure 3.4 Soil pH in five Breton Plot soils with four S treatments after alfalfa growth. Uppercase letters indicate significant differences among soil types and lowercase letters indicate significant differences among S treatments (α=0.05)

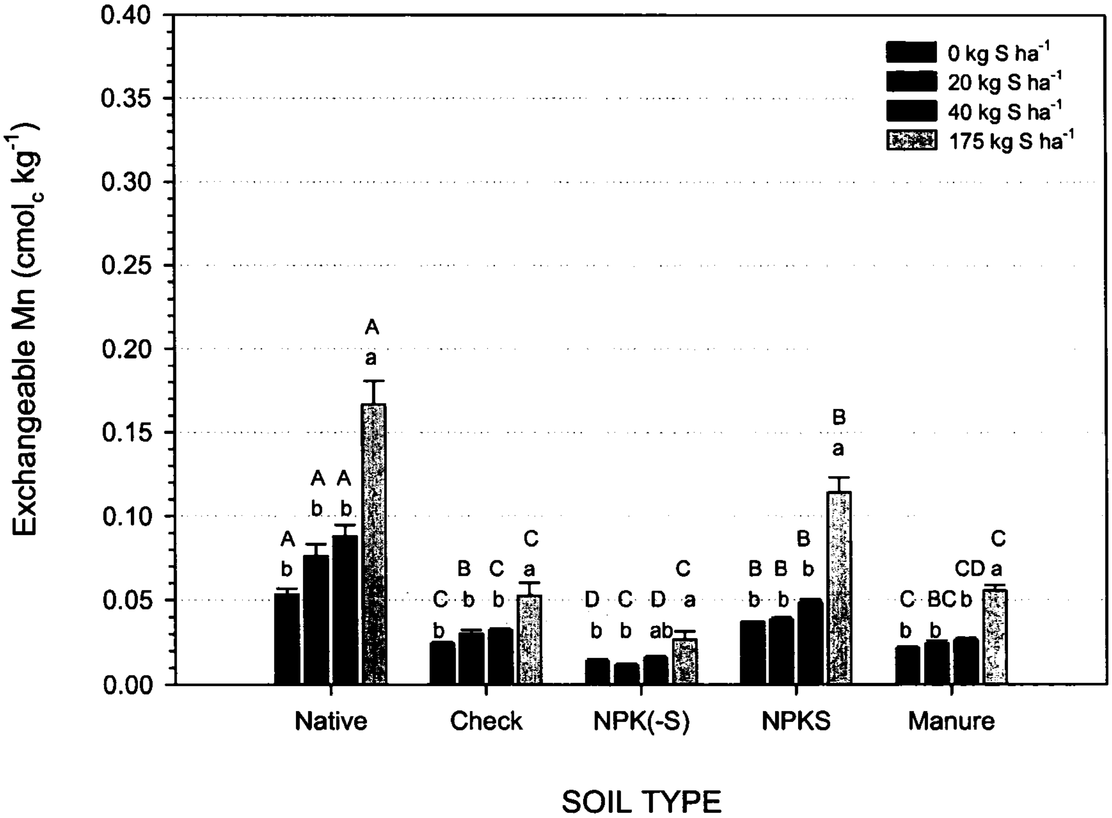

Figure 3.5 Exchangeable Mn in five Breton Plot soils with four S treatments after wheat growth. Uppercase letters indicate significant differences among soil types within the corresponding S treatment and lowercase letters indicate significant differences among S treatments within a particular soil type (α=0.05)

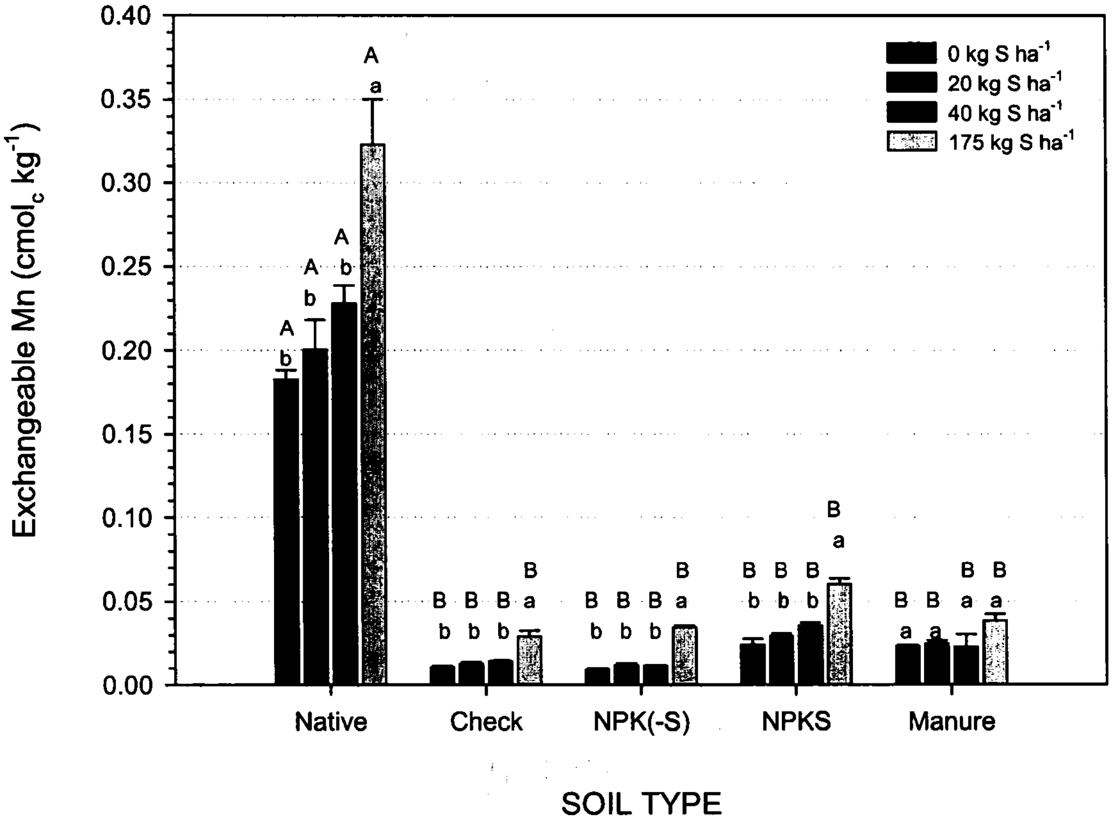

Figure 3.6 Exchangeable Mn in five Breton Plot soils with four S treatments after alfalfa growth. Uppercase letters indicate significant differences among soil types within the corresponding S treatment and lowercase letters indicate significant differences among S treatments within a particular soil type (α=0.05)

