



# Utilization of Point Aconi CFB Ash as an Agricultural Soil Amendment

Final Research Report

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October, 2000

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Second Printing August, 2004

## **ACKNOWLEDGMENTS**

Sincere thanks are extended to:

Peg Cummings, Jim Lewis and others at the Point Edward Resource Centre, who have generously given their time and provided space and equipment for the project.

Bill Richards, of Nova Scotia Power, who generously provided support and assistance throughout this research. Contributions, at various stages, from Gerry Lethbridge, Louis Ferguson, Brian Jennex, Pat Farrell and Carey O'Handley are acknowledged with appreciation.

Alain Joseph, for 3 field seasons of dedicated work.

Ron Korcak, Agricultural Research Service of the United States Department of Agriculture, who provided valuable input on handling and agricultural utilization of CFB ash.

Allen L. Crandlemire, the Coal Research Agreement (Cape Breton Development Corporation, Nova Scotia Power Inc. and Nova Scotia Department of Natural Resources) and the Natural Science and Engineering Research Council of Canada, for providing the research funding.

## ABSTRACT

A three year study was conducted to evaluate Point Aconi Circulating Fluidized Bed (CFB) ash, which is approximately one third each of unreacted sorbent (CaO), gypsum (CaSO<sub>4</sub>), and coal ash, as an agricultural soil amendment and liming agent. The ash utilized in the study, baghouse material (fly ash) captured from combustion of Devco Prince coal, is typical of ash from high sulphur coal-fired fluidized bed combustors. After three years of field testing, CFB ash was found to be an acceptable liming agent for vegetable crops (cabbage and rutabaga) and mixed forage, with no significant adverse effects on crop quality or excessive soil loading of metals. Two years of testing on turfgrass indicates that CFB ash may also be used as a fast-acting limestone substitute on turfs. Within the first year, ash applied at the soil lime requirement increased very low soil pH to a range considered optimal for nutrient availability and crop growth. A high persistence of liming effects in both ash and limestone treatments suggests that the materials have comparable residual activity. There was no yield difference between ash and limestone amended crops, however, both soil treatments significantly improved growth and yield of vegetables and forage compared with unamended controls. Soil levels of As, Ba, Cu, Pb, Sr, Cr, Tl, V, Hg and U were increased significantly by ash treatments. With the exception of Tl, no plant uptake of any of the metals was detected and none of the elements exceeded metal criteria for soils receiving waste materials. Ca:Mg imbalances and Ca-induced Mg deficiency in soils and crops is an important nutrient management issue relating to repeated use of CFB ash as a liming agent. It is recommended that CFB ash be made available for use as a liming agent on both food and non-food crops. As this study demonstrates, however, a number of safety, efficacy, and regulatory issues need to be addressed in order to derive the greatest benefit from utilizing the material as well as minimize potential risks. The report includes recommendations for land application as well as for the development of standards and guidelines for agricultural use of CFB ash in Canada.

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**EXECUTIVE SUMMARY**

After three years of field testing, Point Aconi CFB ash was found to be an effective liming agent for vegetable crops (cabbage and rutabaga) and mixed forage, with no significant adverse effects on crop quality or excessive soil loading of metals. Two years of testing the ash on turfgrass indicates that the material may also be used safely (i.e., without burning) as a fast-acting limestone substitute on turfs. It is therefore concluded that CFB ash is an acceptable liming agent for both food and non-food crops. There are a number of important issues associated with agricultural utilization that need to be addressed, however, in order to derive the greatest amount of benefit and minimize potential risks.

Presented in this Final Research Report are the results obtained on liming efficacy and crop response, as well as element loading in soils and uptake by crops. The implications of these results is presented in the context of improving the prediction of soil and crop liming response to the ash, as well as developing guidelines (i.e., management, monitoring and quality standards) for utilization of the ash in agriculture and as a soil amendment.

**Liming Efficacy**

CFB ash was similar to Mosher (dolomitic) limestone in terms of both liming activity in the soil, as well as crop response to soil treatment. Within the first year of application, CFB ash applied at rates equivalent to the soil lime requirement (21 t/ha), increased very low soil pH (4.9) to a range considered optimal for nutrient availability and crop growth (pH 6.0-6.5). In Years 2 and 3, soil pH in both limestone and CFB ash treatment plots was maintained within or near the optimum range with little or no additional applications.

The ability of a liming material to neutralize soil acidity depends primarily on the neutralizing value, or calcium carbonate equivalence (CCE). Because of a lower CCE (64-80%) compared with Mosher limestone (90-95%), application rates of the ash were increased approximately 30% to provide equivalent acid neutralizing capacity. An important finding of the study is that soil pH response is predictable and similar for liming materials of varying neutralizing value so long as amendment loading is adjusted for the CCE of the material. Variability of the ash with respect to CCE is therefore not considered to be a limitation in terms of use as a liming agent.

CFB ash reacted more quickly than limestone, and the resulting soil pH was higher. The high alkalinity was soon reduced by the carbonation reaction which occurs following application of the ash to soils. Differences in acid-neutralizing behavior of the liming materials is attributed to the high oxide content (15-40%) of the ash, which imparts a high reactivity, high alkalinity (pH >12), and powdery consistency to the material. This is distinct from the crystalline carbonates in limestone, which must be ground in order to react with soil particles and range in pH between pH 8-8.5.

A high persistence of liming effects was observed in both limestone and ash treatments, and in Year 4 there is no indication of declining soil pH in treatments applied at the higher loading rate.

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High liming persistence is attributed to factors which lower the solubility of the liming materials, and therefore reduce the rate of reaction with soil particles. High amendment loading rates (>20 t/ha) and an essentially complete neutralization of soil acidity are two factors which would substantially reduce the solubility of liming materials. While CFB ash contains a greater percentage of highly reactive particles (<0.15 mm) than Mosher limestone (98% compared with 60%), residual activity of the oxide component is increased by the formation of granules of CaCO<sub>3</sub> of relatively low solubility. Thus, despite a fine particle size and high reactivity, liming persistence of CFB ash may not differ significantly from that of carbonate limestones.

While increasing low soil pH is the main reason for liming acid soils, improving soil levels of Ca, or Ca and Mg, is another important usually concurrent function. CFB residues contain large amounts of Ca (24-46%) but are generally Mg depleted (0.3-1%). By comparison, dolomitic limestones contain similar or lower amounts of Ca (21-27%) but significantly more Mg (8-11%). At the relatively high loading rates used in this study, ash treatments had a large impact on soil Ca levels but no effect on soil Mg. The effect of high soil Ca:Mg on nutrient availability to crops grown in ash amended soils, as well as on livestock who may consume low Mg content forage, has implications for both the liming strategy as well as soil and crop monitoring requirements. To prevent Ca-induced Mg deficiency in soils and crops, it is recommended that CFB ash be used only on soils that contain adequate (>10%) Mg. Below 10% soil Mg, dolomitic lime should be used as a liming material to increase soil Mg to at least 12% before further applications of ash. Levels of Mg and other soil nutrients should be monitored following ash application, particularly on sandy soils of low cation exchange capacity (CEC).

Hydrated (conditioned) ash had slightly lower neutralizing value than unhydrated material, and demonstrated a greater tendency to clump and interfere with use of the hand-held Gandhi drop spreader for application. Nonetheless, hydrated ash was preferred because of the less caustic nature and improved dust control compared with the unhydrated material. A separate spreading trial, utilizing a commercial size tandem lime spreader, indicated that hydrated CFB ash can be easily applied using typical farm-scale limestone spreading equipment. Because smaller scale drop spreaders are widely used for applying lime to turfs, spreader trials may be required to determine the best method of application to turfs.

### **Crop Response**

There was no yield difference between ash amended and limestone amended vegetable crops, and all soil amendment treatments significantly improved growth and yield of vegetables when compared with unamended controls. Maximum loading treatments (up to 53 t/ha) indicated no phytotoxicity in vegetable crops at any growth stage, including sensitive stages such as germination and seedling growth.

In the forages, no adverse effects were noted on establishment or growth of forage when ash was soil incorporated in the seeding year. Surface applications of ash in years 2 and 3 were minimal due to target soil pH being reached or exceeded. Total forage yields were similar in the ash and

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Limestone treatments, and within the range reported for mixed forage grown in Nova Scotia (7.5-8 t/ha). Yields in non-limed controls were reduced by 50%, indicating the importance of maintaining correct soil pH in forage production. Forage quality, as indicated by values for crude protein (%CP), digestible energy (%ADF, %TDN and %DE) and nutrient content, was higher in liming treatments compared with unamended controls but not different between ash and limestone treatments. All liming treatments contributed to earlier growth and better persistence of the legume component in the third year.

In the turf grass, no adverse effects on turf (burning, etc.) were noted, even when the ash was applied at a rate (160 kg/100 m<sup>2</sup>) that greatly exceeds what would normally be applied (25 kg/100 m<sup>2</sup>) to turfgrass. Observations on turf quality (greenness, density, % weeds, etc.) did not indicate any effect of liming treatments on turf quality. The lack of quality differences is not surprising, however, given the limited number of treatment applications (once for Low-Ash and Limestone, twice for High-Ash), relatively high initial soil pH, and heterogeneity (i.e., botanical diversity) of the test site.

A similar response of vegetables and forage crops to both ash and limestone treatments indicates that low soil pH was the main factor limiting crop growth. While NPK fertilizer was supplied to all treatments, improved soil levels of macronutrients did not eliminate the consistent and severe yield reduction (>50%) observed in the unlimed Control treatments. Plant tissue Mg was very low in all ash-amended crops, however low Mg did not limit crop yield. The significant crop response to liming obtained in this study highlights the rationale for recommending lime in crop production; that is, to improve crop yield.

### **CFB Ash as a Source of Plant Nutrients**

The clearest demonstration of enhanced plant uptake was for Ca. Plant Ca levels were significantly higher in ash compared with Limestone treatments in both cabbage and forages, but not the rutabaga. There was no evidence of increased S levels in the ash treatments for either of the high-S requiring vegetable crops. While plant B was increased by ash treatments in the cabbage and rutabaga, B was still below sufficiency levels in both crops. CFB ash treatments reduced the severity of B deficiency symptoms (brown heart) in rutabaga but did not replace the need for further B supplementation (i.e., foliar B).

There was little indication of increased plant uptake of Mo, Fe, Cu, Mn or Zn in the ash compared with limestone treatments, and both liming treatments tended to reduce plant uptake of N, Mn and Zn as compared with the controls. Higher plant N in unlimed plots is attributed to lower plant biomass (concentration effect), and increased plant Mn and Zn, to increased solubility and plant availability of these elements at lower soil pH. Both Mosher limestone and ash treatments increased forage Mn above typical levels reported for mixed forage in Nova Scotia, however forage Mn in limed treatments was well below Control levels. The effect of treatments on plant Mn levels is attributed to the significant levels of Mn found in both liming materials. There was no effect of soil treatment on plant Cu.

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In all crops, plant tissue Mg was significantly lower in ash compared with Limestone treatments. This result is of particular concern with forages due to the increased risk of grass tetany (hypomagnesaemia) in ruminant animals who consume the low Mg content forage. The importance of Mg as a macro-nutrient in plant and animal nutrition, as well as the traditional reliance on liming materials to ensure adequate Mg supply, makes Ca-induced Mg deficiency one of the most important management items for agricultural soils amended with CFB ash.

Alkaline conditions and high soil ratios of Ca:Mg and Ca:K can reduce the availability of macronutrients (P, K, and Mg) as well as induce micronutrient deficiencies (B, Cu, Mn, Fe, and Zn). For this reason, liming beyond pH 6.5, or above 75% Ca+Mg, is not recommended, particularly on sandy or weakly buffered soils.

### **Predicting Soil and Crop Liming Response**

The initial characterization of the Point Edward soils as weakly buffered presented some challenges in terms of explaining the results obtained on soil liming response. Consequently, in the 4th year of the study, some additional testing was done on the soils. Two questions posed were: 1) why do sandy loam soils at Point Edward demonstrate such a high lime requirement as well as persistence of liming effects, and 2) do results on soil liming response with CFB ash obtained in this study apply to other soils which differ in terms of buffer acidity and other characteristics?

The main soil characteristics which determine soil lime requirement and liming response are buffer capacity (typically estimated by cation exchange capacity (CEC)) and colloid characteristics (type and amount of clay, organic content). The persistent liming effects observed at Point Edward are attributed mainly to factors which lower the solubility of the liming materials (i.e., high amendment loading rates, near complete neutralization of soil acidity). Laboratory methods used in the initial characterization of the soil may have underestimated soil buffering capacity and overestimated lime requirement of these soils. Thus, there is a possibility that soil test recommendations resulted in a slight over-application of lime to the experimental plots. Supplementary testing done on the soils by the New Brunswick Department of Agriculture lab reported values for CEC that were higher and soil pH and lime requirement values that were lower than values originally reported by the NSDAM soil test lab. Ten lessons learned from the study about soil and crop liming response are presented with a view to developing liming protocols for CFB ash. These lessons highlight the importance of soil testing, not only for effective utilization of the ash but also for the development of liming strategies that are appropriate for the soil type.

### **Potentially Toxic Elements in Soils and Crops**

The ash utilized in this study was relatively high in As, Ba, Fe, Mn, Mo, Pb, Sr, and Zn. This fact was reflected in the soil metal data, which indicated significant increases in As, Ba, Cu, Pb and Sr, and lesser increases (also statistically significant) of Cr, Tl, V, Hg and U in soils from the ash treatments. Five of these elements (As, Cr, Cu, Hg, and Pb) are commonly regulated under federal or provincial laws. From the literature, As is considered the most likely of these to



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accumulate in plants grown on ash amended soils. Despite high amendment loading rates, in the three years of this study, no plant uptake of As or any of the other five regulated metals was detected. None of the metals exceeded criteria for metals in soils. Arsenic, however, exceeded federal limits on As content in fertilizers and supplements. In most cases, soil metal content was below background levels typically reported for uncontaminated soils. For example, in the treatment which had received the maximum loading of ash (53 t/ha), soil As was well below the maximum limit (14 mg/kg) and still within what may be considered a normal soil range (below 7 mg/kg). Levels of Pb in soils from this treatment, while exceeding the values for uncontaminated soil, were still well below the regulated limit for Pb (60 mg/kg). The other three elements (Cr, Cu, and Hg) were present in treated soils at concentrations below the mean levels indicated for uncontaminated soil.

One element, thallium (Tl), may be considered unique in that it increased in both soils and in plant tissues. A significant increase in Tl in both plant tissue and soils in the higher ash treatments, while small, is important due to the toxicity and high bioavailability of this element. Soil Tl levels are normally low, however, Tl is readily taken up by plants, particularly on sandy, low organic matter soils, and increased plant levels of this element may be highly toxic to both plants and animals. Thallium is not one of the dozen or so metals commonly regulated under federal or provincial laws and reported in the literature as environmentally important, and thus the importance of increased soil Tl may be overlooked. Of seven industrialized countries having guidelines for maximum permissible soil metal concentrations, Switzerland is the only country with a limit for Tl (1 mg/kg dw of soil). While levels found in this study are well below the Swiss limits for Tl, our results demonstrate that detectable increases in plant uptake are possible for this element at soil concentrations below the legal soil limit.

The fact that, other than Tl, plant uptake of metals did not occur is notable. At the outset of the study, it was recognized that the ash contained, in addition to the large amounts of beneficial sorbent-derived components, a number of potentially toxic elements which may accumulate in ash amended soils, and/or plants grown on these soils. One of the objectives in establishing the trials - trials involving long-season vegetable crops, grown on a relatively low buffer capacity (i.e. low metal-binding capacity) soil, with amendment loading rates 5 to 10 times higher than those that would normally be applied - was to provide a "worst case scenario" with respect to metal uptake by the crops. While leaching was not measured in this study, the data for net change in soil metals indicates that there were no significant losses of soil metals during the course of the growing season.

Despite the low clay content (4-6%) of the soils used in this study, the soils nonetheless demonstrate a significant ability to immobilize metals. The metal sorbing ability of these soils is attributed to the presence of Fe and Al oxide clays as well as a moderately high organic content (3.3-4.6%) for a sandy soil. Conditions that influence mobility and bioavailability of sorbed metals can change over time, and therefore, when determining amendment loading rates, a conservative approach with respect to metals is always best. Federal limits on levels of As and

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other metals in fertilizers and waste materials<sup>1</sup> provide the greatest margin of safety with respect to variability in metal sorption capacity of soils, soil amendment loading rates, as well as soil pH and redox conditions following application of amendments.

**Requirements for Management, Monitoring and Quality Standards**

While there may be a higher level of management associated with the ash compared with conventional liming materials, as an agricultural soil amendment, the material is not entirely unique in this regard. For example, there are other materials used to raise soil pH and/or supply Ca which are Mg-depleted which, if not used properly, can induce Mg deficiencies in soils and crops. Both compost and sewage sludge have established a precedent for determining input levels of metals prior to waste application, as well as monitoring for compliance with metal criteria for soils and waste materials.

In order to derive the greatest benefit from and minimize risk in using CFB ash on agricultural land, there are a number of testing and monitoring steps which should be followed before and after land application. A list of recommended analytical procedures, as might be included in a land application guideline or monitoring protocol for agricultural use, is provided in this report. Some analyses are routinely performed as part of standard agronomic practice, whereas others are more specific for use of liming materials from industrial processes or other by-products to which metal concerns apply.

There are several aspects to ensuring safe and appropriate ash application rates. Some aspects are addressed by soil testing (lime requirement, soil Mg levels, and pre-amendment soil metals) as well as analyses of the ash (CCE, metal content and other ash quality parameters). Other aspects should be addressed through ash quality standards as well as guidelines for land application of CFB ash.

Two of the recommendations of this study are that 1) ash quality standards, and 2) guidelines for land application of CFB Ash, similar to those prepared by the United States Department of Agriculture but adapted to reflect Canadian environmental standards and legislation, be developed in order to promote safe and efficient use of the material. Ash quality standards should include parameters relating to liming efficacy as well as metal content. Existing metal criteria may not be appropriate for alkaline inorganic materials such as CFB ash which contain a wider range but lower levels of metals than sewage sludge. It is recommended that the guideline for land application include ash safety and efficacy criteria, ash handling and application procedures, agronomic considerations, as well as testing and monitoring protocols for ash, soils and crops.

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<sup>1</sup>as compared with less restrictive provincial (e.g., Nova Scotia sewage sludge) metal criteria.

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**Final Research Report****1. INTRODUCTION**

The Point Aconi Generating Station, in eastern Cape Breton Island, Nova Scotia, uses Circulating Fluidized Bed (CFB) technology to generate 165 MWe for the Nova Scotia Power Inc. (NSPI) grid. The use of large amounts of limestone as a sorbent in the CFB process allows combustion of relatively high sulphur coals while achieving 90% sulphur capture. A high rate of residue production (120 000 tonnes of ash annually) as well as cost of landfilling the material in an environmentally compliant facility has prompted NSPI to seek beneficial uses for CFB ash. Since 1997, researchers from the Nova Scotia Agricultural College have been evaluating the Point Aconi ash, comprised of one-third each of unreacted sorbent (CaO), gypsum (CaSO<sub>4</sub>), and coal ash (oxides of Fe, Al, and Si plus trace elements), as an agricultural soil amendment. The research has been conducted on behalf of NSPI with the objective of improving utilization of the high volume by-product, which remains largely landfilled.

The need to investigate opportunities for ash utilization was identified during the plant's environmental assessment process. The rate of residue production from the CFB process is relatively higher than some other combustion/gas cleanup technologies available, such as flue gas desulphurisation. There are environmental and financial incentives for NSPI to avoid the landfill process for the residue. The landfill is a fully engineered site that is costly to construct and to operate. The site also requires continuous environmental monitoring for ground water quality, material stability, and runoff water treatment.

NSPI initiated this project to investigate the feasibility of using the CFB ash as a soil amendment, thereby using some of the lime-based minerals in the residue as a substitute for the limestone currently used by area farmers. Soils in Atlantic Canada are naturally acidic and leached of basic cations (e.g., Ca, Mg and K), and therefore require regular inputs of limestone and fertilizers in order to remain fertile and productive. If demonstrated to be effective, the practice of using CFB ash as a liming agent and source of plant nutrients, has the potential to provide a competitive commercial advantage to farmers in the area of the plant and to permit NSPI to avoid the placement of this by-product of the CFB process in the landfill.

In the United States, agricultural uses for CFB residues have been evaluated for more than 20 years, however, there has been relatively little work done in this area in Canada. Conditions applying to agricultural use of this material which may be unique to Canada include fuel sources for CFB combustion (influencing ash composition), as well as climate, soils and an agricultural industry that does vary from one region to another. A reduction in subsidies and supports to agriculture within Nova Scotia has intensified the pressure on producers to reduce input costs to remain competitive. Much of the original impetus for this study was provided by Cape Breton farmers who, faced with the loss of a trucking subsidy for limestone, contacted NSPI with a view to utilizing Point Aconi ash as a lower cost limestone substitute.

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The specific objectives for the study were:

1. To determine the efficacy of CFB ash as an agricultural liming agent;
2. To evaluate CFB ash as a source of Ca and other nutrients for vegetable and forage crops;  
and
3. To assess the potential for elemental toxicities in soils and crops resulting from application of CFB ash to soils.

The study has consisted of three years of field trials, involving application of CFB ash to vegetables and forage crops, conducted at the Point Edward Resource Centre in Cape Breton, and two years of testing on turfgrass at the Nova Scotia Agricultural College (NSAC) in Truro. The project has also included an extensive laboratory testing program. In the final year, an investigation was conducted into regulations and standards governing the commercialization and use of by-products such as CFB ash as fertilizers and supplements in Canada.

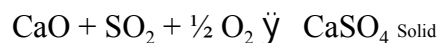
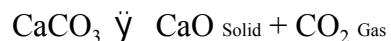
This report describes the methodology and results obtained in the three-year study. Results are presented on liming efficacy and crop response, as well as element loading in soils and uptake by crops. Soil characteristics which are important in soil liming are identified with a view to improving the prediction of soil liming response to the ash as well as the development of appropriate liming strategies for soils having different chemical and physical characteristics. Recommendations for the utilization of CFB ash are provided, with a view to addressing practical challenges which apply in a land application situation, as well as to the development of standards and guidelines to promote safe and efficient use of the material as a soil amendment in Canada.

**Final Research Report****2. LITERATURE REVIEW****2.1 CFB Technology**

Circulating Fluidized Bed (CFB) technology is an advanced coal combustion technology for electric power generating plants that provides a means to utilize low grade fuels (e.g. high sulphur coals, 4 - 8 %) while still achieving stringent air emission requirements (Doiron and Ross 1992). In this process, crushed coal and limestone are fluidized by jets of air and burned at controlled velocity and optimum temperatures. The direct contact between the limestone bed material (sorber) and the solid fuel permits the limestone to absorb sulphur oxides (forming  $\text{CaSO}_4$ ), thus reducing their emission to the atmosphere. Nitrogen emissions are reduced through the relatively low temperature of combustion (Dearborn 1986).

Operating since 1993, the Point Aconi Generating Station uses the Circulating Fluidized Bed (CFB) technology to generate 165 MWe for the NSPI grid. The plant is located on the northeastern coast of Boularderie Island, at the eastern end of Cape Breton Island, Nova Scotia. The location is approximately 10 km east of the Trans Canada Highway on route 162. The plant comprises a CFB boiler in combination with a Toshiba turbine-generator set. The boiler operates at a pressure of 12.8 MPa (1854 PSIG) and a temperature of 540°C (1005°F). The plant is designed to burn approximately 350,000 tonnes (t) of coal and approximately 100,000 t of limestone per year, producing in excess of 120,000 tonnes of residue<sup>2</sup>.

The power plant boiler was designed to burn a wide range of fuels in an environmentally sound manner, limiting sulphur emissions to 10% of the sulphur entering the boiler in the fuel, and thereby reducing NSPI's system wide  $\text{SO}_2$  emissions. To achieve this, the CFB process combines the fuel, primarily petroleum coke and bituminous coal, with limestone in the boiler. The limestone reacts to form lime in the 860°C environment of the boiler. The lime reacts with sulphur dioxide gas to form calcium sulphate. Hence, 90% of the sulphur that enters the boiler as a fuel impurity leaves the boiler as a solid in the ash stream, not as a gaseous emission. The overall chemical reactions are the following:



The boiler is designed to remove ash at two points in the process. Bottom ash is drained directly from the fluid bed combustor. Fly ash is filtered out of the flue gas stream using a baghouse. Because not all of the limestone injected into the boiler reacts to form anhydrite, there is excess limestone and lime in the ash streams. The ash comprises the following major constituents:

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<sup>2</sup>W. Richards, Senior Plant Engineer, Point Aconi Generating Station. Personal communication, July 2000.

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Lime (CaO) - 13.6%; Anhydrite (CaSO<sub>4</sub>) - 34.2%; Limestone (CaCO<sub>3</sub>) - 9.1%; Other calcium compounds (Ca(OH)<sub>2</sub>, CaS, etc.) 6.9%; Coal ash - 35.9% (Jacques Whitford and Assoc. 1997).

Fly ash, removed in the baghouse, is transported pneumatically to a storage silo where it is held until it can be transported to the landfill site or alternate destination. Fly ash destined for the landfill site is mixed (1<sup>st</sup> stage conditioning) with water prior to loading into trucks, and conditioned a second time at the landfill site. The water addition initiates hydration chemical reactions that are necessary to stabilize the material for the landfill process and tends to reduce fugitive dust around the loading facility. Unconditioned fly ash can be loaded into dry tanker trucks at the plant.

**2.2 Properties of CFB Ash**

The properties of coal combustion residues vary with such factors as coal characteristics, combustion conditions, the efficiency of particulate removal, and processes (i.e. conditioning, weathering) that may occur prior to disposal. Additional variables in the CFB process include Ca/S ratio, sorbent characteristics, and conditions during fluidized bed operation (EPS 1982). Depending on cost and availability, other fuels (i.e. oil), some in themselves by-products, may partially replace coal as fuel source. While the variability of coal combustion by-products is a factor that makes it difficult to extrapolate from the literature, there are certain properties of CFB ash that have been used to characterize this material for waste handling, disposal and environmental protection practices (Dearborn 1986).

Chemical, physical, exothermic and leaching properties of CFB ash are described below. Included in the discussion are properties relevant to utilization of the ash as a soil amendment, such as liming efficacy, content of essential and non-essential elements, and physical properties that relate to handling and applying the material.

**2.2.1 Chemical Properties**

CFB ash may be characterized as a mixture of alkaline oxides, unreacted limestone, calcium sulfate, coal ash constituent (Fe, Al and Si oxides), plus small amounts of carbon that remains unburned after combustion. Elemental composition is dominated by five elements, existing primarily in the oxide form, Ca, Si, Al, Fe and S (Jacques Whitford and Assoc. 1997). CFB ash differs chemically from PCF ash in terms of pH and alkaline calcium compounds, as well as solubility of constituents. The utilization of larger quantities of sorbent in the CFB process results in a highly alkaline residue (pH 10-12.5), with Ca compounds comprising up to 80% of the spent bed material and up to 70% of the fly ash (EPS 1982). Unreacted calcium oxide, or quick lime (CaO) and calcium sulfate, or anhydrite (CaSO<sub>4</sub>), are the major constituents, with greater amounts of these compounds present in the spent bed material compared with fly ash (Table 2.1). The other way in which CFB ash differs from PCF ash is that in the lower temperature combustion (CFB), there is no significant reaction between silicate ash and the non-silicate species (e.g., carbonates, chlorides) (Raask 1985). This results in a non-vitrified solids residue that is more soluble and leachable than PCF ashes (Dearborn 1986). Total sulphur



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content is typically 8-14% in the bed material and 4-8% in the fly ash. Total and soluble sulfate concentrations in CFB ashes tend to be similar, indicating that little sulphur exists in the elemental form. Sulphur exists largely as  $\text{CaSO}_4$  (Dearborn 1986). Residues also contain oxides of silicon, iron and aluminum, with generally higher amounts of these constituents associated with fly ash compared with bottom ash. High iron content in residues is generally indicative of pyrite being present in the coal (Jacques Whitford and Assoc. 1997) (Table 2.1). Minor ratios of oxides of potassium, sodium, magnesium, titanium, phosphorus, and sulfur interchangeably exist in the form of sulphates and/or silicates (EPS 1982).

The combination of materials in CFB combustion residues, approximately one-third each coal ash, gypsum and unreacted sorbent ( $\text{CaO}$ ), makes the by-product an attractive soil amendment. The unreacted sorbent can substitute for limestone as a soil pH modifier (discussed in Section 2.2.5) and the gypsum, by virtue of its greater solubility compared to limestone, supplies plant available Ca and S and has a beneficial impact on many soil chemical and physical properties (Shainberg et al. 1989). Ca content in the residue ranges from 24 to 46%, and S content between 7.2 to 14%. The ash component is also a source of several important plant micro-nutrients (B, Mo, Fe, Cu, Mn, and Zn) (Korcak et al. 1997).

**Table 2.1 Major chemical constituents present in CFB residues: bed ash and fly ash (baghouse) samples from Queens\*, Summerside and Point Aconi\*\* CFB units.**

Sample	$\text{CaSO}_4$	$\text{CaO}$	$\text{Ca(OH)}_2$	$\text{CaCO}_3$	Total S	$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$
<b>Bed ash</b>	----- % -----							
Queens	47	40.6	-	2.2	10.8	2.2	-	6
Summerside	47.6	35.9	-	0.8	10.1	1.8	-	10.9
Point Aconi	54.5	13.5	1.6	1.6	13	3.9	4.6	9.3
<b>Fly ash</b>								
Queens	17.3	9.8	-	3.7	4.5	27.2	-	26.6
Summerside	24.4	26.4	-	4.8	5.9	10.2	-	19.9
Point Aconi	34.4	13.6	0.8	9.1	8.2	15.1	5.5	11.4

\* Queens and Summerside data from Dearborn Environmental Consulting Ltd , 1986; results from x-ray diffraction analysis.

\*\* Point Aconi data from Jacques Whitford and Assoc. 1997; results from x-ray diffraction and thermogravimetric analysis.

One frequently cited concern relating to utilization of coal combustion by-products as soil amendments relates to concentrations of minor elements, which include essential, non-essential and toxic elements (i.e. heavy metals). The concentrations of minor elements in CFB fly ash and bed ash as compared with other fossil fuel combustion by-products, sewage sludges, coal and soils are presented in Table 2.2. Concentrations of most minor elements are greater in the combustion by-products when compared with either coal or soils, indicating that the combustion

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process tends to enrich the wastes in the minor elements (Eary et al. 1990). CFB ash is generally lower in minor elements than PCF ash due to the greater amount of sorbent-derived components which comprise 64% of the fly ash and 80% of the bed ash (Jacques Whitford and Assoc. 1997). Compared to sewage sludge from industrialized areas, CFB ash contains low levels of heavy metals (i.e. Cd, Cr, Cu, Hg, Ni, and Zn). Most metals are present in the ash at concentrations less than 1% by weight, and are within ranges normally found in soils (Table 2.2). There are however, a number of minor elements present in CFB residues, which may be of concern, namely B, Mo, Se, As, and Pb. As noted below, other potentially toxic elements (i.e. Cu, Cr, Be, Hg, Ni, Tl, V, and Zn) may also be present at elevated levels, depending on fuel source being utilized (Carlson and Adriano 1993) (Table 2.2). The oxyanions B, Mo, Se, and As are of greater environmental concern than cationic trace elements, due to the generally higher pH of ash-amended soils and the increased solubility of these species due to decreased sorption (Jackson et al. 1999; Khattak et al. 1991). The implications of element content, in terms of utilization of the residue in agriculture and as a soil amendment, is discussed further in Section 2.3.4.

The ranges for various elements in CFB fly ash, bed ash, petroleum coke fly ash and oil derived fuel ash indicates the range in by-product element concentrations, and highlights relationships between fuel source and other variables and ash composition (Table 2.2). Oil derived fuel ash, including petroleum coke fly ash, tends to be enriched in Cu, Pb, Ni, V and Zn. Higher concentrations of As, Mo, Pb and Zn are found in fly ash derived from pyritic (high in FeS<sub>2</sub>) bituminous coals than in fly ash derived from lignite coals (data not shown) (Eary et al. 1990). Element concentrations in fly ash and bed ash samples from Point Aconi CFB units are typical for ash from high sulphur coal-fired fluidized bed combustors (Jacques Whitford and Assoc. 1997). Volatile elements (i.e. As, Se, F, Ba, and Pb) typically concentrate in the fly ash, however, Jacques Whitford and Assoc. (1997) show As with an affinity for the bed ash (Table 2.2). Element concentrations (particularly B and soluble salts) in all ashes may be significantly reduced in weathered or lagooned ash (Carlson and Adriano 1993).

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**Table 2.2 Concentrations of minor elements in fossil fuel wastes, sewage sludge, coal and soils: Prince coal CFB fly ash and bed ash, 30% petroleum coke (Pet coke)/70% Prince coal fly ash, oil ashes, sewage sludges, coal and soils.**

Element	Fly ash		Bed ash	Oil ashes <sup>c</sup>	Sewage sludges <sup>d</sup>	Coal <sup>c</sup>	Soils <sup>d</sup>
	Prince coal <sup>a</sup>	Pet coke <sup>b</sup>	Prince coal				
Al	76,300 <sup>†</sup>	18000	30,300 <sup>†</sup>	-	-	-	10,000-200,000
As	179	140	353	3-10,000	2-26	0.5-106	1-50
Ba	459	340	222	148-1,000	150-4000	150	20-1,500
Be	3.5	nd	2.1	-	4-13	-	0.2-10
B	183 <sup>†</sup>	48	86 <sup>†</sup>	0.5-600	15-1,000	1-360	1-134
Cd	<1	2.2	<1	<11	2-1,500	0.1-6.5	0.01-2.7
Cl	12000	-	1300	-	-	-	-
Cr	136 <sup>†</sup>	20	10 <sup>†</sup>	70-4,400	20-40,600	0-610	1.4-530
Co	13	11	5	-	2-260	-	0.1-65
Cu	69.4	130	70.9	10-130,000	50-3,300	2-190	2-100
F	227	-	81	-	2-740	-	10-1,100
Fe	116,000 <sup>†</sup>	23000	14,600 <sup>†</sup>	-	-	-	10000-300,000
Hg	<0.05 <sup>†</sup>	0.36	2.05 <sup>†</sup>	<1	0.1-55	0.01-1.6	0.01-0.7
Mn	452 <sup>†</sup>	1400	483 <sup>†</sup>	110-1,200	60-3,900	6-180	20-3,000
Mo	14	13	13	<20-780	1-40	0-73	0.2-5
Ni	32	77	9	100-180,000	16-5,300	0.4-104	1-110
Pb	233	170	25	10-100,000	50-3,000	4-220	2-200
Sb	<5	nd	<5	-	-	-	5-10
Se	-	13	-	8-500	2-9	0.4-8	0.1-2
Sr	291	250	348	50-920	40-360	100	5-1,000
Tl	15±3 <sup>†</sup>	5.4	20.6±3 <sup>†</sup>	-	-	-	0.01-2.3
V	59	280	48	10-460,000	20-400	0-1,280	20-500
Zn	238	210	115	40-100,000	700-49,000	0-5,600	10-300

\* Units are mg/kg solid

<sup>†</sup> Prince coal baghouse and bed material from Dearborn 1985.<sup>a</sup> Prince coal fly ash and bed ash data from Jacques Whitford and Assoc. 1997.<sup>b</sup> Pet coke fly ash data from Richards 1999.<sup>c</sup> Oil ashes and coal data from Eary et al. 1990.<sup>d</sup> Sewage sludge and soils data from Kabata-Pendias and Pendias 1991; Bohn et al. 1985

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### 2.2.2 Physical Properties

The spent bed material (bottom ash) is a coarse, sand-sized dry solid, light grey to black in colour and granular in appearance. Fly ash is finer (i.e. silt-sized) and generally darker in colour due to the higher content of unburned carbon. CFB ash particles are vesicular and rounded to amorphous, indicating that the ash has had limited exposure to high combustion temperatures (EPS 1982)<sup>3</sup>. Physical properties of CFB residues considered to be important from a residue management and environmental perspective are particle size distribution, specific gravity, density, permeability, moisture content, and water holding capacity. These properties are also of interest in terms of structural use (Section 2.3.1) and utilization as a soil amendment.

Bottom ash particles range in size from 0.1 to 20 mm in diameter whereas fly ash particles are 1 to 100  $\mu\text{m}$  (Dearborn 1986). Approximately 15% of the bed ash is greater than 2 mm in diameter; of the fraction less than 2 mm, only 4% is silt sized (80  $\mu\text{m}$  or less), whereas 85% of the fly ash is silt sized (Jacques Whitford Assoc. 1997). Under field conditions and after slaking, particle size distributions may be altered due to spalling or fragmentation (also known as decrepitation) caused by the expansion of particles as a result of the reaction between water and the CaO content of the residue. Bottom ash shows a greater tendency for particle fragmentation following slaking compared to fly ash, presumably because of the greater CaO content in the coarser bed material (Dearborn 1985, 1988). Particle size distribution data permits inferences to be made about the disposal and compactability of the residue. For example, bed materials are generally composed of widely varying sized particles, and are therefore easily compacted to obtain high densities and strengths. In contrast, the finer baghouse materials are very fine and uniformly sized making the residue more difficult to compact. To achieve high densities, greater compaction energies and water additions are required to permit particle orientation. In a practical situation, landfilled residue is a mixture of bed and baghouse materials which are blended to produce a homogeneous waste with uniform conditioning requirements to achieve optimum strengths (Dearborn 1988).

Specific gravity and minimum and maximum densities are used in prediction of the behaviour of the ash particles within the landfill with respect to compaction and settling. Bottom and fly ash fractions exhibit specific gravities in a range that is typical of soils, 2.58-2.82 and 2.08-2.77  $\text{g}/\text{cm}^3$ , respectively (Dearborn 1988). Values reported for minimum density of Point Aconi CFB ash are 1010  $\text{kg}/\text{m}^3$  and 1598  $\text{kg}/\text{m}^3$ , for fly ash and bottom ash, respectively. Maximum densities were 1080  $\text{kg}/\text{m}^3$  and 1694  $\text{kg}/\text{m}^3$  for fly ash and bed ash, respectively (Jacques Whitford and Assoc. 1997). The lower minimum densities of the fly ash compared to bottom ash are attributed to a more uniform, smaller particle size distribution. Stone and Kahle (1978) report permeability coefficients of  $3.7 \times 10^{-2}$   $\text{cm}/\text{s}$  for bed material and  $1.9 \times 10^{-3}$   $\text{cm}/\text{s}$  for fly ash. This range of permeability ( $10^{-3}$  to  $10^{-2}$   $\text{cm}/\text{s}$ ) is comparable to that of fine sand. For comparison, permeability coefficients of gravels are greater than 11.6  $\text{cm}/\text{s}$  and those of clays in the order of  $1 \times 10^{-7}$   $\text{cm}/\text{s}$  (Dearborn 1988).

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<sup>3</sup>Typical CFB operating temperatures are 815-950 °C, compared with 1370-1650 °C for PCF boilers.

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Moisture content of unhydrated CFB residues is negligible, 0.0% in the bed material and less than 0.1% in the fly ash, as is expected in products of combustion. Residues readily absorb moisture from the air, however, due to the presence of hygroscopic compounds such as  $\text{CaSO}_4$  and  $\text{CaO}$  (Dearborn 1988). Moisture-density compaction relationships are highly significant in disposal of the residue in terms of minimizing both disposal area requirements as well as leaching potential. Water holding capacity is determined to give some indication of the amount of water that a landfilled waste might retain against the force of gravity before it begins to release leachate. Difficulties in determining water holding capacity of CFB residues include resistance to wetting (i.e. when water is added material floats to the surface) and swelling when wetted (i.e. at least 100% increase in volume). Water holding capacity of the fine textured fly ash (75-90%, w/w) is higher than that of the bed material (40-50%), indicating an earlier release of leachate under saturated conditions in the coarser bed material (Dearborn 1986).

Because of its exothermic and expansive nature, an important management practice in the handling and disposal of CFB ash is conditioning, or hydration (15-45%, w/w), of the ash. Conditioning is generally done at two points in the residue management cycle: at the plant site, during silo-unloading operations, and at the landfill site<sup>4</sup>. Conditioning of CFB residues is done for the following reasons:

- C To permit the hydration reactions, and associated liberation of heat and steam, to take place in a controlled and safe manner;
- C To control the release of fugitive dust emissions during ash-loading and hauling as well as landfilling operations;
- C To facilitate residue expansion prior to landfilling (volume requirements at the landfill site are determined on a hydrated basis);
- C To prevent thermal damage to the landfill liners;
- C To enable landfill operators to achieve required compaction densities (i.e. to within  $\pm$  10% of Modified Proctor Maximum Dry Density) (Doiron and Ross 1992; Dearborn 1986).

Conditioning tests conducted on Point Aconi CFB ash (fly ash, bed ash and 60:40 blend of fly ash and bed ash) indicated that optimum conditioning (associated with 80% conversion of lime to portlandite) was achieved with water additions between 6 and 8 percent (Jacques Whitford and Assoc. 1997).

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<sup>4</sup>W. Richards, Point Aconi Generating Station. Personal communication, May, 1997.

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While all of the above physical properties of CFB ash have implications for use of the material as a soil amendment, hydration behavior and bulk density are likely to be most significant. For example, incomplete hydration of the residue will result in a relatively caustic and dusty product which may be difficult to handle. On the other hand, the addition of too much water may result in formation of rock-hard clumps, equally difficult to handle and apply with conventional lime spreading equipment. Testing may therefore be required to determine the optimum moisture contents for handling and applying the ash for agricultural use. Although individual particles have soil-like densities, bulk density of the residue is low, particularly of the fly ash, because of its small, uniform particle size. The beneficial effect of fly ash on physical properties of both clayey and sandy soils (i.e. increased permeability, porosity, and tilth of clays, and reduced bulk density and increased water holding capacity of sands) are attributed to the silt-sized particles as well as component calcium (Salé et. al 1997; Carlson and Adriano 1993).

### 2.2.3 Exothermic Properties

The presence in the ash of large amounts of unreacted CaO (quicklime) and lesser amounts of CaSO<sub>4</sub> (anhydrite) produces an energetic and exothermic reaction when the ash comes into contact with water. The hydration reaction results in the formation of Ca(OH)<sub>2</sub>, CaSO<sub>4</sub>·2H<sub>2</sub>O, and the liberation of heat. Pure CaO and CaSO<sub>4</sub>, when reacted with water can release 1140 Kcal/kg and 126 Kcal/kg of energy, respectively. The reaction of the ash with water is also accompanied by an increase in crystal volume due to the incorporation of water molecules into the CaO and CaSO<sub>4</sub> crystal structures. The volume change, plus accompanying release of heat of hydration, exerts a great internal expansive force which causes particles to fracture, shatter and then disintegrate completely into microparticles, either as crystalline dust or colloidal suspension. The ratio of water to quicklime determines, in part, the temperature rise (Dearborn 1985).

### 2.2.4 Leaching Properties

Both batch and column leaching tests<sup>5</sup> have been conducted in order to characterize the leachability of CFB residues<sup>6</sup> (Dearborn 1986, 1985, 1988; Jacques Whitford and Assoc. 1997). While column leaching tests are generally considered to be more representative of leachability under field conditions, some of the properties of CFB residues have presented challenges in conducting column leaching studies. For example, in initial column leaching studies, the exothermic and expansive nature of the material when wetted resulted in the destruction of leaching columns and eruption of waste from the columns. Pressures and pozzolanic reactions within the column caused compaction and solidification of residues to the extent that their removal required using a power hand drill with masonry bit (Dearborn 1985). The tendency of CFB residues to solidify when hydrated, as well as the subsequent adsorption/precipitation reactions between ash elemental constituents and the soil, indicates that leachability under field

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<sup>5</sup>Batch and column leaching tests differ with respect to configuration of the waste (suspended within a leaching medium vs compacted within a column) and the method of contacting the waste with the leaching medium (continuous mixing within a sealed container vs slow percolation through a column open to the atmosphere).

<sup>6</sup>Tests are typically conducted on unconditioned, uncompacted material.

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conditions may be considerably less than is suggested by leaching tests. Nonetheless, leaching tests are still considered useful in identifying a worst-case-scenario with respect to leachate characteristics and impact on groundwater.

Leaching tests have demonstrated that CFB residues are relatively soluble in water<sup>7</sup>, and that leachates are highly alkaline (pH typically >12) with high total dissolved solids (TDS) concentrations (>5000 mg/L). The major constituents in the leachates are calcium and sulphate, with minor amounts of chloride, sodium, potassium, fluoride, silicon, aluminum and strontium (Table 2.3). While the dissolved solids are primarily inorganic species, measurable concentrations of total organic carbon (in the range of 2.0 to 52.0 mg/L) may also be present (Dearborn 1986, 1988).

The concentration of most elements in the leachates is very low, and all elements are present at levels several orders of magnitude lower than the two major constituents, calcium and sulphate (Table 2.3). With the exception of these and the seven minor constituents, leachate element concentrations are well below 1.0 mg/L. Concerns with leachate toxicity therefore relate primarily to the high alkalinity of leachates rather than to the presence of metals (Doiron and Ross 1992; Jacques Whitford and Assoc. 1997). Aeration of leachates triggers a recarbonation reaction where the net effect is a reduction in leachate pH and alkalinity as well as concentrations of major dissolved constituents. Bioassays utilizing aeration of leachates to reduce alkalinity to a biologically tolerable range (i.e. pH 7-8) have enabled assessment of aquatic toxicity of CFB residue leachates without the overriding effects of high alkalinity. Results from one study demonstrate a strong correlation between pH and toxicity of leachates. Untreated (alkaline) samples consistently produced toxic responses in Microtox<sup>TM</sup>, algal and *Daphnia magna* tests, whereas aerated (neutralized) samples were accompanied by a large reduction in toxic response (i.e. aerated samples were completely non-toxic for Microtox<sup>TM</sup> and alga, but slightly toxic for *Daphnia magna*) (Dearborn 1988).

A low potential for transfer of most metals from leachates of CFB residues in disposal environments is further reduced by the highly persistent alkalinity. The tendency of a number of metals, in particular Cu, Zn, Ni, Co, Fe, Cd, Pb, Mn, and Hg, to form insoluble compounds under alkaline conditions has been noted (Van Der Sloot et al. 1982, cited in Dearborn 1985; Albasel and Cottenie 1985; Jackson et al. 1999). Similarly, the desorption of trace metals from fly ash in aqueous solutions tends to follow a predictable pattern of decreasing release with increasing pH (Theis and Wirth 1977; Kanungo and Mohapatra 2000). Some metals, however exhibit a reverse trend at high pH (notably As, Se, Mo, V and Cr), therefore a highly alkaline leachate does not guarantee a low concentration of all trace elements which may be of concern (Bohn et al. 1986; Dearborn 1985; Jackson et al. 1999).

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<sup>7</sup>CFB ashes are relatively soluble when compared with PCF ashes. This is because of the high content of CaO and CaSO<sub>4</sub>, which are more soluble than the silicates in PCF residues, as well as the lower temperatures in CFB combustion which results in non-vitrified solids residues that are more leachable than PCF ashes (Dearborn 1986).

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**Table 2.3 Element concentrations reached in CFB residue leachates: bed ash and fly ash from Queens and Summerside<sup>1</sup>, and Point Aconi<sup>2</sup> CFB units.**

Element	Bed ash			Fly ash		
	Queens	Summerside	Point Aconi	Queens	Summerside	Point Aconi
Al	3.99	4.16	<0.1	6.94	4.17	0.19
As	<0.005	<0.005	<0.02	0.035	0.027	<0.02
Ba	0.049	<0.005	0.5	1.03	0.295	0.47
Be	<0.0005	<0.0005	<0.05	<0.0005	<0.0005	<0.05
B	0.071	0.041	<0.05	0.314	0.066	<0.05
Cd	<0.01	<0.01	<0.003	<0.01	<0.01	<0.003
Ca	1490	1450	3460	1790	1440	4000
Cl	20.4	12.2	743	679	36.6	226
Cr	0.01	<0.01	0.024	<0.01	<0.01	<0.02
Co	0.06	<0.05	<0.01	<0.05	<0.05	<0.02
Cu	0.002	0.018	<0.02	0.029	<0.009	<0.02
F	1	1.3	-	5.6	1.9	-
Fe	0.13	0.13	<0.5	0.3	0.13	<0.5
Pb	<0.05	<0.05	0.042	5.21	<0.05	0.0027
Mg	0.1	0.03	0.2	0.26	0.02	0.1
Mn	<0.01	<0.01	<0.02	<0.01	<0.01	0.024
Mo	0.4	0.4	0.16	0.8	0.3	0.13
Ni	0.08	0.07	<0.1	0.08	0.07	<0.1
P	0.6	<0.6	<0.1	0.6	<0.6	<0.01
K	3	2	25.1	47	3	1.45
Si	8.42	4.04	<5	10.6	3.56	<5
Ag	0.015	0.007	<0.005	0.011	0.011	<0.005
Na	2	<1	25	113	2	0.5
Sr	1.58	1.15	2.4	2.39	1.21	1.9
SO <sub>4</sub>	1820	1413	701	1792	1320	781
V	0.018	<0.005	<0.02	0.326	0.028	<0.02
Zn	0.13	0.08	<0.05	1.89	<0.05	<0.05

\* Units are mg/L

<sup>1</sup> Dearborn 1986 -maximum element conc. from serial batch leaching test (20 cycle, leached with deionized water, 20:1 liq to solid ratio) conducted on unconditioned, uncompacted CFB residues.

<sup>2</sup> Jacques, Whitford and Assoc. 1997. Results from leachate extraction procedure 164-GP-IMP (CGSB) on raw Point Aconi fly ash and bed ash.