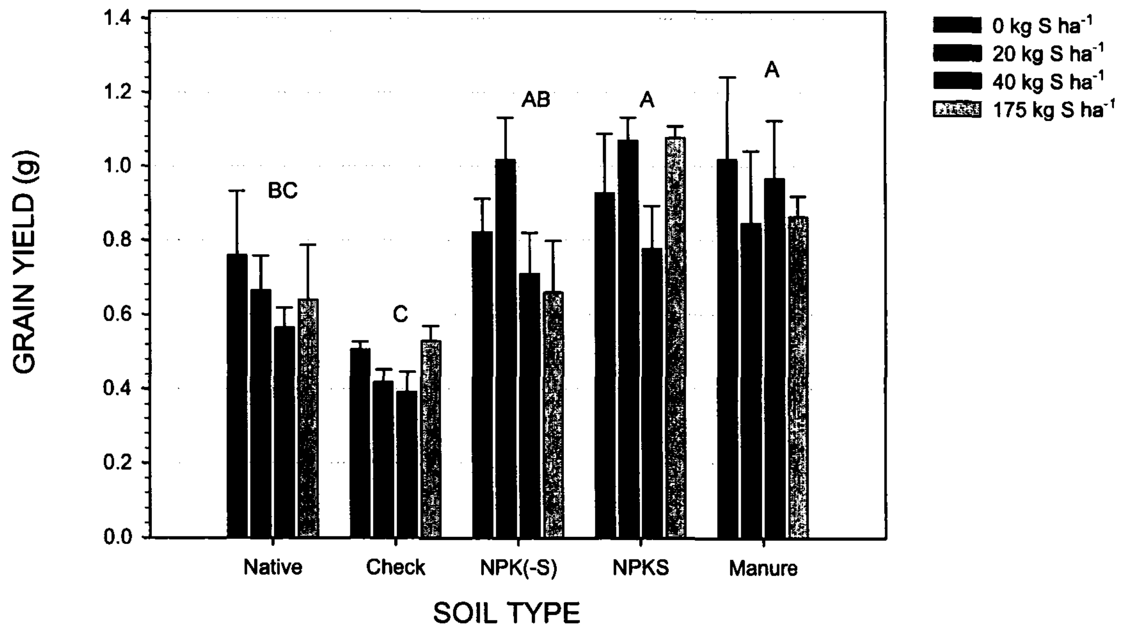

Figure 3.7 Grain yield of wheat grown on five Breton Plot soils with four S treatments. Upper case letters indicate significant differences among soil types (α=0.05)

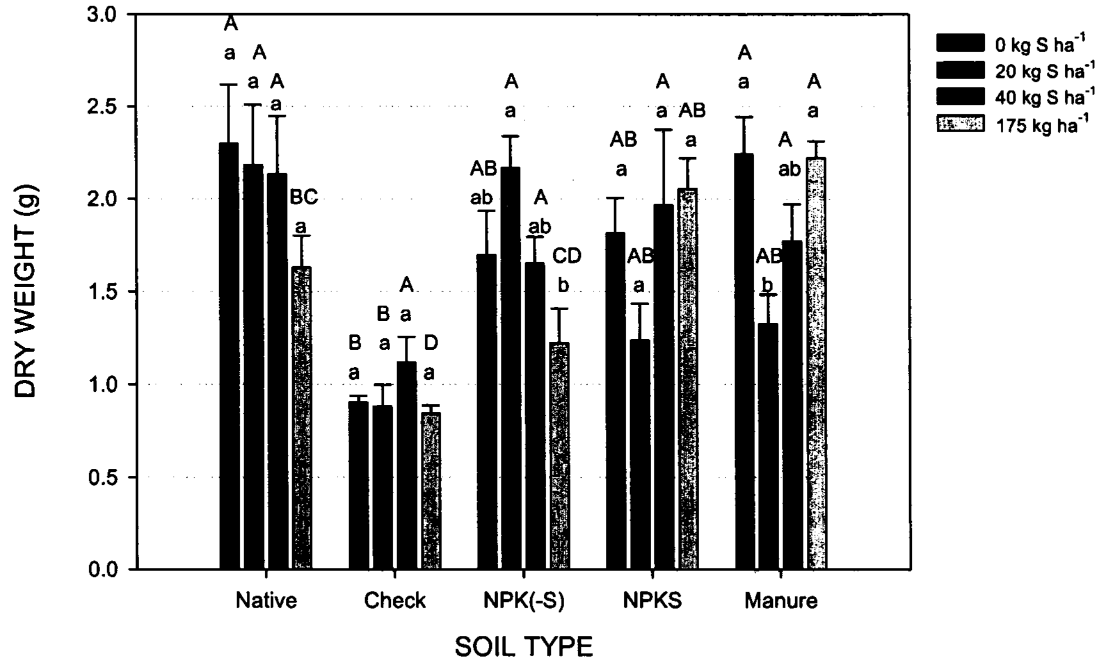

Figure 3.8 Alfalfa dry mass grown on five Breton Plot soils at four S treatment levels. Uppercase letters indicate significant differences among soil types within the corresponding S treatment and lowercase letters indicate significant differences among S treatments within a particular soil type (α=0.05)

4 Synthesis

4.1 Main Findings

Soil properties can be altered in the long-term by agricultural practices such as tillage, summer-fallow, fertilizers, and crop rotations. Natural and anthropogenic environmental factors can also have an effect on soil properties, including concentrations of nutrients such as sulphur (S). Sulphur is a necessary element required by plants and is often referred to as the fourth major nutrient, following nitrogen, phosphorus, and potassium. Gray Luvisols are frequently deficient in S and require S fertilization along with other essential nutrients, to achieve optimum crop yields (Nyborg and Bentley, 1971). Sulphur can also be added to soils through atmospheric deposition in rain and snow, rain intercepted by trees, dry particulates and direct adsorption of SO_2 (Legge, 1988). While S compounds are naturally occurring in the atmosphere, human activities in the past two centuries have had a dramatic effect on global S cycling and increased SO_2 atmospheric levels twenty-fold since the 1800's (Brimblecombe et al., 1989; Schlesinger, 1997). The largest emitter of sulphur oxides is the petroleum industry, followed by coal-fired electric generating stations; smaller contributors include pulp and paper, chemical and fertilizer industries, highways and urban centres (Palmer and Trew, 1987; Legge, 1988).

The main objectives of this study were to 1) evaluate long-term changes in soil chemical properties over time in a Gray Luvisol from the Breton Plots due to several soil amendment practices; 2) evaluate the effects of S addition on wheat and alfalfa growth; and 3) evaluate the effects of S addition on soil chemical properties.

Results from the archived samples showed that some soil properties had been altered by amendment practices over time. These distinctions, however, were not often discreet and had been reduced by lime amendment over the last two decades. Differences among soil management types were confounded by differences among series. Differences among series appeared to be more important than differences among soil management practices in some cases, and were explained by a pre-existing, natural acidity gradient increasing from south to north and east to west across the Breton Plots. Lime amendment had had a considerable effect on soil properties, including: increases in pH and base saturation; decreases in exchangeable acidity; and possibly decreases in exchangeable Al and Mn.

Results from the greenhouse experiment did not indicate any significant effect of S addition on wheat yield. Wheat yield was significantly affected by soil management, with the highest yields observed on the manure and NPKS soils, and the lowest yields on the check and native soils. This may be illustrating the acid tolerance of wheat, although pH values did not drop below 5.5 in the study. S addition and soil management type showed a significant interaction for alfalfa yield. Alfalfa yields did not show a significant decrease with increasing S addition in most soils, with the exception of the NPK(-S) soil at the extreme S amendment (175 kg S ha^{-1}). Alfalfa yields were significantly lower for the check soil than the other soil management types in all S treatments. Some soil properties varied with S treatment, but the effects were not consistent between wheat and alfalfa. Particularly noteworthy were the differences in pH response to S addition between alfalfa and wheat. Following alfalfa growth, there was a significant decrease in pH with increasing S addition for all soil management types. On the other hand, following wheat, the native and NPK(-S) soils were the only ones showing a decrease in pH in response to S addition; furthermore, decreases were only significant at the extreme (175 kg S ha^{-1}) addition rate. These results may be partially explained by the ability of plants to change their rhizosphere pH by releasing H^+ or OH^- to maintain electro-neutrality during nutrient uptake (Riley and Barber, 1971; Nye, 1981; Haynes, 1990; Hinsinger et al., 2002). Legume plants such as alfalfa take up more cations than anions (Bear and Wallace, 1950; Jones, 1967) and extrude H^+ from their roots to counterbalance the excess positive charge (Tang et al., 1998). Conversely, cereals such as wheat, take up more anions than cations and will release OH^- or HCO_3^- to counterbalance the excess of negative charges in their roots (Riley and Barber, 1971; Jarvis and Robson, 1983; Weinberger and Yee, 1984). Although the rhizosphere soil volume is likely small, it is possible that alfalfa growth and S addition had an additive effect on soil pH during the greenhouse experiment, resulting in greater pH decreases than in the case of wheat, which on the other hand likely mitigated the acidifying effect of S addition.

4.2 Soil Acidification through Sulphur Deposition

The native soil in the greenhouse experiment had a pH of 6.4 in the control (0 kg S ha^{-1}) treatment. This is near neutral even though this soil had not been limed, suggesting that atmospheric deposition in the Breton area has not had any acidifying effect on soils. A mathematical exercise can help to quantify the effect S deposition will have on soils from the Breton Plots. Using the Breton Plots buffer curves (unpublished data) from the 1998 soil sampling, an equation was derived to calculate the relationship between pH and H^+. The equation is in the form $y = mX + b$ and is $\Delta pH = -0.2237(\Delta H^+)$ [(H^+ is in mg g^{-1}]. The Breton Plots receive ~3.4 kg S ha^{-1} from S deposition per year according to the most recent information from a monitoring station near the Breton Plots (West Central Airshed Society, 2003). This equates to 210 g H^+ ha^{-1} per year. Using a bulk density of 1.3 Mg m^{-3} the mass of the surface 15 cm of soil is 1.95 x 10^6 kg ha^{-1}. Therefore the H^+ generated is

$$\frac{1.077\times10^{-4}\,mg\ H^{+}}{g\ soil} = 2.4\times10^{-5}\,pH\ units\ (per\ year).$$

This is a very minute amount. Even if H^+ addition were 1000 times greater, the change in pH would only be 0.024 pH units per year. This calculation confirms that S deposition is not currently acidifying soils at the Breton Plots, and that current levels of deposition are not likely to result in measurable changes in pH even in the long term. Instead, the lower pHs observed at some of the plots must be, for the most part, due to agricultural amendments and crops grown. Acidification seems to be primarily due to N fertilizer addition and is controlled with lime on the east half of each plot in the five-year rotation.

4.3 Sulphur Deficiency at the Breton Plots

Gray Luvisols are low in fertility and can be deficient in S (Bentley et al., 1971). Studies at the University of Alberta's Breton Plots in the 1930's were the first to demonstrate that Gray Luvisols can be deficient in S, and that grasses as well as legumes respond to S fertilization on these soils (Newton, 1936; Bentley et al., 1971; Robertson, 1979). Crops at the Breton plots are still benefiting from S fertilization (Figure 4.1 and Figure 4.2). The NPK(-S) yields were lower than the NPKS yields in forage from 1990 to 2003 and wheat from ~1985 to 2003. These plots both receive the same fertilizer rates of N, P, and K and are both limed, when required, to pH 6.5. The only (current) difference in management is the addition of S to the NPKS plot. Prior to 1980 the NPK(-S) plot received LNPKS amendment. It appears the S added had a carry-over effect until ~1990, and then yields decreased, presumably due to S deficiency. S fertilization at the Breton Plots is currently applied at a rate of 5.5 kg S ha^{-1} (1980-current). In this respect atmospheric deposition (3.7 kg S ha^{-1}) should not be considered a negligible input of S to the plots. While not important as an acidifying agent, atmospheric deposition thus may be an important factor for the fertility of the naturally S-deficient Breton soils. Increases in crop yields that were observed in the 1960's may indeed have been due to increases in S deposition at that time.

4.4 Recommendations and Future Work

The study of long-term changes in soil properties was limited by the availability of archived samples from the Breton Plots. It is important that soil samples continue to be archived at regular intervals for use in future studies. Challenges encountered in the greenhouse experiment could be improved upon by future researchers. Both wheat and alfalfa plants exhibited symptoms of water stress during the experiment. The method of watering, while effective in minimizing leaching from the pots, may not have provided sufficient water for optimum growth. The use of deeper pots with smaller diameters may have provided more favourable soil moisture content for the plants, or, an alternate method for minimizing leaching may have also yielded better results. Alfalfa was also affected by a thrips infestation in the first few weeks of the greenhouse experiment.