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### 2.2.5 Liming Efficacy

Liming materials are applied to neutralize soil acidity, raise soil pH and supply Ca and Mg. Attributes of a liming material which affect its reaction with the soil include both chemical properties (CCE, solubility, kind and amount of Ca and Mg compounds) and physical properties (i.e. particle size). Moisture content is also important because water replaces an equivalent weight of potentially reactive agricultural lime (PPIC 1996).

Commonly used liming materials include Ca and Mg oxides, hydroxides, carbonates and silicates (Tisdale et al. 1999). To be considered a liming material the accompanying anion ( $\text{OH}^-$ ,  $\text{HCO}_3^-$ ) must lower  $\text{H}^+$  activity and hence  $\text{Al}^{3+}$  in the soil solution (Tisdale et al. 1999). Gypsum ( $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ ), while not a liming material, is an important Ca source as well as soil conditioner for problem soils (i.e. reducing soluble aluminum in acid soils, and sodium in saline-sodic soils) (Brady and Weil 1999). In Table 2.4, properties used to characterize liming materials are indicated for CFB ash and several other materials used to raise soil pH and/or supply Ca and Mg to soils.

Chemical composition and purity determine how much acid can be neutralized. Pure calcium carbonate ( $\text{CaCO}_3$ ) is the standard against which liming materials are measured, and the acid-neutralizing capacity of liming materials is expressed as a weight percentage of calcium carbonate, or calcium carbonate equivalent (CCE). CCE is the generally accepted term in North America for characterizing acid neutralizing capacity, however, the terms neutralizing value (NV) or total neutralizing value (TNV) are sometimes used interchangeably with CCE<sup>8</sup>. For liming materials derived from industrial processes, 25% is the minimum CCE for the by-product to be considered an effective liming material<sup>9</sup> (BNQ 1997). The CCE of agricultural limestone (high-grade calcitic or dolomitic limestone), is between 90-108% (Table 2.4). The CCE of CFB ash varies primarily with the CaO content, which ranges from 15-40%. Calcium carbonate equivalent of CFB ash ranges from 40-90%; the average is 60% (Stout et al. 1988). Variations in CCE of different batches of ash from the same coal source can be attributed largely to differences in CaO content (a function of coal:sorbent ratios during combustion) and moisture content (i.e., conditioned vs unconditioned ash).

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<sup>8</sup>This can be confusing, as in certain jurisdictions (i.e., most countries within the European Union) neutralizing value refers specifically to CaO equivalence. Conversion for CaO to  $\text{CaCO}_3$  equivalence is 1.786 (BNQ 1997).

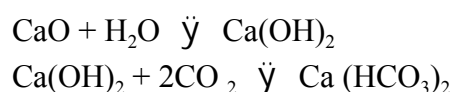
<sup>9</sup>Voluntary industry standard.

**Final Research Report****Table 2.4 Characteristics of materials used to raise soil pH and/or supply Ca and Mg to soils.**

Material	Composition	CCE	CaO equiv	Element		Solubility	Particle size % <0.15 mm
				Ca	Mg		
Burned lime, quicklime	77 CaO 18 MgOA	183	102	55	11	-	-
Slaked/ hydrated lime	75 Ca(OH) <sub>2</sub> 20 Mg(OH) <sub>2</sub> A	136	76	41	8.3	-	-
Calcitic limestone	95 CaCO <sub>3</sub>	90-95	53	32-38	0-3	92	-
Dolomitic limestone	35 CaCO <sub>3</sub> 60 CaMg(CO <sub>3</sub> ) <sub>2</sub> A	95-108	56	21-27	8-11	87	60
Gypsum	CaSO <sub>4</sub> •H <sub>2</sub> O	-	-	23	0-0.2	95	-
CFB residues	15-40 CaO 2-10 CaCO <sub>3</sub> 20-50 CaSO <sub>4</sub> 15-30 FeAlSiO <sub>3</sub>	40-90	22-50	24-46	0.3-1	78-84	98

Sources: Brady and Weil 1999; EPS 1982; Dearborn 1986; Stout et al. 1988.

Compared to the carbonates in agricultural limestone, oxides in CFB ash allow a more rapid neutralization of soil acidity and the resulting soil pH is higher (Brady and Weil 1999). The greater initial reactivity of pure oxides of Ca and Mg compared with carbonates may be attributed to both a higher alkalinity (pH typically > 12) as well as finer particle size. Oxides are inherently unstable, however, and when applied to soils, readily undergo carbonation. Following hydrolysis of the oxide, carbon dioxide from the atmosphere and/or biological respiration combines with Ca<sup>2+</sup> or Mg<sup>2+</sup>, thereby forming more stable calcium or magnesium carbonate compounds of near neutral pH (i.e. pH 7-8) (McCarty et al. 1994; Carlson and Adriano 1993):



While carbonation also occurs with carbonates following application to soils, the associated pH reduction is less pronounced than with oxides and hydroxides due to lower initial alkalinity (Brady and Weil 1999).

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The solubility of liming materials influences the rate of the acid neutralizing reaction in soils, the depth of the liming effect, as well as the extent of release of plant available (exchangeable) Ca and Mg. Solubility is a function of properties of the liming material (chemical composition, particle size), as well as soil conditions (soil pH, concentration of precipitating ions) and the rate and method of application (surface vs incorporated). Other conditions being equal, the solubility of materials from Table 2.4 ranks as follows:

gypsum > calcitic lime > dolomitic lime > CFB ash

The greater solubility of gypsum compared to calcitic or dolomitic lime is attributed to the greater solubility of sulfates compared with carbonates. Calcium carbonate (calcite) is slightly more soluble than magnesium carbonate (dolomite) (Foth and Ellis 1996). While gypsum (or anhydrite,  $\text{CaSO}_4$ ) is a significant component of CFB ash, solubility of the residue is reduced primarily by oxides and carbonates (both sparingly soluble).

In addition to neutralizing value and chemical composition, the other main factor affecting the rate of the acid neutralizing reaction is particle size. Whereas liming materials comprised of oxides/hydroxides, such as CFB ash, are by nature powdery and therefore require no particle size reduction, carbonate limestones must be finely ground in order to react with the soil. Crushing procedures used on carbonate limestones result in a range of particle sizes, and the liming efficiency of different size fractions increases with decreasing particle size, that is 0% efficiency for > 2 mm (9-mesh Tyler sieve); 60% between 0.150 mm and 2 mm; and 100% for < 0.150 mm (100-mesh Tyler sieve) (BNQ 1997). Based on the sieve analysis in Table 2.4, CFB ash has greater liming efficiency (98% of the material less than 0.150 mm) than dolomitic limestone (60% of the material less than 0.15 mm). To meet the desired goal of some neutralization of soil acidity immediately following application, but also continued liming effect for 1 to 4 years after application, agricultural limestone is usually ground so that 40% of the material passes through a 100-mesh sieve, 50% passes 60-mesh, 70% passes 20-mesh and 95% passes an 8-mesh sieve (A&L 1992).

A number of liming studies report a lower liming persistence for CCBs and other lime by-products compared with carbonate limestones (Carlson and Adriano 1993; Muse and Mitchell 1995; Bailey et al 1989; Brady and Weil 1999). Lower residual activity, like greater reactivity, is usually attributed to finer particle size. Other authors (McCarty et al. 1994; Tisdale et. al 1999), however, indicate that the residual activity of oxide materials is increased by the formation of hardened granules of  $\text{CaCO}_3$ , which may remain in the soil for long periods of time. Thus, it is possible that, despite a fine particle size and high reactivity, liming persistence of CFB ash may not differ significantly from that of carbonate limestones.

While the main function of liming materials is raising soil pH, another important, usually concurrent, function, is optimizing the balance and supply of soil calcium and magnesium.

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Calcium is an important structural component of plant cells and stimulates root and leaf development. As the dominant cation in agricultural soils,  $\text{Ca}^{2+}$  also performs important functions in the soil, that is it enhances soil structure, stimulates microbial activity, and acts as a 'nutrient filler', occupying exchange sites on the soil colloid that would otherwise become saturated with acid-forming aluminum and hydrogen, or  $\text{Na}^+$  in sodic soils (Parnes 1990; Bohn et al. 1985). Magnesium, the second most abundant cation in soils, is also critical in plant nutrition. Magnesium is the only metallic constituent of chlorophyll<sup>10</sup>; it is also a factor in enzyme activity and helps regulate the uptake of other nutrients (Tisdale et al. 1999). While soil deficiencies of Ca and Mg are relatively uncommon, these nutrients compete with each other and potassium for uptake by plant roots. The existence of an antagonistic relationship between Ca, Mg and K in the soil means that the ratio of these nutrients can have as much or greater effect on availability to plants as their individual soil concentrations. For example, high levels of soil Ca relative to Mg, or specifically, a soil Ca:Mg ratio greater than 5-7:1, can result in plant deficiencies of Mg. Similarly, high levels of exchangeable soil K can interfere with Mg uptake by crops; K/Mg antagonism is of particular concern in low-magnesium soils. The implication of a magnesium imbalance is far more serious for livestock than for plants. This because of the risk to livestock posed by a potentially fatal condition known as "grass tetany" that can develop when animals consume forage or pasture grasses low in Mg<sup>11</sup> (A&L 1985). While plants are unlikely to show visual Mg deficiency symptoms until soil Mg falls below 5%, the risk of mineral imbalances in forages may occur on soils with <10% Mg (McLean and Brown 1984). Base saturation, or the percentage of the total exchange capacity saturated with exchangeable cations other than hydrogen and aluminum, provides an indication not only of levels of individual nutrients but also of their relationship to one another. While research on varying soil cation ratios has failed to establish a distinct relationship with crop yield, soil base saturation of 50-70% Ca, 8-20% Mg and 2-5% K, is often recommended to maintain an optimum balance, supply and availability of plant nutrients, as well as soil structure and tilth (McLean and Brown 1984; A&L 1992).

Liming soils generally ensures an adequate supply of calcium however, depending on the liming material, may not provide sufficient magnesium. Repeated use of calcitic lime, CaO and other low-Mg liming materials can result in sub-optimal levels of soil Mg, particularly on sandy, low capacity soils. From Table 2.4, CFB residues are generally Mg depleted, and it is well documented that repeated use of CFB residues as a liming material may have a depressing effect on Mg uptake by crops (Section 2.3.4).

### 2.3 Coal Combustion Ash Utilization

The principal applications for which ashes from coal-fired power generation are currently being utilized in Canada and the United States are summarized in the following section. The potential for by-product diversion as well as some of the opportunities and challenges presented by utilizing the material are discussed.

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<sup>10</sup>the chlorophyll molecule imparts green colour to green plants

<sup>11</sup>Grass tetany in ruminant animals is caused by acute Mg deficiency (hypomagnesaemia). Affected animals become hyperirritable, then stagger and fall. If untreated, the condition may be fatal. Grass tetany is associated with blood serum Mg in the animal below 0.001%, or plant tissue Mg less than 0.18% on a dry weight basis.

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While total ash production in the US (more than 50 million tonnes) far exceeds the amount produced in Canada (6 million tonnes), in both countries the percentage of ash being utilized represents 20 - 25% of the total. In both Canada and the US, fly ash accounts for approximately 75% of the total ash production and virtually all of the utilization. The main application for which coal combustion ash is utilized is as a structural/fill material. Other uses currently under investigation include as a substrate for solidifying or stabilizing wastes, alkaline reagent to control acid mine drainage, and utilization in agriculture and as a soil amendment. The current by-product diversion for coal combustion ash in the United States and Canada is summarized in Table 2.5.

The majority of ash utilization in the US involves PCF ashes; in Canada, Point Aconi is the only utility CFB unit therefore essentially all of the Canadian utilization data refers to PCF ash (ACAA 1997; NRCAN 1998). While CFB ash represents a small fraction of the total ash produced, higher alkalinity compared with PCF ashes and other unique properties make it an attractive candidate for agricultural use.

**Table 2.5 Current by-product utilization (million metric tons), and percentage of the total diverted from landfill, represented by various applications for coal combustion ashes.**

Application	United States		Canada	
	Utilization (million tons)	Diversion (% )	Utilization (million tons)	Diversion (% )
Structural/fill material	11.85	22	1.1	17
Waste stabilization	1.7	-	>0.1	>1
Control of Acid Mine Drainage -		-	0.2	3
Soil Amendment	-	-	0	0
Total	-	25	1.3	20

### 2.3.1 Structural Use

In the United States, 11.85 million tonnes of coal combustion fly ash, or approximately 22% of the total amount generated, is utilized in structural or construction-related applications. From Table 2.6, the major usage for fly ash in the US is cement production and/or concrete products, which together account for 60% of the total utilized in construction related activities (ACAA 1997). In Canada, a higher percentage (up to 80%) of the total ash utilized is designated for structural applications, however as noted above, the volumes involved are far below those of the US (data not shown) (NRCAN 1998).

**Final Research Report****Table 2.6 Fly ash construction-related applications in the United States (1996).**

Applications	Quantity used (million tonnes)	Percent of total used
Cement production and/or concrete products	7.2	60
Structural fills or embankments	1.9	17
Stabilization of waste materials	1.7	14
Road base or subbase materials	0.63	5
Flowable fill and grouting mixes	0.27	2
Mineral filler in asphalt paving	0.15	2
Approximate total	11.85	100

Source: American Coal Ash Association 1997. 1996 Coal Combustion Product-Production and Use.

The cementitious properties of fly ash may be attributed to the lime (CaO), which on hydration forms compounds similar to those developed by the hydration of portland cement<sup>12</sup>. Pozzolanic properties are due to the presence of *“siliceous or siliceous and aluminous materials which in themselves possess little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties”* (ASTM C 618-91). Fly ash is considered to be a natural pozzolan. Pozzolans tend to enhance the workability and structural properties of cement admixtures. Fly ash which is to be utilized in portland cement concrete (PCC) must meet the requirements of ASTM C618<sup>13</sup>, a stringent yet widely applied industry standard. Under ASTM C618 two main classes of fly ash are defined 1) Class F fly ash, and 2) Class C fly ash. Fly ash that is produced from the burning of anthracite and bituminous coal is typically pozzolanic and is referred to as a Class F fly ash if it meets the chemical composition and physical requirements specified in ASTM C618. Fly ash that is produced from lignite and subbituminous coal, in addition to having pozzolanic properties, also has some self-cementing properties (ability to harden and gain strength in the presence of water alone). When this fly ash meets the specifications outlined in ASTM C618, it is referred to as a Class C fly ash. Most Class C fly ashes have self-cementing properties (ACAA 1997; SBS 1999).

Essentially all Class C fly ash is used as an additive in cement mixtures or as a cement substitute. Class F fly ash is utilized primarily as structural fill/embankment material (conditioned and compacted as a soil substitute) or flowable fill (aggregate or supplementary cementitious material). The accepted norm for PCC replacement is approximately 25%, however replacement up to 60% has been successfully demonstrated for use of Class F fly ash in flowable fill (CANMET/ACI 1998).

<sup>12</sup> Mostly calcium silicate hydrates.

<sup>13</sup>ASTM C618-92a. 1994. Standard Specification for Fly Ash and Raw or Calcined Natural Pozzolan for Use as Mineral Admixture in Portland Cement Concrete. ASTM, Annual Book of ASTM Standards, Vol. 04.02, West Conshohocken, Pennsylvania.

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There are many advantages and seemingly few disadvantages associated with structural use of coal combustion fly ash. The natural pozzolanic and cementitious properties of fly ash make it well suited for structural applications. While not all fly ashes will meet ASTM C618 standards, this is not necessarily a problem for uses other than cement production. One advantage of structural applications is the diversity of uses, which allows utilization of ash of varying quality and characteristics. Risk to the environment or public health posed by contaminant leaching is very low once the material has solidified into a massive structure with low permeability. Structural use is already a high volume application for the ash, and with the potential for significant increased utilization, a much higher diversion of ash from landfill is possible with this application.

**2.3.2 Waste Stabilization**

Typically, metal contaminated wastes are chemically stabilized using lime and solidified with Portland cement to prevent further contaminant transport. The high volumes of waste involved and cost of treatment materials adds substantially to the overall cost of managing metal contaminated wastes. In an effort to both reduce the costs of waste treatment, and increase flue gas desulfurisation (FGD) by-product use by 100% and overall coal combustion by-product (CCB) use by 10% in the next decade, the US Department of Energy has launched a R&D initiative to develop processes for use of CCBs in treatment of metal-contaminated wastewater, sludge and soil (USDE 1997). In the US, approximately 1.7 million tonnes of fly ash (14% of the total amount utilized) is used for waste stabilization (Table 2.6). While the major application is metal-contaminated sludge stabilization, fly ash is also being evaluated for stabilization of a range of other hazardous (i.e. radioactive) and non-hazardous (i.e. food processing) wastes (CANMET/ACI 1998). The US Department of Agriculture, in collaboration with the US Department of Energy, is currently investigating the utilization of CFB residues to stabilize dairy feedlots to enhance element attenuation and minimize impact of the manure on soil and water quality (Elrashidi et al. 1999).

A considerable amount of information has been gained from leaching experiments conducted in order to evaluate the mobilization of trace elements from CFB ash and other CCBs. Generally, the studies have examined the release of metals from fly ash or fly ash soil mixtures, or mixtures of fly ash, soil and organic/nitrogenous wastes (i.e. sewage sludge, manure) (Jackson et al. 1999; Kanungo and Mohapatra 2000; Elrashidi et al. 1999). Other studies have examined the effect on leachate composition of co-disposal of fly ash with highly acidic pyritic materials (Bhumbla et al. 1996). These studies indicate that the release of metals from alkaline coal ash materials is strongly affected by hydrous Fe and Al oxide content, pH, and redox status of the solids matrix, as well as by soluble organic compounds which may be present. Thus, the amount of metals leached from contaminated wastes stabilized with CCB's will depend on the chemical composition of constituent waste components as well as any new reaction products formed in the admixture.

Stabilization of wastes represents a potentially high volume application for the ash, and depending on the waste material, may be an efficacious, cost-effective and environmentally

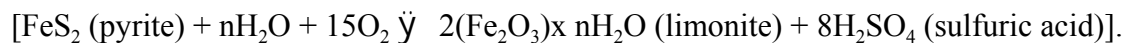
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sound method of managing problem wastes. It is important to note, however, that such approaches, no matter how successful, do not alleviate the larger problem of production of metal-contaminated wastes, and therefore should not deflect attention away from the need for increased efforts in source reduction.

**2.3.3 Abatement of Acid Mine Drainage**

Acid mine drainage (AMD) from underground coal mines, from surface mines, and from coal refuse piles is the largest single environmental problem facing the mining industry today (NRCAN 1999; Mining Watch 1999a). AMD occurs when sulphide-bearing minerals in rock (e.g., pyrite) are exposed to air and water, changing the sulfide sulphur to sulphuric acid. The oxidation and hydrolysis of the ferrous ions produces hydrated iron oxide (limonite) and additional acidity, i.e.,



The resulting leachate is highly acidic ( $\text{pH} < 3$ ), and often contaminated with heavy metals leached out of the waste rock and tailings. AMD results in the destruction of habitat for aquatic life, and places ground water, surface water and drinking water supplies at severe risk of contamination. (NRCAN 1999; Kim et al. 1982). Because the acid-generating potential of the exposed rock and tailings continues indefinitely, an abandoned acid-generating mine has the potential for long-term devastating impacts on rivers, streams and aquatic life, becoming in effect a “perpetual pollution machine” (Mining Watch 1999a). The estimated acidic drainage liability in Canada ranges from \$2.0 billion to 5.0 billion (NRCAN 1999). The cost of AMD to US taxpayers is in the range of \$32 to \$72 billion (Mining Watch 1999a).

Conventional abatement methods for AMD, which include injection of acid-neutralizing chemicals into the mine, or passive methods like diverting leachate through constructed wetlands, have been temporary at best and very costly. Coal combustion by-products (CCB's), by virtue of their alkaline, pozzolan and cementitious properties, have been shown to be effective in mitigating the negative environmental impacts of AMD at significantly less cost than conventional methods (USDE<sup>14</sup> 1998).

CCB's, engineered to produce grout-like materials with low permeabilities, may be injected in large volumes into abandoned underground mines so that most or all of the void spaces are filled (USDE 1998). Grout injection diverts water away from acid-forming materials in the mine, and by filling voids, keeps air out of the workings and helps prevent pyrite oxidation from starting. The alkalinity of the ash also reduces the oxidation rates in areas where air may remain, and neutralizes any acidity already generated. Pyrite encapsulation and water diversion following grouting operations are the most likely mechanisms for longer-term improvements in water quality (Kim et al. 1982). Pneumatic ash injection is another technology for placement of CCB's

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<sup>14</sup>United States Department of Energy.



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in underground mines. Pneumatic ash injection differs from grout-filling in that the ash is injected in a dry form, with advantages in terms of improved void-filling (i.e. better penetration of up-sloping voids), reduced materials handling and reduced cost (USDE 1998).

**2.3.4 Utilization in Agriculture and as a Soil Amendment****2.3.4.1 CFB Ash as an Agricultural Liming Agent**

The development of agricultural uses for CFB ash has been pursued since 1976 by the Agricultural Research Service (ARS) of the United States Department of Agriculture (USDA), with support from the United States Department of Energy (USDE). ARS research has consisted of trials conducted on a range of agricultural crops (i.e. grain and forage legumes, corn, cereal crops, perennial fruit and nut crops, pastures) designed primarily to compare the neutralizing value of CFB residues with that of ground agricultural limestone (Stout et al. 1979; Stout et al. 1988; Korcak 1979, 1980a,b, 1982, 1984, 1985; Bennett et al. 1985; Edwards et al. 1985). The contribution of CFB residue to plant nutrition (i.e. greater plant uptake of Ca and S in ash compared with limestone treatments) is sometimes cited as an additional benefit. CFB ash treatments are typically soil incorporated or surface applied at rates equivalent to the lime requirement of the soil, or at higher rates (i.e. up to 112 Mg/ha) to determine maximum loadings (Korcak 1988). Due to the greater amount of sorbent-derived components in the bed ash (up to 80% compared with 64% in the fly ash) (Jacques Whitford and Assoc. 1997), much of the early agricultural research involved bottom ash or spent bed material (Korcak 1979, 1980ab 1982; Stout et al. 1979). Unique properties (i.e. silt-sized instead of sand-sized particles, element enrichment, pozzolanic properties), combined with a greater proportion of total solids represented by fly ash (60-85%), has led to increased research emphasis on agricultural uses of CFB fly ash (Korcak 1985; McCarty et al. 1993; Carlson and Adriano 1993; Schumann and Sumner 1999).

The conclusions drawn by ARS from this research are that CFB residue, when applied at or near the lime requirement of the soil, is an effective liming agent and source of plant Ca and S with negligible effects on soil concentrations of non-essential trace elements (i.e., metals) (Stout et al. 1988). In order to promote safe and efficacious use of the material, the ARS in 1988 produced a document entitled "Manual for applying Fluidized Bed Combustion Residues to Agricultural Lands" (Stout et al. 1988). This manual is currently under revision, to include updated research progress and address potential concerns with arsenic in CFB residues (Korcak 1997).

A large number of studies have indicated that coal combustion by-products (CCBs) can act as liming agents. McCarty et al. (1993) tested the liming ability of a number of CCBs and found that effectiveness of the by-products for increasing soil pH was directly related to calcium carbonate equivalency (CCE) (i.e. bed ash (97% CCE) > multistage burner residue (68% CCE) > spray drier residue (55% CCE) > fly ash (18% CCE)). By comparison, the CCE of agricultural limestone (high-grade calcitic or dolomitic limestone), is between 90-108%. For liming materials derived from industrial processes, 25% is the minimum CCE for the by-product to be

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considered an effective liming material (BNQ 1997). Various studies indicate that the CCE of fluidized bed materials (36-81%) is much higher than that of other CCB's as a result of the large amounts of sorbent (calclitic or dolomitic limestone) used in the CFB combustion process. The CCE of CFB ash varies primarily with the CaO content, which ranges from 15-40%. Calcium carbonate equivalent of CFB ash ranges from 40-90%; the average is 60% (Stout et al. 1988).

As noted in Section 2.2.5, compared with carbonate limestones, oxide materials such as CFB residues allow a more rapid neutralization of soil acidity and the resulting soil pH is higher. Initial high alkalinity is transient however, due to the carbonation reaction (i.e. conversion of CaO and Ca(OH)<sub>2</sub> to Ca (HCO<sub>3</sub>)<sub>2</sub>) which soon follows. Greater reactivity of CFB residues is attributed to the high alkalinity of the oxide component (pH typically > 12) as well as finer particle size (i.e. 98% of the material less than 100 mesh (Table 2.4) (Brady and Weil 1999; McCarty et al. 1994; Carlson and Adriano 1993). The high liming efficiency of CFB ash may be advantageous where a rapid and large change in soil pH is required (i.e. initially very acid soils with high buffering capacity), however may result in excessively high soil pH (>9) on poorly buffered soils (Carlson and Adriano 1993). Because larger particles reduce the rate of the liming reaction, some slow release activity is also desirable for residual or carryover liming effect (i.e. into the second and third year after application) (Barber 1984). For example, limestone particles passing a 50-100 mesh sieve will have completely reacted after 1 year, whereas only 50% of particles passing a 20-50 mesh sieve will have reacted within the first year. To meet the desired goal of some neutralization of soil acidity immediately following application, but also continued liming effect for 1 to 4 years after application, agricultural limestone is usually ground so that 40% of the material passes through a 100-mesh sieve, 50% passes 60-mesh, 70% passes 20-mesh and 95% passes an 8-mesh sieve (A&L 1992). On the basis of reactivity and particle size, CFB ash is likely to be highly efficient in neutralizing soil acidity in the short term but could have limited residual activity. There is some indication however that carbonation reactions in the soil may prolong the residual activity of oxide materials.

Liming materials are applied not only to neutralize soil acidity, but also to optimize the balance and supply of soil Ca and Mg. It is well established that repeated use of calclitic lime, CaO and other low-Mg liming materials can result in sub-optimal levels of soil Mg, particularly on sandy, low capacity soils. For example, using calclitic lime and CaO to increase pH of some Ohio soils to pH 7 resulted in 17 to 34% reduction in exchangeable Mg, which was believed to have been brought about by the occlusion or co-precipitation of Mg with Al (Foth and Ellis 1996). From Table 2.4, CFB residues are generally Mg depleted, and Mg deficiencies in soils and crops resulting from the use of CFB residues as a liming material have been reported. Soil Mg deficiencies, exacerbated by relatively high applications of fly ash (80 Mg/ha) to maize, were attributed to cation imbalances caused from excess Ca compounds (Schumann and Sumner 1999). High rates (36 kg/m<sup>2</sup>) of fluidized bed material (FBM) applied to apples increased leaf Ca and decreased leaf Mg, whereas low rates (9.2 kg/m<sup>2</sup>) increased leaf Mg, suggesting a Ca-induced suppression of Mg uptake by the plant at high rates of FBM (Korcak 1988). Ca-induced Mg deficiencies resulting from the use of FBM were attributed to the use of calclitic lime as the sorbent in CFB combustion instead of dolomitic lime. Dolomitic lime is the preferred liming

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material when acid soils are low in Mg, and should be used when soil Mg is below 10%. In Indiana, where sandy, low capacity soils are susceptible to Mg deficiencies, dolomitic lime is recommended for every third limestone application as a general practice (McLean and Brown 1984). It is likely that surface-applied CFB residues would, in time, have a similar effect on Ca/Mg distribution in the soil profile as gypsum, i.e. exchangeable Ca is increased uniformly down the soil profile, and Mg is reduced in the upper part but accumulates in the lower portion as an intermediate stage in its removal from the profile (Shainberg et al. 1989). Similar precautions as are noted with the use of gypsum as a fertilizer material (Shainberg et al. 1989) should therefore apply to use of CFB residues; that is, levels of Mg and other soil nutrients should be monitored closely following application of CFB residues, particularly on sandy soils of low CEC.

### 2.3.4.2 CFB Ash as a Nutrient Source

As indicated, calcium and sulfur are two essential plant nutrients present in CFB residues in appreciable amounts. Ca and S content in CFB ash (24 to 46% for Ca, and 7.2 to 14% for S) is similar to the range of these nutrients found in gypsum (23% and 18%, respectively) (Stout et al. 1988; A&L 1992). The ash contains small amounts of K (0.05-0.8%) and Mg (0.5-1.2%), and is a source of important plant micro-nutrients (B, Mo, Fe, Cu, Mn, and Zn) (Stout et al. 1988; Korcak et al. 1997). Despite a substantial nutrient content, reports from the literature on the nutritional benefits of the ash to amended soils and crops are mixed and often inconclusive; the clearest demonstration of nutritional benefit is as a Ca and S source.

In field and greenhouse studies with seedling fruit trees, CFB residues were a more available source of Ca than either calcitic or dolomitic limestone. Leaf Ca in 'Elberta' peach seedlings was increased 29% and 51% by CFB residue compared to the Control treatment in the first and second 12 weeks of growth, respectively, whereas an equivalent rate of calcitic lime only increased leaf Ca by 10% and 11% during the same periods (Edwards et al. 1985). Korcak (1984) compared FBM, applied at one (1x) or two times (2x) the lime requirement, with  $\text{CaCO}_3$  as a Ca and S source for apples. An additional treatment comparison consisted of  $\text{CaCO}_3$  plus gypsum, to apply similar amounts of Ca and S as the FBM. After four years, there was no difference between treatments in terms of either leaf Ca or S, however leaf Mg was significantly lower for FBM applied at the 1x or 2x level compared to  $\text{CaCO}_3$ . In another study, however, when compared with  $\text{Ca(OH)}_2$  as a lime source, applications of FBM resulted in higher levels of both S and Mg in forage crops than the hydrated lime (Stout et al. 1979). It appears that the conclusions to be drawn from these studies depends as much on the composition and type of the contrasting liming treatment as on the composition of the CFB residues.

While there are studies citing the use of coal combustion residues to correct deficiencies of selected nutrients (i.e. boron (Martens 1971; Ransome and Dowdy 1987), magnesium (Hill and Lamp 1980), molybdenum (Doran and Martens 1972; Elseewi et al. 1980), and zinc (Martens 1971; Schnappinger et al. 1975)) there are an equal number which identify nutrient imbalances (deficiencies or excesses) as a limiting factor associated with utilization of such materials. Boron phytotoxicity is cited as the greatest potential problem with high application rates of

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unweathered fly ashes (Carlson and Adriano 1993). Under the alkaline soil conditions following ash amendment, reductions in plant tissue concentrations of P (Elseewi 1980; Molliner and Street, 1982), Cu, Fe, Mn and Zn (Carlson and Adriano 1993) have been cited, as well as excesses in Mo and Se (Codling and Wright (unpublished); Gupta and Gupta 1998). Nutrient imbalances resulting from application of CFB residues to soils can be attributed to the content of elements present in the residue relative to the amounts required by plants. For example, the diagnosis and recommendation integrated system (DRIS) analysis of 24 fly ash samples indicates that Mo and B supply from fly ashes consistently exceeds plant requirements, while P, K, and Mg, elements required by crops in relatively large amounts, are present in fly ashes in low or negligible amounts (Schumann and Sumner 1999). As previously noted, the high levels of Ca in fly ash can reduce plant uptake of Mg and K, despite adequate soil contents of these nutrients, resulting in Mg and K deficiencies in the plant.

**2.3.4.3 Potential for Elemental Toxicities**

A total of 25 potentially toxic elements have been found in measurable amounts in coal combustion fly ashes (Table 2.7) (Keefer 1993). Eight elements - Ba, B, Ca, Mo, Pb, S, Se, and Sr - generally increase in concentration in the soil to which fly ash is applied. Six of these elements, that is Ba, B, Mo, S, Se, and Sr, along with Al and As, have been shown to increase in plants grown in fly ash amended soils (Adriano et al. 1980). This does not pose a phytotoxicity problem for the plants, except B in certain boron-sensitive plants. However, from an animal health standpoint, some of these elements may be potentially toxic to animals. Some of the most toxic elements for animals include As, Cd, Cu, F, Hg, Mo, Pb, and Se (Keefer 1993; Gupta and Gupta 1998). Cadmium, Cu, F, and Pb have not been shown to accumulate to any extent in plants grown on fly ash amended soil, therefore there does not appear to be a problem with these elements (Keefer 1993). On the other hand, Mo and Se are required in small amounts by animals but become toxic when present in large amounts. Plant roots normally represent a “soil-plant barrier”, thereby reducing metal uptake from the soil and entry of metals into the food chain. Mo and Se, along with Cd, however, are readily taken up by plants and therefore escape the soil-plant barrier (Miller et al. 1995).

Arsenic requires careful monitoring, as it is not only toxic to animals, but also accumulates in plants grown on fly ash amended soils. The USDA manual entitled “Manual for applying Fluidized Bed Combustion Residues to Agricultural Lands” (Stout et al. 1988) is currently under revision, to include updated research progress and address potential concerns with arsenic in CFB residues (Korcak 1997). The elements As, Mo and Se, along with B, Cr and V, are present in soils in the form of oxygenated anions, or oxyanions (Bohn et al. 1985). The main electrical charges associated with soil colloids (clays and organic matter) are negative, and most of the ions adsorbed by soil colloids are cations (positively charged ions). Most metal cations become less soluble, and therefore less mobile and plant-available, as soil pH is increased (Section 2.4). The fact that the elements of concern in fly ash are predominantly oxyanions is problematic because a) these elements are less easily held by soils, b) they tend to become more soluble under alkaline conditions, c) some elements which may be toxic to animals (i.e., Mo, Se) are readily taken up by plants, and d) the soil chemistry of anions is more complex and generally

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less well known than that of cations. Thus, there is a need for a different type of research to deal with these elements (Keefer 1993). Another concern with elements present in coal combustion by-products may be the enrichment in elements (Se, V, Be, Tl, etc.) which are not commonly regulated under federal or provincial laws, or reported in the literature as being environmentally important. Thus, the importance of increases in these elements in soils or crops following by-product amendment may be overlooked.

**Final Research Report****Table 2.7 Elements found in fly ash (FA), soils, plants and animals.**

Element in FA	Following FA application			Toxic to plants	Toxic to animals
	Not found in soils	Increased in soils	Increased in plants		
Ag					
Al			Al		
As		As	As		As
Ba		Ba	Ba		
Be	Be				
Bi					
B		B	B	B	
Ca		Ca			
Cd	Cd				Cd
Co					
Cr					
Cu				Cu	Cu
F	F				F
Mn					
Mo		Mo	Mo		Mo
Ni	Ni				
Pb		Pb			Pb
S		S	S		
Sb					
Se		Se	Se		Se
Sr		Sr	Sr		
Ti					
Tl				Tl	Tl
V					
W					
Zn					

Sources: Keefer (1993); Carlson and Adriano 1993; Gupta and Gupta 1998.

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### 2.4. Bioavailability of Metals in Soils

Discussions of metals are often complicated by terminology. Common descriptors are “trace metals/elements” or “heavy metals”, the former being older terms which pre-date rapid, easy detection of elements at very low concentrations, and include both essential and toxic elements. The latter is another imprecise term, which refers to metals having densities greater than 5 gm/cm<sup>3</sup>, or elements in the periodic table with atomic numbers greater than 20<sup>15</sup> (Tiller 1989). Other terms, such as “essential” or “toxic” elements are related to physiological function, and are confusing since their effects on health depend, in most cases, on concentrations (Kabata-Pendias and Pendias 1991). For example, many essential elements are toxic when present in excessive amounts, and a growing number of elements (i.e. V, Ru, Al, Ni, As, Ga) previously considered “non-essential” are now classified as beneficial to some plants or animals or simply as those for which essentiality has not yet been proven (Reilly 1991). While all of these terms are inadequate in one way or another, in this report the terms “metal” and “trace element” are used interchangeably, as terms of convenience and tradition, when referring to elements present in nature at low concentrations which may have toxic effects on living organisms. The term “micronutrient” is used specifically in a nutritional context, when referring to elements (all of them trace elements, many of them metals, some of them toxic at high concentrations) known to be required by plants or animals in small amounts.

Metals occur naturally in all soils, water, and living organisms. While many are essential for healthy life, most metals have severe impact on living systems when present in excess concentrations. The metals Hg, Cu, Ni, Pb, Co, Cd, and possibly also Ag, Be, and Sn, are considered to be the most toxic to living organisms (Kabata-Pendias and Pendias 1991). The most toxic elements for livestock include Cu, Pb, Hg, Mo, and Se, although toxicities of As, Co, F, I, Fe, Mn and Zn have also been reported (Gupta and Gupta 1998). The metals Cd, Cu, Ni, Pb, and Zn are recognized for their prominence in sewage sludge-amended soils (Basta et al. 1993), whereas Be, F, Cr, Ni, Zn, As, Cd, Hg, and Pb are considered the most serious anthropogenic<sup>16</sup> pollutants. Anthropogenic deposition of arsenic (As) may be significant in locations with a history of metallurgical and chemical processing, coal combustion, and use of arsenical pesticides (Kabata-Pendias and Pendias 1991). While reports of As poisoning are rare, the metal is considered a cumulative poison and human carcinogen (Brady and Weil 1999). Chemical form, or speciation, influences both toxicity and bioavailability, e.g. free (hydrated) metal ions are more mobile and toxic than stable complexes, oxygenated anions (AsO<sub>2</sub><sup>-</sup>) are more toxic and easily leached than their simple cations (As<sup>3+</sup>), and reduced forms (As<sup>3+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>) are generally more toxic and soluble than oxidized forms (As<sup>5+</sup>, Fe<sup>3+</sup>, Mn<sup>3+</sup>) (Stevenson and Cole 1999; Kabata-Pendias and Pendias 1991; Bohn et al. 1985; Jacobs et al. 1970). Natural concentrations of metals in soils span a range of 8-9 orders of magnitude, from 10<sup>-2</sup> to 10<sup>6</sup> (Edelman and deBruin 1986). Some elements (Cd, Hg) are so toxic that their concentrations in soil should not exceed 2x10<sup>-1</sup>-2x10<sup>0</sup> µg/gm, whereas others (Mn, V, Zn), while toxic at excessive levels, have a wider acceptable range and may safely be present at soil concentrations of 1-2x10<sup>2</sup> µg/gm (V, Zn) or 1.5x10<sup>3</sup> µg/gm (Mn) (Kabata-Pendias and Pendias 1991). Aluminum is a

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<sup>15</sup>Generally excluding alkali metals and alkaline earths.

<sup>16</sup>Those deposited as a result of man's activities.

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major component of the earth's crust, and occurs in soils in the range  $10^3$ - $10^4$   $\mu\text{g/gm}$ . At very low soil pH (4.0-4.5), however, highly soluble Al and Al phytotoxicity is a major limiting factor to crop growth (Bohn et al. 1985). For any one element, natural concentrations may vary as much as a thousandfold depending on the nature of the soil (notably texture) and its origin. For anthropogenic elements, the range in concentration is even greater (Stevenson and Cole 1999). When evaluating metal additions to soils, it becomes critical to recognize the "boundaries of concentrations that separate healthy from unhealthy organisms, safe food from unsafe food products" (Tiller 1989). As discussed below, however, confusion as to what these concentrations mean often arises, as elements exist in soils in various pools (soluble, exchangeable, adsorbed, etc.) which differ greatly in terms of element concentration, mobility, bioavailability, and toxicity.

Studies have shown that total metal concentrations in the solid matrix are poor indicators for both bioavailability and leachability of metals in soils. Chemical fractionation techniques, in which progressively stronger extraction solutions are used to sequentially extract the various forms of trace metals in soils and other substrates, provide some indication of the speciation, or forms of metals present, as well as the environmental availability of metals (Bourque et al. 1994). Metals (including micronutrient cations) occur in soils in the following forms or pools, listed in order of decreasing availability (Stevenson and Cole 1999; Brady 1984; Kabata-Pendias and Pendias 1991):

- i) Water soluble, as free or complexed ions in solution
- ii) Exchangeable
- iii) Organically bound
- iv) Occluded in Fe and Mn oxides
- v) Held in lattices of secondary minerals e.g. silicate clays, carbonates
- vi) Structurally bound in primary minerals e.g. quartz, muscovite, orthoclase, etc. (residual fraction).

The water soluble plus exchangeable fractions characterize the mobile species of metals in soils. Because of the low solubility of most trace elements, especially cations, a very small percentage of the total soil content occurs in the mobile fraction (generally <2%). The remaining fractions (up to 98% of the total) are more or less immobile (Kabata-Pendias and Pendias 1991). As indicated above, many materials present in soils can react to immobilize trace metals, that is clays, organic matter, hydrous Fe and Mn oxides, carbonates, inorganic chemical compounds, organic acids, amino acids, humic and fulvic acids, biological systems and biological residues (Williams et al. 1980). Most metals have a tendency to precipitate as sparingly soluble oxides and/or hydroxides at alkaline pH values and to form sparingly soluble carbonate, phosphate, and sulfide salts, thereby reducing their bioavailability (Stevenson and Cole 1999).



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The capacity of Fe and Al oxides in sorbing and/or co-precipitating metals has been widely studied. Hydrous oxides of Fe and Al are important soil constituents in soils of Eastern Canada (Spodosols), where they characterize the 'spodic horizon', an illuvial (leached) zone containing precipitates of Fe/Al oxides and organic matter (Brady 1984). Total Fe and/or Al content explained most of the variance for Mn, Ni, Ba, Be, Hg, As, Cd, Cr, Cu, Mo, Pb, and Zn concentrations in 448 Florida soils (mostly sandy soils with low trace element concentrations) (Chen et al. 1999). In a study of the influence of soil physical and chemical properties on trace element movement in soils, soil texture, surface area ( $\text{m}^2/\text{g}$ ), percentage of free Fe oxides and content of free lime (CaO), were identified as the most useful parameters for predicting soils effectiveness for trace element retention (Korte et al. 1976). Surface adsorption (associated with high clay and/or organic content) is the key mechanism for divalent cations (i.e.  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Be}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Hg}^{2+}$ ), whereas free (hydrous) Fe and Al oxide content exerts a strong influence on attenuation of oxyanions ( $\text{AsO}_4^{3-}$ ,  $\text{SeO}_3^{2-}$ ,  $\text{VO}_3^-$ ,  $\text{CrO}_4^{2-}$ ,  $\text{BO}_3^{3-}$ ,  $\text{MoO}_4^{2-}$ ) (Korte et al. 1976; Kabata-Pendias and Pendias 1991). Sesquioxide content plays a particularly key role in As sorption by soils. In both coarse and fine textured Wisconsin soils, retention of As, and the amount of As sorbed from solution, increased as the free  $\text{Fe}_2\text{O}_3$  content of the soils increased (Jacobs et al. 1970). A greater extractability of As with  $\text{NH}_4\text{Cl}$  (immediately available fraction) from the sandy soil (29%) compared with silty-clay (14%) and clay loam (3%) soils suggests that in soils with a low As sorption capacity, a portion of the As is readily mobile. As sorption capacity of the soils was eliminated or appreciably reduced by removing amorphous Fe and Al components, indicating that, while other soil components may sorb As, these are of relatively little importance in As sorption by soils (Jacobs et al. 1970).

Organic matter may play a key role in the availability of some metals in soil. The best-known reactions involve chelation, or the coordinated linkage of a metal ion with soluble organic compounds (ligands). Metal-chelate complexes are recognized for their ability to maintain micronutrients that would otherwise convert to insoluble precipitates at the higher pH (>6.5) of many agricultural soils in slowly available forms (Stevenson and Cole 1999). Organic matter may act as a buffer in ameliorating adverse effects of toxic metals (i.e. Cu, Cd, Pb) in soil, or it may enhance trace element solubility (Jackson et al. 1999). Organo-metal complexes involving insoluble organic matter generally reduce metal bioavailability, whereas soluble organic matter may enhance metal bioavailability. Metals that form strong complexes with organic ligands (i.e. Cu) are influenced to a greater degree than those that form weak complexes (Mn) (Stevenson and Cole 1999; Chirenje and Ma 1999). Organic matter reactions with metal ions are complex and diverse. An important limitation of organo-metal complexes in terms of binding of toxic metals is that the attenuation of metals is relatively short-term (Brady and Weil 1999). For example, early studies by Chaney (1973) and Leeper (1972) on long-term sludge amended soils demonstrate that organically bound forms of Cd are made available when soil organic matter mineralizes (i.e. is depleted) as a result of cropping soils without adequate return of crop residues (Williams et al. 1980).

Sequential extraction and leaching procedures have been used to characterize mobility of metals in soils and make predictions about bioavailability. Metal mobility sequence in 10 soil types

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(across six soil orders ranging from sands to clays with pHs varying from 4.2 to 7.8) was  $\text{Cu} < \text{Cd} < \text{Ni}$  for cations and  $\text{Se} < \text{As} < \text{Cr}$  for oxyanions. The metals were not all leached to the same extent (clays showed higher attenuation capacity than sands), but the order of leaching was generally the same. The soil type (spodosol) show moderate mobility of metals due to the presence of a spodic horizon (Smith et al. 1995, in Chirenje and Ma 1999). Investigations into the movement of metals within soil profiles have shown that most metals stay within the surface. For example, after 12 yrs of adding 84 t/ha of sludge to soil, practically all of the Mn, Zn, Cu, Ni, Co, Cr, Pb, Cd, Hg, As, and Se remained in the surface 20 cm of the soil (Anderson and Nilsson 1972, in Williams et al. 1980). Page and Chang (1975), on reviewing literature on trace element movement, concluded that, except for B, the movement of metals in soils treated with sludges is restricted to the depth of tillage (Williams et al. 1980). Cd and Zn in sludge are more leachable than Cu or Pb. According to Leeper (1972), of the metals Fe, Cr, Cu, Ni, Zn, Pb, Cd, and Mn that may be present in sludge, only Zn and Cd remain mobile and would therefore pose a risk to the food chain. With the exception of Cr and B, leaching of anions from soils is generally negligible (Bohn et al. 1985). All of the oxyanions (As, B, Mo, Se, V, and Cr) are attenuated by hydrous oxides of Fe and Al (Korte et al. 1976), however their reactions in soils are highly dependant on pH and Eh conditions (Kabata-Pendias and Pendias 1991). The case of mercury (Hg) is somewhat unique.  $\text{Hg}^{2+}$  is retained somewhat strongly by soils, and while this oxidation state for Hg is predominant, significant reduction to  $\text{Hg}^0$  is common. Elemental Hg is volatile and can diffuse as a gas through soils pores. Compared to other toxic metals, Hg is therefore relatively mobile in soils. The toxic compound dimethyl mercury ( $\text{Hg}(\text{CH}_3)_2$ ), formed in contaminated and highly reduced aquatic sediments, is fortunately quite rare in soils (Bohn 1986).

Soil pH affects solubility of metals to varying degrees. Metals most likely to be mobilized under acidic conditions are Al, Fe, Mn, Zn, Pb, Cu and Cd (Kabata-Pendias and Pendias 1991). Soil pH is reported to be the predominant soil property affecting Cd, Pb and Cu adsorption (Basta et al. 1993). The dissolution of metal ions at different pH values reflects the forms in which they are held or retained by soils; that is, high leachate concentrations of Al, Si, Fe, Cu, Ni, Co, Mn, Pb, Ba, and Zn between pH 3.0 and 5.5 was attributed to the attack of aluminosilicate clay minerals at acidic pH (Kanungo and Mohapatra 2000). As the pH value is increased from 5.5 to 8.0, most metal ions (except Na, K, Ca and Mg) tend to form neutral metal hydroxides of lower solubility than the free metal ions, hence the potential for leaching is greatest at soil pH below 5.5. Liming acid soils has long been known to reduce phytotoxic levels of soluble Al and Mn, and the reduced solubility of many other metals under alkaline conditions has led some researchers to advocate liming of soils as an effective and practical method of reducing metal uptake by plants. For example, the application of lime to biosolids-amended soils reduced plant uptake of Cd, Cu, Ni, Zn, and Pb (Basta and Sloan 1999). Liming to pH 6.0 or higher can be expected to decrease the availability of Cu, Fe, and Zn but not as sharply as for B and Mn (APASCC 1986). Some highly charged cations (i.e. B, Cr, P, Mo, Se, As) exist in soils primarily as weakly soluble oxyanions. Since anion retention decreases as the pH increases, the availability of the anions As, Mo, Se, V, and Cr increases somewhat with pH (Bohn et al. 1985). Both Mo and Se are strongly mobilized in alkaline soils, while in acid soils they become almost insoluble (Kabata-Pendias and Pendias 1991). For most other anions, the response to soil pH is

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less pronounced. Boron may be considered an exception amongst the anions in that it becomes less available above pH 6.0 (Kabata-Pendias and Pendias 1991). Cr is somewhat unique among toxic anions in that mobility is greatest in well-aerated (oxidized) soils of moderate to high pH (for most metal ions mobility is greatest under reduced, acidic conditions) (Bohn et al. 1996).

The effect of soil pH on solubility of As, as with the other oxyanions, may be seen as secondary. Solubility of As is largely a function of its oxidation state (1-5), which is influenced by soil pH and redox potential (Masscheleyn et al. 1991). Thus, soil oxides and redox potential (Eh) are the main soil parameters controlling As sorption, with pH of the system influencing the concentration of the As species being adsorbed (Kabata-Pendias and Pendias 1991). Studies on the sorption/ desorption behaviour of As in soils and/or fly ash indicate that As mobility is relatively high above pH 9 and below pH 5, and that very little As is mobile within the pH range 6-9 (Kabata-Pendias and Pendias 1991; Chirenge and Ma 1999; Bhumbala et al. 1996; Jacobs et al. 1970; Theis and Wirth 1977). The reduced concentration of As between pH 6 and 9 is attributed to the formation of metal oxides and hydroxides of low solubility, while an increase in soluble As at pH values outside this range is due to the unavailability of free metal ions to cause its precipitation (Kanungo and Mohapatra 2000; Theis and Wirth 1977). Leaching studies with highly alkaline (pH>12) CFB residues indicate that, even at relatively high total As concentrations (i.e. >170 mg/kg As) in the ash, the amount of water soluble As released is negligible (less than 0.02 mg/L) (Jacques Whitford and Assoc. 1997). From these studies, it does not appear that any appreciable leaching or plant uptake of As would result from application of CFB residues to soils, particularly once target pH conditions (5.5-7) have been achieved. Having said this, it should be emphasized that soil pH is not a major factor controlling As mobilization, and that amorphous oxides of Fe exert the primary controls on release of As and other metals from both soils and coal combustion residues (Theis and Worth 1977).