Although S deposition is not important as an acidifier at the Breton Plots it appears it is important as a fertilizer. In order to better understand the role S deposition has as a fertilizer, future studies could investigate the pools of S in the soil including inorganic S, labile organic S, resistant organic S and microbial S. Studies could also be conducted measuring the isotopic composition of S in the soil to determine the relative composition of natural and anthropogenic derived S.

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4.6 Tables and Figures

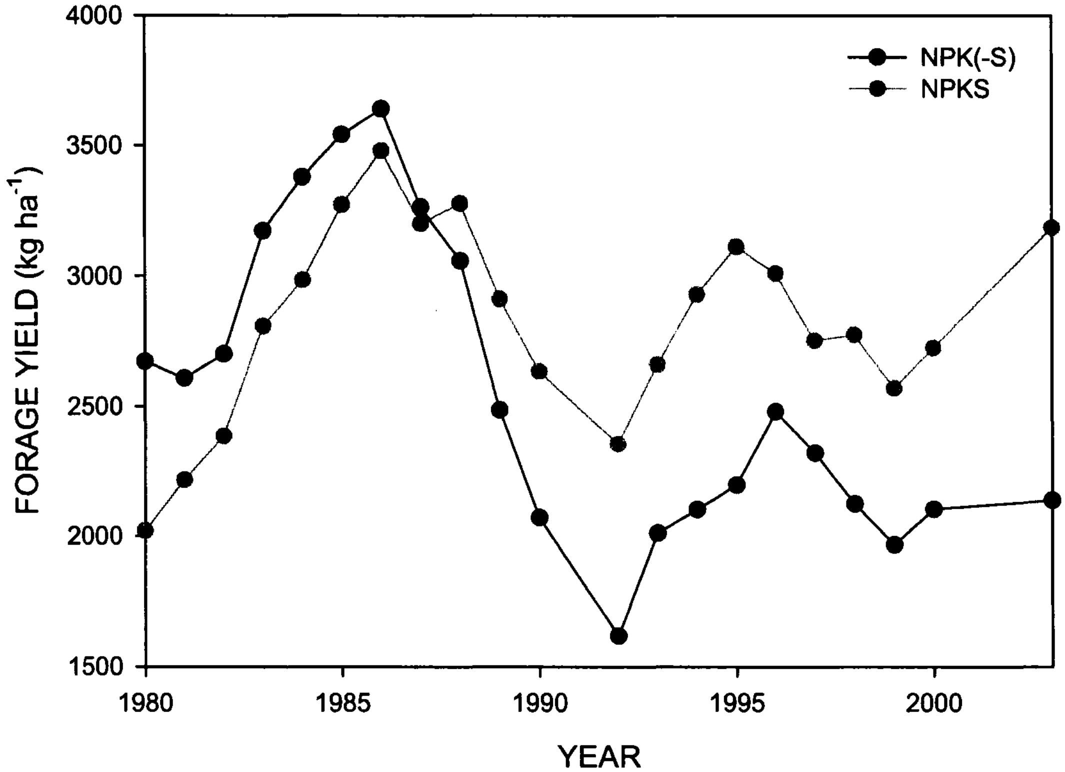

Figure 4.1 Five-year running averages of first year forage yield on the limed half of selected Classical Breton Plots from 1980-2003

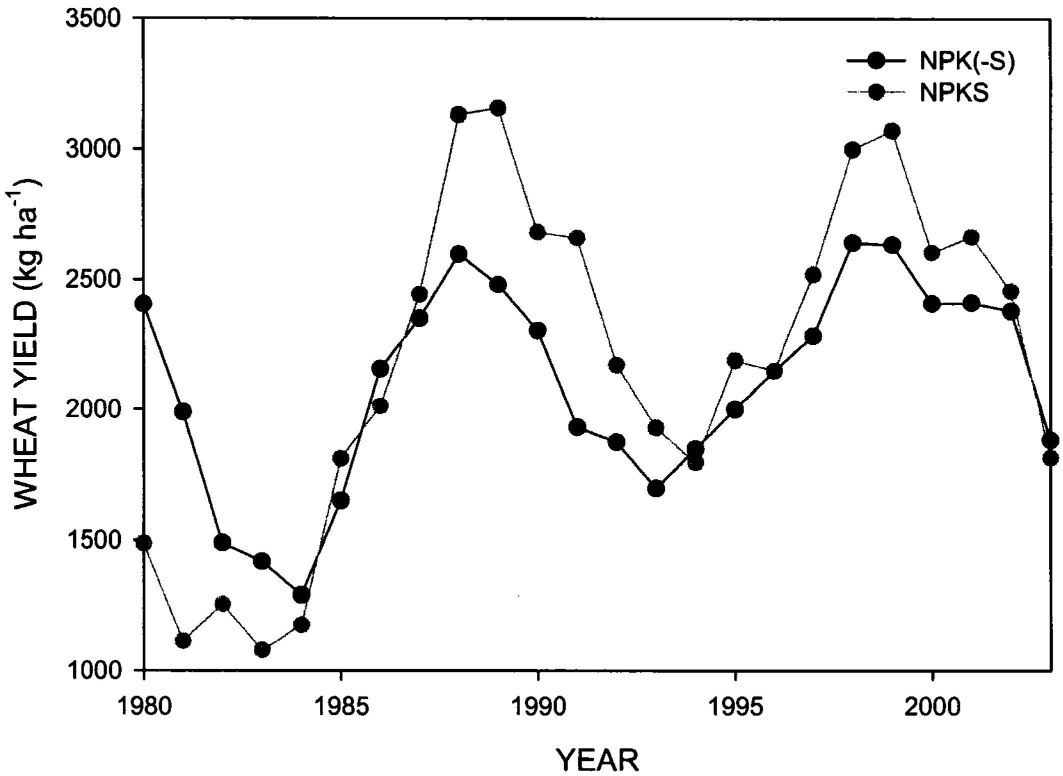

Figure 4.2 Five-year running averages of wheat yield on the limed half of selected Classical Breton Plots from 1980-2003