When predicting metal mobility, loading rate should also be considered. For example, Merry et al. (1986) (in Jiang and Singh 1993) found that As uptake was less sensitive to changes in soil pH than to the amount of As added, and Kabata-Pendias and Pendias (1991) report that mobility of As in soil is proportional to the amount of As added and inversely proportional to time and Fe and Al contents. Thus, predicting the mobility in soils and plant availability of As from CFB residues, requires consideration of As sorption capacity of the soil (soil texture, Fe/Al hydrous oxide content), As loading rate, as well as soil pH and redox conditions following application of the residue.

**Final Research Report****3. METHODOLOGY****3.1 Experimental Site and Soils****3.1.1 Site Selection, Preparation and Management**

The field trials for vegetable and forage crops were established on a 1 hectare field located at the Point Edward Resource Centre, approximately 15 km north of Sydney, Cape Breton. To achieve the greatest crop response to the experimental treatments, a field was required with a high lime requirement and low soil levels of Ca and other nutrients. Identifying a field with the desired soil characteristics involved screening a number of potential sites at the Point Edward Resource Centre. The selection criteria included no history of previous agricultural use, low soil pH, and low soil levels of Ca and other nutrients. After the selection was made in May 1997, an area of approximately one hectare was staked-off. The recently cleared field had never been cultivated, and while mostly free of vegetation, was very rough. At least half of the field was littered with large rocks (15-30 cm diam.) and the whole field was covered with small rocks (5-10 cm diam.). The entire field, excluding an untillable trough which transected the field, had to be rock-picked prior to cultivation. Clearing the field of rocks involved the use of two John Deere 75 HP tractors, and the intermittent use of a mechanical rock picker (Rockmaster XL). Boulders too large to be moved manually were dug out with the tractor. The rock picker was only moderately effective on this field due to the uneven surface. Both large and small rocks were mostly loaded by hand into the bucket of the tractor and dumped in a pile away from the field. The field was then disced several times to obtain a reasonably level surface and a loose, friable seedbed.

Field preparation was required only for the vegetables plots in 1998 and 1999. The forages, a mix of perennial grasses and legumes had been established in 1997. Field preparation for the vegetables was done during the month of June, and involved a combination of chemical weed control and soil cultivation to prepare the seedbed. To prepare a suitable seedbed, soil was cultivated by both mechanical and manual means. Mechanical cultivation involved several passes over the field with a 75 HP John Deere tractor equipped with offset discs. Discs were lifted at the edge of each plot during discing to minimize movement of soil between plots. Due to the unevenness of the field, it was difficult to uniformly tractor-disc the field to the optimum depth (15 cm). In order to achieve a uniform friable seedbed, hand cultivation of each plot was also necessary. The operation involved hand hoeing the field to break up clods and ridges of soil, followed by raking to removed any remaining weeds and to smooth the soil surface.

The turfgrass trial, located at the NSAC, Truro, was established in 1998 on an existing sod and therefore there was no field preparation.

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### 3.1.2 Soil Characteristics

The soils at the Point Edward experimental site span four main soil series, Debert (DRT), Springhill (SGL), Hebert (HBT) and Pugwash (PGW). All soils have developed on coarse loamy glacial till, except the Hebert soil which developed on sandy skeletal glacio-fluvial sediments (NSDAM, 1991). The Hebert soil is well drained, while the other soils are moderately well to imperfectly drained due to the presence of compacted layers within 80 cm of the surface. Differences in the soil series resulted in some variability between the three areas (cabbage, rutabaga and forage) where trials were established. In general, however, all of the soils at this site were sandy loam in texture, well to moderately well-drained, friable and stoney, with a moderate to weak crumb structure. The soils at Point Edward had a low initial soil pH and very low levels of calcium and other nutrients (Appendix 1).

Soils at the NSAC experimental site belong to the Woodville series. The Woodville soils are imperfectly drained, with 40-60 cm sandy loam over firm reddish-brown sandy loam to loam till derived from Triassic sandstone. Compared with other turf areas on the College grounds, turfs at the weather station site have a history of low to medium management, i.e., fertilized once per season instead of three times, and limed once in 3-5 years instead of every 2-3 years<sup>17</sup>. The management history of the site is reflected in the moderate soil acidity (pH 5.8) and low-moderate levels of base cations and other nutrients.

Soil buffering capacity, which determines soil lime requirement and the responsiveness of soils to applied amendments, was characterized from initial measurements of soil texture (size distribution of soil particles), soil cation exchange capacity (CEC), soil organic matter (SOM) content, soil pH/buffer pH, and soil lime requirement (Table 3.1).

**Table 3.1 Characterization<sup>1</sup> of the buffering capacity of soils used in each of the trials.**

Trial	Particle size dust %			Soil texture	CEC (cmol/kg)	SOM %	Soil pH	Buffer pH	Lime Req. (t/ha)	Buffer capacity
	sand	silt	clay							
Cabbage	66.1	29.0	4.9	sandy loam	11.4	3.3	4.9	6.6	18.8	low
Rutabaga	59.7	36.3	4.9	sandy loam	14.3	3.8	4.8	6.4	24.3	low
Forage	58.2	35.0	6.8	sandy loam	13.3	4.6	5.1	6.6	18.3	low
Turf	54.5	41.7	3.8	sandy loam	11.2	3.7	5.8	7.2	6.3	low

<sup>1</sup> based on pre-amendment soil samples taken at the start of the experiment; each value is the average of 4 replicates within each trial. Soil textural analysis by BioScan; all other analyses performed by NSDAM soil test lab.

Based on the initial soil analyses conducted by the NSDAM lab, the buffer capacity was characterized as low. Because of difficulties encountered in interpreting soil liming results and other responses related to soil buffering, two samples of the original soils were sent to the New

<sup>17</sup>Personal communication with Randy Ross, Grounds Maintenance, NSAC.

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Brunswick Department of Agriculture soil test lab for re-analysis in August 2000. The soil test results provided by the New Brunswick lab yielded values for initial soil pH, buffer acidity and CEC that were more consistent with the sandy loam texture, and were therefore better able to explain the liming response and other results obtained at Point Edward. Because of the limited number of samples involved in the latter analysis compared with the initial analysis, only the initial results are presented in Table 3.1. As is noted in the General Discussion (section 5.0) and throughout the report, however, it is likely that the soils at Point Edward had significantly lower initial soil pH, greater buffer capacity (higher CEC), and lower lime requirement<sup>18</sup> than is indicated by the values given in Table 3.1 above.

### **3.1.3 Precipitation**

Precipitation in the Sydney area was quite variable both within the growing seasons and among the growing seasons (Table 3.2). The average precipitation, based on the 30-year normal, is 605.3 mm. In 1997 the average precipitation for the growing season (May - October) was 485.5 mm, well below the normal, in 1998 the average was 873.2, well above normal, and in 1999 the average was 534.4, again below normal. The May average was near normal in 1997 and well above normal for 1998, indicating reasonably moisture charged soil. In contrast the May average for 1999 was well below normal indicating a soil moisture deficit.

The June average was below normal for 1997, and this continued and became more severe in July, less than half the 30-year normal. July is a critical month for crop establishment, and the severe soil moisture deficit at this time presented a challenge in terms of supplying water to meet more than the most conservative plant needs. Generally in a sandy soil, at least 25 mm of moisture are needed per week to ensure the plants demand for water is being met. This amount can vary depending on soil clay content and the water table level. Rainfall in August was above the average and supplied adequate amount of water to sustain plant growth. The averages were below normal for September and October, but with the excess that was received in August crop development continued without being adversely affected.

In 1998, the above average rainfall continued into June and July, falling below normal in August. The average for September was above normal, and below normal in October. The plant did not suffer moisture stress at any point during the growing season.

In 1999, the moisture deficit continued into June, but the average rainfall in July was above normal. The seeding and transplanting occurred at a period of moisture deficit, but the rainfall occurred early enough so that no major adverse effects were sustained by the crop. The above average rainfall continued into August, but fell sharply in September, and was again above average for October. The crop was minimally affected by moisture conditions.

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<sup>18</sup>Results from the New Brunswick soil test lab suggest that initial soil pH was 0.6 units lower, and that buffer capacity may be 30-35% higher and soil lime requirement 25-30% lower, than values presented in Table 3.1.

**Final Research Report****Table 3.2 Monthly precipitation (mm) for Sydney, Cape Breton - 1997, 1998 and 1999 growing seasons compared with 30 year normal\*.**

Month	1997	1998	1999	30 year normal
May	105.0	179.8	51.4	92.5
June	61.2	128.8	52.2	91.2
July	40.2	220.0	118.8	86.2
August	139.1	71.0	100.8	97.3
September	79.2	164.0	47.8	103.2
October	58.8	109.6	163.4	134.9
Growing season total (May-Oct. inclusive)	483.5	873.2	534.4	605.3

\* Source: Atmospheric Environment Branch, Environment Canada and NSDAM Weather Summary.

Precipitation in the Truro area was not quite so variable (Table 3.3), with the seasonal average above normal for both seasons. In May and August 1998 the average rainfall was below the normal average, but not at such a deficit as to hinder plant growth and development. The average rainfall during the first 3 months of 1999 was below normal, resulting in a slight reduction in growth. Precipitation levels were above normal for August and September supplying sufficient moisture for excellent late season growth.

**Table 3.3 Monthly precipitation (mm) for NSAC, Truro - 1998 and 1999 growing seasons compared with 30 year normal\*.**

Month	1998	1999	30 year normal
May	68.9	43.9	93.0
June	110.2	66.4	78.0
July	131.0	44.7	86.8
August	73.1	123.9	99.2
September	139.8	160.7	84.0
October	130.1	90.4	110.9
Growing season total (May-Oct. inclusive)	653.1	530.0	461.9

\* Source: Atmospheric Environment Branch, Environment Canada and NSDAM Weather Summary.

**Final Research Report****3.2 Experimental Protocol****3.2.1 Experimental Layout**

The experiments established at Point Edward consisted of two vegetable trials, cabbage and rutabaga, and one forage trial. In 1997, adjacent to the vegetable trials an equivalent area was seeded to buckwheat as a cover crop (Fig 3.1). In each replicate of cover crop plots, the treatments in the adjacent vegetable trial were duplicated and followed the same sequence, from left to right. The original intention in establishing the cover crop trials, was to provide an area in which to rotate the vegetables from year to year, while maintaining the same sequence, scheduling, and rate of soil treatment applications. Late in the growing season, it was decided not to rotate the vegetable crops but instead to maintain the vegetables in the same area for the duration of the experiment; the rationale being that the benefits from collecting data from the same treatment plots each year, in terms of increased scientific rigour, outweighed any agronomic disadvantages (i.e. greater reliance on agricultural chemicals to control insect pests and diseases) of not practising crop rotation.

In 1998, an additional treatment, Double-Ash, was added to the design (Figure 3.2). This treatment comprised the High-Ash treatment in the cabbage cover-crop plot, and involved the application of very high rates of ash to the plots. Cabbage seedlings were transplanted into this area.

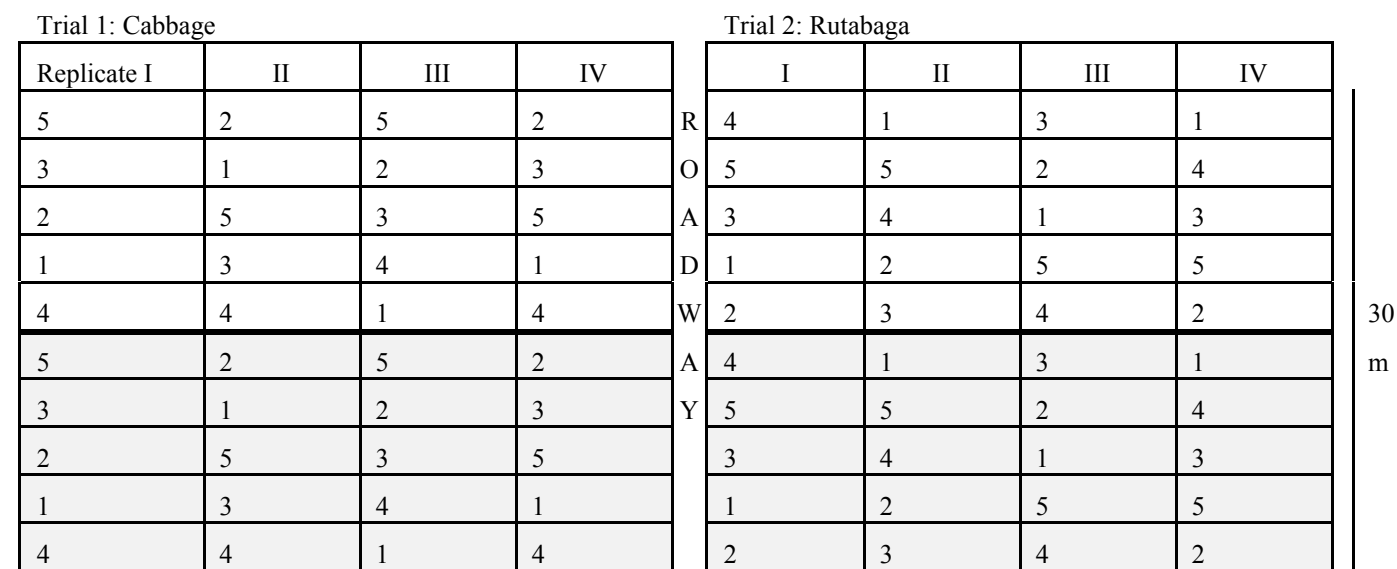
In all trials, treatments were arranged in a randomized complete block design with 4 replicates (Fig. 3.2). The plot size for the vegetable trial was 3m x 10m, and 6m x 20m for the forage trial. An area along the inside border of each plot was maintained as a buffer strip (planted but not sampled or harvested) to minimize interference or contamination between plots. This buffer strip was approximately 0.5 m wide in the vegetable plots and 1.0 m wide in the forage plots. The planted areas for the three trials were 1,200 m<sup>2</sup> for the vegetable trials, 1,200 m<sup>2</sup> for the cover crops, and 2,400 m<sup>2</sup> for the forages, giving a total planted area of 4,800 m<sup>2</sup>.

In order to allow the evaluation of a non-food application for the ash, a turfgrass trial was also added in 1998. The turf trial, located at the NSAC in Truro, involved comparing the effect of two rates of ash with standard agricultural grade limestone on the growth and quality of turfgrass. As with the agricultural trials, experimental treatments for the turf trial were arranged in a randomized complete block design with 4 replicates (Fig. 3.3). Plot size for the turfgrass trial was 2m x 1m.



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**Figure 3.1 Map of Experimental Site (1997)**



Trial 3: Forage

Replicate I	II	III	IV
2	3	5	3
4	4	3	1
1	1	1	5
5	5	2	4
3	2	4	2

30

3 80m°

Legend for Treatments:

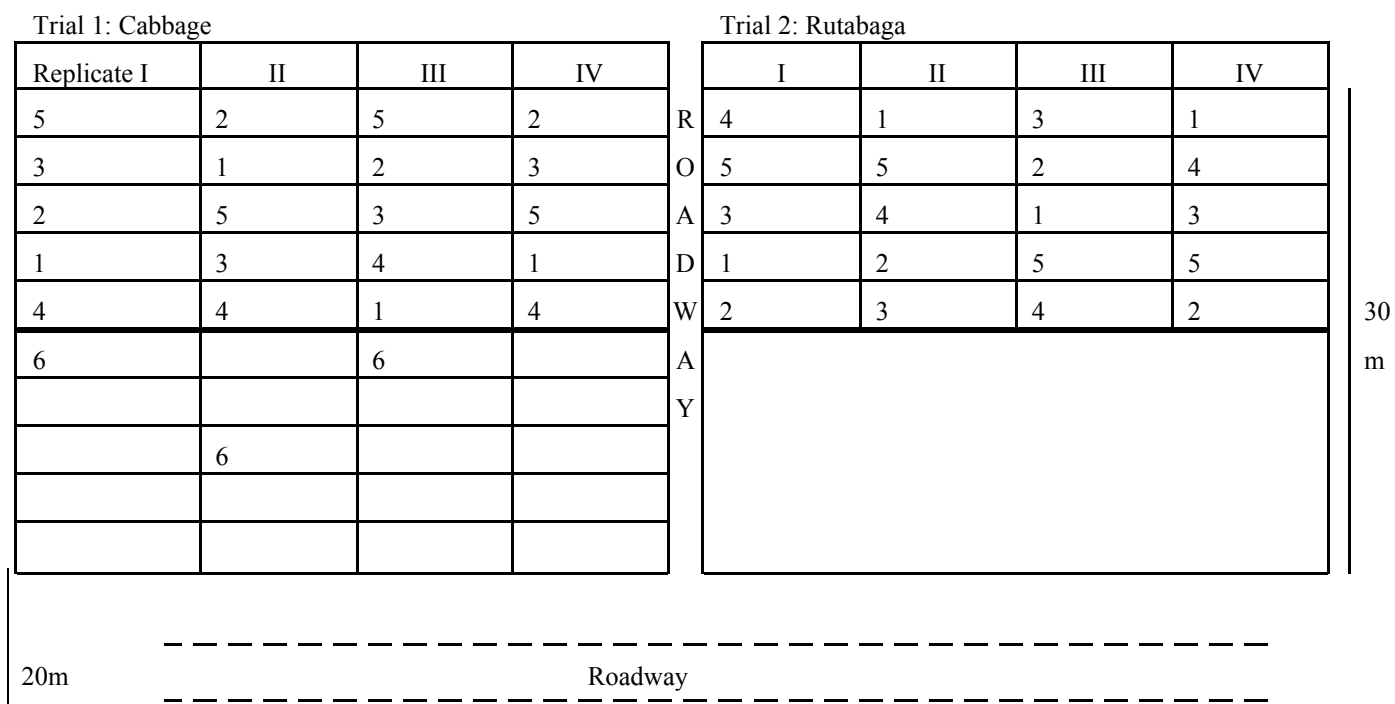
- 1 Control Plot (unamended soil)
- 2 Limestone - 21 t/ha split
- 3 Low-Ash - 17 t/ha

- 4 Split-Ash - 33 t/ha, split application
- 5 High-Ash - 33 t/ha

Cover crop (buckwheat)

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**Figure 3.2 Map of Experimental Site (1998/99)**



Trial 3: Forage

Replicate I	II	III	IV
2	3	5	3
4	4	3	1
1	1	1	5
5	5	2	4
3	2	4	2

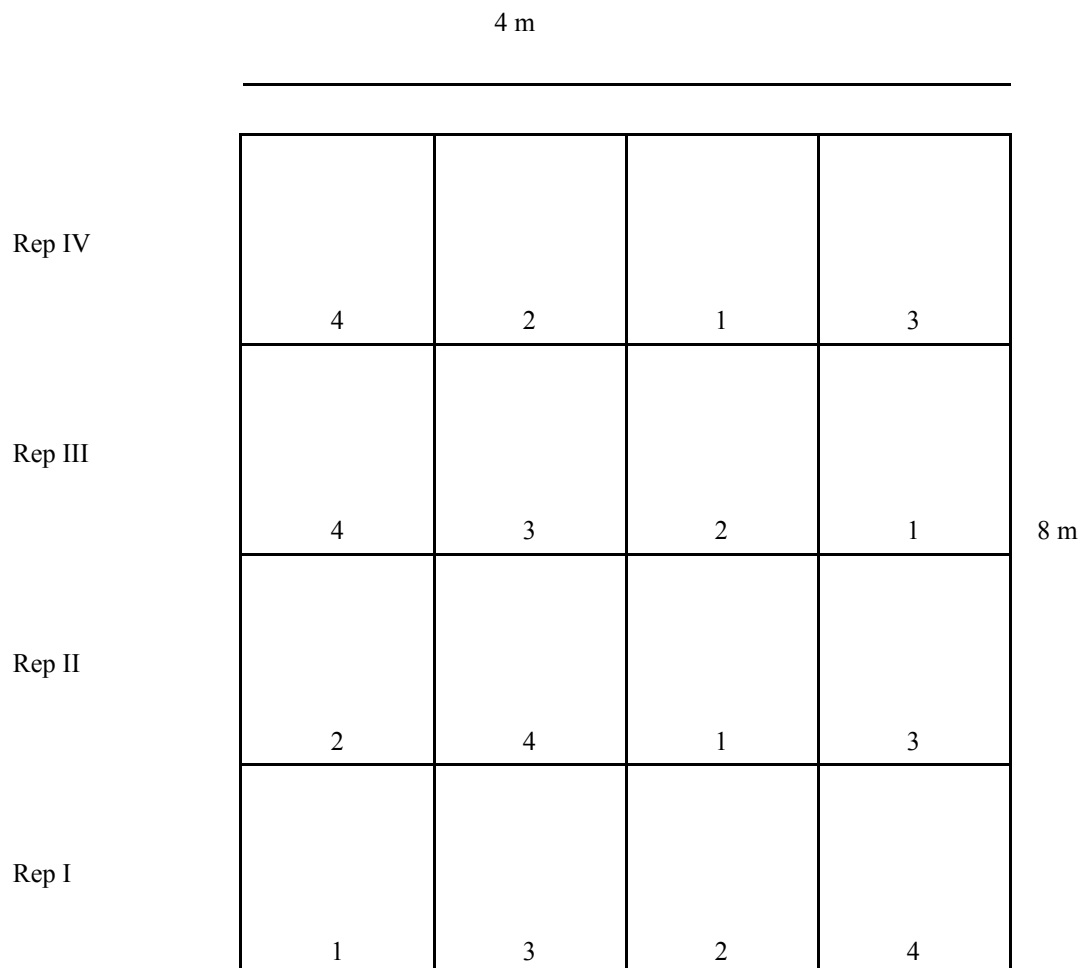
3 80m<sup>o</sup>

**Legend for Treatments:**

- 1 Control Plot
- 2 Limestone
- 3 Low-Ash
- 4 Split-Ash
- 5 High-Ash
- 6 Double-Ash

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**Figure 3.3 Map of Turfgrass Trial**



**Legend for Treatments:**

- 1 Control Plot (unamended)
- 2 Limestone (6.7 t/ha)
- 3 Low-Ash (8 t/ha)
- 4 High-Ash (16 t/ha, split application)
- NV of lime=95%
- NV of ash=79%

**Final Research Report****3.2.2 Experimental Treatments****3.2.2.1 Agricultural Use Trials**

There were five experimental treatments: an unamended control, agricultural limestone, and three levels of CFB ash, and the addition of a sixth ash treatment in 1998 and 1999 to the cabbage (Table 3.4).

Treatment application rates were based on the average lime requirement of the field (21 t/ha) and the calcium carbonate equivalent (CCE) of the limestone and CFB ash (Table 3.5). In 1997, splitting the limestone application so that half of the material was applied in the spring and the other half applied in the fall, improves soil absorption and is a standard practice for soils with a high lime requirement (greater than 6 t/ha).

The Low-Ash treatment (17 t/ha) corresponded to half the lime requirement, corrected for the lower CCE of CFB ash (65%<sup>19</sup>) as compared with agricultural limestone (95%). The Split-Ash treatment (33 t/ha, 16 t/ha in the June and 17 t/ha in October) corresponded to the Limestone treatment (standard practice). The purpose of the High-Ash treatment (33 t/ha, applied all at once in June) was to determine the limits of soil absorption as well as phytotoxicity of high application rates. The Double-Ash treatment consisted of a cumulative application over 2 years (1997-1998) of 53 t/ha. The purpose of this treatment was to determine the effect of applications in excess of the soil lime requirement on soil pH, crop growth and element content of soils and crops.

It is noted that for any given treatment, application rates were similar across the first three trials in 1997, whereas rates differed from trial to trial in 1998 and 1999. The reason for this difference was that in 1997, the initial lime requirement (pre-treatment) was determined from the bulk samples taken in May, which included soil from all three experimental areas, whereas in 1998 and 1999 the lime requirement for each treatment was determined separately for each trial, based on the average of 4 replicate samples per treatment.

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<sup>19</sup>Based on June 11/97 analysis of the ash (Limestone analysis) by NSDAM.

**Final Research Report****Table 3.4 Experimental treatments and amendment loading for the agricultural use trials.**

Treatment	Amendment loading (t/ha)			Cumulative
	1997	1998	1999	
<u>Cabbage</u>				
Control	-	-	-	-
Limestone <sup>1</sup>	21 (split)	3	3	27
Low-Ash <sup>2</sup>	17	1	-	18
Split-Ash <sup>3</sup>	33 (split)	-	2	35
High-Ash <sup>4</sup>	33	1	3	37
Double-Ash <sup>5</sup>	33	20	-	53
<u>Rutabaga</u>				
Control	-	-	-	-
Limestone	21 (split)	7	7	35
Low-Ash	17	3	-	20
Split-Ash	33 (split)	-	4	37
High-Ash	33	-	3	36
<u>Forage</u>				
Control	-	-	-	-
Limestone	21 (split)	4	-	25
Low-Ash	17	1	-	18
Split-Ash	33 (split)	1	-	34
High-Ash	33	-	-	33

<sup>1</sup> Limestone = agricultural grade dolomitic limestone, CCE 90-95%. Rate corresponded to LR required to raise soil pH to 6.5, 1997 rate applied as a split application.

CFB ash treatments: CCE=64-70%.

<sup>2</sup> Low-Ash = Rate applied in 1997 was half the High-Ash rate. In 1998 and 1999, ash was applied to raise soil pH to 5.5.

<sup>3</sup> Split-Ash = Objective was to provide ash treatment equivalent to lime treatment, 1997 rate applied as split application (½ Spring, ½ Fall).

<sup>4</sup> High-Ash = All ash applied in 1997 was applied in spring.

<sup>5</sup> Double-Ash = Objective was to determine maximum rate of loading, cabbage only, for 1998, 1999.

The limestone was Mosher agricultural grade limestone ( $\text{CaMg}(\text{CO}_3)_2$ ), with a CCE of 95% and fineness guarantee of 100% of the material passing through 10 mesh (2.00 mm) and 60% of the

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material passing through 100 mesh (0.15 mm). In 1997, two types of CFB fly ash from the Point Aconi Generating Station were used, conditioned<sup>20</sup> (hydrated) and unconditioned (unhydrated). Conditioned ash was used in the June application and unconditioned ash was used in the October application. All subsequent applications of ash was with conditioned materials. Results of a limestone analysis performed on samples of these two types of ash are provided below (Table 3.5). Results of other analyses performed on the ash (aqueous leach of soluble elements, total and available metals, PAH's and PCB's) are provided in Appendix 3.

**Table 3.5 Limestone analysis of conditioned and unconditioned CFB ash, 1997.**

Analyte	Conditioned (July application)	Unconditioned (October application)	Mosher Limestone
Dry Matter (%)	93.3	as received	as received
Soluble (%)	79.5	77.5	87.0
Ca (%)	24.8	27.5	21.0
Mg (%)	0.4	0.4	9.1
Neutralizing value (%)	64.0	70.0	90.0
pH	12.3	12.1	8.5

### 3.2.2.2 Turfgrass Trail

There were four treatments in the turfgrass trial: 1. Control - no soil amendment; 2. Limestone - agricultural grade limestone; 3. Low-Ash - CFB ash; and 4. High-Ash - CFB ash. The Limestone treatment (6.7 t/ha) corresponded to the lime requirement to raise the soil pH to 6.5, and the Low-Ash treatment (8 t/ha) was the ash equivalent of this treatment, corrected for the lower CCE of the ash. The High-Ash treatment (16 t/ha) was twice the rate of the Low-Ash treatment, with the application split over two years (half was applied in July 1998, and the remainder applied in July 1999).

### 3.2.3 Sampling of Soils and CFB Ash

In 1997, soils at the Point Edward experimental site were sampled on May 13, June 25, July 23, October 3, October 22 and October 25. In 1998 and 1999, soils were sampled in late May, before land preparation, and in October, after harvest. In all sampling events, a representative sample was obtained by taking 10-30 cores from random locations throughout the plot (or replicate), and thoroughly mixing the bulk sample before taking a sub-sample. Bulk samples were divided at least two ways, with one or more sub-samples being packaged and sent to laboratories for analysis, and one sub-sample being dried before transferring to sealed glass jars for archival storage.

<sup>20</sup>Conditioning of the ash is done during the loading operations for dust control, and involves adding sufficient water (25% w/w) to make up for moisture lost to the hydration of CaO and during the generation of steam.

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In 1997, the May 13 sampling was taken as part of the site selection process, as discussed in section 3.1.1. The June 25 sampling occurred prior to the application of soil treatments, and involved sampling (30 or more cores) each of the replications of each trial, including the cover crop area planted. The purpose of this sampling was to establish the background levels of soil parameters in each replicate. Detailed observations on soil texture, colour, uniformity, aggregation and other soil characteristics of the replicate were also recorded at this time. On July 23, soils were sampled from each plot in the vegetable trials. These samples were analysed for available metals, to provide baseline information on the levels of metals in ash-amended soils early in the growing season. Sampling was delayed until 3 weeks after the application of the ash to allow soil absorption of the ash as well as absorption and volatilization of the insecticidal soil drench applied to the cabbage and rutabaga plots after planting. All experimental plots (except cover crop) were sampled on October 25, following harvest and the fall application of amendments. Soils from the vegetable plots were again analysed for available metals, and soil from both vegetable and forage plots were analysed for all standard soil test parameters (see section 3.7 Laboratory Analysis). Soils from the Limestone and Split-Ash plots were also sampled earlier in October to obtain data on the soil pH before applying the second split of the Limestone and ash treatments. In 1998 and 1999, the late May sampling was used to determine the liming requirement, if any, for the crops to be grown; the October sample was used to determine the nutrient requirements for the following growing season, as well as for the elemental analysis for the cabbage and rutabaga plots.

**3.2.4 Sampling of CFB Ash**

Samples of CFB ash were collected prior to application of the material to the experimental area. A similar sampling technique was used to obtain both samples. Approximately 1 to 1.5 litres of ash were removed from 4-6 locations around the perimeter of the pile at three different elevations (15-20 litres in all). The bulk ash sample was then thoroughly mixed and divided several ways to obtain sub-samples for both laboratory analysis and storage.

The June 11, 1997 sample was conditioned material from the ash landfill site, not applied to soils but analysed prior to establishing the experiments in order to determine ash application rates. The June 30 (conditioned) and October 24 (unconditioned) ash samples were from material which was applied at the experimental site. The analyses performed on the samples are outlined in Section 3.7 (Laboratory Analysis). The October sample in all three years was submitted for limestone analysis and an analysis of total metals.

**Final Research Report****3.2.5 Application of Soil Treatments**

In 1997 CFB ash and agricultural Limestone treatments were applied at the end of June and during the last week of October. In the June application, soil treatments were applied one week before seeding to allow soil absorption and to minimize possible phytotoxic effects from the ash. The October applications were applied after vegetable harvest and before the final soil sampling. In 1998 and 1999, required ash applications were applied in late May at the start of land preparation.

The amount of CFB ash required for the field trials was determined from treatment application rates and the plot areas for each treatment. In June 1997, the ash was delivered in bulk in a covered 25 ton earthmoving dump truck. In October 1997 and subsequent years, to reduce dust in transport and handling, the ash was delivered in closed 180 kg barrels. The agricultural limestone was purchased as 55 x 20 kg bags from the United Farmers Co-operative in Sydney River.

A 36" push-handle Gandhi drop spreader was used to apply lime and fertilizers to improve the ease and accuracy of applying the ash. Use of the spreader for applying ash was eventually discontinued, as neither the conditioned nor the unconditioned material demonstrated the uniform, flowable consistency required for use in this type of drop spreader. At least 20% of the conditioned material comprised hard lumps of ash, which clogged the rotors and prevented the spreader wheels from turning. With the unconditioned material, the problem was the fine flour-like ash adhering to the sides of the spreader and caking over the diamond-shaped hopper openings.

In recognition of the poor spreading properties of the ash compared to agricultural limestone, when using the Gandhi spreader, a separate spreading trial with a commercial spreader was conducted at the Point Aconi landfill site. This trial indicated that the CFB ash can be easily applied using typical farm size limestone spreading equipment.

Ash treatments were applied to the vegetable plots by filling a wheelbarrow with ash, transporting the wheelbarrow load to the plot, and distributing the ash evenly over the plot area using small plastic pails. The correct amount of ash for each plot was obtained by determining the mass of a 20 litre hard plastic pail completely filled with ash (26.2 kg). When calculated on a per plot basis, ash treatment application rates were multiples of the filled 20 litre pail (i.e. 2 pails per plot . 17 t/ha, and 4 pails/plot . 33t/ha). Wheelbarrow loads therefore consisted of either 2 or 4 pails of ash. A large amount of dust was generated by shovelling and spreading the ash, and a full set of protective clothing (respirators, goggles, nitrile gloves, disposable coveralls, leather boots) was worn by each worker. A different method of application was employed for the forage trial, where the plot area and amount of ash applied per plot was four times that of the vegetable trials. The bucket of the tractor was calibrated, using the known mass of filled pails of ash, and by marking off the bucket at the level of the required amount. The bucket could then be loaded directly from the ash pile. Applying the ash involved driving the tractor along the plot in



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low gear, while a person walking in front of the bucket used a garden rake to remove the ash from the bucket and spread it over the plot in as even a strip as possible. Neither of the above spreading techniques were very satisfactory, as it was both difficult to control dust and obtain an accurate, uniform application.

The agricultural grade limestone was applied with the Gandhi drop spreader to both vegetable and forage plots. The amount of lime required for each plot was weighed out in pails, placed in the hopper of the spreader, and the unit pulled over the plot at constant walking speed until the hopper was empty. The use of the spreader resulted in the lime being applied with greater speed, ease and precision than the ash. The lime also generated dust, and a dust mask was worn for respiratory protection during spreading.

During the discing operation, care was taken to lift the discs at the edge of each plot so as to minimize the movement of soil into the neighbouring plot. Forage plots were discing only after the June application (before seeding), and all subsequent soil treatments to forages remained as surface applications.

In 1998, soil amendments were applied to the turfgrass in mid-July. Unhydrated ash was used, and was found to be satisfactory for application utilizing the Gandhi drop spreader. Treatment application rates were based on the lime requirement of the soil (average of all plots, 6.7 t/ha) and the neutralizing value of the limestone (95%) and unconditioned ash (79%). Because of the small plot size, the amount of ash and lime required for each plot were pre-weighed and placed in paper bags which were then emptied directly into the Gandhi spreader. Each Limestone treatment (6.7 t/ha) received 1.34 kg of Mosher agricultural grade limestone. For both the Low-Ash (8 t/ha) and High-Ash (16 t/ha) treatments, 1.6 kg of ash was applied to the plots. Because the High-Ash treatment was a split application, an additional 1.6 kg of ash was applied in July 1999.

**3.2.6 Fertilization**

To prevent macro-nutrient deficiencies in crops, N-P-K fertilizer was applied to all of the plots prior to seeding and transplanting. The fertilizer was broadcast over the plots by hand, and incorporated into the soil by lightly discing with the tractor. The rate of fertilizer application was based on soil test results obtained from the June sampling in 1997 and from the October sampling in 1998 and 1999. A further side-dress of N (as 34-0-0) was applied to the cabbage four weeks after transplanting.

For the turfgrass, fertilizer was applied at the same time as the other amendments (mid-July). A 10-10-10 lawn and garden fertilizer was applied uniformly at the rate of 1 lb/1000 ft<sup>2</sup> (1.56 kg of fertilizer) to the entire plot.

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**Final Research Report****3.2.7 Transplanting and Seeding**Cabbage

In each year cabbage (*Brassica oleracea* var. *capitata* f. *alba*) transplants, Lennox cultivar, were purchased from Conrad Neisten, a local vegetable grower. In late June, 3,500 plants (4-leaf stage) in 16 flats were picked up from Hanks Family Farm in North Sydney and transported to the greenhouse at the Point Edward Resource Centre. The transplants were thoroughly soaked with water on arrival. Throughout transplanting, unplanted flats of cabbage were kept out of direct sun in the greenhouse and watered daily.

The field was prepared for planting by measuring off and staking rows at 75 cm centres, the standard row spacing for late planted cole crops. This spacing allowed three harvestable rows and two guard rows in each 3 m wide plot. Strings marked at 45 cm intervals were then strung along the row to guide planting. Using a tree planting shovel, soil was loosened to a depth of 20-25 cm at 45 cm intervals, and sufficient soil removed to make a 15 cm deep hole. Each planting hole was soaked with 1-2 L of water using the lawn tractor-mounted tank sprayer. Transplants were dropped into the planting hole and planted and the soil was firmed around the plug.

The transplanting operation was completed over a 2-day period in late June or early July. In 1997, weather conditions were excessively dry and, at least 3,000 litres of irrigation water using a lawn tractor-mounted 200 litre tank sprayer had to be applied to the field. Weather conditions were optimum for transplanting in 1998, and though dry at the start of the operation in 1999, there was adequate rainfall immediately after transplanting, so that additional irrigation was not required.

Rutabaga

In each year rutabaga (*Brassica napus*) seed, Laurentian cultivar, was obtained from the United Farmers Co-operative. Rows were marked off as above, at a 60 cm row. Marked strings running the length of the rows were used to guide row and seed spacing. The row was prepared for seeding by running a hoe under the string to lightly score the soil surface. Seeding was done by hand, and seeds were planted at 8 cm intervals, and later thinned to 16 cm. Seeds were covered by tamping the soil over the seed row with the flat end of a hoe. One of the three inner rows in each rutabaga plot was randomly assigned as a germination test plot. The purpose of these subplots was to compare percentage germination of rutabaga among the five treatments.

Germination test plots consisted of an 8.5 m section of the row planted at the same 8 cm seed spacing with a package of 100 pre-counted seeds. The beginning and end of the plots were marked with yellow stakes. Generally seeding the rutabaga was completed within one day. An additional germination was conducted in 1998, with the objective of determining if there were phytotoxic effects on seedling germination and establishment as a result of the High-Ash application rate. The test was established in the Double-Ash cabbage treatment plots. The rutabaga were seeded between the rows of transplanted cabbage plants, and monitored for 4 weeks, after which time the plants were removed.

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### Forages

Triple Mix, a commonly used forage mixture consisting of 70% timothy (*Phleum pratense*), 15% red clover (*Trifolium pratense*) and 15% white clover (*Trifolium repens*), was used for the forage trial. Triple Mix was purchased at the United Farmers Co-operative, and seeded on July 14, 1997 at the recommended seeding rate of 13 kg/ha using a push type broadcast seeder. Following seeding, the soil surface was rolled with a Brillion seeder to cover the seed and provide a firmer seedbed.

## 3.3 Site Management

### 3.3.1 Irrigation

In 1997, because of the hot, dry weather in it was imperative that supplemental irrigation be supplied to the crops. Irrigation was provided both at planting, and every 3 or 4 days thereafter during the first 3 weeks of crop establishment. Irrigation consisted of watering crops with a hand held spray gun and hose attached to a lawn tractor-mounted 200 L tank sprayer. Because of the limited capacity of the spray tank, and slow speed of the lawn tractor used to make return trips (0.5 km each) to re-fill the tank, irrigating by this method became a very time consuming occupation (i.e. a day to water each of the vegetable trials). By necessity, irrigation was limited to the cabbage and rutabaga.

Under the high rates of evaporation and extreme soil moisture deficit conditions in July, this method was barely adequate in providing the minimum required irrigation to the vegetables, and failed to supply any irrigation to the large area planted to forages. Towards the end of July, crops were becoming moisture stressed, with the forage seedlings almost wilted beyond recovery. Arrangements were made with Nova Scotia Power to utilize one of the large irrigation trucks used to supply large volumes of water to the ash landfill site. On July 25, a truck carrying approximately 13,700 litres of water was brought to the experimental site. Within 15 minutes, the entire contents of the tank were distributed over the three experiments, with particular emphasis on irrigating the forages.

It is estimated that supplemental irrigation during the month of July provided the equivalent of approximately 4 mm rain to the vegetable crops (delivered in five waterings over the course of three weeks), and 3 mm of rain to all three experiments (delivered in one 15 minute event)<sup>21</sup>.

Supplemental irrigation was not required in 1998, and was only required at the start of transplanting in 1999 (with Day 1 of the Cabbage transplanting).

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<sup>21</sup>Given: 10,000 L of water supplied to the vegetable crops (2,400 m<sup>2</sup> area) by the tractor mounted sprayer, and 13,700 L supplied to the three experiments (4,800 m<sup>2</sup> area) by the irrigation truck.  
Given: 1 m<sup>3</sup> = 1000 L; and vol (m<sup>3</sup>)/area (m<sup>2</sup>) x 1000 = mm

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### 3.3.2 Pest Control

In each year Lorsban (Chlorpyrifos, an organo-phosphate) was applied as a soil drench to cabbage and rutabaga immediately after transplanting and seeding to prevent feeding damage by cutworm (*Noctuidae* spp.) and cabbage root maggot (*Delia radicum* L.). Lorsban was applied at the rate of 500 ml of chemical in 200 L of water using the tractor mounted sprayer also used for irrigation. For the rutabaga, Lorsban was applied as a continuous spray over the soil of the seed row, and for the cabbage, the spray was applied in a circular pattern at the base of each plant. Full protective clothing (pesticide respirator, goggles, nitrile gloves, disposable coveralls, and rubber boots) was worn both during the mixing and application of the pesticide as well as during the cleaning of the spray apparatus. To clean the sprayer, the tank was completely filled and then sprayed out first with water, followed by 5% bleach, and then triple rinsed with water.

During the growing season, the vegetable crops were monitored for population levels of imported cabbage worm (*Pieris rapae*), cabbage looper (*Trichoplusia ni*) and diamondback moth (*Plutella xylostella*). Dipel (Thuricide, a biological) was applied as needed at the rate of 250 g/ha to control populations of those insects. In September, 1997 Dipel was not effective in controlling diamondback moth populations, therefore Ambush (a synthetic pyrethroid) was applied to the cabbage at the rate of 120 ml/ha to control diamondback moth. This provided an effective control, and populations levels were not a serious problem in 1998 or 1999, and two sprays during each season, were successful in controlling insect populations.

### 3.3.3 Weed Control

Weed pressure was not significant in any of the plots, and hand pulling large weeds such as lambs quarters (*Chenopodium album*) generally provided sufficient control. One exception requiring chemical control, was a localized infestation of coltsfoot (*Tussilago farfara*) in the forage trial. A spot treatment of Round-Up (Glyphosate) was applied to the coltsfoot using a backpack sprayer with a hand-held spray gun. In the vegetable plots a treatment of Round-Up was applied to the entire area one week before soil preparation to kill a range of annual and perennial weeds. Round-Up was applied at a rate of 5.0 L/ha (2.5% spray solution). Other than this, weed pressure remained low during the growing season, and hand pulling and hoeing provided adequate control. The land was previously forested and not cultivated, therefore the soil weed-seed bank was limited, both with respect to species diversity and quantity of potential weed seeds.

## 3.4 Crop Monitoring

Crop monitoring consisted of daily site visits, as well as more rigorous procedures conducted on a weekly basis to document growth and general appearance of the crops.

Daily site visits typically involved a walk through the plots to look for signs of moisture stress, insect damage, or other environmentally induced conditions. If any of these were noted, the cause and severity of the condition were evaluated to determine if and what kind of intervention was required. Significant observations were noted in the field data book.

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Weekly site visits were used to collect data on crop growth from all experimental plots. The variables measured included: germination percentage, number of leaves, size and shape of leaves, plant size, growth habit and general vigour, and foliar pigmentation. As cabbage began to form heads (late August), dates at which the inner leaves of the heads began to turn in were recorded for each plot. All data were recorded in the field data book. Observations were also photographed periodically throughout the season.

Determining percentage germination involved walking down the pre-marked germination subplot in each plot, and counting the number of rutabaga seeds germinated.

### **3.5 Harvesting**

Cabbage and rutabaga plots were harvested between October 17 and 20 in each year. The harvesting operation consisted of harvesting, grading, data collecting and recording, and plant sampling. All of these tasks were performed directly in the field. Harvesting equipment (knives, electronic scales, vegetable bins, and coolers for short-term sample storage) was obtained from the Plant Science Department of NSAC. Other equipment used for the harvest (John Deere 75 HP tractor with bucket and an all-terrain vehicle) was provided by the Point Edward Resource Centre.

The area to be harvested was first marked off with fluorescent flagging tape and excluded guard rows and the first and last 0.5 m of each row. Cabbage were cut at the base of the stem using 20 cm long knives, with only the large outer leaves removed. The harvested heads were placed in large bins. Heads were graded as marketable (Canada # 1) or cull according to the Fresh Fruits and Vegetables Products Regulations of the Canada Agricultural Products Act. One person did the grading for all the material to maintain consistency, both during the harvest and for each year. Heads were counted and weighed. All weighing was done using a 40 kg electronic scale with power supplied through an adapter connected to the vehicle cigarette lighter. The data were recorded separately for each category on previously prepared data sheets. To obtain a random sample for tissue sampling every 10th head was placed in a specially marked bin.

Rutabaga were pulled and the roots and leaves trimmed using 20 cm long knives. It was observed that some roots were infected with clubroot, and therefore all roots were first separated into infected or not-infected categories and the number of roots for each were recorded. All roots were graded as marketable (Canada #1) or cull according to similar standards as described for cabbage above. The roots were counted and weighed and the data were recorded separately for each category on previously prepared data sheets. To obtain a random sample for tissue sampling every 15th root was placed in a specially marked bin.

Cabbage heads and rutabaga roots were sampled for plant uptake of nutrients and trace metals. The cabbage heads previously selected at random, were split longitudinally and approximately 50 g of tissue was removed immediately above the stem area. Outer leaves and material with dense veins or stem tissue were avoided. The samples from each plot (8-10 heads) were placed

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into a 5 L plastic pail, the bulk sample was thoroughly mixed then a sub-sample was removed. Four sub-samples were taken per plot, 3 sub-samples were placed in labelled ziploc bags, and one sub-sample was placed in a small paper bag (after sample fresh weight was determined and recorded). This sample was later dried in the NSAC plant drier (65°C for 48 hours) then cooled and weighed. The other three samples were stored in a cooler for transport. Two sets of the samples were shipped to separate labs for analysis (NSDAM for nutrients, and Philip Analytical Services for trace metals), and 1 set was packed for storage and placed in a freezer at the NSAC. Rutabaga were cut in cross section at the hypocotyl-root interface. Approximately 50 g of tissue was removed from the xylem tissues area in both sections of the root. The material was handled similarly as described above for cabbage.

After all data were collected the remaining plant material was loaded into the tractor bucket and transported to a level area located approximately 20 m from the field for composting.

**3.6 Field Clean-up**

The end-of-season field clean-up each year consisted of harvesting and removing guard row plants from the field, collecting and replacing broken and loose plot stakes and doing a general clean-up of the experimental site.

Another task completed at this time was construction of a windrow for composting the harvested plant material. The windrow of compostable material, approximately 4 m wide x 2 m high x 6 m long, was formed using the tractor bucket. At least 20% of the volume of the pile consisted of sawdust (obtained from a portable sawmill installed at the Point Edward Resource Centre), with the remainder of the pile comprised of crop residues. During windrow construction, the pile was turned several times to incorporate the sawdust, and finally covered with a cap of sawdust.

At the termination of the experiment, in July 2000, soil sampling was repeated in all plots to determine soil pH and residual liming activity. Subsequently the vegetable plots were disced and seeded to perennial forage.

**3.7 Laboratory Analysis**

The components analysed, analyses performed and laboratories involved in the testing program are summarized in Table 3.6. Procedures for several of the analyses listed below are provided in Appendix 2. The elements included in the metals analysis are presented in Table 3.7.

**Final Research Report****Table 3.6 Components analysed, analyses performed and laboratories involved.**

<b>Component</b>	<b>Analysis</b>	<b>Laboratory</b>
CFB ash	Limestone analysis (% dry matter, solubility, total neutralizing value (CCE), % Ca, % Mg)	NSDAM <sup>1</sup>
	Total metals (scan of 23 elements) Aqueous leach (soluble forms of 26 elements) Available metals (scan of 22 elements) PAH's, PCB's	PAS <sup>2</sup>
	Aqueous and acidic leachate extraction; Malvern particle size analysis	TUNS <sup>3</sup>
	Hot-water extractable B	PAS
	Radioactivity analysis (U <sup>238</sup> , Th <sup>232</sup> , K <sup>40</sup> , Cs <sup>137</sup> )	NSAC <sup>4</sup>
	Limestone	Limestone analysis (as above)
Limestone	Total Metals (scan of 23 elements)	PAS
	Hot-water extractable B	PAS
Soils	Standard soil test (organic matter, P, K, Mg, Ca, S, soil pH, buffer pH, lime requirement, Zn, Mn, Fe, Cu, B, CEC, % base saturation)	NSDAM NBDARD <sup>5</sup>
	Available metals (scan of 23 elements)	PAS
	Particle size distribution (%sand, silt, clay)	BSAS <sup>6</sup>
Plant Tissue	Standard plant tissue plus S (N, P, K, Mg, Ca, S, Zn, Mn, Fe, Cu, B)	NSDAM
	Standard forage (dry matter, crude protein, ADF, TDN, DE (Mcal/kg), P, K, Mg, Ca, Na, Zn, Mn, Fe, Cu)	
	Available metals (scan of 24 elements)	PAS

<sup>1</sup> Nova Scotia Dept. of Agriculture and Marketing, Quality Eval. Services, Truro, NS

<sup>2</sup> Philip Analytical Services, Halifax, NS

<sup>3</sup> Technical University of Nova Scotia, Halifax, NS

<sup>4</sup> Nova Scotia Agricultural College, Truro, NS

<sup>5</sup> New Brunswick Dept. of Agric. and Rural Development, Fredricton, NB

<sup>6</sup> BioScan Analytical Services, Truro, NS

**Final Research Report****Table 3.7 Elements included in the analysis of metals in CFB ash, soils and crops.**

Element	Symbol
Aluminum	Al
Antimony	Sb
Arsenic	As
Barium	Ba
Beryllium	Be
Boron	B
Cadmium	Cd
Chromium	Cr
Cobalt	Co
Copper	Cu
Iron	Fe
Lead	Pb
Manganese	Mn
Molybdenum	Mo
Nickel	Ni
Selenium	Se
Silver	Ag
Strontium	Sr
Thallium	Tl
Tin*	Sn
Uranium	U
Vanadium	V
Zinc	Zn
Mercury	Hg

\* Available only for tissue metal scan.



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**Final Research Report****3.8 Statistical Analysis**

Prior to final analysis, all data were verified to have satisfied the assumptions for statistical analysis by examining the residuals from the fitted model, including plotting the residuals against the predicted values. Most of the data sets met those assumptions, there were some variables within data sets that did violate the assumptions. In those instances a further examination of the data did identify one or two outliers, and once the outliers were removed the full data sets fell within the assumptions for normality. No further manipulations or transformations were required of the data.

The final statistical analysis utilized a split-block design, with soil amendment (treatment) being the main plot and year the sub-plot. Analysis were conducted separately for each crops, as species, treatment, year interactions were of no interest. The full model was

$$y = \mu + B + T + T*B + Y + Y*B + T*Y + O$$

where  $y$  represents observation;  $\mu$  represents the mean;  $B$  represents blocks (replications);  $T$  represents treatment (soil amendments);  $Y$  represents year; and  $T*Y$  the interaction between treatment and year. The term  $T*B$  was the error term used for  $T$ , and  $Y*B$  was the error term used for  $Y$ . For models that indicated a significant interaction, least significant difference (LSD) was determined ( $P=0.05$ ) for the interaction term. For models for which the interaction was not detected to be significant, the main effects of treatment and/or year (or period) were examined. If either or both were significant then the LSD was determined, using the appropriate error term.

A significant interaction ( $p=0.05$ ) indicates that the response of treatment is dependent on or affected by year, and thus the treatment response had to be analysed within year. When a significant interaction was not detected, the main effects of treatment and year were considered. The main effect of treatment was averaged over years, and the main effect of year was averaged over treatment.

**Final Research Report****4.0 RESULTS****4.1 Liming Efficacy**

There are two main aspects to consider when evaluating the efficacy of liming materials. One is the ability of the material to neutralize soil acidity and increase low soil pH; the other is the ability to improve soil fertility. The soil fertility improvement resulting from liming acidic soils should consist of both increased levels of soil calcium and magnesium, as well as improved availability of other plant nutrients and greater soil biological activity at the more favourable soil pH range. While these two functions of liming soils - neutralizing acidity and improving soil fertility - are in many ways related, it is possible for liming materials to be more effective at one than the other. Liming efficacy in terms of both functions depends on the chemical and physical attributes of the liming material; in particular, calcium carbonate equivalence (CCE), particle size or fineness, and kind and amount of calcium and magnesium compounds (i.e., carbonates, oxides, hydroxides, or silicates of calcium and magnesium) (Foth and Ellis 1996). The amount of lime required by a given soil, as well as the soil liming response (rate and extent of the acid neutralizing reaction), is a function of both the characteristics of the liming material as well as the initial pH and buffering capacity of the soil to which the material is applied (Brady and Weil 1999).

In this section, liming efficacy of CFB ash is evaluated in terms of both acid neutralizing capacity as well as capacity of the material to improve the balance and supply of soil calcium and magnesium when compared with Mosher agricultural limestone. The discussion is based on results obtained between 1997-1999. Some difficulties in interpreting the soil liming responses on the basis of the initial characterization of the soils (i.e., buffer capacity and lime requirement) is noted. A more complete discussion of liming efficacy, which includes additional information on the soils obtained in August of 2000 (re-analysis of initial soil samples by the New Brunswick soil test lab, as well as year 2000 soil pH data) is presented in the General Discussion (section 5.0). Appendix 7 provides background on Soil Acidity and Soil Liming Response.

**4.1.1 Soil pH****4.1.1.1 Vegetables and Forage**

The soil pH data from plots established on this initially very acid soil (Point Edward experimental site) demonstrates the significant acid neutralizing capacity of CFB ash. When considered on the basis of acid neutralizing capacity, CFB ash compared favourably with agricultural grade limestone as a liming agent for vegetable and forage crops. Within the first year of application, ash applied at the soil lime requirement increased very low soil pH (- pH 5.0) to a range considered optimal for nutrient availability and crop growth (pH 6.0-6.5). In terms of soil pH adjustment, apart from initially higher alkalinity in the ash treatments (i.e. Split-Ash treatment in 1997), there was no difference between the Limestone treatment and the two ash treatments applied at an equivalent total liming rate (Split-Ash and High-Ash). That is, the target soil pH range (6.0-6.5) was achieved within the first year in all three equivalent liming

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treatments in both vegetable and forage plots (Table 4.1). In Years 2 and 3, soil pH in both the Limestone and CFB ash treatment plots was maintained within or near the optimum range with low (2-4 t/ha) additional applications. In some cases, no liming treatments were applied, indicating that the target pH range had been achieved or exceeded (i.e. 1998 Split-Ash treatments in the vegetables; 1999 all liming treatments in the forage) (Tables 3.4 and 4.1).

These results are consistent with a large number of other studies which indicate that coal combustion by-products (CCBs) can act as liming agents (Stout et al. 1988; Korcak 1979, 1980ab 1982 1985 1997; Edwards et al. 1985; Carlson and Adriano 1993). McCarty et al. (1993) tested the liming ability of a number of CCBs and found that effectiveness of the by-products for increasing soil pH was directly related to calcium carbonate equivalency (CCE) (i.e. bed ash (97% CCE) > multistage burner residue (68% CCE) > spray drier residue (55% CCE) > fly ash (18% CCE)). Various studies indicate that the CCE of fluidized bed materials (36-81%) is much higher than that of other CCBs, primarily as a result of the large amounts of sorbent (calcitic or dolomitic limestone) used in the CFB combustion process. The calcium carbonate equivalence of the CFB ash used in this study ranged between 64% and 79%. The CCE of ash applied in 1997, the year of highest amendment loading rates, ranged between 64% and 70%. Variations in CCE of different batches of ash from the same coal source can largely be attributed to differences in CaO content (a function of coal:sorbent ratios during combustion) and moisture content (i.e. conditioned vs unconditioned ash).

When application rates are determined on a CCE rather than weight basis, few distinctions remain between liming materials relative to their influence on soil pH (McCarty et al. 1993). Application rates of the Limestone treatment in Year 1 were based on the soil lime requirement, and total applications in the Split-Ash and High-Ash treatments were the equivalent of this treatment adjusted for the lower CCE of the ash (64%) compared to Mosher limestone (95%). The Low-ash treatment was half the total rate of the limestone and other two ash treatments<sup>22</sup>. Applications in Years 2 and 3 in all treatments were based on the lime requirement of the soil in the individual treatments<sup>23</sup>. Given the importance of CCE in determining acid neutralizing capacity, it is not surprising that soil pH adjustment and subsequent liming rates were similar in the three 'calcium carbonate equivalent' treatments (Limestone, Split-Ash and High-Ash). Synchronizing initial applications in terms of CCE of the soil lime requirement in these treatments resulted in similar soil pH adjustment, and consequently, similar and low maintenance applications in the following two seasons (Tables 3.1 and 4.1).

Before discussing differences between treatments and the two liming materials (CFB ash and Mosher limestone), the importance of soil buffer capacity should be noted, as this soil characteristic is central to soil liming response. Soil buffer capacity, or ability of the soil to

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<sup>22</sup>Limestone (21 t/ha) was applied as a split (10.5/10.5) (standard practice for high lime rates). High-Ash and Split-Ash (34 t/ha) were the CCE of Limestone. High-Ash treatment was applied all at once in the spring, whereas Split-Ash was split (17/17). Low-Ash was the ash equivalent of half the Limestone treatment (17 t/ha).

<sup>23</sup>In the Low-Ash treatment, applications in Years 2 and 3 were based on a target soil pH of 5.5 instead of 6.5 in order to maintain a lower total ash loading.

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resist changes in pH, is a function of soil texture (determined from the proportions of sand, silt and clay) and the type and amount of soil colloids (in particular, layer silicate clays and humus). Soil buffering is reported to be more significant than initial soil pH in determining the pH effect of ash addition (Carlson and Adriano 1993). A number of different parameters may be used to characterize soil buffer capacity. These include soil texture, cation exchange capacity (CEC), soil pH/buffer pH, and soil organic content. From the values of these parameters in soil samples obtained from the three areas (cabbage, rutabaga and forage) where trials were established, the soils may be considered to be weakly buffered (Table 3.1, section 3.1.2).

The characterization of the Point Edward soils as weakly buffered, however, presents some challenges in terms of explaining the results obtained on soil liming response. In particular, the very high initial lime requirement of the soil (21 t/ha) is inconsistent with the designation of a low buffer capacity. For example, the rates of liming typically reported for weakly buffered, sandy soils are in the range of 2-7 t/ha per pH unit (sands would be at the low end and sandy loams at the high end of this range) (Rowell 1994; Brady and Weil 1999). With the extent of pH adjustment required, as indicated by initial soil pH values (i.e. from pH 5.0 to 6.5), lime requirement of this soil would not be expected to exceed 10.5 t/ha (half the value determined by the NSDAM soil test lab). The other factor that is largely inconsistent with the designation of low buffering, is the persistence in several treatments of liming effects into the third season (Table 4.1). In all treatments, amendment loading rates in 1997 by far exceeded subsequent additions in the 1998 and 1999 growing seasons (Table 3.4). Thus, soil pH in 1999 represents, to a large extent, the residual liming effects of the initial application. Residual effects are examined more closely in year 2000 (discussed in section 5.0). While there are some reports of more lasting pH effects on poorly buffered soils (Petruzelli et al. 1987, in Carlson and Adriano 1993), the concept usually promoted is that greater leaching on low capacity soils reduces the duration of liming effects so that such soils require lime more often than highly buffered soils (Brady and Weil 1999).

Soil pH data from 1997 highlights some of the differences between liming materials in terms of chemical composition and rate of acid neutralizing reaction (Table 4.1). As already noted, soil pH adjustment within the first year was dramatic and complete (from - 5.0 to greater than 6.0, more than a ten fold increase) in all three treatments applied at an equivalent liming rate. There were differences between treatments, however, in terms of the rate and extent of soil pH adjustment.

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**Table 4.1 Soil pH\* and change in soil pH\*\* in cabbage, rutabaga and forage plots in 1997, 1998 and 1999.**

Treatment	Cabbage		Rutabaga		Forage	
	Soil pH	<sup>a</sup> pH	Soil pH	<sup>a</sup> pH	Soil pH	<sup>a</sup> pH
	1997					
Control	4.4	-0.5	4.3	-0.5	4.8	-0.3
Limestone	6.3	1.4	5.9	1.2	6.5	1.4
Low-Ash	5.3	0.4	4.9	0.1	6.7	1.6
Split-Ash	6.6	1.7	6.8	2.1	7.5	2.4
High-Ash	6.1	1.2	6.1	1.3	6.9	1.8
	1998					
Control	4.2	-0.8	4.4	-0.4	5.0	-0.1
Limestone	6.6	1.7	6.3	1.6	6.4	1.3
Low-Ash	5.2	0.3	5.9	1.2	6.6	1.5
Split-Ash	6.8	1.9	6.7	2.0	7.4	2.3
High-Ash	6.6	1.7	6.7	1.9	7.2	2.1
	1999					
Control	4.9	0.0	4.5	-0.2	4.9	-0.2
Limestone	6.5	1.6	6.1	1.4	6.1	1.0
Low-Ash	5.4	0.4	5.7	1.0	6.8	1.7
Split-Ash	6.8	1.8	6.8	2.1	7.1	2.0
High-Ash	6.3	1.3	6.8	2.1	7.0	1.9

\* Values are averages of four replicates. Soil pH was measured at the end of each growing season (following harvest and the application of fall amendments).

\*\* Change in soil pH (<sup>a</sup> soil pH) = pH<sub>f</sub>(fall or end of growing season soil pH) - pH<sub>i</sub>(initial soil pH (June '97, pre-amendment))

Soil pH adjustment (<sup>a</sup> soil pH, or the difference between fall soil pH and initial or pre-application values) in 1997 was consistently greater for the Split-Ash compared with Limestone or High-Ash treatments. Contrasts were greatest in the rutabaga and forage plots (Table 4.1). Obviously, for Split-Ash treatments in the fall of 1997, the fact that soils had just received a large application of CFB ash (i.e. the second split) is the major factor contributing to elevated soil pH. A similar increase, however, was not noted in the Limestone treatment, which had just been amended with an equivalent loading of Mosher limestone. In most cases, fall soil pH in the Limestone treatments were either similar to or below those obtained in the High-Ash treatments (amended at the beginning of the growing season).

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Differences in acid neutralizing behaviour of the liming materials may be attributed to the high oxide content (15-40%) in the ash, which makes it a highly reactive material that reacts quickly with soil particles<sup>24</sup>. Compared to the crystalline carbonates in limestone which must be ground prior to application to soil, oxides, which are by nature powdery, allow a more rapid neutralization of soil acidity and the resulting soil pH is higher (Brady and Weil 1999). With respect to speed of the acid neutralizing reaction, an application of good quality agricultural limestone typically results in adequate soil pH adjustment in 45-60 days, if properly incorporated (PPIC 1996). The fact that increases in soil pH were detected almost immediately after application of amendment in the Split-Ash but not the Limestone treatment, provides further evidence that CFB ash reacts much more quickly than Mosher limestone. Several authors have noted that the high initial alkalinity associated with application of this material to soil is soon reduced by the carbonation reaction. Carbonation readily occurs in soils when CO<sub>2</sub> from the atmosphere and/or biological respiration combines with Ca<sup>2+</sup> and Mg<sup>2+</sup> upon hydrolysis of the CaO and MgO in the ash, thereby forming more stable Ca and Mg carbonate compounds (i.e. Ca(HCO<sub>3</sub>)<sub>2</sub>, Mg(HCO<sub>3</sub>)<sub>2</sub>) (McCarty et al. 1994; Carlson and Adriano 1993). With respect to persistence of the liming effect, the similar low requirements for additional applications in Limestone and CFB ash treatments in Years 2 and 3 suggests that the materials have comparable residual activity.

In all three years, the effect of liming treatments on soil pH was especially pronounced in the forage plots (Table 4.1). Because of a shallow topsoil overlying the bedrock on this field, the plow-layer<sup>25</sup> was between 8 and 10 cm in depth for much of the field. Plow-layer depth was as little as 4 cm on high spots in the field (crests or ridges). Consequently, the depth to which amendments could be incorporated and soils could be sampled was variable and mostly limited to half the normal depth. Shallow incorporation of applied amendments would result in a concentration gradient of the amendment with soil depth. Shallow incorporation of liming treatments, combined with a shallow sampling depth, is the most likely reason for the generally higher soil pH in forage compared with cabbage and rutabaga plots. Another factor responsible for elevated pH values in certain treatments (i.e. Low-Ash) may be attributed to possible over-application with the less precise method for applying ash<sup>26</sup> that was used in the forage trial.

In 1997, early season liming treatments to forage plots were incorporated (i.e. disced into soil) prior to seeding, whereas all subsequent treatments were surface applications to the established forage stand (Table 3.2). While surface applied liming materials usually react more slowly and not as completely as soil incorporated materials (A&L Labs, Technical Bulletin), in forage plots the advantages of soil incorporation in terms of soil pH adjustment are obscured by the very high

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<sup>24</sup>Pure oxides of Ca or Mg have a CCE of 150-180%, whereas pure CaCO<sub>3</sub> has a CCE of 100%. The CCE of mined deposits of calcitic or dolomitic lime (Ca and CaMg carbonates) ranges from 85-108%.

<sup>25</sup>Upper layer of soil into which soil amendments are incorporated and which is mixed by tillage; it is also the soil layer from which soil samples are routinely taken. The plow-layer is typically 15-20 cm in depth.

<sup>26</sup>Problems using the Gandi spreader for applying ash, combined with the large plot area in the forage trial, required that the ash be applied to forage plots by filling the tractor bucket with the pre-weighed treatments and raking the material off while the tractor was driven slowly across the plot.

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alkalinity of soils immediately following amendment with CFB ash. For example, fall soil pH was higher in 'surface applied' Split-Ash (pH 7.5) compared with 'soil incorporated' High-Ash (pH 6.9) treatments despite the fact that total amendment loading rates were the same (Table 4.1). In this case, it is likely that higher soil pH in the Split-Ash compared with High-Ash treatment plots has more to do with the initial high alkalinity of soils immediately following ash application<sup>27</sup> than it does with method of application (surface vs incorporated) (Table 4.1). The greater initial reactivity of CFB ash compared with Mosher limestone is evident from comparisons of fall soil pH in Limestone and Split-Ash treatments. Despite the fact that timing of application (immediately prior to fall soil sampling), application method (soil surface, non-incorporated), and rate of application (on a 'calcium carbonate equivalent' basis) were the same for the two materials, fall soil pH was 10 times higher in Split-Ash (7.5) compared with Limestone (6.5) treatments plots (Table 4.1).

### 4.1.1.2 Turfgrass

Soil pH in 1998 and 1999, and the change in soil pH from 1998-1999 (<sup>a</sup> Soil pH), were determined for each of the soil treatments in the turfgrass plots (see Section 3.2.2.2 for a description of soil treatments). <sup>a</sup> Soil pH was calculated by subtracting soil pH values for 1998 from 1999 values. In that way a negative number represents a decrease in soil pH and conversely a positive number represents an increase. In order to determine the effect of the treatments on soil pH at different sampling depths, soils were sampled at two depths, an upper (0-7.5 cm) and lower (7.5-15 cm) depth; a third sample, representing soil from the entire sampling depth (0-15 cm), was also taken. The third depth (0-15 cm) is the typical sampling depth on which soil test results are reported.

First the interaction between sampling depth and treatment was tested. There was no significant interaction detected for soil pH in 1998 and the main effect of depth and treatment was then tested. A significant effect of sampling depth on soil pH was detected, however there were no significant differences among treatments. Soil pH was significantly different among the 3 sampling depths in 1998 (Table 4.2). There was a significant sampling depth x treatment interaction for soil pH in 1999 and for <sup>a</sup> Soil pH (Table 4.3).

**Table 4.2 Soil pH response at different sampling depths in turfgrass plots in 1998.**

Sampling depth (cm)	Soil pH
0-7.5	6.03a*
7.5-15	5.73b
0-15	5.89c

\* Values in each column followed by the same letter are not significantly different according to least significant difference tests ( $p < 0.05$ ).

<sup>27</sup>In 1997, Split-Ash plots were amended in both June and October (in the latter event, just prior to soil sampling), whereas High-Ash plots were amended only in June.

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Given the short duration of treatment in the first field season, it is not surprising that there was no treatment effect noted in 1998. Nor is the significant effect of sampling depth in 1998 surprising, where on a long established and managed turf (i.e. limed, mowed, fertilized), repeated surface applications of limestone tend to result in a distinct soil pH gradient with depth.

**Table 4.3 Effect of the interaction between sampling depth and treatment on soil pH in 1999 and the change in soil pH from 1998-1999 (<sup>a</sup> Soil pH) in turfgrass plots.**

Sampling depth (cm)	Treatment	Soil pH	<sup>a</sup> Soil pH
0-7.5	Control	6.18cd*	0.15ab
	Limestone	6.65ef	0.70bc
	Low-Ash	6.75f	0.67bc
	High-Ash	7.17g	1.10d
7.5-15	Control	5.77a	0.00a
	Limestone	5.82ab	0.17b
	Low-Ash	5.82ab	0.05a
	High-Ash	5.57a	-0.15a
0-15	Control	6.05bc	0.15ab
	Limestone	6.42de	0.52b
	Low-Ash	6.30ce	0.42b
	High-Ash	6.82f	0.92cd

\* Values in each column followed by the same letter are not significantly different according to least significant difference tests ( $p < 0.05$ ).

A significant interaction indicates that both the treatment and sampling depth are significant, and that the effect of one is dependent on the level of the other. In 1999, soil pH was significantly greater in the High-Ash treatment at the upper sampling depth (0-7.5 cm) compared to all other treatments (Table 4.3). Correspondingly, the upper depth of the High-Ash treatment supported the greatest <sup>a</sup> Soil pH of any of the treatments. Within this depth, there was no significant difference between the Limestone and Low-Ash treatments. The greater effect of the High-Ash treatment at this depth can be explained by the fact that the only plots in 1999 that received a liming material were the High-Ash plots. As expected, soil pH at the upper depth was significantly lower for the Control treatment compared to all other treatments (Table 4.3).

At the lower sampling depth (7.5-15 cm), there were no significant differences in soil pH detected among treatments in 1999 (Table 4.3). Results for <sup>a</sup> Soil pH at this depth are interesting, however, and may highlight differences between CFB ash and limestone in terms of liming efficacy at different soil depths. A negative result for <sup>a</sup> Soil pH in the High-Ash treatment, while not significantly different from <sup>a</sup> Soil pH in the Control or Low-Ash treatments,



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indicates that soil pH decreased slightly at this depth rather than increased after two years of ash application. Despite the fact that CFB ash was applied in both 1998 and 1999 in the High-Ash treatment, the Limestone treatment alone (applied in 1998) had a significant effect on <sup>a</sup> Soil pH at the lower depth. In other words, it appears that after two years, a single season's application of limestone was more effective than two season's applications of CFB ash in terms of penetrating the soil and effectively increasing soil pH at the lower sampling depth (7.5-15 cm). It is possible that this effect can be attributed to the greater solubility of limestone compared to ash (Table 3.5)

At the third sampling depth (0-15 cm), the Low-Ash treatment was not significantly different from either the Control or the Limestone treatment. These latter two treatments were, however, significantly different from each other (Table 4.3). As in the first sampling depth, soil pH in the combined depth was significantly greater in the High-Ash treatment compared to the other three treatments. Correspondingly, the High-Ash treatment had the greatest <sup>a</sup> Soil pH of any treatment for the third sampling depth. Obviously, the greater effect of the High-Ash treatment compared with other treatments in the combined depth (0-15 cm), can be attributed to the significant impact on surface (0-7.5 cm) soil pH of a current season application of CFB ash.

### 4.1.2 Soil Calcium and Magnesium

CFB ash treatments had a great impact on soil Ca levels but little effect on soil Mg. In 1997, the two higher CFB ash treatments (Split Ash and High Ash) resulted in a 3-5 times greater increase in fall soil Ca over pre-amendment levels (<sup>a</sup> Ca) than the equivalent loading of Mosher limestone, and a 30-50 fold increase over <sup>a</sup> Ca in the Control treatment (Table 4.4).

Soil Mg was increased over pre-amendment levels only by the Limestone treatment (Table 4.4). The existence of an antagonistic relationship between Ca and Mg in the soil means that the ratio of these nutrients can have as much or greater effect on availability to plants as their individual soil concentrations. High levels of soil Ca relative to Mg, or specifically, a soil Ca:Mg ratio greater than 5-7:1, can result in plant deficiencies of Mg. The substantial increases in soil Ca in the ash treatments, with no corresponding increase in Mg, resulted in soil Ca:Mg ratios well above the recommended ratio of 5-7:1 in these treatments (Table 4.4).

The effect of liming treatments on soil Ca and Mg may be explained by differences in the amount and kind of Ca and Mg compounds present in the two liming materials. While CFB residues contain large amounts of Ca (24-46%), they are generally Mg depleted (0.3-1% Mg). In contrast, dolomitic limestones contain similar or lower amounts of Ca (21-27%) but significantly more Mg (8-11%) (Brady and Weil 1999). In addition to a generally higher Ca content, the Ca in CFB residues appears to be much more soluble than the Ca in carbonate limestones. This is due to the highly soluble (95%) CaSO<sub>4</sub>, or gypsum, which makes up a significant portion (20-50%) of the residue (Jacques Whitford and Assoc. 1997).

Another useful soil test parameter in evaluating soil cation balances is percent base saturation, or the percentage of the total exchange capacity saturated with exchangeable cations other than

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hydrogen and aluminum. Soil base saturation of Ca should be in the range of 50-60%, and Mg between 10-15% Mg (A&L 1992). Liming beyond 75% Ca+Mg, however, is generally not recommended. While plants are unlikely to show visual Mg deficiency symptoms until soil Mg falls below 5%, the risk of mineral imbalances in forages<sup>28</sup> may occur on soils with <10% Mg (McLean and Brown 1984). The last column in Table 4.4 (fCa/Mg bsat%), showing the final (October 1999) base saturation of the soil with Ca and Mg, indicates that while Ca base saturation was slightly below optimum in the limestone treatments, Mg base saturation was at the high end of the optimum range. In the ash treatments, however, Ca base saturation was generally above optimum and Mg base saturation was critically below optimum.

Liming soils generally ensures an adequate supply of calcium however, depending on the liming material, may not provide sufficient magnesium. The fact that repeated use of calcitic lime, CaO and other low-Mg liming materials such as CFB residues, can result in sub-optimal levels of soil Mg, as well as reduce Mg uptake by crops, is well documented (Korcak 1988; Schumann and Summer 1999; McLean and Brown 1984; Keefer 1993). Concerns with low soil Mg have led agronomists to recommend dolomitic lime when acid soils are low in Mg, or whenever soil Mg is below 10%. In Indiana, where sandy, low capacity soils are susceptible to Mg deficiencies, dolomitic lime is recommended for every third limestone application as a general practice (McLean and Brown, 1984). Because of the likelihood of a similar effect on Ca/Mg distribution in the profile as is noted with gypsum, precautions as are noted with the use of gypsum as a fertilizer material should also apply to use of CFB residues; that is, levels of Mg and other soil nutrients should be monitored closely following application of CFB residues, particularly on sandy soils of low CEC.

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<sup>28</sup>Risks posed to ruminant animals by low Mg in forage is discussed in section 2.25.

**Final Research Report****Table 4.4 Change in soil Ca and Mg, ratio of soil Ca:Mg, in cabbage, rutabaga and forage plots and final soil Ca/Mg base saturation \*.**

Treatment	1997			1998			1999			fCa/Mg bsat %
	<sup>a</sup> Ca**	<sup>a</sup> Mg**	Ca:Mg	<sup>a</sup> Ca	<sup>a</sup> Mg	Ca:Mg	<sup>a</sup> Ca	<sup>a</sup> Mg	Ca:Mg	
<b>Cabbage</b>										
Control	208	7	6	231	8	8	102	-17	10	4/0.8
Limestone	2014	727	3	2405	827	3	2694	776	3	44/21
Low-Ash	2969	12	59	2879	10	61	2188	-5	66	39/1
Split-Ash	9460	50	107	6385	7	148	5636	-2	160	74/0.8
High-Ash	7169	30	102	5891	24	99	5558	26	75	60/1
<b>Rutabaga</b>										
Control	217	3	6	238	-4	8	258	-16	10	9/2
Limestone	2271	844	3	2492	882	3	2602	825	3	42/23
Low-Ash	3268	20	40	3985	4	56	3482	-3	55	55/4
Split-Ash	9721	61	75	7417	13	90	7594	1	108	81/1
High-Ash	7935	29	76	8177	20	87	8731	4	113	82/1
<b>Forage</b>										
Control	117	-20	6	395	-17	10	185	-28	7	13/3
Limestone	3120	900	4	2102	608	4	2251	531	4	44/18
Low-Ash	8404	66	52	7289	0	72	11417	15	92	84/2
Split-Ash	9562	234	34	9562	283	30	23265	107	112	93/2
High-Ash	9562	129	44	9562	188	35	25030	86	130	93/2

\* Values (kg/ha) are averages of four replicates. Soil Ca and Mg were measured at the end of each growing season (following harvest and the application of fall amendments).

\*\* <sup>a</sup>Ca or Mg = (fall or end of growing season levels) - (initial levels (June '97, pre-amendment))

**4.2 Crop Growth**

In each year cabbage were established as transplants and rutabaga were established by direct seeding. The forage, a perennial crop, was established in 1997 by direct seeding. The weather conditions (precipitation) were quite variable among the years. In 1997 cabbage transplanting, and both forage and rutabaga seeding were compromised by severe drought conditions. Irrigation to supply the minimal water needed to sustain plant growth had to be applied. Though germination was variable at the start of the season, and growth and development was somewhat delayed, above normal precipitation in August allowed for a more normal crop growth and development for the remainder of the season. In 1998 precipitation for the first 3 months of the growing season was above normal resulting in some flooding in the low lying areas and a

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prolonged saturation of the fields. This resulted in some variation and reduction in rutabaga germination, and the mortality of some cabbage plants. There was excellent winter survival in the forage, but the wet weather delayed the first forage harvest. After the first cut conditions were not conducive for optimum drying, and the harvest was lost as far as providing meaningful data. In 1999 conditions were extremely dry at the start of the season, but during the transplant/seeding there was an adequate level of precipitation for plant establishment and growth. Winter survival and re-growth in the forage was excellent, and the dry conditions did not adversely affect either the timing or the yield of the first cut.

### 4.2.1 Vegetables

In each year, germination trials were established in the rutabaga plots. The seedling represents a highly sensitive stage in plant growth and any potential phytotoxic effects would be detected more easily at this growth stage than at later growth stages. There were no detectable differences in germination among the soil amendment treatments, indicating that there were no phytotoxic effects of the ash on seedling development. In 1998, a germination trial was established in the High-Ash treatment cabbage plot. No adverse effects were observed on rutabaga germination and early seedling growth, indicating that even at excess levels of application there are no phytotoxic effects on seedling establishment.

A number of common insect pests of cole crops were observed on cabbage and rutabaga. With the exception in 1997 of an initial outbreak of cutworm in the cabbage, and later in August, imported cabbage worm and diamondback moth, feeding damage was minimal in all years. The population density of these and other insect pests were monitored closely, and controls were applied before significant damage occurred. The insecticidal soil drench applied to both cabbage and rutabaga after planting was effective in controlling cutworms and preventing feeding damage from cabbage root maggot. Apart from a small number of flea beetles (*Phyllotreta* spp.) observed feeding on the rutabaga, insect pest pressure was generally insignificant in the rutabaga.

Clubroot infestation was observed throughout the rutabaga plot in 1997. There was some concern that the degree of infestation would be higher in 1998, especially with the wet conditions early in the season. Observations at harvest in 1998 were that, while there was clubroot throughout the rutabaga plot, the intensity of infections was below that of 1997. There was a similar concern for 1999, but clubroot infestation was at an extremely low level or not detectable throughout all the plots. In all years, there were no incidences of clubroot infection observed in the cabbage plants.

#### 4.2.1.1 Cabbage

A significant interaction (treatment x year) was detected for percent marketable weight, marketable head number, marketable head number percent, cull weight, cull head number, cull head number percent, and total head number. A significant year main effect was detected for marketable weight, average marketable head weight, total weight, average total head weight, and

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percent dry weight. A significant treatment main effect was detected for marketable weight, average marketable head weight, total weight, average total head weight, and percent dry weight.

The marketable weight, average marketable weight, total weight, and average total head weight were significantly increased by the soil amendment treatments compared to the control (Table 4.5). The percent dry weight was significantly reduced by the soil amendment treatments compared to the control. For all the above variables, there were no significant differences detected among soil amendment treatments, indicating that plant growth and development is not different in soils amended with ash compared to soils amended with limestone.

The marketable weight, average marketable weight, total weight, and total average weight were significantly higher in 1997 compared to 1998 and 1999 (Table 4.6). The response in 1998 was significantly lower compared to that in 1999. The percent dry weight was significantly higher in 1997 compared to 1998 and 1999; and was significantly higher in 1998 compared to 1999. Plant growth response was different among years, but for the variables indicated above, the treatment and year effects were independent of each other.

**Table 4.5 Effect of treatment on cabbage yield parameters.**

Variable	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
<u>Marketable</u>					
Weight (kg)	7.62a*	52.81b	49.35b	56.09b	59.62b
Average head weight (kg)	0.53a	1.23b	1.20b	1.29b	1.27b
<u>Total</u>					
Weight (kg)	13.07a	56.78b	53.34b	58.58b	61.76b
Average head weight (kg)	0.27a	1.13b	1.05b	1.56b	1.19b
Dry weight (%)	10.84b	8.79a	9.46a	9.42a	9.15a

\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

**Final Research Report****Table 4.6 Effect of year on cabbage yield parameters.**

Variable	Year		
	1997	1998	1999
<u>Marketable</u>			
Weight (kg)	64.51c*	24.47a	46.31b
Average head weight (kg)	1.47c	0.79a	1.05b
<u>Total</u>			
Weight (kg)	69.77c	28.01a	48.33b
Average head weight (kg)	1.36c	0.61a	0.91b
Dry weight (%)	11.25c	9.05b	8.31a

\* Values in each row followed by the same letter are not significantly different according to least significant tests (p<0.05).

A significant interaction was detected for percent marketable weight, marketable head number, percent marketable head number, cull weight, cull head number, percent cull head number, and total head number.

The percent marketable weight, marketable head number, and percent marketable head number were significantly increased by the soil amendment treatments compared to the Control for all years (Table 4.7a). No significant differences were detected among the soil amendment treatments for 1997 and 1999 in all variables. Significant differences were detected among variables for 1998, resulting in the significant treatment year interaction. The percent marketable weight was significantly reduced in the 1998 Low-Ash treatment compared to the other soil amendment treatments. The marketable head number was significantly higher in the 1998 High-Ash treatment compared to the Limestone and Low-Ash treatments, but not significantly different than the Split-Ash treatment. There were no significant differences detected among the Limestone, Low-Ash and Split-Ash treatments. A similar response was observed for percent marketable head number.

**Final Research Report****Table 4.7a Effect of treatment and year on cabbage yield parameters.**

Variable	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
<u>Marketable</u>					
Weight (%)					
1997	54.54a/x*	93.54b/zy	94.31b/y	94.01b/z	96.94b/z
1998	23.64a/z	85.79c/z	76.65b/z	87.31c/z	93.64c/z
1999	41.44a/y	95.82b/y	95.85b/y	98.81b/z	97.42b/z
Head number					
1997	24.25a/y	49.25b/y	43.75b/y	41.75b/zy	48.50b/z
1998	1.50a/z	32.75bc/z	26.75b/z	33.75bc/z	42.00c/z
1999	4.25a/z	42.25b/y	46.25b/y	49.50b/y	48.25b/z
Head number (%)					
1997	46.32a/y	92.72b/y	87.21b/y	84.04b/zy	97.90b/z
1998	4.89a/z	74.11c/z	56.37b /z	72.00c/z	84.45c/z
1999	8.61a/z	81.90b/zy	86.51b/y	91.98b/y	89.69b/z

\* Values in each row followed by the same letter (a,b,c...) are not significantly different according to least significant tests ( $p < 0.05$ ); values in each column followed by the same letter (z,y,x...) are not significantly different according to least significant tests ( $p < 0.05$ ).

Similarly for cull weight, cull head number, percent cull head number, and total head number the treatment year interaction can be attributed to the response observed in 1998 (Table 4.7b). The cull weight was significantly higher in the 1997 Control treatment compared to soil amendment treatments; the cull weight was significantly higher for the 1998 Low-Ash treatment compared to the Control treatment, but not significantly different from the other soil amendment treatments. The remaining soil amendment treatments were not detected to be different from the Control treatment. There were no significant differences detected among the treatments for 1999. The cull head number was significantly reduced in the soil amendment treatments compared to the Control for 1997 and 1999. There were no significant differences detected among the soil amendment treatments. Similarly in 1998, the cull head number was significantly reduced in the soil amendment treatments compared to the Control. Additionally the cull head number was significantly reduced in the Limestone, Split-Ash and High-Ash treatments compared to the Low-Ash treatment. Similar variation existed in the percent cull head number. There were no significant differences detected in total head number among the treatments for 1998 and 1999. The total head number was significantly reduced by the Control treatment compared to the soil amendment treatments in 1998. There were no significant differences detected among the soil amendment treatments.

The field was monitored during the first two weeks of the season for missed transplants and for weak/diseased plants, and those plants were replaced with more vigorous transplants. This was

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done to eliminate variation due to transplant failure and/or an unequal number of plants in each treatment. The 1998 significant reduction in the Control treatment does indicated that in that year, a significant number of plants did not survive to maturity in the Control plot.

**Table 4.7b Effect of treatment and year on cabbage yield parameters.**

Variable	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
<u>Cull</u>					
Weight (kg)					
1997	11.01b/y*	5.35a/y	4.23a/zy	3.35a/z	2.35a/z
1998	1.95a/z	4.39ab/zy	5.44b/y	3.38ab/z	2.57ab/z
1999	3.41a/z	2.19a/z	2.30a/z	0.72a/z	1.52a/z
Head number					
1997	33.46b/z	2.67a/z	5.71a/z	8.00a/zy	2.67a/z
1998	29.25c/z	10.75a/z	19.75b/y	11.75a/y	7.75a/z
1999	46.25b/y	9.50a/z	7.25a/z	4.50a/z	5.50a/z
Head number (%)					
1997	67.34b/z	5.26a/z	10.98a/z	15.95a/z	5.84a/z
1998	95.11d/y	25.89ab/y	43.63c/y	28.00b/y	15.55a/z
1999	91.39b/y	18.10a/zy	13.49a/z	8.01a/z	10.31a/z
<u>Total</u>					
Head number					
1997	51.25a/y	53.00a/y	50.25a/zy	49.75a/zy	51.25a/z
1998	30.75a/z	43.50b/z	46.50b/z	45.50b/z	49.75b/z
1999	50.50a/y	51.75a/y	53.50a/y	54.00a/y	53.75a/z

\* Values in each row followed by the same letter (a,b,c...) are not significantly different according to least significant tests ( $p < 0.05$ ); values in each column followed by the same letter (z,y,x...) are not significantly different according to least significant tests ( $p < 0.05$ ).

The data for cabbage were re-analysed for 1998 and 1999 with the Double-Ash treatment added to the data set. A significant interaction (treatment x year) was detected for percent marketable weight, cull weight, and for percent cull head number. A significant treatment main effect was detected for marketable weight, average marketable head weight, marketable head number, percent marketable head number, cull head number, total weight, average total head weight, total head number, and percent dry weight.

The marketable weight and average marketable head weight were both increased by the soil amendment treatments compared to the Control treatment (Table 4.8). The weights were increased by the Double-Ash treatment compared to all other soil amendment treatments; there



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were no significant differences detected among the other soil amendment treatments. The marketable head number and percent marketable head number were significantly increased by the soil amendment treatments compared to the Control treatment. The marketable head number was significantly higher for the Split-Ash, High-Ash and Double-Ash treatments compared to the Limestone and Low-Ash treatments; there were no significant differences detected within the treatment groupings. The marketable percent head number was significantly higher for the High-Ash and Double-Ash treatments compared to the Limestone and Low-Ash treatments; there were no significant differences detected within the treatment groups. The marketable percent head number for the Split-Ash treatment was not significantly different when compared the Limestone, Low-Ash, and High-Ash treatments; the number was reduced by the Split-Ash treatment compared to the Double-Ash treatment. The response for total weight and average total head weight was similar to that of the marketable weight and the average marketable head weight. The total head number was increased by the soil amendment treatments compared to the Control treatment. There were no significant differences detected among the soil amendment treatments in total head number. The percent dry weight was significantly decreased by the soil amendment treatments compared to the Control treatment; there were no significant differences detected among soil amendment treatments.

The 1998 percent marketable weight was increased by the soil amendment treatments compared to the Control treatment (Table 4.9). Within the soil amendment treatments the Low-Ash treatment was reduced compared to the other treatments. The Limestone treatment was significantly reduced compared to the High-Ash and Double-Ash treatments; the Split-Ash treatment was significantly reduced compared to the Double-Ash treatment; there was no significant difference detected between the High-Ash and Double-Ash treatments. The 1999 percent marketable weight was significantly increased for the soil amendment treatments compared to the Control treatment. There were no significant differences detected among the soil amendment treatments. The effect of cull weight was variable for both years. The 1998 cull weight was significantly reduced by the Double-Ash treatment compared to all other treatments; the 1999 cull weight was significantly reduced by the Double-Ash treatment compared to the Control, Limestone and Low-Ash treatments; there were no significant differences detected among the Split-Ash, High-Ash, and Double-Ash treatments. The addition of the Double-Ash treatment did not alter the relationship between soil amendment treatments and the Control treatment.

The high loading rate of ash, as indicated by the Double-Ash treatment, did not have a negative effect on plant growth and development. The opposite effect was observed. The number of heads in the soil amendment treatment plots were not significantly different from each other, but the total and marketable weights were significantly increased by the Double-Ash treatment compared to all other soil amendment treatments. Though there was an overall increase in yield, the level of ash applied for this treatment was in excess of any amount that would be applied for normal agricultural production. The objective was to determine if phytotoxic effects could be induced at a high (excess) rate of ash application. The application rate at which phytotoxic effects are induced was not achieved.

**Final Research Report****Table 4.8 Effect of treatment on cabbage yield parameters, with Double-Ash treatment.**

Variable	Treatment					
	Control	Limestone	Low-Ash	Split-Ash	High-Ash	Double-Ash
<u>Marketable</u>						
Weight (kg)	3.83a*	39.38b	37.72b	49.52b	48.85b	71.77c
Average head weight (kg)	0.43a	1.04b	0.97b	1.13b	1.07b	1.47c
Head number	3.96a	37.50b	36.50b	41.62bc	45.12c	48.12c
Head number (%)	8.71a	78.00b	71.44b	81.99bc	87.07cd	97.80d
<u>Cull</u>						
Head number (%)	91.28d	22.00bc	28.56c	18.01b	12.93ab	2.20a
<u>Total</u>						
Weight (kg)	6.50a	42.67b	41.59b	51.57b	50.90b	72.15c
Average head weight (kg)	0.15a	0.89b	0.81b	1.01b	0.98b	1.46c
Head number	38.75a	47.62b	50.00b	49.75b	51.75b	49.42b
Dry weight (%)	10.30b	7.86a	8.36a	8.50a	8.31a	8.52a

\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

**Final Research Report****Table 4.9 Effect of treatment and year on cabbage yield parameters, with Double-Ash treatment.**

Variable	Treatment					
	Control	Limestone	Low-Ash	Split-Ash	High-Ash	Double-Ash
<u>Marketable</u>						
Weight (%)						
1998	24.22a/z	85.79c/z	76.65b/z	87.31cd/z	93.64de/z	98.37e/z
1999	42.02a/y	95.81b/y	95.85b/y	98.81b/y	97.42b/z	99.56b/z
<u>Cull</u>						
Weight (kg)						
1998	2.38b/z	4.39cd/y	5.44d/y	3.38bc/y	2.57b/z	0.39a/z
1999	2.95c/z	2.19bc/z	2.30bc/z	0.72a/z	1.52abc/z	0.36a/z
Head number (%)						
1998	25.57b/z	10.75a/z	19.75b/y	11.75a/y	7.75a/z	1.57a/z
1999	44.01c/y	9.50b/z	7.25ab/z	4.50ab/z	5.50ab/z	1.01a/z

\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

**Final Research Report****4.2.1.2 Rutabaga**

A significant interaction (treatment x year) was detected for marketable root number, cull weight, and total weight. A significant year main effect was detected for percent marketable weight, cull root number, total root number, and percent dry weight. A significant treatment main effect was detected for marketable weight, percent marketable weight, percent marketable root number, percent cull root number, total root number, boron, and percent dry weight.

The marketable weight was significantly increased by the soil amendment treatments compared to the Control treatment (Table 4.10). There were no significant differences detected among soil amendment treatments. A similar response was observed for percent marketable root number and total root number.

**Table 4.10 Effect of treatment on rutabaga yield parameters.**

Variable	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
<u>Marketable</u>					
Weight (kg)	3.43a*	16.74b	18.45b	17.39b	18.56b
Weight (%)	28.97a	38.32ab	44.30b	44.33b	49.06b
Root number (%)	14.44a	35.37b	40.95b	41.88b	41.06b
<u>Cull</u>					
Root number (%)	85.45b	64.62a	59.05a	58.12a	58.94a
<u>Total</u>					
Root number	60.00a	106.67b	109.08b	108.17b	121.50b
Boron**	2.37b	2.42b	1.04a	0.29a	0.58a
Dry weight (%)	9.94b	7.64a	10.23b	10.66b	10.67b

\* Values in each row followed by the same letter are not significantly different according to least significant tests (p<0.05).

\*\* Boron deficiency scale: 0-none; 1-low; 2-moderate; 3-severe.

The percent marketable weight was significantly increased by the ash treatments compared to the Control treatment. The Limestone treatment was not detected to be significantly different from the Control nor from the ash treatments. The percent cull root number was significantly reduced by the soil amendment treatments compared to the Control treatment. There were no significant differences detected among the soil amendment treatments. The boron deficiency rating was significantly reduced by the ash treatment compared to the Control and Limestone treatments; there were no significant differences detected within the two treatment groups. The lower boron

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deficiency rating indicates less evidence of boron deficiency observed in the roots. It is standard to recommend the application of 2 or 3 foliar boron applications to rutabaga during the growing season in the Atlantic regions; there were no B applications to the rutabaga crop to allow for a comparison of the effect of fly-ash on crop response to this element. The ash did reduce the severity of B deficiency, but did not supply B in sufficient quantity for crop growth. Foliar application of B is required to prevent deficiency symptoms when using ash as a soil amendment. The percent dry weight was significantly reduced by the Limestone treatment compared to all other treatments, there were no significant differences detected among the other treatments.

The percent marketable weight, cull root number, and total root number were higher in 1999 compared to 1997 and 1998 (Table 4.11). There were no significant differences observed between 1997 and 1998. The percent dry weight was significantly difference among all three years, with the highest value occurring in 1997 and the lowest in 1998.

**Table 4.11 Effect of year on rutabaga yield parameters.**

Variable	Year		
	1997	1998	1999
<u>Marketable</u>			
Weight (%)	30.32a*	31.53a	64.14b
<u>Cull</u>			
Root number	47.30a	52.50a	86.55b
<u>Total</u>			
Root number	71.55a	89.90a	141.80b
Dry weight (%)	12.02c	8.08a	9.38b

\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

The marketable root number was significantly increase by the soil amendment treatments compared to the Control treatment in 1997 and 1999 (Table 4.12); there were no significant differences detected among the soil amendment treatments. In 1998, marketable root number was significantly increase by the Split-Ash and High-Ash treatments compared to the Control and Limestone treatments. There were no significant differences detected among the Control, Limestone and Low-Ash treatments, between the Low-Ash and Split-Ash treatments, and between the Split-Ash and High-Ash treatments. In 1997 and 1998 the cull weight was significantly increased by the soil amendment treatments compared to the Control, with some variation within the soil amendment treatments in both years. In 1999 there were no differences

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detected among the treatments. The total weight was significantly increased by the soil amendment treatments compared to the Control treatment in all years. There was significant variation among the soil amendment treatments for 1997 and 1998; there were no significant differences detected among soil amendment treatments for 1999.

Growth and development of rutabaga was significantly increased by the soil amendment treatments. Except for B deficiency symptoms there was little variation among the soil amendment treatments. Seasonal variations were observed.

As observational data only, corky periderm was found to be present in the Limestone treatment only. This contributed to the cull portion for this treatment, but as indicated by the percent cull root number, it does not appear to have significantly altered the cull relationship.

**Table 4.12 The effect of treatment and year on rutabaga yield parameters.**

Variable	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
<u>Marketable</u>					
Root number					
1997	3.75a/z*	28.25b/z	30.00b/z	30.50b/z	28.75b/z
1998	13.75a/z	22.00a/z	37.00ab/z	50.50bc/zy	63.75c/y
1999	14.00a/z	72.75b/y	74.75b/y	55.75b/y	59.00b/y
<u>Cull</u>					
Weight (kg)					
1997	2.76a/z	35.62c/y	28.39bc/y	22.30b/y	26.22b/y
1998	6.94a/z	53.08c/x	29.30b/y	29.64b/y	29.14b/y
1999	5.39a/z	9.04a/z	8.36a/z	7.10a/z	7.91a/z
<u>Total</u>					
Weight (kg)					
1997	5.35a/z	48.91c/y	41.47bc/zy	36.64b/z	39.02bc/y
1998	11.07a/z	64.83c/x	47.38b/y	51.75b/y	55.72bc/x
1999	8.96a/z	34.59b/z	32.57b/z	23.84b/z	24.21b/z

\* Values in each row followed by the same letter (a,b,c...) are not significantly different according to least significant tests ( $p < 0.05$ ); values in each column followed by the same letter (z,y,x...) are not significantly different according to least significant tests ( $p < 0.05$ ).