5 Appendices

5.1 Breton Annual Precipitation

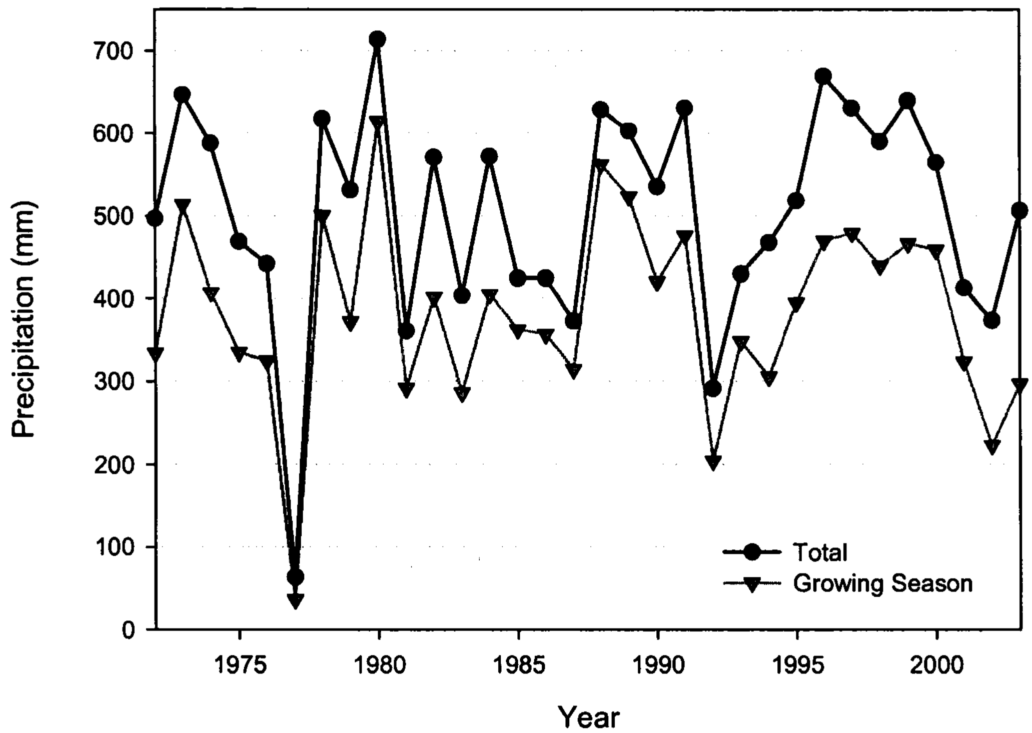

Figure 5.1 Precipitation data for the Breton area divided into total annual precipitation and growing season precipitation (May–September) as collected from Environment Canada's archives (http://climate.weatheroffice.ec.gc.ca/advanceSearch/searchHistoricDataStations_e.html)

5.2 Determination of Sulphur Levels

Method:
1) Measure 5 g of soil into small bottle
2) Add 5 ml of dionized water
3) Let stand for 10 minutes
4) Swirl and take pH
5) Add acid solution and dionized water for a total of 20 ml
6) Shake for 10 minutes
7) Allow to stand for 30 mintues
8) Swirl and take pH second time

Table 5.1 Pre-trial H_2SO_4 amendment experiment

Rotation	Plot	H_2SO_4 (ml)	Orig. pH	Final pH
2-year	Manure	0	6.98	7.25
2-year	Manure	1	7.10	5.66
2-year	Manure	5	7.08	3.43
2-year	Manure	10	7.01	2.46
2-year	Manure	15	7.03	2.05
2-year	Manure	20	7.11	1.82
Native	N/A	0	6.74	6.94
Native	N/A	1	6.72	5.38
Native	N/A	5	6.77	3.95
Native	N/A	10	6.74	2.72
Native	N/A	15	6.76	2.31
Native	N/A	20	6.77	2.00
5-year	NPK	0	7.30	7.42
5-year	NPK	1	7.26	6.17
5-year	NPK	5	7.24	4.00
5-year	NPK	10	7.29	2.94
5-year	NPK	15	7.26	2.35
5-year	NPK	20	7.14	2.05
5-year	Check	0	7.40	7.24
5-year	Check	1	7.39	5.95
5-year	Check	5	7.26	3.70
5-year	Check	10	7.41	2.65
5-year	Check	15	7.40	2.18
5-year	Check	20	7.26	1.90
5-year	NPKS	0	7.16	7.31
5-year	NPKS	1	7.20	5.93
5-year	NPKS	5	6.83	3.83
5-year	NPKS	10	6.97	2.74
5-year	NPKS	15	7.15	2.23
5-year	NPKS	20	7.21	1.93
5-year	Manure	0	7.15	7.36
5-year	Manure	1	7.04	6.06
5-year	Manure	5	7.24	3.96
5-year	Manure	10	7.20	2.89
5-year	Manure	15	7.18	2.31
5-year	Manure	20	7.02	2.01

5.3 Complete Results of the Greenhouse Experiment

Table 5.2 Soil EC on five Breton Plot soils with four S treatments after wheat production

	Sulphur								
	0 kg S ha^{-1}		20 kg S ha^{-1}		40 kg S ha^{-1}		175 kg S ha^{-1}		Average
Soil	Mean (dS m^{-1})	SD	Mean (dS m^{-1})	SD	Mean (dS m^{-1})	SD	Mean (dS m^{-1})	SD	Mean
Native	2.15	0.29	2.19	0.17	2.65	0.18	3.76	0.43	2.68 A*
Check	2.03	0.21	2.44	0.20	2.62	1.14	3.52	0.07	2.65 A
NPK	1.71	0.20	1.95	0.17	2.18	0.11	3.11	0.33	2.24 B
NPKS	1.66	0.08	1.71	0.13	2.17	0.17	2.94	0.04	2.12 B
Manure	2.33	0.15	2.41	0.01	2.67	0.07	3.43	0.07	2.70 A
Mean	1.97 d**		2.14 c		2.46 b		3.35 a		

** Lowercase letters indicate significant differences among S treatments at α=0.05

* Uppercase letters indicate significant differences among soil types at α=0.05

Table 5.3 Soil EC on five Breton Plot soils with four S treatments after alfalfa production

	Sulphur							
	0 kg S ha^{-1}		20 kg S ha^{-1}		40 kg kg S ha^{-1}		175 kg S ha^{-1}	
Soil	Mean (dS m^{-1})	SD	Mean (dS m^{-1})	SD	Mean (dS m^{-1})	SD	Mean (dS m^{-1})	SD
Native	2.41 b* A**	0.16	2.61 b A	0.26	2.92 b A	0.35	4.07 a A	0.24
Check	2.04 b A	0.18	2.06 b A	0.15	2.13 b B	0.19	2.93 a C	0.14
NPK	2.18 b A	0.22	2.35 b A	0.16	2.57 b AB	0.19	4.18 a A	0.09
NPKS	2.17 b A	0.40	2.09 b A	0.64	2.37 b AB	0.42	3.56 a B	0.12
Manure	2.16 c A	0.19	2.48 bc A	0.04	2.62 b AB	0.17	3.51 a B	0.35