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### 4.2.3 Forage

The highest forage yields (total yield) were obtained in the Low-Ash, Limestone, and Split-Ash treatments (Table 4.13). Total yields in the High-Ash treatment were lower but not significantly different from the Limestone or Split-Ash treatments. Forage yields in the soil amendment treatments were typical of or slightly above those obtained for mixed forages on Nova Scotia farms (7.5-8 t/ha). Yields in the non-limed Controls were reduced by more than 50%, indicating the importance of maintaining correct soil pH in forage production. First cut yield typically accounts for 60-70% of the total forage yield. Despite the dry conditions that prevailed during May and June, first-cut yields still accounted for an average of 65% of the total yield.

**Table 4.13 The effect of treatment on the yield of forage**

Yield Component*	Treatments				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
First Cut	2.42a**	5.24bc	6.14c	4.48b	4.25b
Second Cut	0.78a	3.04bc	2.40b	3.68c	2.72bc
Total Yield	3.20a	8.28bc	8.54c	8.16bc	6.97b

\* Yield - t/ha.

\*\* Values in each row followed by the same letter are not significantly different according to least significant difference tests ( $p < 0.05$ ).

### 4.3 Nutrient Content of Plant Tissue

As some of the trace metals are also essential plant nutrients, certain elements (namely B, Fe, Mn, Cu, and Zn) are discussed in both this and the following sections. It should be noted that the laboratory procedures used in the two analyses (standard analysis for plant nutrients and trace metals in plant tissues) differ significantly and therefore a valid comparison cannot be made between the two data sets. Generally the term content is used when referring to nutrients and level when discussing metals. Of the 16 elements that are considerable essential for plant growth, the tissue analysis examined 11 (N, P, K, Ca, Mg, B, Fe, Mn, Cu, Zn, and S). Of the remaining 5, C, H, O were not considered as they are provided to the plants via water and air; Cl was not considered as it is ubiquitous and is never deficient or in excess.

Plant tissue analysis is commonly used as a tool to evaluate a soil fertility program, and therefore for that purpose should occur early in the production cycle to allow for adjustments or additions to fertility management (Walsh & Beaton 1973). An actively growing plant part is selected (e.g. the youngest fully mature leaf or the petiole of such a leaf) to obtain data that can be later be correlated with production. The results are influenced by cultivar, environment, soil type, plant part, maturity, etc.; this can make direct comparisons difficult. In this study mature plant material was used and there is little data published on the nutrient levels of mature tissue, so the comparison among treatments is considered to be more important than absolute levels.

**Final Research Report****4.3.1 Cabbage**

A significant interaction (treatment x year) was detected for Ca and Fe. A significant year main effect was detected for B, K, Mg, N, P, S, and Zn. A significant treatment main effect was detected for B, Mg, Mn, N, and Zn. No significant effects were detected for Cu.

The tissue boron content was significantly increased by the ash treatments compared to the Control and Limestone treatments (Table 4.14). The tissue boron content was significantly reduced by the Limestone treatment compared to the Control treatment. Mg content was decreased by the ash treatment compared to the Control treatment; there were no significant differences detected among the ash treatments. Mg content was increased by the Limestone treatment compared to the Control treatment. Mn, N and Zn content were decreased by the soil amendment treatments compared to the Control treatment; there were no significant differences detected among the soil amendment treatments. Geraldson et al. (1977, in Walsh and Beaton 1977) reported the Mg content of a mature head of cabbage to be 0.14 - 0.20% and 25 - 50 ppm for Mn. The Mg was found to be below this range in the ash treatments, but within this range for the Control and Limestone treatments. Atlantic soils are low in Mg, and traditionally dolomitic limestone has been the source for this element. This result is indicating that additional Mg may be required when using ash as a soil amendment. The Mn content was within an acceptable range for all soil amendment treatments, and the Control treatment was found to be within the broader sufficiency range (25 -200 ppm) reported by Mills and Jones (1996) in mature cabbage wrapper leaves. Atlantic soils are low in B, but this element was not added as a nutrient for this crop. Mills and Jones (1996) have reported a sufficiency range of 30 -100 ppm for B content in mature cabbage wrapper leaves, and Warncke et al. (1994) have reported 40 ppm as an optimum content for cabbage. The B content was well below the range and the suggested target for cabbage, indicating that the crop did experience a B deficiency, though there were not visible signs expressed for this deficiency. The recommended practice of foliar B applications would apply with the use of ash as a soil amendment. Cabbage rarely exhibit Zn deficiency and a Zn content of 20 ppm (Warncke et al. 1994) is adequate for cabbage growth. Plant tissue levels were found within or close to this range.

There is no data for the N content in cabbage tissue located in the interior of the head. The N content would be very different between the interior tissue and the outer wrapper leaves, which are also the actively photosynthesizing area. Based on visual appearance during the growing season, and high yields, there was no evidence that N levels were deficient during the growing season.



**Final Research Report****Table 4.14 The effect of treatment on the nutrient status of cabbage.**

Element	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
B ppm	14.00b*	10.67a	18.69c	20.14c	18.00c
Mg %	0.16b	0.19c	0.12a	0.12a	0.12a
Mn ppm	80.06b	31.90a	42.75a	42.51a	43.80a
N %	3.20b	2.92a	2.77a	2.82a	2.84a
Zn ppm	33.50b	16.48a	20.63a	21.72a	19.09a

\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

The tissue content for B, K, N, P, S, and Zn was significantly lower in 1997 compared to 1998 and 1999; Mg content was significantly lower in 1997 and 1999 compared to 1998 (Table 4.15). The tissue content for B, N, P, and Zn was significantly higher for 1998 compared to 1997 and 1999. The tissue content for K and S was significantly higher for 1999 compared to 1997 and 1998. Geraldson et al. (1973, in Walsh and Beaton 1977) reported the K content in a mature cabbage head to be 30 - 40%. Mills and Jones (1996) reported a range of 2 - 4% for K content in mature wrapper cabbage leaves, 0.30 - 0.65% for P content, and 0.30 - 0.75% for S content. The K and P content in the cabbage tissue is within the ranges reported these nutrients. The S content was found to be at the upper end of the range indicating the ash to be a good S source. The findings were also consistent with literature in that the nutrient content of plant tissue was affected by the environmental conditions during growth, as indicated by the significant year main effect or the significant interaction.

**Table 4.15 The effect of year on the nutrient status of cabbage.**

Element	Year		
	1997	1998	1999
B ppm	11.48a*	21.53c	16.40b
K %	2.27a	2.81b	3.01c
Mg %	0.13a	0.16b	0.14a
N %	2.22a	3.52c	2.98b
P %	0.23a	0.35c	0.27b
S %	0.47a	0.72b	0.85c
Zn ppm	18.18a	27.22c	21.46b

\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

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The significant interaction indicated that the effect of the treatments was directly influenced by the environmental conditions during the growth period. The significant interaction indicated that the effect of the treatments was directly influenced by the environmental conditions during the growth period. The Ca tissue content was significantly increased by the ash treatment compared to the Control and Limestone treatments in 1997 and 1999; there were no significant differences detected within the groups (Table 4.16). There were no significant differences detected among the treatments in 1998. The Fe content was quite variable among years. The Fe content was significantly increased by the Split-Ash treatment compared to Control in 1997; no other treatment was detected to be significantly different from the Control in 1997. There were no significant differences detected among treatments in 1998. The Fe content was significantly increased by the Low-Ash treatment compared to all other treatments in 1999; there were no significant differences detected among the other treatments. Geraldson et al. (1977, in Walsh and Beaton 1977) reported Ca content in a mature cabbage head to be 0.4 - 0.6%, and the Fe content to be 40 - 50 ppm. For all treatments, the Ca content was below this range in 1997; all were within this range in 1998; and in 1999 all were within range except for the Limestone treatment which was below range. The results indicate that over time Ca became more available for plant uptake and that the ash was a better source of Ca compared to the limestone.

The Fe content was within the recommended range for all treatments in all years except in the Control and Limestone treatments in 1997.

**Table 4.16 The effect of treatment and year on the nutrient status of cabbage.**

Element	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
Ca %					
1997	0.19a/z*	0.20a/z	0.35b/z	0.38b/z	0.37b/z
1998	0.44a/y	0.42a/y	0.45a/zy	0.46a/z	0.42a/z
1999	0.40a/y	0.33a/y	0.55b/y	0.58b/y	0.59b/y
Fe ppm					
1997	38.64ab/z	28.37a/z	57.03bc/z	60.94c/z	45.93ab/z
1998	70.67a/y	62.04a/y	61.69a/z	54.43a/z	59.53a/z
1999	66.02a/y	45.56a/zy	95.77b/y	56.08a/z	49.03a/z

\* Values in each row followed by the same letter (a,b,c...) are not significantly different according to least significant tests ( $p < 0.05$ ); values in each column followed by the same letter (z,y,x...) are not significantly different according to least significant tests ( $p < 0.05$ ).

The relationship between the ash treatments and the Control and Limestone treatments was not significantly altered with the addition of the Double-Ash treatment (Table 4.17). The relationship of the Ca content between the ash treatments and the Control and Limestone treatments was similar, the difference being the interaction with year was not detected to be

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significant. The relationship between the soil amendment treatments and the Control remain unchanged with the addition of the Double-Ash treatment. There was a more variable response detected for N content with less separation out of the treatment effects.

**Table 4.17 The effect of treatment on the nutrient status of cabbage, with Double-Ash treatment.**

Element	Treatment					
	Control	Limestone	Low-Ash	Split-Ash	High-Ash	Double-Ash
B ppm	16.72a*	13.55a	21.00b	22.78b	20.76b	21.59b
Ca %	0.42ab	0.38a	0.50c	0.52c	0.50c	0.49bc
Mg %	0.17b	0.20b	0.13a	0.12a	0.14a	0.11a
Mn ppm	78.59b	32.84a	43.26a	41.69a	46.88a	31.90a
N %	3.43c	3.37bc	3.08ab	3.19bc	3.20bc	2.69a
Zn ppm	37.09b	18.14a	22.61a	22.43a	21.43a	24.67a

\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

There were no significant differences detected among treatments in Fe content for 1998 (Table 4.18). For 1999, there were no significant differences detected among the Split-Ash, High-Ash, and Double-Ash treatments, nor were there significant differences detected between those ash treatments and the Limestone treatment nor between those ash treatments and the Control treatment. The Fe content was significantly decreased by the Limestone treatment compared to the Control treatment. The Fe content was significantly increased by the Low-Ash treatment compared to all other treatments. There was a significant year main effect (data not shown) detected for N, P, Ca, Mg, B, Mn, Zn and S.

**Table 4.18 The effect of treatment and year on the nutrient status of cabbage, with Double-Ash treatment.**

Element	Treatment					
	Control	Limestone	Low-Ash	Split-Ash	High-Ash	Double-Ash
Fe ppm						
1998	70.67a/z*	62.04a/z	61.69a/z	54.43a/z	59.53a/z	54.24a/z
1999	66.02b/z	42.56a/z	95.77c/y	56.08ab/z	49.03ab/z	56.34ab/z

\* Values in each row followed by the same letter (a,b,c...) are not significantly different according to least significant tests ( $p < 0.05$ ); values in each column followed by the same letter (z,y,x...) are not significantly different according to least significant tests ( $p < 0.05$ )/kg, dry weight basis.

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### 4.3.2 Rutabaga

There is no published data available on the nutrient ranges in rutabaga root tissue. The data available for rutabaga leaf tissue cannot be used for comparison purposes with the root tissue. A significant interaction (treatment x year) was detected for Ca, Fe, Mg, N, P, and Zn tissue content. A significant year main effect was detected for B, K, and S tissue content; a significant treatment main effect was detected of B, K, Mn, and S tissue content.

The B tissue content was significantly increased by the ash treatments compared to the Control and Limestone treatments (Table 4.19). There were no significant differences detected among the ash treatments nor between the Control and Limestone treatments. The relationship between the ash treatments and the Control and Limestone treatments is similar to and consistent with the observations for the visible deficiency severity rating (Table 4.10). This corroborates that the ash does supply some B but not in sufficient quantity to meet the minimum requirement for rutabaga growth.

The K tissue content was significantly increased by the Limestone treatment compared to all other treatments. There were no significant differences detected among the remaining treatments. The Mn tissue content was significantly reduced by the ash treatments compared to the Control and Limestone treatments. The Mn tissue content was significantly reduced by the Limestone treatment compared to the Control treatment. The S tissue content was significantly increased by the Limestone and Split-Ash treatments compared to the Control. There were no significant differences detected among the soil amendment treatments, nor between the Low-Ash and High-Ash treatments and the Control treatment.

**Table 4.19 The effect of treatment on the nutrient status of rutabaga.**

Element	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
B ppm	12.95a*	11.37a	16.65b	16.35b	17.09b
K %	2.70a	3.58b	2.79a	2.65a	2.62a
Mn ppm	122.91c	48.74b	28.34a	25.06a	20.71a
S %	0.36a	0.46b	0.41ab	0.44b	0.42ab

\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

The B tissue content was significantly different among the three years, with the content in 1997 being the lowest and the content in 1998 being the highest (Table 4.20). The K tissue content was significantly lower in 1997 and 1999 compared to 1998; there was no significant difference detected between 1997 and 1999. The S content was significantly lower in 1997 and 1998 compared to 1999; there was no significant difference detected between 1997 and 1998.

**Final Research Report****Table 4.20 The effect of year on the nutrient status of rutabaga.**

Element	Year		
	1997	1998	1999
B ppm	10.37a*	20.83c	13.44b
K %	2.62a	3.42b	2.56a
S %	0.35a	0.37a	0.53b

\* Values in each row followed by the same letter are not significantly different according to least significant tests (p<0.05).

There were no significant differences detected among ash treatments within year for Ca tissue content (Table 4.21). In 1997, the ash treatments were not detected to be significantly different from the Control treatment. The Ca tissue content was significantly increased by the Limestone treatment compared to the ash treatments. In 1998 the Ca tissue content was significantly reduced by the ash treatments compared to the Control treatment, there was no significant difference detected between the two in 1999. The Ca tissue content was significantly increased by the Limestone treatment compared to Control in 1998 and 1999. The Fe tissue content response was variable among treatments for 1997 and 1999; there were no significant differences detected among treatments in 1999. The Mg tissue content was significantly reduced by the ash treatments and the Limestone treatment compared to the Control treatment in all years. The Mg tissue content was significantly reduced by the ash treatments compared to the Limestone treatment; there were no significant differences detected among the ash treatments. The response of N tissue content was variable among treatments and within years. The P tissue content was significantly reduced by the ash treatments compared to the Control treatment for 1998 and 1999, but there was no significant difference for 1997. The Zn tissue content response was somewhat variable, with the content for the Control treatment generally being significantly higher than for the ash treatments and the Limestone treatment.

**Final Research Report****Table 4.21 The effect of treatment and year on the nutrient status of rutabaga.**

Element	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
<b>Ca %</b>					
1997	0.20ab/z*	0.25b/z	0.19a/z	0.18a/z	0.18a/z
1998	0.32b/y	0.43c/y	0.25a/y	0.24a/y	0.25a/y
1999	0.28a/y	0.46b/y	0.26a/y	0.28a/y	0.27a/y
<b>Fe ppm</b>					
1997	57.80b/z	32.25a/z	61.63bc/z	71.39c/z	50.33ab/z
1998	83.50a/y	98.33ab/x	110.98bc/y	115.48bc/y	120.99c/x
1999	64.47a/zy	67.82a/y	63.86a/z	69.77a/z	79.50a/y
<b>Mg %</b>					
1997	0.13b/z	0.16c/z	0.07a/z	0.07a/z	0.06a/z
1998	0.12b/z	0.22c/y	0.08a/z	0.07a/z	0.07a/z
1998	0.13b/z	0.22c/y	0.09a/z	0.08a/z	0.08a/z
<b>N %</b>					
1997	1.82c/z	1.73bc/z	1.57bc/z	1.46ab/z	1.22a/z
1998	2.05b/zy	2.76c/y	1.97b/y	1.79ab/y	1.74a/y
1999	2.49b/y	2.53b/y	1.79a/zy	2.00a/y	1.75a/y
<b>P %</b>					
1997	0.35a/z	0.49b/z	0.40a/zy	0.39a/zy	0.36a/z
1998	0.51b/x	0.68b/x	0.46a/y	0.42a/y	0.43a/y
1999	0.44b/y	0.58c/y	0.37ab/z	0.35a/z	0.34a/z
<b>Zn ppm</b>					
1997	25.94b/z	17.25a/z	18.71a/zy	17.65a/z	14.98a/z
1998	26.07b/z	27.16b/y	22.99b/y	18.00a/z	19.14ab/z
1999	31.31c/y	24.91b/y	17.32a/z	16.20a/z	15.41a/z

\* Values in each row followed by the same letter (a,b,c...) are not significantly different according to least significant tests ( $p < 0.05$ ); values in each column followed by the same letter (z,y,x...) are not significantly different according to least significant tests ( $p < 0.05$ ).

**4.3.3 Forage**

Forage quality is indicated by crude protein (%CP), digestible energy (% ADF and % TDN) and nutrient content of the forage. Because ADF constituents (see footnotes, Table 4.24) are relatively indigestible, ADF is a negative indicator of energy level of forages (i.e., as ADF increases, digestible energy decreases). ADF, CP and net energy are highly influenced by time of cutting (maturity) and species composition of the forage. For example, ADF and net energy

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are higher in early compared to late cut forages, and higher in legumes compared with grasses at comparable stages of maturity. CP content in the forage also increases with the proportion of legume in the mix. Optimum values for forage quality parameters in a legume/grass hay are 18-20% CP, 25-30% ADF, and 65-70% TDN<sup>29</sup>.

A significant interaction (treatment x cutting date) was detected for ADF, TDN, D.E., P, and K. A significant cutting date main effect was detected for Crude Protein, Mg, Fe, Mn, Cu, and Zn; a significant treatment main effect was detected for Crude Protein, Ca, Mg, Mn, Cu, and Zn.

Crude Protein content was significantly increased by the soil amendment treatments compared to the Control; there were no significant differences detected among the soil amendment treatments (Table 4.22). Ca content was significantly increased by the soil amendment treatments compared to the Control treatment; the Ca content was significantly increased by the ash treatments compared to the Limestone treatment. The Mg content was significantly increase by the Limestone treatment compared to all other treatments; there were no significant differences detected among the other treatments. The Mn and Zn content was significantly decreased by the soil amendment treatments compared to the Control treatment; there were no significant differences detected among the soil amendment treatments. The Cu content was significantly increased by the ash treatments compared to the Control and Limestone treatments, there were no significant differences detected within the treatment groups.

**Table 4.22 The effect of treatment on the feed value of forage.**

Variable	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
Crude Protein* (%)	14.95a**	17.08b	17.29b	17.60b	16.93b
Ca (%)	0.27a	0.52b	0.79c	0.86c	0.84c
Mg (%)	0.15a	0.26b	0.11a	0.13a	0.11a
Mn (ppm)	241.68b	86.79a	98.50a	121.44a	96.49a
Cu (ppm)	4.68a	4.26a	5.94b	6.56b	6.17b
Zn (ppm)	32.01b	22.63a	21.08a	24.10a	21.36a

\* CP% = crude protein: total protein content of feed.

\*\* Values in each row followed by the same letter are not significantly different according to least significant tests (p<0.05).

The Crude Protein, Mg, Fe, Mn, Cu, and Zn content was significantly higher in Cut 2 compared to Cut 1 (Table 4.23)

<sup>29</sup>W. Thomas, Provincial Forage Specialist, NSDAM. Personal communication, August 1998.

**Final Research Report****Table 4.23 The effect of cutting date on the feed value of forage.**

Variable	Cut 1	Cut 2
Crude Protein* (%)	14.83a	18.56b
Mg (%)	0.13a	0.17b
Fe (ppm)	58.43a	68.85b
Mn (ppm)	109.12a	148.84b
Cu (ppm)	4.06a	6.98b
Zn (ppm)	22.17a	26.31b

\* CP% = crude protein: total protein content of feed.

\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

The ADF content was significantly increased by the Limestone treatment compared to all other treatments for cut 1; there were no significant differences detected among the other treatments (Table 4.24). The TDN and D.E. content was significantly decreased by the Limestone treatment compared to all other treatments for cut 1. For all three variables there were no significant differences detected among treatments for cut 2, and the Limestone content was significantly different between cuts 1 and 2. There were no significant differences detected among treatment in P content for cut 1. The P content was significantly increased by the soil amendment treatments compared to the Control treatment for cut 2. The P content was significantly lower for cut 1 compared to cut 2, within all treatments. There were no significant differences detected in K content among treatments for cut 1. The K content was increased by the soil amendment treatments compared to the Control for cut 2; there were no significant differences detected among soil amendment treatments. The K content was significantly lower for cut 1 compared to cut 2, within all treatments.



**Final Research Report****Table 4.24 The effect of cutting date and treatment on the feed value of forage.**

Variable	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
ADF* (%)					
Cut 1	26.42a/z**	29.10b/y	26.80a/z	26.07a/z	27.07a/z
Cut 2	26.96a/z	26.36a/z	26.21a/z	27.37a/z	26.57a/z
TDN* (%)					
Cut 1	70.57b/z	67.12a/z	70.07b/z	71.00b/z	71.02b/z
Cut 2	69.87a/z	70.65a/y	70.84a/z	69.34a/z	70.37a/z
D.E.* (Mcal/kg)					
Cut 1	3.10b/z	2.95a/z	3.08b/z	3.12b/z	3.12b/z
Cut 2	3.07a/z	3.11a/z	3.12a/z	3.05a/z	3.09a/z
P (%)					
Cut 1	0.20a/z	0.21a/z	0.20a/z	0.20a/z	0.21a/z
Cut 2	0.23a/y	0.30c/y	0.27b/y	0.29bc/y	0.38bc/y
K (%)					
Cut 1	2.03a/z	2.03a/z	2.13a/z	1.98a/z	1.93a/z
Cut 2	2.68a/y	3.13b/y	3.10b/y	3.13b/y	2.99b/y

\* ADF= acid detergent fibre: consists of cellulose, lignin, bound protein and acid insoluble ash; TDN= total digestible nutrient: used to express the energy value of feed, TDN is the sum of the digestible portions of protein, fat, fibre and nitrogen-free extract; DE= caloric expression of digestible energy, derived from ADF values.

\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

Tissue Ca levels were higher in forage from the ash treatments compared with Limestone treatments (Table 4.22), and were at the high end of the range reported for Ca in red clover/timothy hay in NS (0.65-0.80%)<sup>30</sup>. This indicates that Ca is supplied by the ash in a more readily available form when compared with Mosher limestone and other commonly used liming materials. Forage Mg levels in the ash treatments (0.11-0.13%), however, may be considered critically low, as plant Mg below 0.18% in forage is a risk factor for grass tetany in livestock who consume the forage (A&L 1985). The low plant Mg content in forage grown in ash treatments is consistent with the results obtained for the vegetables (Tables 4.14, 4.17, 4.21).

Higher soil alkalinity following fly ash amendment has been reported to reduce plant uptake of one or more of the following: P, Cu, Fe, Mn and Zn (Schumann and Sumner 1999; Carlson and Adriano 1993). Fe was not measured in the forage. Plant tissue P was at the low end of the optimum range (0.20-0.25%) in all treatments at first cut, and optimum in both liming treatments

<sup>30</sup>W. Thomas, Provincial Forage Specialist, NSDAM. Personal communication, August 1998.

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at second cut (Table 4.24). Plant tissue Cu and Zn were within a normal range for mixed forage (5-7 ppm and 17-25 ppm, for Cu and Zn, respectively) (A&L 1985), and not significantly reduced by ash treatments compared with Limestone treatments (Table 4.22). The Control treatment forage contained very high levels of Mn (Table 4.22). This effect is attributed to the greatly increased solubility and plant availability of Mn at lower soil pH. Relatively high Mn levels were also found in both Limestone and ash treatments (Table 4.22), where forage Mn was substantially higher than typical levels reported for NS mixed forage (25-55 ppm) (Thomas 1998). The high levels of plant Mn found in this study is attributed to the significant levels of total Mn in both liming materials (Appendix 3). While it is unlikely that this Mn level in the forage would result in excessive intake by a ruminant animal, it is important to maintain total Mn content of the ration within the range of 50-150 ppm. A level of Mn exceeding 500 ppm in the total ration is considered excessive for dairy cows (A&L 1985). Other trace elements which have been reported to occur at excessive levels in plant tissues following fly ash amendment (Mo, Se, B) were not measured in the forage. Plant B was increased by ash treatments in the vegetables, however uptake of this nutrient remained sub-optimal relative to plant requirements (Section 4.31). There was no detectable uptake of either Mo or Se in the vegetables (Section 4.41 and 4.42). It is therefore assumed that these elements would not be problematic in the forage.

Forage K levels at second cut in all soil treatments are well above optimum (1.60-2.10%) (Table 4.24), probably as a result of high K fertilization. Excessive K in the forage can result in poor assimilation of Ca and Mg by the animal, and may be of particular concern in cases such as this when plant Mg content is also low. Levels of K are generally not problematic, however, so long as the ratio of tissue K to (Ca + Mg) is less than 5.5 (A&L 1985), as is the case here (data not shown). In the current study, the ratio of Ca:Mg in soils and crops is considered to be the most important nutrient management issue relating to repeated use of CFB ash as a liming agent.

### 4.4 Metal Content of Plant Tissue

A total of 24 elements were included in the analysis for the metal content in plant tissue (Table 3.7). The following elements were below detectable levels for both species Ag, As, Ba, Be, Cd, Cr, Co, Cu, Mo, Ni, Pb, Sb, Se, Sn, Sr, U, V and Hg and therefore excluded from the statistical analysis. Analyses were completed for Al, B, Fe, Mn, Tl and Zn separately for both species.

#### 4.4.1 Cabbage

In cabbage, significant effects were detected for B, Fe, Mn, and Zn. A significant interaction (treatment x year) was detected for Mn level. A significant year main effect was detected for B, Fe, and Zn; a significant treatment main effect was detected for B, Fe, and Zn.

The B tissue level was increased by the ash treatment compared to the Control treatment (Table 4.25). The B tissue level was reduced by Limestone treatment compared to the Control treatment. The Fe tissue level was reduced by the Limestone treatment compared to all other treatments; there were no significant differences detected among the other treatments. The Zn

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tissue level was reduced by the soil amendment treatments compared to the Control treatment; there were no significant differences detected among the soil amendment treatments.

**Table 4.25 The effect of treatment on the level\* of trace metals in cabbage tissue.**

Element	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
B	0.46b**	0.00a	1.04c	1.46cd	1.59d
Fe	6.09b	3.96a	7.99b	7.15b	6.23b
Zn	3.07b	1.34a	1.71a	1.68a	1.27a

\* Units = mg/kg, dry weight basis

\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

The tissue levels for B, Fe and Zn were significantly lower in 1997 than for 1998 and 1999 (Table 4.26). There were no significant differences detected between 1998 and 1999 for tissue levels for B and Fe. The Zn tissue level was significantly higher in 1988 compared to 1999.

**Table 4.26 The effect of year on the level\* of trace metals in cabbage tissue.**

Element	Year		
	1997	1998	1999
B	0.60a**	1.09b	1.04b
Fe	4.81a	7.57b	6.47b
Zn	1.57a	2.04c	1.84b

\* Units = mg/kg, dry weight basis

\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

The Mn level was significantly reduced by the soil amendment treatments compared to the Control for all years (Table 4.27). There were no significant differences detected among soil amendments treatments in 1997 and 1998. In 1999, the Mn tissue level was significantly reduced by the Limestone treatment compared to the ash treatments.

**Final Research Report****Table 4.27 The effect of treatment and year on the level\* of trace metals in cabbage tissue.**

Element	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
Mn					
1997	7.64b/z**	3.77a/y	4.45a/z	4.65a/y	3.37a/z
1998	10.30b/y	2.57a/zy	3.30a/z	3.10a/z	3.32a/z
1999	9.65c/y	2.32a/z	4.35b/z	3.27a/b	3.50ab/z

\* Units = mg/kg, dry weight basis.

\*\* Values in each row followed by the same letter (a,b,c,...) are not significantly different according to least significant tests ( $p < 0.05$ ); values in each column followed by the same letter (z,y,x,...) are not significantly different according to least significant tests ( $p < 0.05$ ).

The addition of the Double-Ash treatment did not significantly alter the observed response to the treatments (Table 4.28). The B tissue level was significantly increase by the ash treatments compared to the Control; the level was significantly reduced by the Limestone treatment compared to the Control. The Fe tissue level was more variable among treatments. The Mn tissue level was significantly reduced by the soil amendment treatments compared to the Control; there were no significant differences detected among the soil amendment treatments. The Zn tissue level was significantly reduced by the soil amendment treatments compared to the Control. There was also a significant year main effect detected for Zn (data not shown).

**Table 4.28 The effect of treatment on the level\* of trace metals in cabbage tissue, with Double-Ash treatment .**

Element	Treatment					
	Control	Limestone	Low-Ash	Split-Ash	High-Ash	Double-Ash
B	0.68b**	0.00a	1.15bc	1.79d	1.71d	1.70cd
Fe	7.01b	5.09ab	9.09c	7.46bc	6.47ab	3.12a
Mn	9.97b	2.45a	3.82a	3.19a	3.41a	2.90a
Zn	3.40d	1.46ab	1.79bc	1.71bc	1.33a	2.03c

\* Units = mg/kg, dry weight basis.

\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

**4.4.2 Rutabaga**

In rutabaga, significant differences were detected for B, Mn, Tl and Zn. A significant interaction (treatment x year) was detected for Mn and Zn tissue levels. A significant year main effect was detected for Tl tissue level; a significant treatment main effect was detected for B and Tl tissue levels.

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The B tissue level was significantly increased by the ash treatments compared to the Control treatment (Table 4.29). The B tissue level was significantly decreased by the Limestone treatment compared to the Control. The Tl tissue level was significantly increase by the ash treatments compared to the Control and Limestone treatments.

**Table 4.29 The effect of treatment on the level\* of trace metals in rutabaga tissue.**

Element	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
B	0.12a**	0.00a	1.22b	1.57b	1.67b
Tl	0.00a	0.00a	0.03b	0.03b	0.05c

\* Units = mg/kg, dry weight basis.

\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

A significant year main effect was detected for Tl (Table 4.30). The Tl tissue level in 1999 was significantly lower compared to 1997; the level in 1998 was not detected to be significantly different from either 1997 or 1999.

**Table 4.30 The effect of year on the level\* of trace metals in rutabaga tissue.**

Element	Year		
	1997	1998	1999
Tl	0.025b	0.023ab	0.016a

\* Units = mg/kg, dry weight basis

\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

The Mn tissue level was significantly reduced by the soil amendment treatments compared to the Control in all years (Table 4.31). In 1998 and 1999 the ash treatments significantly reduced Mn tissue level compared to the Limestone treatment. In 1997 there were no differences detected among soil amendment treatments. The Zn tissue level was significantly reduced by the soil amendment treatments in 1997 and 1999; there were no significant differences detected among the soil amendment treatments. There were no significant differences detected among the treatments in 1998.

**Final Research Report****Table 4.31 The effect of treatment and year on the level\* of trace metals in rutabaga tissue.**

Element	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
<b>Mn</b>					
1997	13.27b/z**	3.72a/z	3.30a/z	3.15a/z	2.35a/z
1998	11.05c/y	4.15b/z	2.12a/z	2.22a/z	1.77a/z
1999	8.72c/x	3.12b/z	2.37a/z	1.60a/z	1.32a/z
<b>Zn</b>					
1997	2.55b/z	1.23a/z	1.70a/z	1.55a/z	1.30a/z
1998	1.97a/z	1.55a/zy	1.55a/z	1.57a/z	1.42a/z
1999	2.72b/z	1.85a/y	1.72a/z	1.57a/z	1.32a/z

\* Units = mg/kg, dry weight basis.

\*\* Values in each row followed by the same letter (a,b,c,...) are not significantly different according to least significant tests ( $p < 0.05$ ); values in each column followed by the same letter (z,y,x,...) are not significantly different according to least significant tests ( $p < 0.05$ ).

#### 4.5 Metal Content of Soils

In 1997 soils were sampled on June 25, prior to the application of soil treatments, and on July 22 and October 25, following the first and second applications of treatments, respectively. In 1998 and 1999 soils were sampled in October following the final harvest. A total of 23 elements were included in the available metals digest (Table 3.7). The data for all elements for each treatment are provided in Appendix 6. Seven elements (Ag, B, Be, Cd, Mo, Sb, and Se) were below detectable levels, and were therefore excluded from the statistical analysis. Results for the 16 elements (Al, As, Ba, Cr, Co, Cu, Fe, Hg, Mn, Ni, Pb, Sr, Tl, U, V, and Zn) which were at or above the detectable level are presented in three sections. First, the data for loading, or element addition as a result of the application of the soil amendments, and relative to the pre-treatment element level; second, the level of elements in soils at the end of the season; and third, the net change in the level of soil elements over the course of the growing season.

##### 4.5.1 Soil Metal Loading

Initial loading was determined by calculating the difference between soil element levels in the pre-application (June 25) and first application (July 22) soil samples (L1). The difference between the October element levels and the pre-application element level was determined for each year (October 1997 - L2; October 1998 - L3; October 1999 - L4). A positive number indicates an increase, a negative number indicates a decrease in soil element level. The analysis was completed separately for each species plot. In 1998 the Double-Ash treatment was added for cabbage, the data were re-analysed for 1998 and 1999 for the cabbage plot with that treatment added.

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In the cabbage plot there was a significant interaction (treatment x loading period) detected for As, Ba, Cu, Mn, Pb, and Sr. A significant loading period main effect was detected for Al, Fe, Ni, U, and Zn; a significant treatment main effect of treatment was detected for Tl.

The soil Tl level was significantly increase by the Split-Ash and High-Ash treatments compared to the Control, Limestone and Low-Ash treatments (Table 4.32).

**Table 4.32 The effect of treatment on element loading level\* in cabbage plot.**

Element	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
Tl	0.00a**	0.00a	0.00a	0.04b	0.06

\* Units = mg/kg, dry weight basis

\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

The soil Al loading level was increased for period L1, L2, and L3 but there were no significant differences detected among the periods (Table 4.33). The Al loading level was negative for period L4, and this response was significantly different from the other loading periods. A similar response was observed for Fe loading level. The response is an indication of change over time. The loading levels for the first 3 periods was positive, indicating an increase in available Al and Fe; the decrease in period L4 indicates that the Al and Fe have been bound or absorbed to the soil particles. The Ni loading level was negative for the 4 periods; with the decrease in period L4 significantly lower compared to period L3. Examining the response over loading period there is no significant change in Ni losses or gains. The U loading level was positive for the 4 periods, with then increase in period L4 significantly higher than for the other periods. The Zn loading level was significantly lower for periods L3 and L4 compared to period L1 and L2. Examining the response over time Zn levels, or soil availability, is declining.

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**Table 4.33** The effect of loading period on element loading level\* in cabbage plot.

Element	Loading Period**			
	L1	L2	L3	L4
Al	1078.50b ***	1188.00b	1267.50b	-1085.00a
Fe	1096.50b	970.00b	665.50b	-100.00a
Ni	-2.55ab	-1.90ab	-1.00b	-2.80a
U	0.14a	0.11a	0.22a	0.36b
Zn	3.45b	2.65b	0.80a	-0.90a

\* Units = mg/kg, dry weight basis

\*\* L1: July, 1997; L2: October 1997; L3: October 1998; L4: October 1999.

\*\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

The soil As loading level was significantly increased by the ash treatments compared to the Control and Limestone treatments for periods L1 and L2 (Table 4.34). The As loading level for the ash treatments separate out for periods L3 and L4, with the loading level for the Low-Ash treatment being significantly lower than the Split-Ash and High-Ash treatments. The loading level for the Low-Ash treatment was not significantly different compared to the Control and Limestone treatments. In examining the response of the ash treatment across loading period, there were no significant differences detected for the Split-Ash and High-Ash treatments across loading period. This indicates that beyond the initial loading there were no significant changes to the soil As as a result of those treatments. There was a significant difference observed for the Split-Ash treatment. The period L2, L3 and L4 loading levels were significantly higher than for period L1; there was no significant difference in loading levels among loading periods L2, L3 and L4. This response reflects the fact that after the initial ash application for the Split-Ash treatment there was an increase in loading, as compared to the Control treatment in period L1. The significant difference between L1 and L2 reflects the second loading as a result of the fall (split) application for that treatment in 1997. The lack of a significant difference among L2, L3 and L4 indicates there were no changes in As soil levels as a result of that treatment. This response within the Split-Ash across loading period was consistent for the other elements (Ba, Cu, Mn, Pb, and Sr). In addition, generally the Split-Ash and High-Ash treatments has a significantly higher loading rate compared to the other treatments. The Mn level was unique in that all soil amendment treatments significantly increased the soil loading levels relative to the Control, and the loading level for the Control was negative for all periods.



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**Table 4.34 The effect of treatment and loading period on element loading level\* in cabbage plot.**

Element	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
<b>As</b>					
L1**	0.50a/z***	0.52a/zy	2.82b/z	2.50b/z	4.15c/z
L2	0.00a/z	0.00a/z	2.00b/z	5.30d/y	3.77c/z
L3	1.75ab/y	1.00a/zy	2.75b/z	4.50c/y	4.00c/z
L4	0.50a/z	1.50ab/y	2.50b/z	4.75c/y	4.75c/z
<b>Ba</b>					
L1	3.25a/z	3.75a/z	15.50b/z	13.00b/z	29.75c/zy
L2	0.75a/z	2.75ab/z	9.25b/z	34.50c/y	24.25c/z
L3	2.00a/z	1.75a/z	13.50b/z	31.25c/y	32.50c/y
L4	1.75a/z	2.75a/z	13.50b/z	37.25c/y	37.25c/y
<b>Cu</b>					
L1	-0.75a/z	0.00ab/z	1.00bc/z	-0.50a/z	1.50c/z
L2	-1.00a/z	0.00a/z	0.00a/z	1.50b/z	1.50b/z
L3	1.00a/y	0.00a/z	0.50a/z	1.75b/y	1.75b/z
L4	-0.50a/z	-0.50a/z	0.00ab/z	0.75b/y	2.00c/z
<b>Mn</b>					
L1	-2.25a/zy	33.75b/z	28.75b/zy	-6.00a/z	36.25b/z
L2	-9.50a/zy	53.75c/zy	16.25b/zy	38.35bc/yx	48.75c/z
L3	7.50a/y	73.75c/y	38.75b/y	48.75b/x	58.75bc/z
L4	-24.25a/z	46.25cd/z	6.25b/z	23.25bc/y	56.25d/z
<b>Pb</b>					
L1	-0.30a/z**	0.75a/z	3.25b/z	0.75a/z	3.50b/zy
L2	-1.42a/z	1.15b/z	1.25b/z	2.45b/zy	2.25b/z
L3	0.37ab/z	-0.67a/z	2.00b/z	3.50b/y	3.25b/zy
L4	-0.10a/z	-0.07a/z	2.00ab/z	4.00bc/y	5.00c/y
<b>Sr</b>					
L1	0.00a/z	0.00a/z	1.75ab/z	2.75b/z	9.25c/y
L2	0.00a/z	0.00a/z	1.25a/z	9.75c/x	7.25b/zy
L3	0.00a/z	0.00a/z	0.00a/z	6.25b/y	6.75b/z
L4	0.00a/z	1.25a/z	0.00a/z	6.25b/y	6.75b/z

\* Units = mg/kg, dry weight basis.

\*\* L1: July, 1997; L2: October 1997; L3: October 1998; L4: October 1999.

\*\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

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The addition of the Double-Ash treatment did not alter the basic relationship among the treatments (Table 4.35). The Split-Ash and High-Ash treatments increased the loading level for Al, Ba, Cu, Sr and Tl compared to the other treatments; the response for the Double-Ash treatment was not significantly different from the Split-Ash and High-Ash treatments. The Mn loading level was variable among the soil amendment treatments; all were significantly increased compared to the Control treatment. The loading level was positive for the soil amendment treatments and negative for the Control treatment.

**Table 4.35 The effect of treatment on element loading level\* in cabbage plot, with Double-Ash treatment.**

Element	Treatment					
	Control	Limestone	Low-Ash	Split-Ash	High-Ash	Double-Ash
Al	1.12a**	1.25a	2.62b	4.62c	4.37c	3.12b
Ba	1.87a	2.25ab	13.50b	34.25c	34.87c	40.42c
Cu	0.25a	-0.25a	0.25a	1.25b	1.87b	3.08c
Mn	-8.37a	60.00c	22.50ab	36.00bc	57.50bc	42.00bc
Sr	0.00a	0.62a	0.00a	6.25b	6.75b	5.92b
Tl	0.00a	0.00a	0.00a	0.05b	0.06b	0.07b

\* Units = mg/kg, dry weight basis

\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

There was a significant effect of loading period for Al, Ni, U, and Mn (data not shown). This indicates a significant difference between periods L3 and L4.

In the rutabaga plot there was a significant interaction (treatment x loading period) detected for As, Ba, Cu, Pb, Sr, Tl and U. A significant loading period main effect was detected for Al, Hg, and V; a significant treatment main effect was detected for Hg, V, and Zn.

The Hg loading level was negative across all treatments (Table 4.36). The Hg loading was significantly lower for the Control and Limestone treatments compared to the ash treatments. The V loading level was significantly different between the Split-Ash and High-Ash treatments and the Control, Limestone and Low-Ash treatments. The loading level was negative for the later treatment grouping and positive for the former treatment grouping. The Zn loading level was significantly higher for the Split-Ash and High-Ash treatments compared to the Control, Limestone and Low-Ash treatments.

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**Table 4.36 The effect of treatment on element loading level\* in rutabaga plot.**

Element	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
Hg	-0.072a**	-0.070ab	-0.059bc	-0.050c	-0.048c
V	-0.62a	-0.50a	-1.75a	5.50b	4.62b
Zn	-0.31a	0.81a	0.87a	6.56b	4.06ab

\* Units = mg/kg, dry weight basis

\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

There was no significant difference detected on Al loading level among the L1, L2 and L3 periods (Table 4.37). The Al loading level was significantly different for the L4 period compared to L1, L2 and L3. The loading levels were positive for the L1, L2 and L3 periods indicating an increase in soil levels, the level was negative for period L4 indicating a decrease in soil level. This suggest that the Al was being bound to the soil particles. The Hg loading level was not available for period L1, and was negative for periods L2, L3 and L4, indicating a decrease in soil Hg levels. The most significant decrease occurred for period L2. The V loading level was positive for all periods indicating an addition to the soil. The levels were not detected to be difference among periods L1, L2 and L3; the loading level for period L4 was significantly higher compared to periods L1, L2 and L3.

**Table 4.37 The effect of loading period on element loading level\* in rutabaga plot.**

Element	Loading Period**			
	L1	L2	L3	L4
Al	429.50b***	543.00b	693.00b	-1495.00a
Hg	NA	-0.066a	-0.057b	-0.057b
V	0.60a	1.35a	1.40a	2.45b

\* Units = mg/kg, dry weight basis.

\*\* L1: July, 1997; L2: October 1997; L3: October 1998; L4: October 1999.

\*\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

The soil As level was significantly increased by the Split-Ash and High-Ash treatments compared to Control in all loading periods (Table 4.38). The As level was significantly increased by the Low-Ash treatment compared to the Control treatment for all periods except for period L2. The response of the treatments across loading period was similar to that observed above in the cabbage plot. The increase in soil Ba and Cu levels was significantly higher in the ash treatments compared to the Control treatment. The increase in soil Sr level was significantly

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higher in the Split-Ash and High-Ash treatments compared to Control. The response in soil Tl, U and Pb levels was more variable. There were no significant differences detected among treatments for period L1. The soil Tl and U levels were significantly increased in the Split-Ash and the High-Ash treatments compared to the Control treatment for periods L2, L3 and L4. The soil Pb level was significantly higher for the High-Ash treatment compared to all other treatments for period L1. For periods L2, L3 and L4, soil Pb levels were significantly higher in the Split-Ash and High-Ash treatments compared to the Control.

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**Table 4.38 The effect of treatment and loading period on element loading level\* in rutabaga plot.**

Element	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
<b>As</b>					
L1**	0.55a/z***	0.50a/z	2.30b/zy	2.17b/z	5.12c/y
L2	0.50a/z	0.00a/z	1.17a/z	5.50c/y	3.45b/z
L3	1.50a/z	1.00a/z	3.00b/y	6.75d/x	5.00c/y
L4	1.00a/z	1.00a/z	2.75b/y	5.00c/y	5.00c/y
<b>Ba</b>					
L1	5.0a/z	6.0ab/z	19.75b/z	18.50b/z	42.75c/y
L2	0.00a/z	1.75a/z	15.50b/z	51.75c/y	24.25b/z
L3	1.00a/z	4.25a/z	25.75b/z	56.75c/y	44.00bc/z
L4	2.25a/z	4.75a/z	25.25b/z	47.50c/y	52.00c/y
<b>Cu</b>					
L1	-0.25a/z	0.00ab/zy	0.75b/zy	0.75b/z	3.00c/yx
L2	-0.75a/z	-0.50a/z	0.00a/z	2.75c/y	1.25b/z
L3	0.00a/z	0.75ab/y	1.50b/y	3.75c/x	3.50c/x
L4	-0.50a/z	0.25a/zy	1.25b/y	2.75c/y	2.50c/y
<b>Pb</b>					
L1	-0.45a/z	0.20a/z	1.35a/z	2.12a/z	5.37b/zy
L2	-1.25a/z	-1.10a/z	2.30b/zy	6.87c/y	3.62b/z
L3	-0.25a/z	1.12a/z	3.82b/zy	7.87c/y	6.87c/yx
L4	-0.07a/z	0.87a/z	4.87b/y	8.12c/y	9.62c/x
<b>Sr</b>					
L1	0.00a/z**	1.25a/z	5.25b/zy	5.50b/z	11.25c/y
L2	0.00a/z	1.25ab/z	3.00b/z	11.75d/x	8.00c/z
L3	0.00a/z	1.25a/z	6.00a/y	10.50b/yx	9.50b/zy
L4	0.00a/z	1.25a/z	3.00a/z	8.25b/zy	9.25b/zy
<b>Tl</b>					
L1	0.00a/z	0.00a/z	0.00a/z	0.00a/z	0.05a/z
L2	0.00a/z	0.00a/z	0.00a/z	0.10b/y	0.02a/y
L3	0.00a/z	0.00a/z	0.02a/z	0.10b/y	0.10b/y
L4	0.00a/z	0.00a/z	0.02a/z	0.10b/y	0.10b/y
<b>U</b>					
L1	0.10a/zy	0.02a/z	0.10a/z	0.10a/z	0.10a/z
L2	0.05a/z	0.02a/z	0.12ab/z	0.22b/y	0.17b/z
L3	0.20a/yx	0.17a/y	0.47b/x	0.40b/x	0.30ab/y
L4	0.27a/x	0.22a/y	0.30ab/y	0.37ab/x	0.40b/y

\* Units = mg/kg, dry weight basis.

\*\* L1: July, 1997; L2: October 1997; L3: October 1998; L4: October 1999.

\*\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

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### 4.5.2 Final Soil Metal Levels

The final-level data are from the soil metal analysis for the October soil sampling period. The 16 metals that were at a detectable in the soil were analysed. The data presented are for the actual levels in the soil at the date of sampling.

For the cabbage plot no significant effects were detected for Cr, Co, V, Zn, Fe, and Hg, nor was a significant interaction (treatment x year) detected for any element. A significant year main effect was detected for Al, Mn, Ni, and U; a significant treatment main effect was detected for Al, Ba, Cu, Mn, Pb, Sr, and Tl.

The soil As level was significantly increased by the ash treatments compared to the Control and Limestone treatments (Table 4.39). The soil As level was significantly increased more by the Split-Ash and High-Ash treatments compared to the Low-Ash treatment. A similar response was observe for soil Ba level. The soil Cu level was significantly increased by the Split-Ash and High-Ash treatments compared to the Control, Limestone and Low-Ash treatments; there were no significant differences detected within the treatment groupings. A similar response was observed for soil Sr and Tl levels. The soil Mn level was significantly increased by the Limestone, Split-Ash and High-Ash treatments compared to the Control treatment. The response to the Low-Ash treatment was not detected to be significantly different from the Control treatment nor from the other soil amendment treatments. The soil Pb level was significantly increase by the Split-Ash and High-Ash treatments compared to the Control treatment. There were no significant differences detected among the Control, Limestone and Low-Ash treatments, between the Low-Ash and Split-Ash treatments, nor between the Split-Ash and High-Ash treatments.

**Table 4.39** The effect of treatment on the level\* of trace metals in cabbage plot.

Element	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
As	0.75a**	0.83a	2.42b	4.85c	4.17c
Ba	12.00a	12.91a	22.58b	44.83c	41.83c
Cu	4.08a	4.08a	4.42a	5.58b	6.00b
Mn	100.00a	166.67b	129.17ab	145.50b	163.33b
Pb	10.12a	10.63a	12.25ab	13.82bc	14.00c
Sr	0.00a	0.42a	0.42a	7.42b	6.92b
Tl	0.10a	0.10a	0.10a	0.15b	0.15b

\* Units = mg/kg, dry weight basis

\*\* Values in each row followed by the same letter are not significantly different according to least significant tests (p<0.05).

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The soil Al level was significantly lower for 1997 and 1998 compared to 1999 (Table 4.40). The soil Mn level was significantly lower for 1997 and 1999 compared to 1998. The soil Ni level was significantly lower in 1999 compared to 1998; the soil Ni level in 1997 was not detected to significantly different from either 1998 or 1999. The soil U level was significantly different for all years; 1997 was the lowest and 1999 was the highest.

**Table 4.40 The effect of year on the level\* of trace metals in cabbage plot.**

Element	Year		
	1997	1998	1999
Al	13363.00b**	13344.50b	11090.00a
Mn	138.25a	154.25b	130.30a
Ni	5.60ab	6.50b	4.70a
U	0.41a	0.52b	0.66c

\* Units = mg/kg, dry weight basis

\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

The addition of the Double-Ash treatment resulted in two additional elements, Hg and U, showing significant treatment effects (Table 4.41). As above the soil As level was significantly increased by the ash treatments compared to the Control and Limestone treatments. The Double-Ash treatment increased soil As level significantly higher compared to the remaining ash treatments. Similarly the soil Ba and Sr levels were increased significantly by the Double-Ash treatment compared to the Control and the other soil amendment treatments. The soil Cu, Mn, Pb, and Tl levels for the Double-Ash treatment were not detected to be significantly different compared to the High-Ash treatment. There were no significant differences detected between the Limestone, Low-Ash, Split-Ash, and High-Ash treatments compared to the Control treatment for soil Hg and U levels; the Double-Ash treatment significantly increased soil Hg and U levels compared to all other treatments. A significant year main effect was detected for Al, Ni, Mn, and U (data not shown).

**Final Research Report****Table 4.41 The effect of treatment on the level\* of trace metals in cabbage plot, with Double-Ash treatment.**

Element	Treatment					
	Control	Limestone	Low-Ash	Split-Ash	High-Ash	Double-Ash
As	1.12a**	1.25a	2.62b	4.62c	4.37c	6.12d
Ba	12.37a	12.75a	24.00a	44.75b	45.37b	88.35c
Cu	4.50ab	4.00a	4.50ab	5.50bc	6.12cd	7.33d
Hg	0.047a	0.040a	0.051a	0.055a	0.056a	0.077b
Mn	100.37a	168.75b	131.25a	144.75ab	166.25ab	151.42ab
Pb	10.64ab	10.12a	12.50bc	14.25c	14.62cd	18.75d
Sr	0.00a	0.62a	0.00a	6.25b	6.75b	11.92c
Tl	0.10a	0.10a	0.10a	0.15b	0.16bc	0.20c
U	0.56ab	0.66bc	0.51a	0.56ab	0.67ab	0.73c

\* Units = mg/kg, dry weight basis

\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

In the rutabaga plot a significant effect was detected for all elements to be found at or above a detectable level in the soil, except for Ni. A significant interaction (treatment x year) was detected for Ba and Tl. A significant year main effect was detected for Al, As, Cu, Hg, Mn, Pb, and U; a significant treatment main effect was detected for As, Cr, Cu, Hg, Pb, Sr, U, V, and Zn.

The soil As level was significantly increased by the ash treatments compared to the Control and Limestone treatments (Table 4.42). Within the ash treatments levels were significantly higher for the Split-Ash treatment compared to the other two, and significantly lower in the Low-Ash treatment compared to the other two. The soil Cu, Hg, Pb, and Sr levels were significantly increased by the ash treatments compared to the Control treatment. The soil Cr, V, and Zn levels were significantly increase by the Split-Ash and High-Ash treatments compared to the Control treatment. The soil U level was significantly increased by the Low-Ash and Split-Ash treatments compared to the Control treatment.



**Final Research Report****Table 4.42 The effect of treatment on the level\* of trace metals in rutabaga plot.**

Element	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
As	1.00a**	0.67a	2.31b	5.77d	4.48c
Cr	5.00ab	5.08abc	4.75a	6.00c	5.92bc
Cu	2.83a	3.42ab	4.17b	6.33c	5.97c
Hg	0.032a	0.035ab	0.046bc	0.055c	0.057c
Pb	11.10a	11.92ab	15.29bcd	19.25d	18.33cd
Sr	0.00a	0.46a	4.00b	10.17c	8.92c
U	0.45a	0.42a	0.58b	0.61b	0.57ab
V	19.00a	19.17a	17.83a	25.50b	24.67b
Zn	21.25a	22.25a	22.67a	29.00b	25.50ab

\* Units = mg/kg, dry weight basis

\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

The soil Al level was significantly lower in 1999 compared to 1997 and 1998 (Table 4.43). The soil As, Hg and U levels were significantly lower in 1997 compared to 1998 and 1999. The soil Cu level was significantly different for all years; the level was lowest in 1997 and highest in 1998. The soil Mn level was significantly higher in 1998 compared to 1997; there were no significant differences detected between the level in 1999 and the other years. The soil Pb level was significantly higher in 1999 compared to the level in 1998; there were no significant differences detected between the level in 1998 and the other years.

**Final Research Report****Table 4.43 The effect of year on the level\* of trace metals in rutabaga plot.**

Element	Year		
	1997	1998	1999
Al	9738.00b**	9888.00b	7700.00a
As	2.13a	3.45b	2.95b
Cu	3.80a	5.15c	4.50b
Hg	0.039a	0.048b	0.048b
Mn	271.17a	322.15b	301.95ab
Pb	13.71a	15.51ab	16.31b
U	0.39a	0.58b	0.59b

\* Units = mg/kg, dry weight basis

\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

The soil Ba level was significantly increased by the ash treatments compared to Control and Limestone treatments (Table 4.44). The level within the Low-Ash and High-Ash treatments were significantly lower in 1997 compared to 1998 and 1999. The level within the Split-Ash treatment was significant different among all year. The soil Tl level was significantly increased by the Split-Ash treatment compared to all other treatments in 1997. In 1998 and 1999, the soil Tl level was increased by the Split-Ash and High-Ash treatments compared to all other treatments.

**Table 4.44 The effect of treatment and year on the level\* of trace metals in rutabaga plot.**

Element	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
Ba					
1997	19.75a/z**	21.50a/z	35.25b/z	56.05d/z	44.00c/z
1998	20.75a/z	24.00a/z	45.50b/y	76.50d/x	63.75c/y
1999	22.00a/z	24.50a/z	45.00b/y	67.25c/y	71.75c/y
Tl					
1997	0.10a/z	0.10a/z	0.10a/z	0.20b/z	0.12a/z
1998	0.10a/z	0.10a/z	0.12a/y	0.20b/z	0.20b/y
1999	0.10a/z	0.10a/z	0.12a/y	0.20b/z	0.20b/y

\* Units = mg/kg, dry weight basis.

\*\* Values in each row followed by the same letter (a,b,c...) are not significantly different according to least significant tests ( $p < 0.05$ ); values in each column followed by the same letter (z,y,x...) are not significantly different according to least significant tests ( $p < 0.05$ ).

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### 4.5.3 Net Change in Soil Metal Levels

The net change in the level of soil metals during the course of the growing season (i.e. as a result of the fall application of amendments, plant uptake, soil fixation, or leaching) was calculated by subtracting the soil analyses values for soil metal levels of the first application (July) from those of the second application (October) for 1997, and for 1998 and 1999 by subtracting the October soil analysis from that of the previous year. The data set was constructed for the 16 elements at or above soil detectable levels.

In the cabbage plot no significant effects were detected for Cr, Co, Tl, U, Zn, or Hg. This indicates that there was no detectable change in those elements within treatment, or over years. A significant interaction (treatment x year) was detected for As, Ba, and Sr. A significant year main effect was detected for Al, Cu, and Ni; a significant treatment main effect was detected for Cu, Fe, Mn, Pb, and V.

The soil Cu and Pb level was significantly increased by the Split-Ash treatment compared to the Control (Table 4.45). There were no significant differences detected among the remaining treatments; the response for the Split-Ash treatment was not significantly different compared to the High-Ash treatment. The soil Fe and V levels was increased by the High-Ash treatment, and this response was significantly different compared to all other treatments. There were no differences detected among the other treatments, and levels were reduced. The soil Mn level was increase by the Limestone, Split-Ash and High-Ash treatments; there were no significant differences detected among those treatments. The soil Mn level was decreased by the Control and Low-Ash treatments, and were not detected to be significantly different. The two treatment grouping were significantly different.

**Table 4.45 Effect of treatment on end of season change in element level\* in cabbage plot.**

Element	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
Cu	0.00ab*	-0.67a	-1.00a	0.58c	0.33bc
Fe	-508.33a	-566.67a	-675.00a	-377.50a	133.33b
Mn	-7.33a	4.17b	-7.50a	9.75b	6.67b
Pb	0.07ab	-0.27ab	-0.42a	1.08c	0.50bc
V	-0.25a	-0.33a	-0.25a	-0.17a	0.67b

\* Units = mg/kg, dry weight basis

\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

Soil Al, Cu, and Ni levels were increased in 1997 and 1998, and there were no significant differences detected between years within each element (Table 4.46). Levels were decreased in 1999, and this effect was significantly different compared to 1997 and 1998 within each element.

**Final Research Report****Table 4.46 Effect of year on end of season change in element level\* in cabbage plot.**

Element	Year		
	1997	1998	1999
Al	109.50b*	79.50b	-2352.50a
Cu	0.15b	0.60b	-1.20a
Ni	0.65b	0.90b	-1.80a

\* Units = mg/kg, dry weight basis

\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

The soil As level was significantly increased in 1997 by the Split-Ash treatment compared to the Control treatment, and was significantly decreased in 1998 (Table 4.47). In both years there were no significant differences detected among the remaining treatments. In 1999 there were no significant differences detected among treatments. The soil Ba level was increased in 1997 by the Split-Ash treatment compared to the Control, and the other soil amendment treatments. There were no significant differences detected among treatments in 1998 and 1999. A similar response was observed for Sr.

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**Table 4.47** Effect of treatment and year on end of season change in element level\* in cabbage plot.

Element	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
As					
97	-0.50a/z*	-0.52a/z	-0.82a/z	2.80b/y	-0.37a/z
98	1.75b/y	1.00ab/z	0.75ab/z	-0.80a/z	0.22ab/z
99	-1.25a/z	0.50a/z	-0.25a/z	0.25a/z	0.75a/z
Ba					
97	-2.50a/z	-1.00a/z	-6.25a/z	21.50b/y	-5.50a/z
98	1.25a/z	-1.00a/z	4.25a/z	-3.25a/z	8.25a/y
99	-0.25a/z	1.00a/z	0.00a/z	6.00a/z	4.75a/zy
Sr					
97	0.00a/z	0.00a/z	-0.50a/z	7.00b/y	-2.00a/z
98	0.00a/z	0.00a/z	-1.25a/z	-3.50a/z	-0.50a/z
99	0.00a/z	1.25a/z	0.00a/z	0.00a/z	0.00a/z

\* Units = mg/kg, dry weight basis

\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

The data for the cabbage plot were re-analysed with the addition of the Double-Ash treatment (for 1998 and 1999). A significant interaction was detected for Sr. A significant year main effect was detected for Cu and Mn (data not shown); a significant treatment main effect was detected for Ba, Cu, Mn, and V.

The addition of the Double-Ash treatment significantly increased the soil Ba, Cu, Mn, and V levels compared to all other treatments (Table 4.48). There were no significant differences detected among the remaining treatments.

**Final Research Report****Table 4.48 Effect of treatment on end of season change in element level\* in cabbage plot, with Double-Ash treatment.**

Element	Treatment					
	Control	Limestone	Low-Ash	Split-Ash	High-Ash	Double-Ash
Ba	0.50a*	0.00a	2.12a	1.37a	6.50a	25.54b
Cu	0.12a	-1.00a	-1.00a	-0.12a	0.50a	2.71b
Hg	0.00a	0.002a	0.002a	0.001a	0.001a	0.020b
Mn	-7.37a	-3.75a	-5.00a	-7.50a	3.75a	27.67b
V	-0.12a	-0.75a	-0.37a	-0.12a	0.50a	2.54b

\* Units = mg/kg, dry weight basis

\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

The soil Sr level was increased by the Double-Ash treatment compared to all other treatments in 1998 (Table 4.49). There were no significant differences detected among the other treatments. There were no significant differences detected among treatments in 1999.

**Table 4.49 Effect of treatment and year on end of season change in element level\* in cabbage plot, with Double-Ash treatment.**

Element	Treatment					
	Control	Limestone	Low-Ash	Split-Ash	High-Ash	Double-Ash
Sr						
98	0.00a/z*	0.00a/z	-1.25a/z	-3.50a/z	-0.50a/z	7.10b/y
99	0.00a/z	1.25a/z	0.00a/z	0.00a/z	0.00a/z	-1.60a/z

\* Units = mg/kg, dry weight basis

\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

In the rutabaga plot a significant interaction (treatment x year) was detected for As, Ba, Cu, Sr, Tl, and U. A significant year main effect was detected for Al; there were no significant treatment main effects detected.

The soil Al level was decreased in 1999; levels were increased in 1997 and 1998 (Table 4.50). The response in 1999 was significantly different from that of 1997 and 1998.

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**Table 4.50** Effect of year on end of season change in element level\* in rutabaga plot.

Element	Year		
	1997	1998	1999
Al	113.50b*	150.00b	-2188.00a

\* Units = mg/kg, dry weight basis

\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

The soil As, Cu, Ba, Tl, and Sr levels were increased by the Split-Ash treatment for 1997, and this response was significantly different from all other treatments (Table 4.51). There were no significant difference detected among the other treatments, and the change was zero or negative. There were no significant differences detected in soil As, Ba, and Sr levels among treatments for 1998 and 1999. The soil Cu level was increased by the High-Ash treatment in 1998, and by the Split-Ash and High-Ash treatments in 1999, and those responses were significantly different compared to the other treatments. The soil Tl level was increased by the High-Ash treatment in 1998, and this response was significantly different compared to the other treatments; there were no significant differences detected among treatment in 1999. There were no significant difference detected in soil U level between the soil amendment treatments and Control in 1997 and 1998; in 1999 soil U level was significantly decreased by the Low-Ash treatment compared to Control.

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**Table 4.51** Effect of treatment and year on end of season change in element level\* in rutabaga plot.

Element	Treatment				
	Control	Limestone	Low-Ash	Split-Ash	High-Ash
As					
97	-0.05a/z	-0.50a/z	-1.12a/z	3.37b/x	-1.67a/z
98	1.00a/z	1.00a/z	1.82a/y	1.20a/y	1.55a/y
99	-0.50a/z	0.00a/z	-0.25a/z	-1.75a/z	0.00a/zy
Ba					
97	-5.00a/z	-4.25a/z	-4.25a/z	33.25b/z	-18.50a/z
98	1.00a/z	2.50a/z	10.25a/z	5.00a/z	19.75a/y
99	1.25a/z	0.50a/z	-0.50a/z	-9.25a/z	8.00a/y
Cu					
97	-0.50a/y	-0.50a/y	-0.75a/z	2.00b/y	-1.75a/z
98	0.75a/y	1.25ab/x	1.50ab/y	1.00ab/zy	2.25b/y
99	-2.25a/z	-1.75ab/z	-0.50b/z	0.00c/z	0.00c/y
Sr					
97	0.00a/z	0.00a/z	-2.25a/z	6.25b/y	-3.25a/z
98	0.00a/z	0.00a/z	3.00a/y	-1.25a/z	1.50a/y
99	0.00a/z	0.00a/z	-3.00a/z	-2.25a/z	-0.25a/zy
Tl					
97	0.00a/z*	0.00a/z	0.00a/z	0.10b/y	-0.03a/z
98	0.00a/z	0.00a/z	0.03a/z	0.00a/z	0.08b/y
99	0.00a/z	0.00a/z	0.00a/z	0.00a/z	0.00a/z
U					
97	-0.05a/z	0.00a/z	0.02a/z	0.12a/z	0.07a/z
98	0.15ab/z	0.15ab/z	0.35b/y	0.17ab/z	0.12a/z
99	0.07b/z	0.05b/z	-0.17a/z	-0.02ab/z	0.10b/z

\* Units = mg/kg, dry weight basis

\*\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).



**Final Research Report****4.6 Metal Content of Plant Tissues and Soil**

Except where noted, similar results on metal content in plants and soils were obtained for cabbage and rutabaga, therefore results for these two plant species are discussed together.

The metals in plant tissues for which significant treatment effects were determined were B, Fe, Zn, Mn and Tl. Four of these metals (B, Fe, Zn, and Mn) are essential plant nutrients, and have been discussed in Section 4.3. Thus, the only metal in plant tissues discussed here is Tl.

Thallium is unique amongst the metals found in this study in that it increased in both soils (discussed below) and in plant tissues (Table 4.30 and 4.31). A significant increase in Tl in rutabaga tissues was noted in all three of the ash treatments (Table 4.30). While the levels present in the rutabaga were very low, the result is significant due to the toxicity and high bioavailability of this element. Plant Tl levels are normally low; the natural range in edible plants is 0.02 to 0.125 mg/kg (dry weight), however Tl is readily taken up by plants (particularly on sandy, low organic matter soils), and increased plant levels of this element are highly toxic to both plants and animals. Elevated plant levels (up to 2.8 ppm) have been reported in localized areas (i.e. in the vicinity of potash fertilizer works, smelter and bituminous coal plant sites) (Kabata-Pendias and Pendias 1991).

The detection of Tl is notable due to the availability and potential toxicity of this relatively obscure element. It should be emphasized, however, that element concentrations in vegetable tissues did not at any point during the study represent a hazard to humans or livestock who may consume the produce. This was confirmed in 1999 by the Chemical Health Hazard Assessment Division of Health Canada, who reviewed analytical data on the trace metal content of vegetables grown on soils amended for 2 years with CFB ash. The data included treatments which had received the maximum loading (53 t/ha) of CFB ash. The conclusion of Health Canada's assessment was that the reported levels of trace metals in the cabbage and rutabaga would not be considered to represent a health hazard to consumers.

The results for soil element loading correspond closely to those obtained for final levels of soil metals, indicating that increased soil element concentrations at the end of the season are a function of amendment loading in the different treatments. The data for net change in soil metals indicates that, with the exception of Al in 1999, levels of most metals tended to increase over the course of the growing season. Year effects did not reflect differences between years in terms of loading, as expected. In other words, the greatest increase in soil metals did not occur in 1997 (year of maximum loading<sup>31</sup>), but rather, in the second year (1998). This effect, however, is likely to be more related to solubility/precipitation reactions controlling the chemical forms of

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<sup>31</sup>The highest loading (equivalent of 21 t/ha in Limestone, Split-Ash and High Ash) occurred in 1997 (L1 and L2), and loading in 1998 and 1999 (L3 and L4) consisted of low (average 2 t/ha), additional applications based on soil lime requirement. An exception to this was the Double-Ash treatment in the cabbage trial, where in 1998, an additional 20 t/ha of ash was applied to the High Ash treatment to determine the effect of very high loading rates.

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metals in the soil and extracted by the HNO<sub>3</sub> digest<sup>32</sup> than it is to actual or total amounts of metals present.

There are essentially three groups of metals which may be distinguished on the basis of their tendency to increase or decrease in soils as a result of the soil treatments or years: those which increased, those which decreased, and those whose levels were not affected by treatment or year. Meaningful interpretation of these results requires consideration of both 1) the significance of the levels obtained, as indicated by the literature and metal criteria for soils and wastes, and 2) soil conditions and other factors which influence bioavailability (potential for uptake by plants and other living organisms) and mobility of the metals in soils.

Metals that increased in soils included As, Ba, Cr, Cu, Hg, Mn, Pb, Sr, Tl, U, and V (Tables 4.40 to 4.45, inclusive). Similar results were obtained in cabbage and rutabaga, with the exception that soil Cr and V were increased only in the rutabaga plot (Table 4.43). With the exception of Mn, these metals were increased only in CFB ash treatments (Table 4.40, 4.42, and 4.43). The soil loading data (Section 4.5.1) indicates that the ash treatments provided significant amounts of As, Ba, Pb and Sr (Table 4.35, 4.36, and 4.39), and lesser amounts of Tl and V (Table 4.36 and 4.37). This is consistent with the ash analysis (Appendix 3), which indicates that the ash utilized in this study, while typical of ash from high sulphur coal-fired fluidized bed combustors, is relatively high in As, Ba, Fe, Mn, Mo, Pb, Sr, and Zn (Jacques Whitford and Assoc. 1997). The increase in several of these elements (As, Ba, Pb, and Sr) on fly ash amended soils is well documented (Keefer 1993; Carlson and Adriano 1993; Adriano et al. 1980). Other elements commonly reported to be increased in soils with fly ash application (i.e. B, Mo, Se) (Keefer 1993; Jackson et al. 1999; Gupta and Gupta 1998) were not increased in soils in this study. Some metals which showed a slight increase (Cr, Cu, Hg) are more commonly associated with sewage sludge than fly ashes (Basta and Sloan 1999; Williams et al. 1980; Stout et al. 1988). Others (Tl and V) are relatively bioavailable and may be toxic when present at excessive levels, however there is a paucity of literature on their environmental significance (Kabata-Pendias and Pendias 1991).

It is important to note that of the eleven metals which were increased in soils, five (As, Cr, Cu, Hg, and Pb) are commonly regulated under federal or provincial laws. All of these elements may be toxic to animals. Copper and Pb are strongly sorbed by soils above pH 6.0 (Basta et al. 1993), however, and are not generally considered a problem with fly ash use (Keefer 1993). Mercury is highly toxic and relatively mobile in soils; Cr, while an essential micronutrient in animal nutrition, is also toxic at elevated concentrations (Bohn et al. 1986). Neither soil accumulation nor plant uptake of Hg or Cr, however, have been reported to any extent following application of fly ash to soils. Arsenic may be present in fly ash in significant amounts, and while this element is strongly sorbed by soils, under alkaline and/or reducing conditions, As becomes relatively soluble and bioavailable (Theis and Wirth 1977; Masscheleyn et al. 1991).

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<sup>32</sup>HNO<sub>3</sub> digest provides a measure of total concentrations that are exchangeable or adsorbed on the surfaces of soil components (i.e. clays, Fe and Mn hydroxides or organic matter). Because the digest does not dissolve soil minerals, it does not include trace elements associated with silicates (Loro et al. 1996).

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Arsenic is therefore the most likely metal<sup>33</sup> to accumulate in plants grown on ash amended soils (Keefer 1993; Jackson et al. 1999). Soils with low to moderate buffer capacity, such as were used in this study, tend to have low As sorption capacity, and will therefore release a greater proportion of the As which is applied (Jacobs et al. 1970). Despite high amendment loading rates, in the three years of this study, no plant uptake of As or any of the other above metals was detected (Section 4.4). None of the metals exceeded criteria for metals in soils receiving waste materials (Appendix 4). In most cases, soil metal content was below background levels typically reported for uncontaminated soils. For example, in the Double Ash treatment, which had received the maximum loading of ash (53 t/ha), soil As was well below the maximum limit (14 mg/kg) and still within what may be considered a normal soil range (below 7 mg/kg) (Table 4.42). Levels of Pb in soils from this treatment, while exceeding the values for uncontaminated soil, were still well below the regulated limit for Pb (60 mg/kg) (Table 4.42). The other three elements (i.e. Cr, Cu, and Hg) were present in treated soils at concentrations below the mean levels indicated for uncontaminated soils (Tables 4.42 and 4.43 and Appendix 4).

One element, Tl, may be considered unique in that it increased in both soils (Tables 4.40, 4.42, 4.45), and in plant tissues (Tables 4.30 and 4.31). A significant increase in soil Tl in the higher ash treatments, while small, is important due to the toxicity and high bioavailability of this element. Soil Tl levels are normally low; the natural range is 0.01 to 2.3 µg/gm dry weight, however, soils in industrialized areas<sup>34</sup> may contain much higher Tl levels (i.e. above 10 µg/gm). As indicated previously, Tl is readily taken up by plants, particularly on sandy, low organic matter soils, and increased plant levels of this element are highly toxic to both plants and animals (Kabata-Pendias and Pendias 1991). Thallium is also important in that it flags what may be considered gaps in our understanding and control of anthropogenic metals. Tl is not one of the dozen or so metals commonly regulated under federal or provincial laws and reported in the literature as environmentally important, and thus the importance of increased soil Tl may be overlooked. Of seven industrialized countries having guidelines for maximum permissible soil metal concentrations, Switzerland is the only country with a limit for Tl (1 mg/kg dry weight of soil) (Webber and Bates 1997). While levels found in this study are well below the Swiss limits for Tl, our results demonstrate that detectable increases in plant uptake are possible for this element at soil concentrations below the legal soil limit.

The fact that, other than Tl, plant uptake of metals did not occur to any appreciable extent is notable. At the outset of the study, it was recognized that the ash contained, in addition to the large amounts of beneficial sorbent-derived components (CaO, CaSO<sub>4</sub>), a number of potentially toxic elements which may accumulate in ash amended soils, and/or plants grown on these soils. One of the objectives in establishing the trials - trials involving long-season vegetable crops, grown on a poorly buffered (i.e. low metal-binding capacity) soil, with amendment loading rates 5 to 10 times higher than those that would normally be applied - was to provide a “worst case

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<sup>33</sup>Arsenic is actually a metalloid, with properties intermediate between metals and non-metals (electrical semi-conductors, amphoteric oxides, etc).

<sup>34</sup>The largest anthropogenic sources of Tl are coal combustion, heavy metal smelting, cement industry and refining processes (Kabata-Pendias and Pendias 1991).

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scenario” with respect to metal uptake by the crops. While leaching was not measured in this study, the data for net change in soil metals indicates that, other than Al, there were no significant losses of soil metals during the course of the growing season. Leaching and uptake of metals both involve the soil liquid phase, and it follows that lack of evidence of either process suggests low solution concentrations of metals (de Haan and Van Riemsdijk 1986). It is well established that a very low percentage of total soil metals occur in the mobile fraction (generally <2%), and that many materials present in soils (e.g., clays, organic matter, hydrous Fe and Mn oxides, carbonates, inorganic chemical compounds, organic acids, and biological residues) can react to immobilize the remaining 98% (Stevenson and Cole 1999; Williams et al. 1980; Kabata-Pendias and Pendias 1991). Despite the low clay content (4-6%) of the soils used in this study, the soils nonetheless demonstrate a significant ability to immobilize metals. The metal sorbing ability of these soils is attributed to the presence of Fe and Al oxide clays<sup>35</sup> as well as a moderately high organic content (3.3-4.6%) for a sandy soil. Having said that metals exist in soils in predominantly fixed or immobilized forms, when soils contain appreciable amounts of sorbed metals, the potential for dissolution and desorption always exists, with the attendant risk that small amounts of available metals will gain entry into the food web. It is well known that conditions that influence mobility and bioavailability of sorped metals (soil pH, redox potential, organic matter content, loading of additional metals or other nutrients) can change over time, and therefore, when determining amendment loading rates, a conservative approach with respect to metals is always best. This is one of the reasons why Canada and several other countries have adopted what may be considered stringent metal criteria for soils and waste materials; that is, so that the standards hold up under “worst case scenarios”. With respect to arsenic, it would appear that the relatively stringent federal limits on level of As in fertilizers and waste materials<sup>36</sup> provide a high margin of safety with respect to variability in As sorption capacity of soils, soil amendment loading rates, as well as soil pH and redox conditions following application of amendments.

Soil Mn was the only element increased by both liming materials (Table 4.40 and 4.42). From the elemental analysis of the ash and limestone, both materials have a significant Mn content, particularly the Mosher limestone (Appendix 3). Manganese is an important element in both plant and animal nutrition, as well as in oxidation-reduction reactions. For example, the oxidation of metals such as As, Cr, V, Se, and Hg by Mn-oxides is important in reducing the bioavailability and toxicity of these metals (Kabata-Pendias and Pendias 1991). On the other hand, Mn may reach phytotoxic levels under highly acidic and/or reducing soil conditions (Bohn et al. 1986). Most soils contain very large amounts of Mn. Further soil additions, however, from materials such as Mosher limestone or CFB ash should not be a problem owing to the low solubility of Mn at elevated soil pH. As with other metals, however, soil redox conditions often over-ride soil pH in controlling solubility of Mn. As a result, Mn toxicity has been known to

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<sup>35</sup>While there was no determination of the type of clays present, evidence of Fe oxide content is provided by the red-brown soil color and presence of a spodic horizon (illuvial zone of accumulated organic matter and oxides of Al and Fe).

<sup>36</sup>Federal (Agriculture and Agri-Food Canada) guidelines for maximum metal concentrations in fertilizers and waste materials may be more conservative than provincial (e.g., Nova Scotia sewage sludge) guidelines. For example, federal limits on As in fertilizers is 75 mg/kg, whereas provincial limit for As is 170 mg/kg.

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occur at higher pH levels in poorly drained (poorly aerated) soils (Kabata-Pendias and Pendias 1991).

There were two elements (Al and Fe) that, despite very high initial loading (Table 4.34), did not increase in soils. Soil Al levels decreased in 1999 (Table 4.47), and soil Fe neither increased nor decreased in soils despite the high loading. CFB residues contain large amounts of Fe and Al (Appendix 3) which exist in the ash as sparingly soluble oxides, yet are, nonetheless, readily extracted by an available metals digest<sup>37</sup>. The year effect for Al (Tables 4.41 and 4.44) was due to a large reduction in HNO<sub>3</sub>-extractable Al in the third year. While lowered availability of soil Al is expected above pH 5.5, reasons for the delay in reduced soil concentrations (i.e. large amounts of Al were extracted in 1998, despite soil pH above 6.5 in ash treatments) are unknown at this time.

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<sup>37</sup>Recoveries of HNO<sub>3</sub>-extractable Fe and Al are 60% and 66%, compared with total (HClO<sub>4</sub>:HNO<sub>3</sub>:HF-extractable) forms of the metals (Philip Analytical).

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**Final Research Report****5. GENERAL DISCUSSION**

In the following discussion, CFB ash and Mosher limestone are compared on the basis of results obtained on liming efficacy and crop response. Soil characteristics which are important in soil liming are identified with a view to improving the prediction of soil liming response to the ash as well as the development of appropriate liming strategies for soils having different chemical and physical characteristics. Results obtained on element loading in soils and uptake by crops are summarized, and the implications of these results is discussed in the context of recommended management, monitoring and quality standards for agricultural utilization of the ash.

**5.1 Liming Efficacy and Crop Response****5.1.1 Similarities between Liming Materials**

The ash was as effective as Mosher limestone as a liming agent, both in terms of extent of acid neutralizing reaction as well as sustained liming effect. Within the first year of application, CFB ash applied at rates equivalent to the soil lime requirement (21 t/ha), increased very low soil pH (pH 4.9) to a range considered optimal for nutrient availability and crop growth (pH 6.0-6.5). A substantial reduction in soil acidity was achieved. Because soil pH is a logarithmic scale, an increase in one pH unit (i.e., from pH 5.0 to 6.0) represents a 10-fold reduction in  $H^+$  ion concentration<sup>38</sup>, or soil acidity (Brady and Weil 1999). The capacity of the ash to raise soil pH to near optimum values (i.e. soil pH at or near 6.5) was demonstrated in all five trials conducted as part of this study<sup>39</sup>.

Results obtained in this study are consistent with the large body of literature which indicates that coal combustion by-products (CCBs) can act as liming agents. The ability of a liming material to neutralize soil acidity depends primarily on the neutralizing value, or calcium carbonate equivalent (CCE). The CCE of materials used in this study, 64-80% for CFB ash and 90-95% for the Mosher dolomitic limestone, were within the ranges typically reported for these materials. The CCE of fluidized bed materials (36-81%), while lower than carbonate limestones (90-108%), is much higher than most other CCBs due to the large amounts of sorbent used in the CFB combustion process, i.e., unreacted sorbent ( $CaO$ ,  $CaCO_3$ ) comprises approximately one-third of the material (Korcak 1997). A key concept demonstrated by soil liming studies is that similar soil pH adjustment can be expected when liming materials are applied on a CCE basis. This concept is of great practical significance to agricultural use of CFB ash, as it means that soil pH response is predictable and similar for ash of varying neutralizing value, so long as amendment loading is adjusted for CCE of the ash. In this study, it was critical that three of the experimental treatments (Limestone, Split-Ash and High-Ash) were applied on an equivalent CCE basis, as this allowed a comparison of liming effect as well as crop response to the

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<sup>38</sup>Soil pH is defined as the negative logarithm of the hydrogen ion concentration, or  $\log 1/[H^+]$ .

<sup>39</sup>The five trials referred to here are the Cabbage, Rutabaga, Forage and Pet coke ash trials conducted at Point Edward, and the Turfgrass trial conducted at NSAC. Three additional experiments conducted by A. Joseph, evaluating CFB ash as a source of calcium and boron for crops, are described fully in his MSc thesis.

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materials. Synchronizing initial applications in these treatments in terms of CCE of the soil lime requirement resulted in similar soil pH adjustment, and consequently, similar and low additional applications in the following two seasons. The fact that a similar target pH was achieved in ash and limestone treatments applied at equivalent loading indicates that there is no difference between the liming materials in terms of the acid neutralizing reaction.

A number of liming studies report a lower liming persistence for CCBs and other lime by-products compared with carbonate limestones (Carlson and Adriano 1993; Muse and Mitchell 1995; Bailey et al 1989; Brady and Weil 1999). Lower residual activity, like greater reactivity, is usually attributed to finer particle size. In this study, a high persistence of liming effects was observed in both limestone and ash treatments. Based on soil samples taken in July 2000, there is no indication of declining soil pH in any of the treatments in Year 4 (Appendix 8). In fact, the opposite effect is observed, with soil pH increased over 1999 values in all trials and in all of the liming treatments. While residual activity is partly a function of particle size, chemistry of the liming material and the soil is also a factor. The high liming persistence noted in this study is attributed largely to factors which lower the solubility of the ash, and therefore reduce the rate of reaction with soil particles. High amendment loading rates (>20 t/ha) and an essentially complete neutralization of soil acidity, are two factors which would substantially reduce the solubility of liming materials. There is a possibility that the elevated soil pH observed in 2000 is the result of an excessive lime application. This latter possibility is discussed in section 5.2.2. While additional liming applications and elevated soil pH may hamper the evaluation of residual activity in liming treatments applied at high rates, the persistence for 4 years of soil pH between 5.5-6.0 in the Low-Ash treatment (Tables 4.1 and 5.1), with little or no additional liming applications, indicates that the ash has significant residual activity. Several authors (Tisdale et. al 1999; McCarty et. al 1994; Carlson and Adriano 1993) have indicated that the residual activity of oxide-based liming materials is greatly increased by hydration/carbonation reactions which take place following application to soils. Thus, it may be surmised that, despite a fine particle size and high reactivity, liming persistence of CFB ash is not significantly different from that of carbonate limestones.

For both cabbage and rutabaga, both total yield and marketable yield were significantly increased by liming treatments compared with yields in the unlimed controls. There was no difference in marketable yield or quality (percentage culls) between ash and limestone treatments applied at equivalent loading. In other words, crop response to the two liming materials was similar. An important additional result obtained in the cabbage was that marketable yield was increased, and correspondingly, percentage of culls decreased, by the Double-Ash or maximum loading treatment compared with all other treatments. While the high liming rates in this treatment are not recommended liming practice, the results are important in demonstrating that, even at rates far in excess of what would normally be applied<sup>40</sup>, there is no negative impact of ash application on crop yield. The low phytotoxicity of the ash was further demonstrated by results

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<sup>40</sup>Liming applications are typically in the range of 4-8 t/ha, or the ash equivalent of 5-10 t/ha. Thus the cumulative loading in the Double Ash treatment (53 t/ha within two years) is 5-10 times in excess of "normal" application rates.

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obtained on germination and seedling growth. Rutabaga were seeded between the rows of transplanted cabbages in the Double-Ash plots and monitored for four weeks before being removed. The absence of phytotoxicity to high rates of ash at this highly sensitive growth stage indicates that there is no risk to plant growth from application of the ash at normal or recommended input levels.

Similarly, in the forages, no adverse effects were noted on establishment or growth of forage when ash was soil incorporated in the seeding year. Surface applications of ash in years 2 and 3 were minimal due to target soil pH being reached or exceeded. Total forage yields were similar in the ash and Limestone treatments, and within the range reported for mixed forage grown in Nova Scotia (7.5-8 t/ha). Forage quality, as indicated by crude protein (% CP), digestible energy (%ADF, %TDN and %DE) and nutrient content of the forage, was higher in liming treatments compared with unamended controls but not greatly different between ash and limestone treatments. All liming treatments contributed to earlier growth and better persistence of the legume component in the third year. Differences between ash and limestone treatments were found, however, in terms of nutrient content of the forage (see section 5.2).

In the turfgrass, no adverse effects on turf (e.g., burning) were noted, even when the ash was applied at a rate (160 kg/100 m<sup>2</sup>) that greatly exceeds what would normally be applied (25 kg /100 m<sup>2</sup>) to turf. Observations on turf quality (greenness, density, % weeds, etc.) did not indicate any effect of liming treatments on turf quality. The lack of quality differences is not surprising, however, given the limited number of treatment applications (once for Low-Ash and Limestone, twice for High-Ash), relatively high initial soil pH, and heterogeneity (i.e. botanical diversity) of the test site.

A similar response of vegetables and forage crops to both ash and limestone treatments indicates that low soil pH was the main factor limiting crop growth. The macronutrients, N, P, and K, supplied to all treatments by N-P-K fertilizer, were initially deficient on the acid, infertile soils at Point Edward. Improved soil levels of these three macronutrients, however, did not eliminate the consistent and severe yield reduction (>50%) observed in the unlimed Control treatments. Other than greater plant uptake of Ca in cabbage and forage, and partial alleviation of B-deficiency in rutabaga, we did not see a major nutritional benefit from the ash compared with limestone. Plant tissue Mg (discussed below) was very low in all ash-amended crops, however low Mg did not limit crop yield. Given the severe yield reduction in fertilized but unlimed Controls, similar high crop yield and quality in ash and limestone treatments, indicates first, that low soil pH was the main barrier to crop growth, and second, that the two liming materials were equally effective in removing this barrier.

The significant crop response to liming obtained in this study highlights the rationale for recommending lime in crop production. The main reason for recommending lime to increase pH of acid soils to 6.0-6.5 is to improve crop yield. Data from more than 1,500 plant species indicate that relative crop yields at pH 4.7 are only 32% compared to 98% at pH 6.8 (Foth and Ellis 1996). Within the pH range of 4 to 10, the primary effect of soil pH on plant growth is not



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the  $H^+$  activities *per se* but the associated chemical environments. In general, the major influence of pH is on ion activities that affect the toxicity of elements like Al and Mn and availability of essential plant nutrients (in particular, Ca, Mg, P, K, S, B, Mo, and Zn). Large yield decreases can be expected below pH 5.5, at which point many soils become less than 100% basic cation saturated and amounts of exchangeable Al increases rapidly. On strongly acid soils (pH 5.1-5.5), root growth is restricted due to Al toxicity and a deficiency of Ca and/or Mg. Legume crops are particularly intolerant of soil acidity, due to the sensitivity of their associated N-fixing *Rhizobium* bacteria and the generally higher requirements of legumes for elements such as Mo and Ca (Kamprath 1970).

### 5.1.2 Differences between Liming Materials

One important difference between CFB ash and agricultural grade carbonate limestones is the lower and more variable calcium carbonate equivalent (CCE) of the ash. As indicated previously, the CCE of fluidized bed materials is reported to range from 36-81%, whereas carbonate limestones generally have a CCE between 90 and 108%. The wider variation in CCE of the ash may be attributed to differences in CaO content (a function of coal:sorbent ratios during combustion) and moisture content (i.e., conditioned vs unconditioned ash). There are several implications, in terms of agricultural use of the ash, of having a lower and more variable CCE compared with agricultural grade limestones. An obvious consequence of lower CCE is that higher amendment loading is required in order to neutralize soil acidity. In this study, application rates of the ash were increased approximately 30% to provide equivalent acid neutralizing capacity to Mosher limestone. While an increase of this magnitude is not likely to be problematic at typical liming rates (4-8 t/ha, or the ash equivalent of 5-10 t/ha), higher amendment loading as a result of using lower CCE ash may be a limitation when:

- there are significant transportation costs involved (i.e, at sites far from ash source);
- high loading rates are applied to poorly buffered soils;
- sources of ash containing higher levels of trace elements are used.

The importance of the last two issues (soil type and ash quality) with respect to amendment loading are discussed below in sections 5.3 and 5.4.

A second difference between the materials was that CFB ash reacted more quickly than limestone, and the resulting soil pH was higher. The high initial alkalinity in ash treatments appeared to be transient, however. Both greater reactivity and higher transient alkalinity in the ash are attributed to its significant oxide content (15-40%). Pure oxides are highly alkaline (pH >12) materials with a high CCE (>180%). Compared with the crystalline carbonates in limestone, which must be ground in order to react with soil particles, oxides, which are powdery by nature, allow a more rapid neutralization of soil acidity and the resulting soil pH is higher (Brady and Weil 1999). As previously noted, oxides are inherently unstable, and when applied

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to soils, readily undergo carbonation (McCarty et al. 1994; Carlson and Adriano 1993). Thus, in terms of acid neutralization, when applied on a CCE basis the net effect of oxide materials on soil pH is similar to carbonate limestones.

A third difference noted between dolomitic limestone and CFB ash is the ratio of Ca to Mg in the materials. Because calcitic lime is generally used as the sorbent, CFB residues contain large amounts of Ca (24-46%) but are generally Mg depleted (0.3-1%). By comparison, dolomitic limestones contain similar or lower amounts of Ca (21-27%) but significantly more Mg (8-11%). At the relatively high loading rates used in this study, ash treatments had a large impact on soil Ca levels but no effect on soil Mg. The existence of an antagonistic relationship between Ca and Mg in the soil means that the ratio of these nutrients can have as much or greater effect on availability to plants as their individual soil concentrations. The implications of a high Ca to Mg ratio in the ash, in terms of both crop nutrition and soil management and monitoring requirements, is discussed in more detail below and in section 5.4.

**5.2 CFB Ash as a Source of Plant Nutrients**

Previous research on CFB ash suggests that the material is superior to carbonate limestones, and similar to gypsum, as a source of Ca and S. Increased plant uptake of micronutrients such as B, Cu, Fe, Mn and Mo, as well as reduced uptake of P, Mg and Zn, have also been reported in crops grown on ash-amended soils.

In the present study, the clearest demonstration of enhanced plant uptake was for Ca. Plant Ca levels were significantly higher in ash compared with Limestone treatments in both cabbage and forages, but not the rutabaga. There was no evidence of increased S levels in the ash treatments for either of the high-S requiring vegetable crops.

Boron is an important micronutrient for most vegetable crops (in particular, rutabaga) as well as legume crops. Because of the low B requirement of most crops and elevated B levels in many coal combustion ashes, B phytotoxicity is cited as the greatest potential problem with high application rates of fly ash (Carlson and Adriano 1993). Even at very high rates of ash application (53 t/ha), B phytotoxicity was not observed in this study. While plant B was increased by ash treatments in the cabbage and rutabaga, B was still below sufficiency levels in both crops. CFB ash treatments reduced the severity of B deficiency symptoms (brown heart) in rutabaga, however, did not replace the need for further B supplementation (i.e., foliar B). The lack of B phytotoxicity is attributed to the use of highly leached, nutrient depleted soils and relatively low B-content ash.

There was no indication of increased plant uptake of Mo, Fe, Cu, Mn or Zn in the ash compared with limestone treatments, and both liming treatments tended to reduce plant uptake of N, Mn and Zn compared with the controls. Higher plant N in unlimed plots is attributed to lower plant biomass (concentration effect). Lower plant Mn and Zn in liming treatments is predictable with the decreased solubility and plant availability of these elements at higher soil pH. Crop deficiencies of Zn and P are a frequently cited concern with the use of fly ash as a liming material. In this study, there was no effect of liming treatments on plant P levels, and while both liming materials reduced plant uptake of Zn, tissue concentrations of this micronutrient were

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within plant sufficiency ranges for all crops. Both Mosher limestone and ash treatments increased forage Mn above typical levels reported for mixed forage in Nova Scotia, however forage Mn in limed treatments was well below Control levels. The effect of treatments on plant Mn levels is attributed to the significant levels of Mn found in both liming materials. There was no effect of soil treatment on plant Cu.

The only serious nutrient imbalance associated with use of CFB ash in this study was very low soil and crop levels of Mg relative to Ca. As noted previously, high levels of soil Ca relative to Mg, or specifically, a soil Ca:Mg ratio greater than 5-7:1, can result in plant deficiencies of Mg. The substantial increases in soil Ca in the ash treatments, with no corresponding increase in Mg, resulted in soil Ca:Mg well above the recommended ratio of 5-7 to 1 in these treatments. Consequently, plant tissue Mg was significantly lower for all crops in ash compared with Limestone treatments. While no yield depression occurred with ash treated crops and there were no visible symptoms of Mg deficiency, levels of Mg were critically low in both soils and plant tissues. Magnesium deficiency is of particular concern in the forages due to the increased risk of grass tetany (hypomagnesaemia) in ruminant animals who consume the low Mg content forage.

While CFB ash may be a poor source of Mg, it should be noted that among materials used to raise soil pH and/or supply Ca, it is not unique in this regard. Other materials which may be Mg-depleted include quick lime (CaO), hydrated lime (Ca(OH)<sub>2</sub>), calcitic lime (CaCO<sub>3</sub>), as well as gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), a widely used Ca source and soil conditioner for problem soils. The fact that repeated use of coal combustion ashes and other low-Mg materials can result in sub-optimal levels of soil Mg as well as reduce Mg uptake by crops, is well documented (Korcak 1988; Schumann and Summer 1999; McLean and Brown 1984; Keefer 1993).

Concerns with low soil Mg have led agronomists to recommend dolomitic lime when acid soils are low in Mg, or whenever soil Mg is below 10%. In Indiana, where sandy, low capacity soils are susceptible to Mg deficiencies, dolomitic lime is recommended for every third limestone application as a general practice (McLean and Brown 1984). Because of the likelihood of a similar effect on Ca/Mg distribution in the profile with CFB ash as is noted with gypsum<sup>41</sup> (Shainberg et al. 1989), precautions noted with the use of gypsum as a fertilizer material should also apply to use of CFB residues; that is, levels of Mg and other soil nutrients should be monitored closely following application of CFB residues, particularly on sandy soils of low CEC.

Alkaline conditions and high soil ratios of Ca:Mg and Ca:K can reduce the availability of macronutrients (P, K, and Mg) as well as induce micronutrient deficiencies (B, Cu, Mn, Fe, and Zn). For this reason, liming beyond pH 6.5, or above 75% Ca+Mg, is generally not recommended, particularly on sandy or weakly buffered soils (Liebhardt 1981). In this study, the persistence of elevated soil pH (i.e., pH > 6.5) in several treatments provides an opportunity

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<sup>41</sup>exchangeable Ca is increased uniformly down the soil profile, and Mg is reduced in the upper part but accumulates in the lower portion as an intermediate stage in its removal from the profile.

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to examine the effects of high rates of ash application on soil and plant concentrations of elements whose solubility is either increased or decreased by more alkaline conditions. With the exception of Ca and Mg, soil nutrient levels have not been closely examined. Thus, a more complete discussion of the effect of the ash on plant nutrition will require including the soil nutrient and pH data in the analysis.

### **5.3 Predicting Soil and Crop Liming Response**

#### **5.3.1 Soil Characteristics**

In any agricultural field trial, an important question is, to what extent was the observed response influenced by unique conditions at the experimental site? As indicated above, liming response will vary to some degree with the liming material (e.g. more rapid neutralization, transient higher alkalinity with oxides), however, soil pH adjustment is largely predictable and similar for materials of varying neutralizing value so long as amendment loading is adjusted for CCE. Soil characteristics will also influence the liming response, however, and ultimately determine the appropriate liming strategy for a given site (i.e., the type of liming material used, amount and frequency of liming applications).

Given that: a) testing in this study was conducted on soils which had similar physical and chemical characteristics<sup>42</sup>, and b) the high lime requirement and persistent liming effects at Point Edward were difficult to explain on the basis of the initial characterization of the soils, some additional testing was done on the soils in order to address the following questions:

1. Why were the liming results obtained at Point Edward? Specifically, why did these sandy loam soils (4-6% clay) with reportedly low buffer acidity have such a high lime requirement (21 t/ha)? And why do liming effects persist strongly in Year 4?
2. Do the results on liming response with CFB ash obtained in this study apply to other soils which differ significantly in terms of soil acidity and other chemical and physical characteristics?

In other words, what is the role of soil characteristics in determining the soil lime requirement and liming response (rate and extent of pH adjustment following liming, persistence of liming effects) and what soil factors influence the liming strategy (rate and frequency of applications) with respect to the utilization of CFB ash?

The main soil characteristics which have the greatest influence on soil liming response are soil buffer capacity and colloid characteristics. The role of soil pH relates primarily to effects on the solubility of liming materials as well as precipitating ions. As outlined in the following section (5.3.2), accounting for the results obtained at Point Edward requires examining not only the relevant soil parameters but also laboratory methods used to determine parameters related to soil buffering and lime requirement.

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<sup>42</sup>Soils at both the Point Edward and NSAC experimental sites had sandy loam texture, low clay content (4-6%), soil organic content of 3-4% and CEC in the range of 11-14 cmol/kg.

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Soil buffering is of great practical significance in soil liming. Not only is it a key factor in determining soil lime requirement, it also influences the rate and extent of pH adjustment as well as the persistence of liming effects. For example, soils of low buffering capacity (low CEC soils) require less lime for a given required change in soil pH compared with more highly buffered soils. Because of a low amount of reserve and exchangeable acidity, neutralization of total acidity on these soils is likely to be more rapid than on highly buffered soils.