* Lowercase letters across a row indicate significant differences among S treatments within the corresponding soil type at α=0.05

**Uppercase letters within a column indicate significant differences among soil types within the corresponding S treatment at α=0.05

Table 5.4 Soil SAR on five Breton Plot soils with four S treatments after wheat growth

	Sulphur								
	0 kg S ha^{-1}		20 kg S ha^{-1}		40 kg S ha^{-1}		175 kg S ha^{-1}		Average
Soil	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean
Native	1.64	0.26	1.42	0.10	1.29	0.15	1.88	0.92	1.56 A**
Check	1.16	0.12	1.12	0.09	0.89	0.08	1.09	0.29	1.07 C
NPK	1.11	0.20	1.14	0.16	0.90	0.15	0.86	0.10	1.00 C
NPKS	1.59	0.22	1.34	0.07	1.22	0.18	1.19	0.09	1.33 AB
Manure	1.31	0.17	1.19	0.25	0.98	0.11	1.10	0.09	1.14 BC
Mean	1.36 a*		1.24 ab		1.05 b		1.22 ab		

** Uppercase letters indicate significant differences among soil types at α=0.05

* Lowercase letters indicate significant differences among S levels at α=0.05

Table 5.5 Soil SAR on five Breton Plot soils with four S treatments after alfalfa growth

	Sulphur											
	0 kg S ha^{-1}			20 kg S ha^{-1}			40 kg kg S ha^{-1}			175 kg S ha^{-1}		
Soil	Mean		SD	Mean		SD	Mean		SD	Mean		SD
Native	1.43 a*	A**	0.10	1.20 b	B	0.10	1.13 b	AB	0.09	1.10 b	A	0.07
Check	1.31 a	AB	0.08	1.10 b	B	0.09	1.07 b	B	0.07	0.87 c	BC	0.11
NPK	1.18 ab	B	0.08	1.25 a	AB	0.08	1.11 b	B	0.05	0.80 c	C	0.08
NPKS	1.34 ab	AB	0.02	1.16 bc	B	0.06	1.40 a	A	0.21	1.03 c	AB	0.08
Manure	1.42 a	A	0.15	1.40 a	A	0.04	1.27 ab	AB	0.08	1.14 b	A	0.10

* Lowercase letters across a row indicate significant differences among S treatments within the corresponding soil type at α=0.05

** Uppercase letters within a column indicate significant differences among soil types within the corresponding S treatment at α=0.05

Table 5.6 Soil CEC_e in five Breton Plot soils with four S treatments after wheat growth

	Sulphur								
	0 kg S ha^{-1}		20 kg S ha^{-1}		40 kg kg S ha^{-1}		175 kg S ha^{-1}		Average
Soil	Mean (cmol$_c$ kg^{-1})	SD	Mean (cmol$_c$ kg^{-1})	SD	Mean (cmol$_c$ kg^{-1})	SD	Mean (cmol$_c$ kg^{-1})	SD	Mean (cmol$_c$ kg^{-1})
Native	17.66	1.23	17.75	1.59	18.44	0.90	17.08	1.19	17.73 A*
Check	15.32	1.31	14.30	0.49	15.05	0.45	14.45	0.29	14.78 B
NPK	17.71	0.17	18.02	0.28	16.30	2.27	16.92	0.38	17.24 A
NPKS	14.78	0.14	14.89	0.33	15.60	0.54	15.11	0.37	15.10 B
Manure	18.39	0.54	18.38	0.56	17.84	0.26	17.64	0.40	18.06 A
Mean	16.77		16.67		16.65		16.24		

* Uppercase letters indicate significant differences among soil types at α=0.05

Table 5.7 Soil CEC_e in five Breton Plot soils with four S treatments after alfalfa growth

	Sulphur											
	0 kg S ha^{-1}			20 kg S ha^{-1}			40 kg kg S ha^{-1}			175 kg S ha^{-1}		
Soil	Mean ($cmol_c\ kg^{-1}$)		SD	Mean ($cmol_c\ kg^{-1}$)		SD	Mean ($cmol_c\ kg^{-1}$)		SD	Mean ($cmol_c\ kg^{-1}$)		SD
Native	17.38 a*	AB**	0.47	17.30 a	B	0.86	18.87 a	A	1.61	18.31 a	A	1.50
Check	15.20 a	C	0.16	15.11 a	C	0.20	14.88 ab	B	0.42	14.39 b	B	0.22
NPK	17.06 bc	B	0.15	16.88 bc	B	0.17	17.28 b	A	0.04	17.42 ab	A	0.29
NPKS	15.61 a	C	0.24	15.18 ab	C	0.39	15.25 a	B	0.09	14.63 b	B	0.21
Manure	18.01 a	A	0.45	18.43 a	A	0.37	18.41 a	A	0.19	18.31 a	A	0.36

* Lowercase letters across a row indicate significant differences among S treatments within the corresponding soil type at α=0.05

** Uppercase letters within a column indicate significant differences among soil types within the corresponding S treatment at α=0.05

Table 5.8 Percent base saturation in five Breton Plot soils with four S treatments after wheat growth

	Sulphur											
	0 kg S ha^{-1}			20 kg S ha^{-1}			40 kg kg S ha^{-1}			175 kg S ha^{-1}		
Soil	Mean (%)		SD	Mean (%)		SD	Mean (%)		SD	Mean (%)		SD
Native	99.55 a*	B**	0.05	99.45 a	C	0.10	99.40 a	B	0.08	98.87 b	C	0.20
Check	99.64 ab	B	0.03	99.76 a	A	0.03	99.75 a	A	0.04	99.54 b	AB	0.10
NPK	99.85 a	A	0.12	99.84 a	A	0.09	99.75 ab	A	0.15	99.51 b	AB	0.15
NPKS	99.65 a	B	0.03	99.65 a	B	0.01	99.62 a	A	0.06	99.19 b	B	0.03
Manure	99.82 a	A	0.09	99.66 ab	B	0.11	99.72 a	A	0.08	99.50 b	AB	0.06

* Lowercase letters across a row indicate significant differences among S treatments within the corresponding soil type at α=0.05

** Uppercase letters within a column indicate significant differences among soil types within the corresponding S treatment at α=0.05

Table 5.9 Percent base saturation in five Breton Plot soils with four S treatments after alfalfa growth

	Sulphur											
	0 kg S ha^{-1}			20 kg S ha^{-1}			40 kg kg S ha^{-1}			175 kg S ha^{-1}		
Soil	Mean (%)		SD	Mean (%)		SD	Mean (%)		SD	Mean (%)		SD
Native	98.95 a*	D**	0.04	98.24 a	C	0.21	99.85 a	C	0.16	98.79 b	C	0.01
Check	99.75 ab	BC	0.03	99.74 ab	B	0.05	99.86 a	AB	0.06	99.69 b	A	0.12
NPK	99.95 a	A	0.01	99.93 a	A	0.02	99.93 a	A	0.01	99.80 b	A	0.02
NPKS	99.74 a	C	0.13	99.81 a	AB	0.02	99.77 a	B	0.03	99.42 b	B	0.08
Manure	99.87 a	AB	0.01	99.87 a	AB	0.02	99.88 a	A	0.08	99.79 a	A	0.03

* Lowercase letters across a row indicate significant differences among S treatments within the corresponding soil type at $\alpha=0.05$

** Uppercase letters within a column indicate significant differences among soil types within the corresponding S treatment at $\alpha=0.05$

Table 5.10 Exchangeable Mn in five Breton Plot soils with four S treatments after wheat growth

	Sulphur							
	0 kg S ha^{-1}		20 kg S ha^{-1}		40 kg kg S ha^{-1}		175 kg S ha^{-1}	
Soil	Mean (cmolc kg-1)	SD	Mean (cmolc kg-1)	SD	Mean (cmolc kg-1)	SD	Mean (cmolc kg-1)	SD
Native	0.053 b* A**	0.007	0.076 b A	0.015	0.088 b A	0.014	0.167 a A	0.028
Check	0.025 b C	0.002	0.030 b B	0.004	0.032 b C	0.002	0.053 a C	0.016
NPK	0.014 b D	0.002	0.011 b C	0.002	0.016 ab D	0.002	0.027 a C	0.009
NPKS	0.037 b B	0.001	0.039 b B	0.002	0.049 b B	0.004	0.115 a B	0.017
Manure	0.022 b C	0.002	0.025 b BC	0.004	0.027 b CD	0.002	0.055 a C	0.007

* Lowercase letters across a row indicate significant differences among S treatments within the corresponding soil type at α=0.05

** Uppercase letters within a column indicate significant differences among soil types within the corresponding S treatment at α=0.05

Table 5.11 Exchangeable Mn in five Breton Plot soils with four S treatments after alfalfa growth

	Sulphur											
	0 kg S ha^{-1}			20 kg S ha^{-1}			40 kg kg S ha^{-1}			175 kg S ha^{-1}		
Soil	Mean (cmol$_c$ kg^{-1})		SD	Mean (cmol$_c$ kg^{-1})		SD	Mean (cmol$_c$ kg^{-1})		SD	Mean (cmol$_c$ kg^{-1})		SD
Native	0.183 b*	A**	0.011	0.201 b	A	0.036	0.228 b	A	0.021	0.323 a	A	0.055
Check	0.011 b	B	0.002	0.013 b	B	0.002	0.014 b	B	0.001	0.029 a	B	0.006
NPK	0.009 b	B	0.001	0.012 b	B	0.002	0.011 b	B	0.001	0.034 a	B	0.002
NPKS	0.024 b	B	0.007	0.029 b	B	0.003	0.036 b	B	0.004	0.060 a	B	0.007
Manure	0.023 a	B	0.001	0.025 a	B	0.004	0.023 a	B	0.015	0.039 a	B	0.007

* Lowercase letters across a row indicate significant differences among S treatments within the corresponding soil type at α=0.05

** Uppercase letters within a column indicate significant differences among soil types within the corresponding S treatment at α=0.05

Table 5.12 Exchangeable Al in five Breton Plot soils with four S treatments after wheat growth

	Sulphur							
	0 kg S ha^{-1}		20 kg S ha^{-1}		40 kg kg S ha^{-1}		175 kg S ha^{-1}	
Soil	Mean (cmol$_c$ kg^{-1})	SD	Mean (cmol$_c$ kg^{-1})	SD	Mean (cmol$_c$ kg^{-1})	SD	Mean (cmol$_c$ kg^{-1})	SD
Native	0.027 a* A**	0.002	0.020 a AB	0.004	0.022 a A	0.008	0.024 a AB	0.010
Check	0.031 a A	0.003	0.005 b B	0.003	0.005 b A	0.006	0.014 b B	0.013
NPK	0.014 b A	0.021	0.019 b AB	0.018	0.025 ab A	0.030	0.057 a A	0.027
NPKS	0.014 a A	0.005	0.013 a AB	0.002	0.010 a A	0.006	0.008 a B	0.009
Manure	0.013 a A	0.017	0.038 a A	0.017	0.023 a A	0.016	0.033 a AB	0.004

* Lowercase letters across a row indicate significant differences among S treatments within the corresponding soil type at α=0.05

** Uppercase letters within a column indicate significant differences among soil types within the corresponding S treatment at α=0.05

Table 5.13 Exchangeable Al in five Breton Plot soils with four S treatments after alfalfa growth

	Sulphur							
	0 kg S ha^{-1}		20 kg S ha^{-1}		40 kg kg S ha^{-1}		175 kg S ha^{-1}	
Soil	Mean (cmol$_c$ kg^{-1})	SD	Mean (cmol$_c$ kg^{-1})	SD	Mean (cmol$_c$ kg^{-1})	SD	Mean (cmol$_c$ kg^{-1})	SD
Native	0.000 a* B**	0.000	0.000 a B	0.000	0.000 a A	0.000	0.000 a B	0.000
Check	0.028 a A	0.004	0.026 a A	0.007	0.007 b A	0.010	0.015 ab AB	0.013
NPK	0.000 a B	0.000	0.000 a B	0.000	0.000 a A	0.000	0.000 a B	0.000
NPKS	0.017 a AB	0.021	0.000 a B	0.000	0.000 a A	0.000	0.025 a A	0.019
Manure	0.000 a B	0.000	0.000 a B	0.000	0.000 a A	0.000	0.000 a B	0.000

* Lowercase letters across a row indicate significant differences among S treatments within the corresponding soil type at α=0.05

** Uppercase letters within a column indicate significant differences among soil types within the corresponding S treatment at α=0.05