Correspondingly, fluctuations in soil pH (active acidity) due to the effects of leaching or crop removal of basic cations, acidifying fertilizers, or applied liming materials, are greater. Thus, on low buffer capacity soils there is a much greater risk of overliming. Transient increases in soil pH following the application of oxides or other highly reactive liming materials will also be more pronounced on these soils. Some authors report more lasting pH effects from the application of alkaline fly ash to poorly buffered soils (Petruzzelli et al. 1987, in Carlson and Adriano 1993). More commonly, the consensus is that greater leaching on low capacity soils reduces the duration of liming effects so that such soils require lime more often than highly buffered soils (Brady and Weil 1999). The response of soils to liming according to the amount of buffering affects the liming strategy. On weakly buffered soils, frequent light applications are recommended, whereas on more strongly buffered soils, larger amounts may be applied less often (Tisdale et al. 1999). Based on the limits of soil adsorption, maximum liming rates are 7-9 t/ha<sup>43</sup>. Thus, for acid soils with high buffer capacity (8-10 t/ha/pH unit), lime applications are usually spread over 1-2 years. Rates for lower buffer capacity soils (2-7 t/ha/pH unit) should not exceed 4-6 tons/ha in any given application (Brady and Weil 1999; Rowell 1994). Actual rates of application depend on the amount of soil buffer acidity (as indicated by the soil test), target pH and crop requirements, as well as CCE of the liming material.

Do the results on liming response obtained in this study apply to other soils which differ in terms of buffer acidity and other chemical and physical characteristics? From the standpoint of pH adjustment, the answer is yes, as there is a wide consensus that soil pH response to liming materials is predictable when amendment loading is adjusted for CCE. As far as soil lime requirement and liming strategy are concerned, however, the response must be no. As indicated above, in order to determine an appropriate liming strategy (rate and frequency of applications), and more fully anticipate the soil liming response (rate of acid neutralization, fluctuation in pH following liming, etc.), one needs to examine the characteristics of the soil which define the buffer capacity.

### 5.3.2 The Role of Soil Testing

Given that buffering largely determines not only soil requirements for lime and fertilizers, but also influences the type of management required to keep the soils productive, it would appear that providing estimates of soil buffer capacity is one of the more important functions of the soil test. Because buffer capacity is a function of the exchange capacity of the soil colloids, estimates of soil CEC, and sometimes soil organic content, can provide a reasonable estimation of the buffer capacity. Fortunately, both CEC and organic content are commonly reported on soil tests. In terms of soil buffer capacity, however, CEC and organic content are not the complete story, as the other important colloids are the clay particles. In addition, methodology

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<sup>43</sup>Based on a liming material with neutralizing value of 90-95%.

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and interpretation of CEC and organic matter tests often limits the usefulness of these analyses<sup>44</sup>. More detailed characterization of the clay (amount and type) and humus fractions provides information not only on the exchange capacity of the soil but also the charge properties i.e., whether the soil charge, or ability to hold acidifying or nutrient cations, is pH dependant or permanent (Brady and Weil 1999). The existence of significant pH dependant charge in naturally acidic, infertile soils, such as are found in Atlantic Canada, has significant management implications. Both liming and maintaining soil organic content can produce significant increases in the CEC, thereby increasing the buffering and nutrient holding capacity of these soils (Foth and Ellis 1996). As one might expect, determining the percentages of soil separates (sand, silt and clay) as well as the characterization of clay and humus colloids, are specialized procedures which are not performed on a routine basis.

The other soil test parameter indicative of buffer capacity is the soil lime requirement. Various approaches have been used to estimate soil lime requirement, however, most routine or batch analyses utilize buffered solutions as a means to estimate a proportion of the total acidity. Different buffering solutions are used for soils with different cation exchange capacities. The SMP (Shoemaker McLean and Pratt) buffer test is best suited to soils with appreciable buffer acidity and exchangeable Al. The reliability of this test for moderate to high buffer acidity soils, along with its speed and simplicity, has made it the most widely used buffer lime requirement test in soil test labs in Canada and the United States. Despite having similar soils, the four Atlantic Canadian provinces use different buffer lime requirement tests. Prince Edward Island and New Brunswick currently use the SMP buffer, while Nova Scotia and Newfoundland use the Adams and Evans buffer (Warman et al. 1996). The Adams and Evans buffer is recommended for low activity clay soils with low effective CEC and low lime requirement, and is therefore not widely employed outside the southeastern United States (Foth and Ellis 1996). Reasons for the use of this buffer by provincial labs<sup>45</sup> in Nova Scotia and Newfoundland are not known. It would appear, however, that many of the soils (mostly Spodosols<sup>46</sup>, with low to high variable charge and variable buffer acidity) tested by the labs would frequently exceed the low limits for exchangeable acidity for the test (8 meq per 100 g soil) (Foth and Ellis 1996). For example, exchangeable acidity in soils from the Point Edward experimental site, which may be considered fairly representative of Cape Breton soils, ranged from 9-17 meq per 100 g soil. While this amount of buffer acidity is low compared with amounts of exchangeable H<sup>+</sup> associated with higher exchange capacity permanent charge soils (i.e., 18-60 meq per 100 g soil), the amount of acidity in these soils does exceed the range recommended for the Adams and Evans buffer method (Brady and Weil 1999; Rowell 1994).

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<sup>44</sup>Petra Loro, Manager, Soil and Analytical Services Section, New Brunswick Dept. of Agriculture and Rural Development. Personal communication, August, 2000.

<sup>45</sup>For example, the NS Dept. of Agriculture and Marketing (NSDAM) soil test lab in Truro.

<sup>46</sup>Spodosols: coarse-textured mineral soils formed under forest vegetation through a process of intensive acid leaching. Spodosols are the dominant soils not only on Cape Breton Island, but also in much of eastern Canada and the northeastern United States, where soil acidity and low base saturation are a major limiting factor to agricultural productivity of soils (Brady and Weil 1999; Webb et al 1991; Hilchey et. al 1963).

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Suspecting that buffer method may have influenced the very high lime requirement values reported for the Point Edward soils, two archived samples of the original soils were sent to the New Brunswick Department of Agriculture soil test lab and analyzed using the SMP buffer test. While the soils tested by the New Brunswick lab still demonstrate a very high lime requirement (16 t/ha to increase soil pH from 4.2 to 6.5), both soil pH and lime requirement are considerably lower than the NSDAM lab values. In addition, CEC was significantly higher (36%) in samples analyzed by the New Brunswick lab compared with the NSDAM lab.

The lower values for initial soil pH and lime requirement reported by the New Brunswick lab<sup>47</sup> result in more reasonable lime recommendations which fall within the ranges reported in the literature for sandy loam soils (6 t of limestone per ha per pH unit to raise soil pH to 6.5) (Rowell 1994). Furthermore, the relatively high CEC values for a sandy loam soil reported by New Brunswick (19-22 cmol/kg) are more consistent with a high lime requirement than CEC values reported by the NSDAM lab (12-14 cmol/kg). These results indicate the possibility that buffer capacity of the soils may be underestimated while lime requirement, and possibly even soil pH, is overestimated by the NSDAM lab.

One implication of the possible overestimation of lime requirement is, obviously, that there was an overapplication of lime to the experimental plots. Given that increase in soil pH between pH 4.5 and pH 7 is essentially linear, an overapplication of approximately 30% would increase soil pH by about 0.3 units above the target pH, or to pH 6.8 (McLean 1973). The observation in Year 4, of soil pH values of 6.8 or more in essentially all treatments but the Control and Low-Ash treatments, is consistent with the supposition of overliming. It should be noted that this supposition is based on limited sampling and analysis; i.e., the comparison of buffer lime requirements methods is based on only two samples. More importantly, even if there were a slight over-application of lime, this would have no effect on the essential lessons (listed below in 5.3.3) which may be drawn from the soil and crop liming response data.

Despite the fact that soil test information is often variable, being highly dependant on the quality and conformity of procedures (from sampling and analysis to interpretation and recommendations) soil testing remains the most practical way of characterizing soils as well as monitoring levels of nutrients (deficiencies, excesses, imbalances) and contaminants over time. It is generally recommended that soil testing for pH and lime requirement be done every 3 three years. In practice, many farmers soil test every year, particularly on soils intended for vegetables or other high-value crops, in order to determine fertilizer requirements. Because of the large influence of soil pH on ion activities and nutrient availability, levels of soil nutrients should be monitored before and after liming. Alkaline conditions and high soil ratios of Ca:Mg and Ca:K can reduce the availability of macronutrients (P, K, and Mg) as well as induce micronutrient deficiencies (B, Cu, Mn, Fe, and Zn). Levels of soil Mg and the ratio of Ca:Mg will also determine the choice of liming material. Thus, all of the standard (i.e., routinely determined) soil test parameters are important for soil liming. Recommended monitoring and analytical procedures to be used in a testing program for land application of CFB ash are presented in Table 5.1 (section 5.4.2).

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<sup>47</sup>soil pH of 4.1-4.3 instead of 4.7-4.9, and lime requirement of 13-19 t/ha instead of 18-24 t/ha.

**Final Research Report****5.3.3 Towards a Liming Protocol for CFB Ash**

Summarized below are 10 essential lessons learned from this study about soil and crop liming response to CFB ash. These lessons may be helpful in terms of improving the prediction of liming response to the ash on different soils, as well as enabling users to derive the most benefit from using this material as an agricultural liming agent. Further recommendations with respect to safety and minimizing metal loading in soils and crops are provided in section 5.4. It is hoped that the information provided below and in section 5.4 will contribute to the development of guidelines and standards for utilization of CFB ash as soil amendment.

1. When applied to soils on a chemically equivalent (calcium carbonate equivalent, or CCE) basis, CFB ash has an acid neutralizing capacity equivalent to that of Mosher dolomitic limestone. In other words, when amendment loading is adjusted for CCE, the ash is as effective a liming agent as agricultural limestone.
2. Crop response, in terms of both yield and quality, to CFB ash and Mosher dolomitic limestone is the same, indicating that the materials are equally effective in removing the main factor which limits crop yields on acid soils (i.e. soil acidity and the attendant low base saturation).
3. The ash is a good source of Ca to crops, however is generally depleted in Mg. Because of the high Ca to Mg ratio, the ash should not be applied to low Mg (<10%) soils. When soil Mg is low (below 10%), dolomitic lime should be used as a liming material to increase soil Mg to at least 12% before further applications of ash. Soil levels of Mg should be monitored following ash application, particularly on sandy soils of low cation exchange capacity (CEC).
4. Depending on the source, the ash contains significant amounts of boron and may therefore be used to supplement boron requirements in high B-requiring crops (i.e. rutabaga, alfalfa). In this study, CFB ash did not supply the entire B requirement of rutabaga.
5. Because soil pH adjustment is predictable and similar for liming materials of varying neutralizing value, so long as amendment loading is adjusted for calcium carbonate equivalence (CCE), variability of the ash with respect to neutralizing value is not a limitation to use of the material.
6. The ash is more reactive (i.e., fast acting) in soils than carbonate limestones, however, appears to have similar residual activity. Reactivity will be greater, and residual activity somewhat less, on sandy soils with low buffer capacity compared with more highly buffered soils. Residual activity of the ash is affected not only by characteristics of the



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- ash but also factors which lower the solubility of the material in the soil (i.e., high loading rates, complete neutralization of soil acidity, concentration of precipitating ions).
7. Hydrated ash has slightly lower neutralizing value than unhydrated material, and demonstrates a greater tendency to clump. Hydrated ash may be preferred as a liming material, however, because of the less caustic nature and improved dust control compared with the unhydrated material.
  8. Liming applications should always be based on soil test information. Additional soil testing should be conducted following ash application to monitor levels of nutrients and metals in the soil. Soil liming strategy will vary from one soil to another. As with any liming material, frequent light applications of ash are more effective on weakly buffered soils, whereas larger amounts may be applied less often on more strongly buffered soils. For acid soils with high lime requirement (8-10 t/ha/pH unit), applications should be spread over 1-2 years.
  9. While this study has demonstrated the low phytotoxicity of the ash, even at very high loading rates (53 t/ha), applications in excess of the soil lime requirement are not recommended. Risks associated with excessive application include high alkalinity, accelerated build-up of metals in soils, and increased potential for uptake of metals by crops. To avoid nutrient tie-ups in soils and crops, liming beyond pH 6.5 or above 75% Ca+Mg, should be avoided, particularly on sandy or weakly buffered soils.
  10. Soil test methods which are calibrated for local soil types and conditions should be used wherever possible. The suitability of the low soil buffer acidity Adams and Evans lime requirement test for Nova Scotia soils, which have variable amounts of buffer acidity, should be examined.

**5.4 Management Implications of Element Loading in Soils and Uptake by Crops**

The metal content of plant tissues and soils is discussed in detail in section 4.6. Summarized below are some of the implications of these results in the context of soil management and monitoring requirements, as well as standards and quality criteria for CFB ash, when the material is utilized as a soil amendment.

**5.4.1 Potentially Toxic Elements in Soils and Crops**

Soil levels of As, Ba, Cu, Pb, Sr, Cr, Tl, V, Hg and U were increased significantly by ash treatments, however none of the elements exceeded metal criteria for soils receiving waste materials (Appendix 4). The use of long-season vegetable crops, a poorly buffered (i.e. low metal-binding capacity) soil, and high amendment loading rates was considered to represent a “worst case scenario” with respect to metal uptake by the crops. With the exception of Tl, no plant uptake of any metals was detected, even at the highest rate of ash loading (greater than 50

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t/ha). While leaching was not measured in this study, the data for net change in soil metals indicated that there were no significant losses of soil metals during the course of the growing season. On the basis of these results, metal loading in soils and crops is not considered to be a limitation to use of the material as an agricultural liming agent. It is emphasized that this conclusion is based on relatively short-term (three-year) loading on one soil type with one particular source of ash. Thus, there is a need to collect soil metal data across a range of soil types (for example, at farms or other locations where ash is being applied) which would allow a better prediction of metal loading on a given soil type, as well as number of years to reach maximum loading, based on a given metal content of the ash and ash application rate.

While metal loading from CFB ash may not prohibit agricultural use, the study does identify a number of potentially toxic elements in the ash (As, B, Be, Cd, Hg, Mo, Pb, Se, Tl, V) whose levels need to be closely monitored if the material is to be used in food production and/or as a liming agent. Potential concerns with these elements range from phytotoxicity (B), immediate or eventual hazard to human and animal health via the food chain (As, Mo, Se, Cd, Pb, Tl, Hg), as well as possible respiratory hazard to unprotected or inadequately protected applicators (Be, Cd, Ni, Pb, V). The ash utilized in this study consisted of baghouse material (fly ash) captured from combustion of Devco Prince coal. While the ash contains significant amounts of As, Ba, Fe, Mn, Pb, Sr and Zn, it is typical of ash from high sulphur coal-fired fluidized bed combustors. As noted in Appendix 6, higher or lower concentrations of a number of elements in the ash are possible when a different fuel source is utilized. For example, the 30% petroleum coke/70% Prince coal fly ash blend tested on beans and sunflowers in 1999 contained higher levels of As, B, Cd, Cu, Pb, Mo, Ni, Se, Tl, U, V, Zn and Hg than the main source of ash (1997-98 Prince coal fly ash) utilized in this study (Appendix 3). The relationship between fuel source and other variables and ash composition, both in terms of metal content and neutralizing value of the ash, has important implications for use of the material in agriculture and as a liming agent.

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### 5.4.2 Requirements for Management, Monitoring and Quality Standards

While there may be a higher level of management (i.e., increased safety precautions and greater requirements for testing and monitoring) associated with the ash compared with conventional liming materials, it is emphasized that the material is not unlike other agricultural soil amendments in this regard. As noted previously, there are, in addition to CFB ash, a number of materials used to raise soil pH and/or supply Ca which are Mg-depleted (i.e., quick lime, hydrated lime, calcitic lime, and gypsum). If not used properly, any one of these materials can induce Mg deficiencies in soils and crops. With respect to metals, both compost and sewage sludge have established a precedent for determining input levels of metals prior to waste application, as well as monitoring for compliance with metal criteria for soils and waste materials.

With the aim of minimizing risk by applying greater control and expertise to ash handling/land application procedures, some power utilities in the United States have adopted a third-party approach to hauling and spreading the ash. In other words, rather than leaving the hauling/spreading up to the farmer or any number of small trucking/lime spreading contractors, an independent hauler is contracted by the utility to both transport and apply the material. This approach offers advantages in terms of both risk avoidance for the utility as well as convenience to the farmer. An additional service which could be included in the cost/ton is taking any soil samples which may be required in order to determine appropriate application rates. Obviously, the feasibility of this approach depends in part on whether or not the market accepts a reduced competitive advantage for the ash by increasing costs per ton.

There are several aspects to determining safe and appropriate ash application rates. Some of these are addressed by soil testing (lime requirement, soil Mg levels, and pre-amendment soil metals) as well as analyses of the ash (CCE, metal content and other ash quality parameters). Other aspects could be addressed by a guideline for land application of CFB ash, similar to that developed by the USDA<sup>48</sup>. For example, the USDA manual provides a flow chart or decision tool to assist users in determining when land application is appropriate or safe, points at which monitoring or analysis is required, as well as steps involved in determining metal loading with different ash application rates.

A list of recommended monitoring and analytical procedures, as might be included in a land application guideline or monitoring protocol for agricultural use, is provided in Table 5.1 (below). Some of the analyses are routinely performed (i.e., standard agronomic practice), whereas others are more specific for use of liming materials from industrial processes or other by-products to which metal concerns apply. The standard soil analysis, as well as the limestone analysis, are available in Nova Scotia and other provinces at relatively low cost (- \$10-15/sample) from soil test labs associated with provincial agriculture departments. These tests are also available from private labs (i.e., A&L, Brookside) which specialize in agricultural testing.

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<sup>48</sup>Stout et al 1988. Manual for Applying Fluidized Bed Combustion Residue to Agricultural Lands. United States Department of Agriculture. Agricultural Research service, ARS-74, 15 pp.

**Final Research Report****Table 5.1 Recommended monitoring and analytical procedures to be used in a testing program for land application of CFB ash.**

<b>Monitoring</b>	<b>Analysis</b>	<b>When conducted</b>
Determining the agronomic justification for liming (soil pH), acceptability of cation ratios (soil Mg>10%), and soil lime requirement.	Standard soil analysis <sup>a</sup>	Pre-application; generally every 2-3 years.
Establishing pre-amendment levels of metals in soils at the land application site.	Available metals in soils <sup>b</sup>	Pre-application
Establishing liming efficacy of the ash and determining amendment loading.	Limestone analysis <sup>c</sup>	Pre-application
Determining the acceptability of ash for land application (compliance with metal criteria), input levels of metals prior to application.	Total metals in ash <sup>d</sup>	Pre-application
Monitoring changes in soil pH, organic content, nutrient status (deficiencies, excesses, imbalances), post-application.	Standard soil analysis <sup>a</sup>	1 year following application; as required thereafter.
Monitoring changes in soil metals, post-application.	Available metals in soils <sup>b</sup>	Every 3-10 years, depending on frequency and rate of ash application.
Monitoring nutrient content of plant tissues, post application.	Standard plant tissue or forage analysis <sup>e</sup>	As required.

<sup>a</sup>organic matter, soil pH, buffer pH, lime requirement, P, K, Ca, Mg, S, Zn, Mn, Fe, Cu, B, CEC, % base sat

<sup>b</sup>available metals =HNO<sub>3</sub>-extractable; <sup>d</sup>total metals =HClO<sub>4</sub>:HNO<sub>3</sub>:HF-extractable; both are multi-element scans

<sup>e</sup>% dry matter, solubility, CCE, %Ca, %Mg <sup>e</sup>macro- and micronutrients; forage quality parameters

Metals analyses are also readily available from both private and publically funded labs, however, costs of the analyses are considerably higher. Metal scans of 20-25 elements usually cost between \$75-\$150/sample, depending on the lab, elements included in the analysis, etc. The available metals and total metals digests represent increasingly stronger extraction procedures, and therefore remove fractions of metals of decreasing biological availability. The available metals digest (USEPA 3050) provides a measure of total concentrations that are exchangeable or adsorbed by soil components but excludes silicate-bound fractions (Loro 1997). Thus, this test is the most useful in terms of predicting bioavailability and mobility of metals in soils. It is also the relevant test in terms of regulatory guidelines or soil metal criteria. Alternatively, by

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extracting a higher proportion of silicate or structurally bound and oxide-occluded metals, the total metals analysis (USEPA method 3052) provides a more meaningful characterization of the total concentrations present in wastes and other materials applied to soils. When requesting a metals analysis, it is therefore important to specify both the sample matrix (soil, sediment, ash, etc.) and required analysis (total vs available metals digest) to ensure that results are obtained for the relevant metal fraction.

To ensure that minimum standards for safety and efficacy are met in the ash being made available for agricultural use, a set of ash quality criteria or standards needs to be developed. Quality standards for the ash should include parameters relating to liming efficacy, such as CCE, CaO content, Ca and Mg content, moisture content, and solubility, as well as content of metals. The BNQ standard *Liming Materials from Industrial Processes*, while not specifically designed for CFB ash, is a detailed and useful reference for this purpose. The ash utilized in this study appeared to meet or exceed all of the BNQ standards that would apply to this material. Until specific standards for CFB ash are developed, a minimum CCE > 50%, to provide liming efficacy and prevent excessive loading, is recommended. When marketed within Canada as a liming agent, CFB ash is subject to regulation under the federal Fertilizers Act and Regulations, and therefore must comply with the metal criteria for fertilizers and supplements specified in the Act (see CFIA metal criteria in Appendix 4). As noted below, these criteria may not be entirely appropriate for alkaline inorganic materials containing a wider range but lower levels of metals than sewage sludge. Therefore, any standards writing initiative should include an assessment of the applicability of existing metal criteria to CFB ash. Additional short-term plant growth experiments (i.e., bioassay) may be required to assess phytotoxicity or bioavailability of specific elements in the ash which are not captured in existing metal criteria (e.g., Tl, V). Because the ash contains varying levels of metals which are toxic by inhalation, such as Be, Cd, Ni, Pb, and V, personal respiratory protection<sup>49</sup> is recommended when handling and applying the ash. There may be a need for further assessment of the potential respiratory hazards to inadequately protected users.

Finally, a longer term challenge to be addressed is the present lack of guidelines, either federal or provincial, specific to land application of CFB ash in Canada. It is therefore recommended that guidelines, similar to those prepared by the USDA, be developed and made available to applicators and users of the ash to promote safe and efficient use of the material. Differences between Canada and the United States require that the guideline be adapted to reflect Canadian environmental and agricultural legislation and policy. There are a number of overlapping federal and provincial regulations that provide metal criteria for soils, waste materials, as well as fertilizers and supplements sold in Canada. None of these regulations, however, adequately address all of the unique challenges and opportunities presented by the utilization of an alkaline, inorganic by-product such as CFB ash. For example, existing federal and provincial metal criteria were developed largely to address heavy metal concerns with land application of sewage sludge, and may not be entirely appropriate for CFB ash. Not only does CFB ash contain low levels of most of the metals of concern in sewage sludge (Cd, Cr, Cu, Hg, Ni, and Zn), it may be

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<sup>49</sup> for example, half-face respirator with HEPA cartridge for toxic particulates.

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enriched in other elements (As, Mo, Se, V, Be, Tl) for which metal criteria are lacking or inconsistently applied, and which are less commonly reported in the literature as being environmentally important. Thus, the importance of increases in these elements in soils or crops following ash amendment may be overlooked. The development of reliable metals criteria (i.e., which, when used to determine amendment loading rates, hold up under “worst case scenarios”) must account for not only differences in the solubility of metals but also differences in solubility under varying soil conditions (soil pH, redox status, etc). For example, heavy metals exist in soils primarily as metal cations, however, several of the elements of interest in CFB ash (As, Mo, Se, B, Cr, V) are present as oxygenated anions, or oxyanions. While the solubility and mobility of the heavy metal cations decreases with increasing soil pH, the reverse tends to be true with the oxyanions. Thus, the alkaline soil conditions following application of CFB ash will decrease the solubility of most metal cations but may actually increase solubility of elements such as As, Mo, Se, V and Cr. The development of appropriate metal criteria for materials such as CFB ash must therefore be based on a solid understanding and knowledge of the specific elements present in the ash, as well as the factors which determine their solubility (and hence, mobility and bio-availability) under the alkaline conditions existing in ash amended soils.

**Final Research Report****6. CONCLUSION AND RECOMMENDATIONS**

After three years of field testing, Point Aconi CFB ash was found to be an effective liming agent for vegetable crops (cabbage and rutabaga) and mixed forage, with no significant adverse effects on crop quality or excessive soil loading of metals. Two years of testing the ash on turfgrass indicates that the material may also be used safely (i.e., without burning) as a fast-acting limestone substitute on turfs. Crop yields were similar in ash amended and limestone amended treatments, and maximum loading treatments (53 t/ha) indicated no phytotoxicity in vegetable crops at any growth stage. The ash was superior to dolomitic limestone as a source of Ca to crops. There was no evidence of enhanced S uptake, however, ash treatments did alleviate severe B deficiency symptoms in high B-requiring crops (rutabaga).

In this study, no single factor was identified that would prohibit use of CFB ash as an agricultural soil amendment and liming agent. It is therefore concluded that the material is an acceptable liming agent for both food crops and non-food crops. It is recognized, however, that there are a number of important issues associated with agricultural utilization that need to be addressed in order to derive the greatest amount of benefit and minimize potential risks. First of all, there is a potential for element imbalances and toxicities in soils and crops as well as applicator health concerns, that may require greater management and monitoring in using the material compared with agricultural (dolomitic or calcitic) limestones. Secondly, trace element content and other qualities which determine suitability for agricultural use can vary significantly with fuel source and other variables in the combustion process. Thirdly, in Canada there is currently a lack of guidelines and criteria specific to CFB ash that would promote the safe and efficient use of this material for use in agriculture and as a soil amendment.

One important finding of the study is that soil pH response is predictable and similar for liming materials of varying neutralizing value, so long as amendment loading is adjusted for the calcium carbonate equivalence (CCE) of the material. Variability of the ash with respect to CCE, or neutralizing value, is therefore not considered to be a limitation in terms of use as a liming agent. Furthermore, it is proposed that both the potential for element imbalances and toxicities in soils and crops as well as applicator health concerns, can be addressed through the development of coherent ash quality standards as well as criteria and guidelines for land application.

The following recommendations are offered as possible steps towards addressing some of the outstanding ash utilization issues identified in this report. Some of the recommendations are of a practical nature and may therefore apply immediately in a land application situation. All of the recommendations listed below are intended to contribute to the development of standards and guidelines for the utilization of CFB ash as a soil amendment in Canada.

**Final Research Report****RECOMMENDATIONS:**

1. It is recommended that Point Aconi CFB ash be made available for use as a liming agent on both food crops and non-food crops.
2. Until more detailed ash quality standards are developed, a minimum standard of calcium carbonate equivalence (CCE) > 50%, to provide liming efficacy and prevent excessive loading, is recommended. As a liming agent sold within Canada, the ash must comply with metal criteria specified for fertilizers and supplements under the Fertilizers Act and Regulations (see CFIA metal criteria in Appendix 4 of this report).
3. To prevent Ca-induced Mg deficiency in soils and crops, CFB ash should only be used on soils that contain adequate (>10%) Mg. When soil Mg base saturation is low (below 10%), dolomitic lime should be used as a liming material to increase soil Mg to at least 12% before further applications of ash. Soil levels of Mg should be monitored following ash application, particularly on sandy soils of low cation exchange capacity (CEC).
4. Liming applications should always be based on soil test information. Additional soil testing should be conducted following ash application to monitor levels of nutrients and metals in the soil.
5. While this study has demonstrated the low phytotoxicity of the ash, even at very high loading rates (53 t/ha), applications in excess of the soil lime requirement are not recommended. Risks associated with excessive application include high alkalinity, accelerated build-up of metals in soils, and increased potential for uptake of metals by crops. To avoid nutrient tie-ups in soils and crops, liming beyond pH 6.5 or above 75% Ca+Mg, should be avoided, particularly on sandy or weakly buffered soils.
6. Soil test methods which are calibrated for local soil types and conditions should be used wherever possible. The suitability of the low soil buffer acidity Adams and Evans lime requirement test<sup>50</sup> for Nova Scotia soils, which have variable amounts of buffer acidity, should be examined.
7. For reasons of safety and improved dust control, hydrated ash is recommended over unhydrated ash as a liming material. Hydrated ash was easily applied using farm-scale limestone spreading equipment, however the tendency of the material to clump interfered with use of a hand-held Gandhi drop spreader. Spreader trials may be required to determine the best method of application to turfs.

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<sup>50</sup>method currently used by Nova Scotia Department of Agriculture and Marketing soil test lab.



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8. Personal respiratory protection (i.e., half-face respirator; HEPA cartridge for toxic particulates) is recommended when handling and applying the ash. Further assessment of potential respiratory hazards to inadequately protected users may be required.
9. Guidelines for Land Application of CFB Ash, similar to those prepared by USDA but adapted to reflect Canadian environmental standards and legislation, need to be developed and made available to applicators and users of the ash to promote safe and efficient use of the material. As a minimum, it is recommended that the guideline include ash safety and efficacy criteria (metal content, CCE, etc.), ash handling and application procedures, agronomic considerations, and testing and monitoring protocols for ash, soils and crops.
10. Ash quality standards need to be developed for agricultural use. Quality standards should include parameters relating to liming efficacy as well as metal content. Existing federal and provincial metal criteria may not be appropriate for alkaline inorganic materials, and therefore any standards writing initiative should include an assessment of the applicability of existing criteria to CFB ash.
11. With the aim of applying greater control and expertise to ash handling/land application procedures, the feasibility of sole-sourcing/sub-contracting both hauling and spreading of the ash should be explored.
12. A soil metal data base should be developed in order to allow a better prediction of element loading over time on different soil types, based on a given element content of the ash and ash application rate. Soil data from farms or other locations where the ash is being applied, and the corresponding ash analyses, could be utilized for this purpose.

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**Final Research Report****APPENDIX 1 INITIAL SOIL ANALYSIS REPORT****Results of soil analyses for the Point Edward experimental site<sup>1</sup>.**

Organic matter %	Soil pH	Buffer pH	Phosphate		Potash		Calcium		Magnesium		Sulfur S kg/ha
			P <sub>2</sub> O <sub>5</sub> kg/ha	L-	K <sub>2</sub> O <sub>5</sub> kg/ha	L	Ca kg/ha	L-	Mg kg/ha	L	
3.9	4.9	6.5	32	L-	116	L	240	L-	81	L	67
Lime Req	CEC		Iron		Manganese		Copper		Zinc		Boron
t/ha	meq/100 g		Fe ppm		Mn ppm		Cu ppm		Zn ppm		B ppm
21	13.3		246		12		0.67		1.7		0.31

<sup>1</sup>Based on soil samples taken June 25 prior to establishing the experiments; each value is the average of 4 replicates of three trials). Analyses performed by the NSDAM soil test lab, Truro, NS.

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**APPENDIX 2 LABORATORY METHODS**

**Limestone Analysis**

The methods described below for Limestone Analysis have been provided by the Nova Scotia Department of Agriculture and Marketing, Plant Industry Branch, Harlow Institute, NSAC, Truro, NS.

Solubility

Reagent

1. Concentrated HCl
2. Concentrated HNO<sub>3</sub>

Procedure:

1. Weigh approximately 2.0 g of oven-dried sample into 250 ml pyrex beaker. Record weight to four decimal places (W1)
2. Add 25 ml of distilled water and swirl.
3. Add 10 ml of concentrated HCl plus a few drops of concentrated HNO<sub>3</sub>.
4. Boil for 10 minutes and cool.
5. Filter into 1 L volumetric, using Whatman No. 5 paper.
6. Wash with deionized water.
7. Make filtrate to 1 L and save for calcium and magnesium analysis.
8. Place residue and filter paper in a tarred porcelain crucible (W2) and dry at 105°C for 4 hours.
9. Ash in furnace at 650°C. Cool and weigh (W3).

Calculation:

$$\% \text{ Soluble} = 100\% - [(W3 - W2) / W1] \times 100$$

Calcium and Magnesium

Procedure:

1. Pipette 5 ml of the one L filter from “% Soluble” analysis into a 25 ml volumetric and make to volume.
2. Analyse by ICAP according to manufacturer’s instructions.

Calculation:

$$\% \text{Ca (or \%Mg)} = \text{ppm Ca (Mg) from ICAP} \times (1000 / W1) \times (25 / 5) \times 10^{-4}$$

Neutralizing Value

Neutralizing value of a liming material is defined as the calcium carbonate equivalent of the material and is calculated as the atomic weight equivalent to CaCO<sub>3</sub>. Pure calcium carbonate has an atomic weight of 100 and, therefore, a neutralizing value of 100.

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Examples:

Dolomite

$$NV = (\%Ca \times (mw \text{ CaCO}_3 / aw \text{ Ca}) + [\%Mg \times (mw \text{ of MgCO}_3 / aw \text{ Mg}) \times (mw \text{ CaCO}_3 / mw \text{ MgCO}_3)])$$
$$NV = (\% \text{ Ca} \times 100/40) + [\%Mg \times (84.3/24.3) \times (100/84.3)]$$
**pH**

Principle:

This method is used to determine the pH of a soil in 1:1 soil:water suspension. pH is defined as the negative logarithm, to the base 10, of the hydrogen ion concentration. Since the pH is logarithmic, the hydrogen ion concentration in solution increases 10 times when the pH is lowered one unit.

Scope:

This method is applicable to all inorganic soils with pH between 3.5 and 9.0. In the case of high organic, or muck soils, it is necessary to increase the ratio of water to soil to a point where at least a slurry is obtained.

Apparatus:

1. No. 10 (2mm opening) stainless steel sieve.
2. 10 cm<sup>3</sup> stainless steel or plastic scoop.
3. Steel rod and glass rods.
4. Waxed paper cups.
5. pH meter with reproducibility of at least 0.05 units.
6. 20 ml dispenser.

Reagents:

1. pH 7.0 Buffer Sol'n - Dissolve 3.3910 g citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>) and 23.3844 g disodium phosphate (Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O) in re-distilled water and make 1 litre, or use a commercially available buffer solution.
2. pH 4.0 Buffer Sol'n - Dissolve 11.8060 g citric acid and 10.9468 g disodium phosphate in re-distilled water and make to 1 litre, or use a commercially available buffer solution.

Procedure:

1. Mix soil sample well, using a scoopula.
2. Dip a 20 ml stainless steel scoop into the centre of the soil sample deep enough to fill the scoop above the rim.
3. Strike the handle of the scoop 3 times with a steel rod.
4. Level the soil in the scoop with ONE pass of the steel rod.
5. Place the 20 ml of soil into a 5 oz disposable sample cup.
6. Add 20 ml of distilled water using the dispenser. Up to two batches of 48 samples each are done simultaneously along with the quality control.
7. Stir thoroughly and intermittently for 30 minutes and let stand for an additional 30 minutes. Read pH and record to ONE decimal place.

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8. The electrodes must be gently placed in the soil solution so as not to damage the ceramic membrane of the reference electrode. The reference electrode (containing 4M KCl) should be mounted 1/4 inch higher than the pH electrode. This allows the pH electrode to be placed in the soil suspension and the reference electrode in the supernatant.

**Quality Control:**

1. A composite sample is run with every batch of samples. Results of the composite are put on the composite sheet provided.
2. pH meter is calibrated every day using pH buffers 4 and 7. An efficiency of at least 95% is required before accepting the calibration and proceeding.
3. Electrodes are cleaned every Friday.
4. Care must be exercised to prevent scratching of the glass electrode, since a scratch electrode will give erratic results. Likewise, a reference electrode with restricted flow of filling solution will cause unstable readings.
5. Pepsin is used to regenerate electrodes. Make sure at the end of analysis that the temperature probe is not put into the pepsin with the electrodes.

**Lime Requirement (Adams-Evans Buffer Method)****Principle**

The Adams-Evans lime requirement method is based on separate measures of soil pH determined in water and buffer. Soil pH is used as a measure of acid saturation of the soil while buffer pH is used as a measure of acid saturation of the soil while buffer pH is used as a measure of total soil acids. (For a full description of the method principle, see "Handbook on Reference Methods for Soil Analysis", 1992, Soil and Plant Analysis Council.)

Lime requirement of an acid soil is defined as the amount of lime or other base which, when incorporated into the soil to a given depth, will increase the pH of the soil to a selected level.

**Scope**

This method is applicable to soils with exchangeable acidity of less than 8 meq/100g and pH less than 6.5. Sensitivity is within 0.5 t/ha. The target pH for the calculations listed in this procedure is 6.5.

**Reagents**

1. Para-nitrophenol - technical grade, 800 g
2. Boric acid - reagent grade, 600 g
3. Potassium hydroxide - reagent grade, 420 g
4. Potassium chloride - reagent grade, 2960 g

**Buffer Solution - preparation**

1. Weigh out the above quantities of reagents.
2. Heat four, 4-L beakers, each containing 3 L of distilled water to steaming on a hot plate.
3. Dissolve the 420 g of KOH in 700 ml of distilled water in a one L beaker.
4. Add 10 L of distilled water to a 40 L carboy.
5. Dissolve the 2960 g of KCl in the 10 L of distilled water in the carboy.
6. Dissolve the 600 g of boric acid equally between two of the beakers of hot distilled water.



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7. Dissolve the 800 g of p-nitrophenol equally between two of the beakers of hot distilled water.
8. Add the contents of the one L beaker containing KOH to the carboy. Mix by rotating the carboy.
9. Add the contents of the two, 4 L beakers containing the boric acid to the carboy and mix.
10. Add the contents of the two, 4 L beakers containing the para-nitrophenol to the carboy. Handle the beakers carefully as they are still hot. Mix entire solution.
11. Make to slightly less than 40 L and allow to cool.
12. Make to 40 L with distilled water.
13. Adjust to pH 8.00 with either KOH or HCl. Buffer pH must be 8.00 +/-0.05.
14. Check pH of buffer solution weekly and adjust if necessary.

#### Procedure

1. Add 20 ml of the buffer solution to the suspension used to determine pH.
2. Stir THOROUGHLY using a glass rod.
3. Let stand for a minimum of 10 minutes. Stir intermittently and just before reading buffer pH.
4. Standardize the pH meter using 7.00 and 4.00 buffers.
5. Measure the pH of the soil-buffer suspension. Record to two decimals on report sheets.
6. Rinse the electrodes off after each reading.

#### Calculation

$$\text{Lime Requirement (t/ha)} = (((-0.00011 \times \text{BpH}) + 0.00088) / X) \times (X - 0.25) \times 18700$$

$$\text{where } X = (5.55 - \text{SQRT}(30.80 - (9.08 \times (7.79 - \text{pH})))) / 4.54$$

#### Quality Control

1. Composite sample from pH procedure is carried over to lime requirement. Buffered reading is taken and results are put on the composite sheet.
2. Buffer pH is determined and adjusted if it is outside 8.00 +/-0.05.
3. See pH Method for care and precautions relative to the electrodes.

**Final Research Report****Method Summary**

The method summaries for the procedures listed below have been provided by Philip Services Corp. as the procedures used for all samples submitted to them for analysis. The summaries are presented in the order listed below.

Mercury in Biota Materials

Trace Metals in Terrestrial Biota Samples

Polychlorinated Biphenyls and Organochlorine Pesticides in Soil/Sediment

Polynuclear Aromatic Hydrocarbons in Soils and Sediments

Mercury in Soils and Sediments

Total Trace Metals in Soils and Sediments

Available Trace Metals in Soils and Sediments

**Title: Mercury in Biota Materials**

**SOP #:** 3410

**Reference:** USEPA Method 245.6

**Effective Date:** January, 1994 **Revision Date:** July, 1997

**1. Scope and Application**

This method is designed for the digestion and analysis of total mercury in biota samples as referenced in EPA Method 245.6. The LOQ for this procedure is 0.01 mg/kg wet weight based upon an initial biota as received weight of 2.0 grams.

**2. Summary of Method**

Approximately 2 - 2.5 grams of homogenized biota sample is accurately weighted into pre-cleaned 35 ml polypropylene centrifuge tubes. Sulphuric acid (5 ml) is added to the samples and allowed to stand overnight. Alternatively, a 10 ml aliquot of the digest prepared for total metals analysis may be pipetted into pre-cleaned 35 ml polypropylene centrifuge tubes and acidified with 5 ml of sulphuric acid (Note: All relevant QC samples for the metals digest must be analysed by the same procedure). The samples are then digested for two hours at 60°C in a convection oven. After cooling, two ml of nitric acid is added to the samples, which are then digested for another 2 hours at 60°C. After cooling, an excess of potassium permanganate is added to ensure that all samples remain in an oxidized state. All prepared solutions are analysed for mercury using a LDC Analytical UV Detector (Fixed Wavelength Mercury Monitor). The solutions are transferred to a sparging vessel and the excess potassium permanganate is destroyed with the addition of hydroxylamine hydrochloride. The mercury present in the samples is then reduced to its atomic state by the addition of stannous chloride and sparged. The instrument signal (absorbance) is directly proportional to the concentration of mercury in the sample. Digested standards are used for daily calibration, and additional standards are analysed in order to monitor instrumental drift.

**Final Research Report****3. Quality Assurance**

Reagent blanks, certified reference materials, and method spikes are prepared and analysed in the same manner as mentioned above for the samples. A minimum of one reagent blank, one duplicate, one spike, and one certified reference material (DORM-1 or DORM-2) is analysed for each set of samples. A minimum QC effort of 10% should be maintained.

**Title: Trace Metals in Terrestrial Biota Samples**

**SOP #:** 3010/4081

**Reference:** USEPA Method 200.8

**Effective Date:** August, 1995

**Revision Date:** July, 1997

**1. Scope and Application**

This method is designed for the digestion and analysis of trace metals in terrestrial biota samples. Analytes and LOQs (dry weight basis) are as listed below:

Analyte	LOQ (mg/kg)	Analyte	LOQ (mg/kg)
Aluminum	0.5	Manganese	0.1
Antimony	0.1	Molybdenum	0.1
Arsenic	0.1	Nickel	0.1
Barium	0.25	Selenium	0.1
Beryllium	0.25	Silver	0.025
Boron	0.25	Strontium	0.25
Cadmium	0.02	Thallium	0.01
Chromium	0.1	Tin	0.1
Cobalt	0.05	Uranium	0.01
Copper	0.1	Vanadium	0.1
Iron	1	Zinc	0.1
Lead	0.025		

**2. Summary of Method**

A 0.25 gram portion of the cleaned and air dried biota sample is accurately weighed into pre-cleaned 50 ml polypropylene centrifuge tubes. Approximately 2 ml of high purity HNO<sub>3</sub> is added to each sample, and allowed to stand overnight. The samples are then slowly warmed until the reaction subsides, and then heated in a boiling water bath until the acid volume is reduced to less than 1 ml. Another 2 ml of HNO<sub>3</sub> is added and the samples are heated again until the acid volume is less than 1 ml. Approximately 1 ml additional HNO<sub>3</sub> plus 10 ml of distilled, deionized water is then added to the samples which are gently heated for a period of twenty minutes. After cooling, the samples are diluted to a final volume of 25 ml. The samples are then diluted ten fold and analysed directly using a Sciex/Perkin-Elmer Elan 5000 ICP-MS in accordance to EPA Method 200.8.

**Final Research Report****3. Quality Assurance**

Reagent blanks, certified reference material, and method spikes are prepared and analysed in the exact same fashion as mention above for the samples. A minium of one reagent blank and two different biota reference material (usually NBS 1571 and NBS 1575) are prepared and analysed with every 20 samples. Spiking of samples at a level appropriate to the matrix is performed at a frequency of 10%. Duplicate digestion and analysis of samples is also performed at a frequence of 10%.

**Title: Polychlorinated Biphenyls and Organochlorine Pesticides in Soil/Sediment****SOP #:** 8020**Reference:** USEPA Method 8080 and 8081**Effective Date:** January 17, 1996**Revision Date:** July, 1997**1. Scope and Application**

This method is applicable to the determination of polychlorinated biphenyls (PCBs) and organochlorine (OC) pesticides in soil and sediment. The reporting limit of PCBs in soil is 0.050 mg/kg and 0.010 mg/kg for sediments. The reporting limit of OC pesticides ranges from 0.002 to 0.02 mg/kg. The following compounds can be determined using this method:

Polychlorinated Biphenyls: Aroclors 1016, 1242, 1248, 1254, 1260

Organochlorine Pesticides

Aldrin

Alpha-BHC; Beta BHC; Delta-BHC; Gamma-BHC (Lindane)

Chlordane

o, p-DDE; p,p-DDE

o, p-DDD; p,p-DDD

o, p-DDT, p,p-DDT

Dieldrin

Endosulphan I; Endosulphan II; Endosulphan Sulphate

Endrin; Endrin Aldehyde; Endrin Ketone

Hexachlorobenzene

Heptachlor, Heptachlor Epoxide

Methoxychlor

Mirex

Toxaphrene

**2. Summary of Method**

Ten gram samples of soil or sediment are extracted by shaking for 2 hurs with 50 ml of acetone/hexane on a paint shaker. A portion of the extract is concentrated and cleaned up on a Florisil column. The extract is then concentrated by nitrogen evaporation and exchanged into isooctane. The extracts are analysed on a gas chromatograph equipped with capillary columns and dual electron capture dectors.

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The GC system is calibrated regularly with PCB/OC standards of known concentration. The areas of the individual peaks are integrated and automatic data analysis routines within the instrument software are used to prepare the calibration curves. The day-to-day stability of the calibration is confirmed by analyzing calibration check solutions with each batch of samples. The components in the samples are identified using the retention time criteria obtained on two GC columns (with different phases). After being detected, the individual peaks are then integrated and quantified. Total PCBs are quantified by comparing to the nearest Aroclor or mix of Aroclors.

**3. Quality Assurance**

In the case of sediments, two National Research Council reference sediments (HS-1 and HS-2) are extracted and analysed with each batch of samples. For soil samples, sodium sulphate is spiked twice at one level with known concentrations of PCB. A quality control sample, PS-97, is also available for the analysis of PCBs, to determine accuracy. The results of these evaluations are provided with the sample results.

**Final Research Report****Title: Polynuclear Aromatic Hydrocarbons in Soils and Sediments**

SOP #: 7010

Reference: USEPA Method 8270A

Effective Date: January 17, 1996

Revision Date: July, 1997

**1. Scope and Application**

This method is applicable to the determination of polynuclear aromatic hydrocarbons (PAHs) in soils and sediments with a reporting limit of 0.01 mg/kg. The following compounds are routinely determined:

Analyte	Analyte
Naphthalene	Pyrene
1-Methylnaphthalene	Benz[ <i>a</i> ]anthracene
2-Methylnaphthalene	Chrysene
1-Chloronaphthalene	Benzo[ <i>b</i> ]fluoranthene
2-Chloronaphthalene	Benzo[ <i>k</i> ]fuoranthene
Acenaphthylene	Benzo[ <i>a</i> ]pyrene
Acenaphthene	Indeno[ <i>1,2,3-cd</i> ]pyrene
Fluorene	Dibenz[ <i>a,h</i> ]anthracene
Phenanthrene	Benzo[ <i>ghi</i> ]perylene
Anthracene	Fluoranthene

**2. Summary of Method**

A 10 gram portion of wet soil is weighed out and spiked with 4 deuterated surrogate PAH compounds (these compounds represent a range of volatilities and are used to monitor the efficiency of the sample preparation steps). The sample is mixed with sodium sulphate until it becomes free flowing and is then extracted for two hours by vigorous shaking with 75%/25% (v/v) n-pentane/methylene chloride. If required, an aliquot of the extract is removed and interfering compounds are eliminated using a silica gel column clean-up procedure. The extract is then solvent exchanged into isooctane and analysed by gas chromatography/mass spectrometry (GC/MS) using selected ion monitoring mode.

The GC/MS system is calibrated at least once per week with PAH standards of known concentration. The area of the individual peaks are integrated and automatic data analysis routines within the instrument software are used to store the mass spectra of the various peaks and to prepare the calibration curves. Calibration accuracy is verified by analysing an independent reference standard. The day-to-day stability of the calibration is confirmed by analysing calibration check solutions with each batch of samples. The components in the samples are identified using retention time criteria and qualifier ion ratios. After being detected, the individual peaks are integrated and quantified. The wet weight concentrations are converted to a dry weight basis using the moisture content of the sample obtained by gravimetric analysis.

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**3. Quality Assurance**

A National Research Council reference sediment (HS-6), containing 20% added moisture, is extracted and analysed with each batch of samples. Process spikes, method blanks and duplicate samples are also prepared and analysed. The results of these evaluations, along with the deuterated surrogate recoveries, are provided with the sample results.

**Title: Mercury in Soils and Sediments**

**SOP #:** 3410

**Reference:** USEPA Method 245.5

**Effective Date:** January, 1994 **Revision Date:** July, 1997

**1. Scope and Application**

This method is designed for the digestion and analysis of total mercury in soil and sediment samples referenced in EPA Method 245.5. The LOQ for this procedure is 0.01 mg/kg based upon an initial soil dry weight of 0.3 grams.

**2. Summary of Method**

Approximately 0.30 grams of air dried and sieved sample is accurately weighed into 80 ml glass tubes. Sulphuric acid (5 ml) and two ml of nitric acid is added to the samples. The samples are then digested for 2 hours at 60°C in a convection oven. After cooling, an excess of potassium permanganate is added to ensure that all samples remain in an oxidized state. All prepared solutions are analysed for mercury by CVAAS with a LDC Analytical UV Detector (Fixed Wavelength Mercury Monitor). The solutions are transferred to a sparging vessel and the excess potassium permanganate is destroyed with the addition of hydroxylamine hydrochloride. The mercury present in the samples is then reduced to its atomic state by the addition of stannous chloride and sparged. The instrument signal (absorbance) is directly proportional to the concentration of mercury in the sample. Digested standards are used for daily calibration, and additional standards are analysed in order to monitor instrumental drift.

**3. Quality Assurance**

Reagent blanks, certified reference materials, and method spikes are prepared and analysed in the same manner as mentioned above for the samples. A minimum of one reagent blank, one duplicate, one spike and one certified reference material (MESS-1) is analysed for each set of samples. A total QC effort of 10% should be maintained.