Table 5.14 Exchangeable acidity in five Breton Plot soils with four S treatments after wheat growth

	Sulphur									
	0 kg S ha^{-1}		20 kg S ha^{-1}		40 kg kg S ha^{-1}		175 kg S ha^{-1}		Average	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	
Soil	($cmol_c$ kg^{-1})		($cmol_c$ kg^{-1})		($cmol_c$ kg^{-1})		($cmol_c$ kg^{-1})		($cmol_c$ kg^{-1})	
Native	0.047	0.002	0.047	0.007	0.046	0.003	0.055	0.024	0.049	A*
Check	0.012	0.004	0.017	0.004	0.020	0.002	0.021	0.013	0.018	D
NPK	0.041	0.007	0.033	0.013	0.042	0.003	0.038	0.003	0.039	BC
NPKS	0.028	0.002	0.027	0.001	0.031	0.001	0.041	0.009	0.032	C
Manure	0.041	0.010	0.040	0.001	0.038	0.003	0.042	0.004	0.040	B
Mean	0.034		0.033		0.035		0.039			

* Uppercase letters indicate significant differences among soil types at α=0.05

Table 5.15 Exchangeable acidity in five Breton Plot soils with four S treatments after alfalfa growth

	Sulphur											
	0 kg S ha^{-1}			20 kg S ha^{-1}			40 kg kg S ha^{-1}			175 kg S ha^{-1}		
Soil	Mean (cmol$_c$ kg^{-1})		SD	Mean (cmol$_c$ kg^{-1})		SD	Mean (cmol$_c$ kg^{-1})		SD	Mean (cmol$_c$ kg^{-1})		SD
Native	0.141 c*	A**	0.009	0.161 bc	A	0.008	0.173 ab	A	0.008	0.200 a	A	0.021
Check	0.027 a	B	0.005	0.025 a	C	0.017	0.028 a	BC	0.005	0.028 a	B	0.036
NPK	0.032 ab	B	0.004	0.033 a	BC	0.004	0.022 b	C	0.008	0.033 ab	B	0.002
NPKS	0.034 a	B	0.004	0.034 a	BC	0.001	0.034 a	BC	0.003	0.042 a	B	0.008
Manure	0.038 a	B	0.001	0.042 a	B	0.010	0.037 a	B	0.002	0.037 a	B	0.004

* Lowercase letters across a row indicate significant differences among S treatments within the corresponding soil type at α=0.05

** Uppercase letters within a column indicate significant differences among soil types within the corresponding S treatment at α=0.05

Table 5.16 Percent carbon in five Breton Plot soils with four S treatments after wheat growth

	Sulphur								Average	
	0 kg S ha^{-1}		20 kg S ha^{-1}		40 kg kg S ha^{-1}		175 kg S ha^{-1}			
Soil	Mean (%)	SD	Mean (%)	SD	Mean (%)	SD	Mean (%)	SD	Mean	
Native	3.35	0.16	3.04	0.72	3.17	0.20	2.96	0.25	3.13	A*
Check	1.93	0.04	1.91	0.08	1.93	0.10	1.87	0.05	1.91	C
NPK	1.97	0.04	1.93	0.11	2.06	0.06	2.02	0.09	2.00	BC
NPKS	2.14	0.08	2.12	0.10	2.11	0.07	2.17	0.06	2.13	B
Manure	3.24	0.08	3.18	0.12	3.35	0.15	3.27	0.13	3.26	A
Mean	2.53		2.44		2.52		2.46			

* Uppercase letters indicate significant differences among soil types at α=0.05

Table 5.17 Percent carbon in five Breton Plot soils with four S treatments after alfalfa growth

	Sulphur							
	0 kg S ha^{-1}		20 kg S ha^{-1}		40 kg kg S ha^{-1}		175 kg S ha^{-1}	
Soil	Mean (%)	SD	Mean (%)	SD	Mean (%)	SD	Mean (%)	SD
Native	3.69 a* A**	0.33	4.05 a A	0.33	3.41 a A	0.25	3.46 a A	0.53
Check	1.90 a B	0.04	1.89 a C	0.06	1.91 a B	0.09	1.85 a B	0.05
NPK	1.98 a B	0.09	1.91 a C	0.04	1.99 a B	0.09	1.98 a B	0.08
NPKS	2.10 a B	0.06	2.16 a C	0.04	2.16 a B	0.09	2.22 a B	0.02
Manure	3.30 a A	0.02	3.26 a B	0.22	3.32 a A	0.07	3.34 a A	0.10

* Lowercase letters across a row indicate significant differences among S treatments within the corresponding soil type at α=0.05

**Uppercase letters within a column indicate significant differences among soil types within the corresponding S treatment at α=0.05

Table 5.18 C:N in five Breton Plot soils with four S treatments after wheat growth

	Sulphur									
	0 kg S ha^{-1}		20 kg S ha^{-1}		40 kg kg S ha^{-1}		175 kg S ha^{-1}		Average	
Soil	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	
Native	15.83	0.12	14.52	2.40	15.43	0.27	15.61	0.44	15.35	A*
Check	10.06	0.07	10.09	0.16	10.18	0.52	10.16	0.19	10.12	C
NPK	10.21	0.11	10.22	0.19	10.49	0.22	10.24	0.23	10.29	C
NPKS	10.99	0.47	11.30	0.19	10.96	0.13	10.52	0.07	10.94	B
Manure	10.52	0.13	10.47	0.05	10.64	0.13	10.43	0.03	10.51	BC
Mean	11.52		11.32		11.54		11.39			

* Uppercase letters indicate significant differences among soil types at α=0.05

Table 5.19 C:N in five Breton Plot soils with four S treatments after alfalfa growth

	Sulphur								Average	
	0 kg S ha^{-1}		20 kg S ha^{-1}		40 kg kg S ha^{-1}		175 kg S ha^{-1}			
Soil	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	
Native	15.33	0.73	15.52	0.62	15.87	0.51	15.32	0.33	15.51	A*
Check	10.08	0.26	10.04	0.55	10.31	0.24	9.97	0.13	10.10	C
NPK	10.08	0.26	9.97	0.23	9.94	0.25	10.15	0.22	10.03	C
NPKS	10.58	0.15	10.74	0.14	10.80	0.16	10.59	0.19	10.67	B
Manure	10.69	0.16	10.65	0.46	10.74	0.07	10.93	0.29	10.75	B
Mean	11.35		11.45		11.42		11.43			

* Uppercase letters indicate significant differences among soil types at α=0.05