**Final Research Report****Title: Total Trace Metals in Soils and Sediments**

SOP #: #3010/#4079

Reference: USEPA Method 3052 and Method 200.8

Effective Date: August, 1995

Revision Date: July, 1997

**1. Scope and Application**

This method is designed for the digestion and analysis of total trace metals in soil and sediment samples. Analytes and their routine LOQs are listed below:

Analyte	LOQ (mg/kg)	Analyte	LOQ (mg/kg)
Aluminum	10	Manganese	2
Antimony	2	Molybdenum	2
Arsenic	2	Nickel	2
Barium	5	Selenium	2
Beryllium	5	Silver	n/a
Boron	n/a	Strontium	5
Cadmium	0.3	Thallium	0.1
Chromium	2	Tin	2
Cobalt	1	Uranium	0.1
Copper	2	Vanadium	2
Iron	20	Zinc	2
Lead	0.5		

**2. Summary of Method**

A 0.500 gram portion of air-dried sieved sample is accurately weighed into a 100 ml Teflon beaker. An acid mixture (HClO<sub>4</sub>:HNO<sub>3</sub>:HF) is added, and the samples are allowed to stand overnight. After a repeat addition of the acid mixture, the samples are slowly heated to dryness on a hotplate. The samples are then cooled, and HCl and HNO<sub>3</sub> are added. After gentle warming for a few minutes, approx.. 20 ml of reagent grade water is added and the samples are heated for another 20 minutes. The samples are then allowed to cool and are transferred quantitatively to a 50 ml polypropylene centrifuge tube and made to volume with reagent grade water. The samples are then diluted ten fold and analysed directly using a Sciex/Perkin Elmer Elan 5000 ICP-MS in accordance with EPA Method 200.8.

**3. Quality Assurance**

Reagent blanks, certified reference materials, and method spikes are prepared and analysed in the exact same fashion as mentioned above for the samples. A minimum of one reagent blank and two different certified sediment reference materials (usually MESS-2 and BCSS-1) are prepared and analysed with every 20 samples. Spiking of samples at a level appropriate to the matrix is performed at a frequency of 10%. Duplicate digestion and analysis of samples is also performed at a frequency of 10%.



**Final Research Report****Title: Available Trace Metals in Soils and Sediments**

SOP #: 3010/4080

Reference: USEPA Method 200.8/3050A

Effective Date: August 1995

Revision Date: October, 1997

**1. Scope and Application**

This method is designed for the digestion and analysis of available trace metals in soils and sediment samples. Analytes and their routine LOQs are as listed below:

Analyte	LOQ (mg/kg)	Analyte	LOQ (mg/kg)
Aluminum	10	Manganese	2
Antimony	2	Molybdenum	2
Arsenic	2	Nickel	2
Barium	5	Selenium	2
Beryllium	5	Silver	0.5
Boron	5	Strontium	5
Cadmium	0.3	Thallium	0.1
Chromium	2	Tin	n/a
Cobalt	1	Uranium	0.1
Copper	2	Vanadium	2
Iron	20	Zinc	2
Lead	0.5		

**2. Summary of Method**

A 0.500 gram portion of the air-dried sieved sample is accurately weighed into a 50 ml polypropylene tube. Nitric acid is added and the samples are digested at 95°C for ~2.5 hours. After the addition of hydrogen peroxide, followed by another digestion period, the samples are allowed to cool and made to volume. The samples are then diluted ten fold and analysed directly using a Sciex/Perkin Elmer Elan 5000 ICP-MS in accordance with EPA Method 200.8.

**3. Quality Assurance**

Reagent blanks, certified reference materials, and method spikes are prepared and analysed in the exact same fashion as mentioned above for the samples. A minimum of one reagent blank and two certified sediment reference materials (usually an ERA SRM) are prepared and analysed with every 20 samples. Spiking of samples at a level appropriate to the matrix, as well as duplicate digestion and analysis of samples, is performed at a frequency of 10%.

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## APPENDIX 3 ASH ANALYSIS

**Table A3.1 Total metals analysis\* of CFB ash (1997 and 1998), limestones (1998) and 30% petroleum coke/70% Prince coal fly ash blend (1999).**

Element**	CFB ash 1997	CFB ash 1998	Calcitic limestone	Dolomitic limestone***	Pet coke /Prince coal ash blend
Al	25000	23100	13000	1600	18000
Sb	3	<2	<2	<2	<2
As	110	120	<2	9	140
Ba	290	560	600	5600	340
Be	<5	<5	<5	<5	<5
B	8	6	<5	21	48
Cd	1.1	1.1	0.7	<0.3	2.2
Cr	20	20	3	4	20
Co	8.1	11	<10	<10	11
Cu	70	88	83	14	130
Fe	33000	41600	1100	7200	23000
Pb	120	130	10	50	170
Mn	1100	1400	1100	5000	1400
Mo	8	11	<2	2	13
Ni	23	26	<20	<20	77
Se	8	11	<2	<2	13
Ag	-	-	<0.5	<0.5	<0.5
Sr	200	190	240	280	250
Tl	3.4	3.8	<0.1	<0.1	5.4
Sn	<2	-	-	-	-
U	3.6	4.8	3.8	1	6.9
V	35	41	4	4	280
Zn	140	130	49	12	210
Hg	0.01	0.1	-	-	0.36

\* Total Metals Digest (HClO<sub>4</sub>-HNO<sub>3</sub>-HF) Philip Analytical Services, Halifax, NS.

\*\* Units - mg/kg.

\*\*\* Mosher limestone.

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Table A3.2 Leachate Analysis\* for CFB ash, 1997.

Element**	Total***	HNO <sub>3</sub> -HClO <sub>3</sub>	Water
Ca %	16.50	16.50	5.53
Mg	3700	3500	8
Fe	53300	45100	23
Na	23200	1590	85
Al	22500	21500	530
K	5750	4870	2940
SO <sub>4</sub> %	19.07	-	7.14
S (Total) %	6.43	-	-
Ni	34	33	<2
Cu	82	80	<1
Co	11	10	<1
Pb	145	150	<2
Zn	175	174	5
Cd	1.2	1.0	<0.2
Mn	1011	1026	4
As	110	140	10
Hg	0.020	0.020	0.005
Mo	18	12	<5
Ag	1.0	0.9	<0.3
V	36	29	10
Sr	157	150	44
Sb	<10	<10	<10
Ba	1000	500	31
Cr	42	38	<5
Be	2.6	2.4	<0.5
B	4760	34	10
Se	<10	<10	<10
U	4.0	3.0	0.8
Tl	3.2	3.2	<0.5

\* Technical University of Nova Scotia (TUNS), Halifax, NS.

\*\* Units: ppm, unless otherwise indicated.

\*\*\* HCl-HNO<sub>3</sub>-HF HClO<sub>4</sub>-extracted.

**Final Research Report****APPENDIX 4 CRITERIA FOR METALS IN SOILS AND WASTES.****Criteria for Metals in Soils and Wastes**

Element	MMC <sup>1</sup> soil	MPMC <sup>2</sup> soil	MPMA <sup>3</sup> soil	MPMCS <sup>4</sup> waste	CFIA <sup>5</sup> fert/supp
As	7	14	14	170	75
Cd	0.8	1.6	1.6	34	20
Co	5	20	20	340	150
Cr	15	120	210	2800	-
Cu	25	100	150	1700	-
Hg	0.1	0.5	0.8	11	5
Mo	2	4	4	94	20
Ni	16	32	32	420	180
Pb	15	60	90	1100	500
Se	0.4	1.6	2.4	34	14
Zn	55	220	330	4200	1850

1 MMC- Mean Metal Content in uncontaminated Ontario soils (mg/kg).

2 MPMC - Maximum Permissible Metal Content in soils receiving waste materials (mg/kg).

3 MPMA - Maximum Permissible Metal Addition to uncontaminated soil (kg/ha).

4 MPMCS - Maximum Permissible Metal Content in sludge (mg/kg).

5 CFIA - Canadian Food Inspection Agency, maximum acceptable metal concentrations in fertilizers and supplements sold in Canada.

**Sources:**

1-3, Guidelines for the Utilization of Biosolids and Other Wastes on Agriculture Land. 1996. Ontario Ministry of Environment & Ministry of Agriculture, Food and Rural Affairs.

3-4, Nova Scotia Standards and Guidelines Manual for the Collection, Treatment and Disposal of Sanitary Sewage, 1992. NS Dept of Environment.

5, Canadian Food Inspection Agency, Trade memorandum T-4-93. Fertilizers Act and Regulations.

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## APPENDIX 5 SOIL METAL DATA - 1997, 1998, 1999

Cabbage - Pre-treatment - June 1997												
Rep	Treatment	Al	Sb	As	Ba	Be	B	Cd	Cr	Co	Cu	Fe
1	Control	12400	0	0	10	0	0	0	7	3.0	4	11900
1	Limestone	12400	0	0	10	0	0	0	7	3.0	4	11900
1	Low-Ash	12400	0	0	10	0	0	0	7	3.0	4	11900
1	Split-Ash	12400	0	0	10	0	0	0	7	3.0	4	11900
1	High-Ash	12400	0	0	10	0	0	0	7	3.0	4	11900
2	Control	10800	0	0	9	0	0	0	5	2.3	6	10900
2	Limestone	10800	0	0	9	0	0	0	5	2.3	6	10900
2	Low-Ash	10800	0	0	9	0	0	0	5	2.3	6	10900
2	Split-Ash	10800	0	0	9	0	0	0	5	2.3	6	10900
2	High-Ash	10800	0	0	9	0	0	0	5	2.3	6	10900
3	Control	14100	0	0	11	0	0	0	6	3.1	4	12600
3	Limestone	14100	0	0	11	0	0	0	6	3.1	4	12600
3	Low-Ash	14100	0	0	11	0	0	0	6	3.1	4	12600
3	Split-Ash	14100	0	0	11	0	0	0	6	3.1	4	12600
3	High-Ash	14100	0	0	11	0	0	0	6	3.1	4	12600
4	Control	11400	0	0	12	0	0	0	5	2.5	3	10700
4	Limestone	11400	0	0	12	0	0	0	5	2.5	3	10700
4	Low-Ash	11400	0	0	12	0	0	0	5	2.5	3	10700
4	Split-Ash	11400	0	0	12	0	0	0	5	2.5	3	10700
4	High-Ash	11400	0	0	12	0	0	0	5	2.5	3	10700

**Final Research Report**

Cabbage - Pre-treatment - June 1997													
Rep	Treatment	Pb	Mn	Mo	Ni	Se	Ag	Sr	Tl	U	V	Zn	Hg
1	Control	20.0	130	0	10	0	0	0	0.1	0.3	18	37	0.04
1	Limestone	20.0	130	0	10	0	0	0	0.1	0.3	18	37	0.04
1	Low-Ash	20.0	130	0	10	0	0	0	0.1	0.3	18	37	0.04
1	Split-Ash	20.0	130	0	10	0	0	0	0.1	0.3	18	37	0.04
1	High-Ash	20.0	130	0	10	0	0	0	0.1	0.3	18	37	0.04
2	Control	0.0	97	0	7	0	0	0	0.1	0.3	17	31	0.05
2	Limestone	0.0	97	0	7	0	0	0	0.1	0.3	17	31	0.05
2	Low-Ash	0.0	97	0	7	0	0	0	0.1	0.3	17	31	0.05
2	Split-Ash	0.0	97	0	7	0	0	0	0.1	0.3	17	31	0.05
2	High-Ash	0.0	97	0	7	0	0	0	0.1	0.3	17	31	0.05
3	Control	11.0	110	0	7	0	0	0	0.1	0.3	18	37	0.05
3	Limestone	11.0	110	0	7	0	0	0	0.1	0.3	18	37	0.05
3	Low-Ash	11.0	110	0	7	0	0	0	0.1	0.3	18	37	0.05
3	Split-Ash	11.0	110	0	7	0	0	0	0.1	0.3	18	37	0.05
3	High-Ash	11.0	110	0	7	0	0	0	0.1	0.3	18	37	0.05
4	Control	11.0	98	0	6	0	0	0	0.1	0.3	17	30	0.06
4	Limestone	11.0	98	0	6	0	0	0	0.1	0.3	17	30	0.06
4	Low-Ash	11.0	98	0	6	0	0	0	0.1	0.3	17	30	0.06
4	Split-Ash	11.0	98	0	6	0	0	0	0.1	0.3	17	30	0.06
4	High-Ash	11.0	98	0	6	0	0	0	0.1	0.3	17	30	0.06

## Final Research Report

Rutabaga - Pre-treatment - June 1997												
Rep	Treatment	Al	Sb	As	Ba	Be	B	Cd	Cr	Co	Cu	Fe
1	Control	6030	0	0	21	0	0	0	3	1.4	2	4600
1	Limestone	6030	0	0	21	0	0	0	3	1.4	2	4600
1	Low-Ash	6030	0	0	21	0	0	0	3	1.4	2	4600
1	Split-Ash	6030	0	0	21	0	0	0	3	1.4	2	4600
1	High-Ash	6030	0	0	21	0	0	0	3	1.4	2	4600
2	Control	7450	0	0	18	0	0	0	4	1.9	2	8070
2	Limestone	7450	0	0	18	0	0	0	4	1.9	2	8070
2	Low-Ash	7450	0	0	18	0	0	0	4	1.9	2	8070
2	Split-Ash	7450	0	0	18	0	0	0	4	1.9	2	8070
2	High-Ash	7450	0	0	18	0	0	0	4	1.9	2	8070
3	Control	12000	0	0	20	0	0	0	7	4.9	5	15600
3	Limestone	12000	0	0	20	0	0	0	7	4.9	5	15600
3	Low-Ash	12000	0	0	20	0	0	0	7	4.9	5	15600
3	Split-Ash	12000	0	0	20	0	0	0	7	4.9	5	15600
3	High-Ash	12000	0	0	20	0	0	0	7	4.9	5	15600
4	Control	11300	0	0	20	0	0	0	6	6.3	4	14900
4	Limestone	11300	0	0	20	0	0	0	6	6.3	4	14900
4	Low-Ash	11300	0	0	20	0	0	0	6	6.3	4	14900
4	Split-Ash	11300	0	0	20	0	0	0	6	6.3	4	14900
4	High-Ash	11300	0	0	20	0	0	0	6	6.3	4	14900

## Final Research Report

Rutabaga - Pre-treatment - June 1997													
Rep	Treatment	Pb	Mn	Mo	Ni	Se	Ag	Sr	Tl	U	V	Zn	Hg
1	Control	9.5	81	0	6	0	0	0	0.1	0.2	14	14	0.30
1	Limestone	9.5	81	0	6	0	0	0	0.1	0.2	14	14	0.30
1	Low-Ash	9.5	81	0	6	0	0	0	0.1	0.2	14	14	0.30
1	Split-Ash	9.5	81	0	6	0	0	0	0.1	0.2	14	14	0.30
1	High-Ash	9.5	81	0	6	0	0	0	0.1	0.2	14	14	0.30
2	Control	11.0	120	0	6	0	0	0	0.1	0.2	19	17	0.03
2	Limestone	11.0	120	0	6	0	0	0	0.1	0.2	19	17	0.03
2	Low-Ash	11.0	120	0	6	0	0	0	0.1	0.2	19	17	0.03
2	Split-Ash	11.0	120	0	6	0	0	0	0.1	0.2	19	17	0.03
2	High-Ash	11.0	120	0	6	0	0	0	0.1	0.2	19	17	0.03
3	Control	13.0	420	0	9	0	0	0	0.1	0.4	23	29	0.05
3	Limestone	13.0	420	0	9	0	0	0	0.1	0.4	23	29	0.05
3	Low-Ash	13.0	420	0	9	0	0	0	0.1	0.4	23	29	0.05
3	Split-Ash	13.0	420	0	9	0	0	0	0.1	0.4	23	29	0.05
3	High-Ash	13.0	420	0	9	0	0	0	0.1	0.4	23	29	0.05
4	Control	13.0	630	0	9	0	0	0	0.1	0.3	22	28	0.04
4	Limestone	13.0	630	0	9	0	0	0	0.1	0.3	22	28	0.04
4	Low-Ash	13.0	630	0	9	0	0	0	0.1	0.3	22	28	0.04
4	Split-Ash	13.0	630	0	9	0	0	0	0.1	0.3	22	28	0
4	High-Ash	13.0	630	0	9	0	0	0	0.1	0.3	22	28	0.04



## Final Research Report

Cabbage - July 1997												
Rep	Treatment	Al	Sb	As	Ba	Be	B	Cd	Cr	Co	Cu	Fe
1	Control	12300	0	2.0	14	0	0	0	6	2.4	3	13300
1	Limestone	11900	0	0.0	14	0	0	0	6	2.8	4	12600
1	Low-Ash	11700	0	2.9	24	0	0	0	6	2.4	5	14300
1	Split-Ash	12900	0	2.6	23	0	0	0	6	3.0	4	12500
1	High-Ash	10100	0	4.4	43	0	0	0	5	2.5	6	11200
1	Double-Ash	.	.	.	.	.	.	.	.	.	.	.
2	Control	12300	0	0.0	13	0	0	0	6	2.8	4	13200
2	Limestone	12400	0	2.1	14	0	0	0	6	2.9	4	12500
2	Low-Ash	17100	0	4.0	35	0	0	0	7	3.6	6	15000
2	Split-Ash	12000	0	2.3	18	0	0	0	5	2.4	3	12600
2	High-Ash	14100	0	5.4	48	0	0	0	7	3.8	7	13100
2	Double-Ash	.	.	.	.	.	.	.	.	.	.	.
3	Control	14600	0	0.0	10	0	0	0	6	2.5	3	12400
3	Limestone	14400	0	0.0	15	0	0	0	8	3.6	4	13200
3	Low-Ash	14000	0	2.2	21	0	0	0	7	3.0	5	13200
3	Split-Ash	17200	0	2.6	23	0	0	0	8	3.1	5	14100
3	High-Ash	10400	0	3.9	40	0	0	0	5	2.2	5	10200
3	Double-Ash	.	.	.	.	.	.	.	.	.	.	.
4	Control	12100	0	0.0	18	0	0	0	5	1.9	4	11200
4	Limestone	16100	0	0.0	14	0	0	0	8	4.1	5	14500
4	Low-Ash	18300	0	2.2	24	0	0	0	8	4.0	5	15600
4	Split-Ash	6870	0	2.5	30	0	0	0	3	1.1	3	5830
4	High-Ash	14300	0	2.9	30	0	0	0	6	2.8	5	11900

## Final Research Report

Cabbage - July 1997													
Rep	Treatment	Pb	Mn	Mo	Ni	Se	Ag	Sr	Tl	U	V	Zn	Hg
1	Control	10.0	110	0	4	0	0	0	0.1	0.3	20	34	.
1	Limestone	11.0	140	0	5	0	0	0	0.1	0.3	18	34	.
1	Low-Ash	12.0	130	0	5	0	0	0	0.1	0.4	22	31	.
1	Split-Ash	12.0	130	0	5	0	0	5	0.1	0.4	18	39	.
1	High-Ash	14.0	140	0	5	0	0	10	0.2	0.4	17	34	.
1	Double-Ash	.	.	.	.	.	.	.	.	.	.	.	.
2	Control	12.0	150	0	5	0	0	0	0.1	0.6	19	37	.
2	Limestone	11.0	160	0	5	0	0	0	0.1	1.0	19	34	.
2	Low-Ash	15.0	160	0	7	0	0	7	0.1	0.4	21	49	.
2	Split-Ash	10.0	120	0	4	0	0	0	0.1	0.4	19	30	.
2	High-Ash	17.0	220	0	6	0	0	11	0.2	0.5	19	46	.
2	Double-Ash	.	.	.	.	.	.	.	.	.	.	.	.
3	Control	8.8	85	0	4	0	0	0	0.1	0.3	18	32	.
3	Limestone	12.0	130	0	5	0	0	0	0.1	0.5	20	44	.
3	Low-Ash	15.0	110	0	5	0	0	0	0.1	0.4	18	40	.
3	Split-Ash	12.0	98	0	6	0	0	0	0.1	0.4	20	45	.
3	High-Ash	12.0	110	0	4	0	0	9	0.2	0.5	16	30	.
3	Double-Ash	.	.	.	.	.	.	.	.	.	.	.	.
4	Control	10.0	81	0	4	0	0	0	0.1	0.5	17	29	.
4	Limestone	11.0	140	0	6	0	0	0	0.1	0.5	19	46	.
4	Low-Ash	13.0	150	0	7	0	0	0	0.1	0.4	20	53	.
4	Split-Ash	11.0	63	0	2	0	0	6	0.1	0.3	11	19	.
4	High-Ash	13.0	110	0	5	0	0	7	0.1	0.4	17	38	.

**Final Research Report**

Rutabaga - July 1997												
Rep	Treatment	Al	Sb	As	Ba	Be	B	Cd	Cr	Co	Cu	Fe
1	Control	6190	0	0.0	25	0	0	0	2	1.0	0	3200
1	Limestone	6580	0	0.0	32	0	0	0	3	1.3	3	4500
1	Low-Ash	7040	0	0.0	27	0	0	0	3	1.3	2	4500
1	Split-Ash	6300	0	0.0	36	0	0	0	3	1.5	2	5680
1	High-Ash	8320	0	6.9	90	0	0	0	4	1.9	6	6210
2	Control	7890	0	0.0	19	0	0	0	4	2.1	3	9780
2	Limestone	7970	0	0.0	23	0	0	0	4	2.0	2	7990
2	Low-Ash	7150	0	3.5	56	0	0	0	3	1.5	4	5700
2	Split-Ash	11300	0	3.2	33	0	0	0	7	3.2	5	14000
2	High-Ash	9450	0	4.4	46	0	0	0	5	2.6	5	11600
3	Control	11500	0	2.2	29	0	0	0	7	4.1	4	16100
3	Limestone	11800	0	2.0	25	0	0	0	7	4.0	5	16000
3	Low-Ash	11100	0	3.2	36	0	0	0	6	3.5	5	14700
3	Split-Ash	10600	0	2.5	42	0	0	0	7	3.8	4	14200
3	High-Ash	11800	0	5.6	70	0	0	0	7	5.9	9	16300
4	Control	12300	0	0.0	26	0	0	0	7	6.3	5	14400
4	Limestone	10100	0	0.0	23	0	0	0	6	3.7	3	13500
4	Low-Ash	12100	0	2.5	39	0	0	0	7	6.6	5	15900
4	Split-Ash	12400	0	3.0	42	0	0	0	7	6.5	5	14600
4	High-Ash	10600	0	3.6	44	0	0	0	6	5.2	5	15200

## Final Research Report

Rutabaga - July 1997													
Rep	Treatment	Pb	Mn	Mo	Ni	Se	Ag	Sr	Tl	U	V	Zn	Hg
1	Control	7.8	43	0	2	0	0	0	0.1	0.3	9	12	.
1	Limestone	13.0	98	0	3	0	0	5	0.1	0.2	11	20	.
1	Low-Ash	7.9	61	0	3	0	0	0	0.1	0.3	12	13	.
1	Split-Ash	11.0	140	0	3	0	0	5	0.1	0.3	20	14	.
1	High-Ash	17.0	120	0	4	0	0	17	0.2	0.5	16	22	.
2	Control	8.9	150	0	3	0	0	0	0.1	0.3	22	19	.
2	Limestone	9.3	100	0	3	0	0	0	0.1	0.3	21	20	.
2	Low-Ash	14.0	120	0	3	0	0	10	0.1	0.3	17	24	.
2	Split-Ash	13.0	190	0	5	0	0	5	0.1	0.4	27	30	.
2	High-Ash	13.0	220	0	4	0	0	9	0.1	0.3	24	25	.
3	Control	15.0	340	0	6	0	0	0	0.1	0.4	24	30	.
3	Limestone	13.0	340	0	11	0	0	0	0.1	0.4	20	31	.
3	Low-Ash	13.0	300	0	5	0	0	6	0.1	0.4	20	27	.
3	Split-Ash	15.0	310	0	6	0	0	6	0.1	0.4	27	30	.
3	High-Ash	20.0	600	0	6	0	0	12	0.2	0.4	28	35	.
4	Control	13.0	580	0	6	0	0	0	0.1	0.5	19	31	.
4	Limestone	12.0	350	0	5	0	0	0	0.1	0.3	22	27	.
4	Low-Ash	17.0	730	0	6	0	0	5	0.1	0.5	21	30	.
4	Split-Ash	16.0	610	0	6	0	0	6	0.1	0.4	20	35	.
4	High-Ash	18.0	600	0	5	0	0	7	0.1	0.3	22	29	.

## Final Research Report

Cabbage - October 1997												
Rep	Treatment	Al	Sb	As	Ba	Be	B	Cd	Cr	Co	Cu	Fe
1	Control	11900	0	0.0	10	0	0	0	6	2.3	3	12200
1	Limestone	11500	0	0.0	11	0	0	0	5	2.3	3	12300
1	Low-Ash	11300	0	2.7	22	0	0	0	6	2.6	4	12300
1	Split-Ash	15300	0	5.9	48	0	0	0	7	4.1	7	14000
1	High-Ash	9700	0	3.2	32	0	0	0	6	2.7	5	11100
1	Double-Ash	12200	0	3.0	35	0	0	0	5	2.0	5	13600
2	Control	10500	0	0.0	9	0	0	0	5	2.4	3	11100
2	Limestone	14900	0	0.0	14	0	0	0	7	3.3	6	14100
2	Low-Ash	17600	0	3.3	24	0	0	0	8	3.4	4	15500
2	Split-Ash	12500	0	4.1	39	0	0	0	5	2.5	5	12200
2	High-Ash	15800	0	5.2	43	0	5	0	8	4.2	8	14200
2	Double-Ash	12400	0	3.0	36	0	0	0	5	2.0	5	10800
3	Control	17700	0	0.0	10	0	0	0	7	2.4	3	13900
3	Limestone	14600	0	0.0	13	0	0	0	7	3.3	4	13400
3	Low-Ash	11300	0	2.0	16	0	0	0	6	3.1	4	11100
3	Split-Ash	16800	0	7.0	54	0	5	0	8	3.1	7	14800
3	High-Ash	10900	0	4.5	43	0	0	0	5	2.4	6	10700
3	Double-Ash	11700	0	3.0	29	0	0	0	7	2.0	4	11000
4	Control	12800	0	0.0	16	0	0	0	5	2.2	4	11200
4	Limestone	17900	0	0.0	15	0	0	0	8	4.0	4	15400
4	Low-Ash	14900	0	0.0	17	0	0	0	7	3.4	5	13600
4	Split-Ash	5960	0	4.2	39	0	0	0	3	1.1	4	4900
4	High-Ash	13400	0	2.2	21	0	0	0	6	2.8	4	11900

## Final Research Report

Cabbage - October 1997													
Rep	Treatment	Pb	Mn	Mo	Ni	Se	Ag	Sr	Tl	U	V	Zn	Hg
1	Control	8.9	120	0	5	0	0	0	0.1	0.4	20	31	0.04
1	Limestone	8.6	150	0	4	0	0	0	0.1	0.3	18	29	0.03
1	Low-Ash	12.0	130	0	5	0	0	5	0.1	0.8	20	32	0.04
1	Split-Ash	15.0	230	0	7	0	0	9	0.2	0.5	19	49	0.04
1	High-Ash	13.0	180	0	6	0	0	7	0.1	0.4	18	33	0.05
1	Double-Ash	14.0	140	0	5	0	0	6	0.2	0.3	20	31	0.04
2	Control	8.9	110	0	4	0	0	0	0.1	0.4	17	28	0.04
2	Limestone	18.0	180	0	6	0	0	0	0.1	0.6	21	39	0.04
2	Low-Ash	13.0	130	0	8	0	0	0	0.1	0.4	23	47	0.05
2	Split-Ash	12.0	120	0	5	0	0	8	0.1	0.4	18	35	0.04
2	High-Ash	15.0	190	0	8	0	0	8	0.2	0.5	21	51	0.06
2	Double-Ash	15.0	110	0	7	0	0	7	0.1	0.4	17	28	0.06
3	Control	8.5	89	0	5	0	0	0	0.1	0.3	19	35	0.05
3	Limestone	9.0	160	0	6	0	0	0	0.1	0.4	19	35	0.03
3	Low-Ash	11.0	120	0	5	0	0	0	0.1	0.3	18	36	0.04
3	Split-Ash	15.0	150	0	6	0	0	13	0.2	0.4	20	47	0.08
3	High-Ash	12.0	160	0	5	0	0	9	0.1	0.4	17	30	0.06
3	Double-Ash	13.0	89	0	7	0	0	5	0.1	0.3	16	27	0.05
4	Control	10.0	78	0	5	0	0	0	0.1	0.3	16	31	0.04
4	Limestone	11.0	160	0	7	0	0	0	0.1	0.4	20	44	0.03
4	Low-Ash	11.0	120	0	6	0	0	0	0.1	0.4	20	40	0.04
4	Split-Ash	9.8	88	0	3	0	0	9	0.1	0.3	10	19	0.04
4	High-Ash	11.0	100	0	6	0	0	5	0.1	0.4	17	37	0.05

**Final Research Report**

Rutabaga - October 1997												
Rep	Treatment	Al	Sb	As	Ba	Be	B	Cd	Cr	Co	Cu	Fe
1	Control	5100	0	0.0	18	0	0	0	2	0.0	0	2600
1	Limestone	6180	0	0.0	26	0	0	0	3	1.1	2	4300
1	Low-Ash	6720	0	0.0	32	0	0	0	3	1.3	2	3600
1	Split-Ash	6760	0	6.6	110	0	0	0	3	2.7	5	8260
1	High-Ash	6770	0	3.1	48	0	0	0	4	1.8	3	5200
2	Control	7980	0	0.0	15	0	0	0	4	2.1	2	10200
2	Limestone	8630	0	0.0	21	0	0	0	4	2.0	2	8910
2	Low-Ash	7220	0	0.0	44	0	0	0	3	1.4	3	4900
2	Split-Ash	11400	0	5.8	59	0	0	0	6	3.0	6	13400
2	High-Ash	10100	0	4.2	42	0	0	0	6	2.8	5	11600
3	Control	10900	0	2.0	24	0	0	0	7	3.4	3	15700
3	Limestone	10800	0	0.0	18	0	0	0	5	3.6	4	14300
3	Low-Ash	11000	0	2.6	32	0	0	0	5	2.9	4	13300
3	Split-Ash	10900	0	4.8	61	0	0	0	7	3.7	6	14400
3	High-Ash	13100	0	4.2	51	0	0	0	7	4.3	6	18600
4	Control	13900	0	0.0	22	0	0	0	7	6.3	5	16700
4	Limestone	10600	0	0.0	21	0	0	0	6	3.6	3	13600
4	Low-Ash	11800	0	2.1	33	0	0	0	6	6.8	4	15100
4	Split-Ash	12700	0	5.0	56	0	0	0	7	7.0	7	15100
4	High-Ash	12200	0	2.3	35	0	0	0	7	5.7	4	17000

**Final Research Report**

Rutabaga - October 1997													
Rep	Treatment	Pb	Mn	Mo	Ni	Se	Ag	Sr	Tl	U	V	Zn	Hg
1	Control	5.8	30	0	2	0	0	0	0.1	0.2	7	10	0.01
1	Limestone	10.0	87	0	3	0	0	0	0.1	0.3	11	17	0.02
1	Low-Ash	8.7	44	0	3	0	0	0	0.1	0.5	11	14	0.02
1	Split-Ash	22.0	730	0	4	0	0	14	0.2	0.5	24	21	0.03
1	High-Ash	10.0	98	0	4	0	0	8	0.1	0.4	16	17	0.03
2	Control	9.7	160	0	3	0	0	0	0.1	0.2	24	20	0.02
2	Limestone	9.1	110	0	4	0	0	0	0.1	0.3	24	20	0.02
2	Low-Ash	18.0	93	0	3	0	0	7	0.1	0.3	13	20	0.04
2	Split-Ash	16.0	190	0	5	0	0	12	0.2	0.5	27	32	0.04
2	High-Ash	14.0	200	0	5	0	0	9	0.1	0.5	27	25	0.03
3	Control	14.0	290	0	5	0	0	0	0.1	0.4	25	26	0.06
3	Limestone	12.0	350	0	5	0	0	0	0.1	0.3	20	25	0.04
3	Low-Ash	13.0	200	0	4	0	0	5	0.1	0.4	19	26	0.05
3	Split-Ash	18.0	320	0	7	0	0	11	0.2	0.5	32	33	0.04
3	High-Ash	21.0	440	0	6	0	0	10	0.2	0.5	33	31	0.08
4	Control	12.0	560	0	9	0	0	0	0.1	0.5	19	33	0.05
4	Limestone	11.0	270	0	8	0	0	5	0.1	0.3	20	26	0.04
4	Low-Ash	16.0	620	0	7	0	0	0	0.1	0.4	21	30	0.05
4	Split-Ash	18.0	640	0	8	0	0	10	0.2	0.5	20	36	0.06
4	High-Ash	16.0	470	0	8	0	0	5	0.1	0.4	24	30	0.05



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Cabbage - October 1998												
Rep	Treatment	Al	Sb	As	Ba	Be	B	Cd	Cr	Co	Cu	Fe
1	Control	11700	0	3	11	0	0	0	5	2	4	11400
1	Limestone	10800	0	2	11	0	0	0	5	2	3	11800
1	Low-Ash	13100	0	3	25	0	0	0	6	2	5	14300
1	Split-Ash	12600	0	4	42	0	0	0	6	3	6	11300
1	High-Ash	11200	0	4	47	0	0	0	5	2	6	11800
1	Double-Ash	11900	0	6	59	0	0	0	6	3	7	11700
2	Control	10100	0	0	10	0	0	0	5	2	4	9640
2	Limestone	13200	0	2	13	0	0	0	6	3	4	11800
2	Low-Ash	16600	0	3	27	0	0	0	7	3	5	13800
2	Split-Ash	13100	0	5	47	0	0	0	6	3	7	12500
2	High-Ash	11200	0	4	36	0	0	0	5	3	5	11200
2	Double-Ash	11700	0	6	65	0	0	0	6	2	7	9840
3	Control	20300	0	2	11	0	0	0	7	3	4	15700
3	Limestone	11500	0	0	12	0	0	0	5	3	4	10300
3	Low-Ash	12800	0	2	20	0	0	0	6	3	4	11900
3	Split-Ash	17000	0	5	35	0	0	0	7	3	6	14400
3	High-Ash	10800	0	4	47	0	0	0	5	2	6	10700
3	Double-Ash	14200	0	6	73	0	0	0	6	2	8	11500
4	Control	13200	0	2	18	0	0	0	5	2	9	11600
4	Limestone	16100	0	0	13	0	0	0	7	4	6	13600
4	Low-Ash	17300	0	3	24	0	0	0	8	4	5	15300
4	Split-Ash	6650	0	4	43	0	0	0	3	1	5	5370
4	High-Ash	19600	0	4	42	0	0	0	7	3	7	15400

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Cabbage - October 1998													
Rep	Treatment	Pb	Mn	Mo	Ni	Se	Ag	Sr	Tl	U	V	Zn	Hg
1	Control	9.3	110	0	6	0	0	0	0.1	0.5	18	30	0.04
1	Limestone	8.3	160	0	5	0	0	0	0.1	0.6	18	25	0.04
1	Low-Ash	12.0	130	0	8	0	0	0	0.1	0.5	21	31	0.06
1	Split-Ash	16.0	210	0	6	0	0	6	0.2	0.6	16	40	0.05
1	High-Ash	15.0	170	0	7	0	0	7	0.2	0.5	16	31	0.04
1	Double-Ash	18.0	180	0	6	0	0	11	0.2	0.7	18	38	0.06
2	Control	9.4	150	0	4	0	0	0	0.1	0.4	14	28	0.04
2	Limestone	10.0	240	0	5	0	0	0	0.1	0.7	17	35	0.04
2	Low-Ash	13.0	150	0	7	0	0	0	0.1	0.5	19	40	0.06
2	Split-Ash	13.0	160	0	8	0	0	7	0.2	0.6	18	38	0.06
2	High-Ash	12.0	170	0	5	0	0	5	0.1	0.6	17	33	0.04
2	Double-Ash	17.0	200	0	5	0	0	14	0.2	0.9	18	37	0.08
3	Control	9.8	110	0	5	0	0	0	0.1	0.5	22	35	0.07
3	Limestone	9.0	160	0	5	0	0	0	0.1	0.5	15	29	0.03
3	Low-Ash	12.0	130	0	5	0	0	0	0.1	0.4	17	37	0.04
3	Split-Ash	14.0	160	0	6	0	0	5	0.1	0.5	20	45	0.07
3	High-Ash	13.0	190	0	7	0	0	8	0.2	0.6	17	30	0.06
3	Double-Ash	19.0	140	0	7	0	0	12	0.2	0.7	20	39	0.07
4	Control	15.0	95	0	13	0	0	0	0.1	0.5	19	28	0.06
4	Limestone	12.0	170	0	9	0	0	0	0.1	0.5	18	43	0.06
4	Low-Ash	13.0	180	0	7	0	0	0	0.1	0.5	22	48	0.06
4	Split-Ash	13	100	0	4	0	0	7	0.1	0.4	11	21	0.05
4	High-Ash	15	140	0	8	0	0	7	0.1	0.6	20	44	0.08

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Rutabaga - October 1998												
Rep	Treatment	Al	Sb	As	Ba	Be	B	Cd	Cr	Co	Cu	Fe
1	Control	6080	0	0	22	0	0	0	2	1	2	3400
1	Limestone	6890	0	0	28	0	0	0	3	1	3	4700
1	Low-Ash	5400	0	2	36	0	0	0	3	1	3	4000
1	Split-Ash	6410	0	5	64	0	0	0	3	2	5	6310
1	High-Ash	8190	0	5	71	0	0	0	4	2	6	6170
2	Control	8180	0	2	17	0	0	0	5	2	3	9600
2	Limestone	8210	0	0	23	0	0	0	4	2	3	8010
2	Low-Ash	7700	0	3	54	0	0	0	4	2	4	6000
2	Split-Ash	10700	0	7	70	0	0	0	6	3	7	11800
2	High-Ash	10400	0	6	72	0	0	0	6	3	7	11000
3	Control	11600	0	2	22	0	0	0	6	4	4	15400
3	Limestone	13300	0	2	21	0	0	0	8	4	6	16900
3	Low-Ash	11700	0	3	33	0	0	0	6	3	6	15500
3	Split-Ash	10900	0	6	72	0	0	0	7	4	7	14800
3	High-Ash	12000	0	5	60	0	0	0	7	5	7	15800
4	Control	12500	0	2	22	0	0	0	7	7	4	15100
4	Limestone	10700	0	2	24	0	0	0	6	3	4	13600
4	Low-Ash	12600	0	4	59	0	0	0	7	7	6	16500
4	Split-Ash	13500	0	9	100	0	0	0	8	7	9	16100
4	High-Ash	10800	0	4	52	0	0	0	6	6	7	15200

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Rutabaga - October 1998													
Rep	Treatment	Pb	Mn	Mo	Ni	Se	Ag	Sr	Tl	U	V	Zn	Hg
1	Control	8.8	43	0	3	0	0	0	0.1	0.3	9	10	0.02
1	Limestone	12.0	110	0	4	0	0	5	0.1	0.4	11	17	0.04
1	Low-Ash	8.8	70	0	4	0	0	5	0.1	0.5	12	10	0.03
1	Split-Ash	15.0	250	0	4	0	0	9	0.2	0.5	21	16	0.06
1	High-Ash	15.0	130	0	5	0	0	11	0.2	0.5	17	18	0.06
2	Control	9.7	190	0	4	0	0	0	0.1	0.5	25	19	0.02
2	Limestone	12.0	130	0	4	0	0	0	0.1	0.3	23	19	0.02
2	Low-Ash	17.0	130	0	4	0	0	7	0.1	0.8	17	22	0.04
2	Split-Ash	19.0	200	0	5	0	0	10	0.2	0.6	25	30	0.06
2	High-Ash	18.0	230	0	5	0	0	11	0.2	0.7	25	28	0.05
3	Control	14.0	370	0	6	0	0	0	0.1	0.4	24	24	0.05
3	Limestone	14.0	370	0	6	0	0	0	0.1	0.6	23	30	0.06
3	Low-Ash	14.0	320	0	6	0	0	5	0.1	0.8	22	28	0.06
3	Split-Ash	21.0	420	0	7	0	0	10	0.2	0.7	28	33	0.06
3	High-Ash	21.0	520	0	8	0	0	9	0.2	0.6	27	31	0.06
4	Control	13.0	650	0	7	0	0	0	0.1	0.7	20	35	0.03
4	Limestone	13.0	280	0	6	0	0	0	0.1	0.5	20	25	0.04
4	Low-Ash	22.0	750	0	5	0	0	7	0.2	0.9	23	31	0.07
4	Split-Ash	23.0	720	0	7	0	0	13	0.2	0.9	22	40	0.07
4	High-Ash	20.0	560	0	5	0	0	7	0.2	0.5	24	28	0.06

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Cabbage - October 1999												
Rep	Treatment	Al	Sb	As	Ba	Be	B	Cd	Cr	Co	Cu	Fe
1	Control	11000	0	0	11	0	0	0.0	5	2	3	11000
1	Limestone	9600	0	2	11	0	0	0.0	5	2	3	11000
1	Low-Ash	12000	0	3	24	0	0	0.0	6	3	4	13000
1	Split-Ash	10000	0	4	41	0	0	0.0	6	3	5	11000
1	High-Ash	11000	0	4	39	0	0	0.0	6	3	5	12000
1	Double-Ash	12000	0	9	120	0	0	0.0	8	4	10	13000
2	Control	9500	0	2	12	0	0	0.0	6	2	4	11000
2	Limestone	11000	0	2	14	0	0	0.0	7	3	4	12000
2	Low-Ash	13000	0	3	27	0	0	0.0	6	2	4	13000
2	Split-Ash	10000	0	4	49	0	0	0.0	6	2	5	11000
2	High-Ash	12000	0	6	64	0	0	0.0	7	4	8	12000
2	Double-Ash	11000	0	4	50	0	0	0.0	6	2	6	12000
3	Control	14000	0	0	9	0	0	0.0	6	2	4	12000
3	Limestone	10000	0	2	14	0	0	0.0	6	3	4	11000
3	Low-Ash	9500	0	2	22	0	0	0.0	6	2	4	10000
3	Split-Ash	13000	0	5	35	0	0	0.0	6	3	5	13000
3	High-Ash	10000	0	5	47	0	0	0.0	6	3	6	11000
3	Double-Ash	11000	0	5	59	0	0	0.0	6	2	7	11000
4	Control	9500	0	0	17	0	0	0.0	5	2	4	10000
4	Limestone	13000	0	0	14	0	0	0.0	7	4	4	12000
4	Low-Ash	14000	0	2	23	0	0	0.0	8	4	5	14000
4	Split-Ash	5700	0	6	66	0	0	0.0	3	1	5	5500
4	High-Ash	14000	0	4	41	0	0	0.0	7	3	6	13000

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Cabbage - October 1999													
Rep	Treatment	Pb	Mn	Mo	Ni	Se	Ag	Sr	Tl	U	V	Zn	Hg
1	Control	9.4	92	0	4	0	0	0	0.1	0.6	17	27	0.04
1	Limestone	8.7	140	0	4	0	0	0	0.1	0.6	17	25	0.04
1	Low-Ash	13.0	130	0	5	0	0	0	0.1	0.6	21	32	0.05
1	Split-Ash	14.0	160	0	5	0	0	5	0.1	0.7	18	36	0.04
1	High-Ash	15.0	170	0	5	0	0	6	0.1	0.7	19	36	0.05
1	Double-Ash	25.0	210	0	7	0	0	14	0.3	1.1	22	47	0.09
2	Control	10.0	100	0	4	0	0	0	0.1	0.9	18	29	0.04
2	Limestone	11.0	210	0	5	0	0	5	0.1	1.0	19	33	0.04
2	Low-Ash	12.0	110	0	5	0	0	0	0.1	0.5	19	35	0.05
2	Split-Ash	13.0	130	0	4	0	0	6	0.2	0.6	18	32	0.05
2	High-Ash	18.0	220	0	6	0	0	8	0.2	0.9	19	42	0.05
2	Double-Ash	15.0	140	0	4	0	0	8	0.1	0.5	22	29	0.08
3	Control	9.2	83	0	4	0	0	0	0.1	0.5	18	32	0.05
3	Limestone	10.0	140	0	4	0	0	0	0.1	0.8	18	30	0.03
3	Low-Ash	12.0	100	0	4	0	0	0	0.1	0.6	17	30	0.04
3	Split-Ash	14.0	140	0	5	0	0	5	0.1	0.6	18	39	0.06
3	High-Ash	15.0	160	0	5	0	0	7	0.2	0.8	18	35	0.06
3	Double-Ash	17.0	130	0	5	0	0	9	0.2	0.7	22	31	0.08
4	Control	13.0	63	0	4	0	0	0	0.1	0.6	18	22	0.04
4	Limestone	12.0	130	0	6	0	0	0	0.1	0.6	18	40	0.04
4	Low-Ash	13.0	120	0	6	0	0	0	0.1	0.5	21	42	0.05
4	Split-Ash	17.0	98	0	3	0	0	9	0.2	0.5	12	20	0.06
4	High-Ash	14.0	110	0	6	0	0	6	0.2	0.7	21	40	0.07

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Rutabaga - October 1999												
Rep	Treatment	Al	Sb	As	Ba	Be	B	Cd	Cr	Co	Cu	Fe
1	Control	4400	0	0	23	0	0	0.0	2	1	0	2900
1	Limestone	5100	0	0	26	0	0	0.0	3	1	2	3900
1	Low-Ash	5000	0	2	38	0	0	0.0	2	1	2	4600
1	Split-Ash	4800	0	4	61	0	0	0.0	3	2	4	6100
1	High-Ash	6900	0	4	68	0	0	0.0	4	2	4	6500
2	Control	5400	0	0	16	0	0	0.0	4	2	2	7600
2	Limestone	5900	0	0	22	0	0	0.0	4	2	2	7100
2	Low-Ash	6300	0	2	53	0	0	0.0	4	2	4	6200
2	Split-Ash	8400	0	5	64	0	0	0.0	6	3	6	12000
2	High-Ash	8000	0	6	81	0	0	0.0	6	3	6	11000
3	Control	8400	0	2	24	0	0	0.0	6	3	4	14000
3	Limestone	10000	0	2	26	0	0	0.0	7	4	5	15000
3	Low-Ash	11000	0	3	37	0	0	0.8	7	4	6	17000
3	Split-Ash	8500	0	5	72	0	0	0.0	7	4	7	13000
3	High-Ash	10000	0	6	87	0	0	0.0	8	6	7	18000
4	Control	10000	0	2	25	0	0	0.0	8	8	5	14000
4	Limestone	9100	0	2	24	0	0	0.0	8	4	5	14000
4	Low-Ash	9100	0	4	52	0	0	0.0	7	7	6	14000
4	Split-Ash	10000	0	6	72	0	0	0.0	9	7	7	15000
4	High-Ash	7700	0	4	51	0	0	0.0	6	4	6	13000

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Rutabaga - October 1999													
Rep	Treatment	Pb	Mn	Mo	Ni	Se	Ag	Sr	Tl	U	V	Zn	Hg
1	Control	6.5	38	0	2	0	0	0	0.1	0.5	7	8	0.02
1	Limestone	10.0	100	0	2	0	0	0	0.1	0.4	10	15	0.03
1	Low-Ash	11.0	61	0	3	0	0	0	0.1	0.4	11	11	0.03
1	Split-Ash	17.0	250	0	3	0	0	6	0.2	0.5	23	15	0.04
1	High-Ash	15.0	130	0	4	0	0	9	0.2	0.7	19	17	0.05
2	Control	8.7	110	0	3	0	0	0	0.1	0.4	23	16	0.02
2	Limestone	10.0	120	0	3	0	0	0	0.1	0.4	22	15	0.02
2	Low-Ash	17.0	110	0	3	0	0	6	0.1	0.4	19	19	0.04
2	Split-Ash	18.0	160	0	5	0	0	9	0.2	0.6	28	27	0.06
2	High-Ash	20.0	190	0	4	0	0	11	0.2	0.7	26	25	0.07
3	Control	15.0	260	0	7	0	0	0	0.1	0.6	23	22	0.04
3	Limestone	15.0	310	0	6	0	0	5	0.1	0.7	21	29	0.05
3	Low-Ash	16.0	260	0	6	0	0	0	0.1	0.7	23	31	0.06
3	Split-Ash	22.0	340	0	7	0	0	9	0.2	0.8	34	30	0.06
3	High-Ash	31.0	660	0	6	0	0	11	0.2	0.8	33	31	0.08
4	Control	16.0	740	0	6	0	0	0	0.1	0.7	22	32	0.05
4	Limestone	15.0	360	0	7	0	0	0	0.1	0.5	25	29	0.04
4	Low-Ash	22.0	690	0	5	0	0	6	0.2	0.8	23	30	0.06
4	Split-Ash	22.0	650	0	6	0	0	9	0.2	0.7	22	35	0.08
4	High-Ash	19.0	500	0	5	0	0	6	0.2	0.5	25	25	0.06



**Final Research Report****APPENDIX 6 THE USE OF PET COKE ASH AS A SOIL AMENDMENT**

During the summer of 1999, Kelly Bowes, a summer student employed by the project, conducted an experiment designed to evaluate and compare limestone, coal fly ash and pet coke ash as soil amendments. The experiment was conducted as part of the requirement for her fourth-year BSc. Honours thesis at the NSAC. Summarized below is the methodology used and results obtained on soil pH and soil and plant metal content for the bean and sunflower trials. Kelly will be presenting a full report on her experiment in November, 2000.

In this summary, it is emphasized that the Pet coke ash trial was a student designed and directed experiment conducted over one growing season, with no unamended controls and limited replication in some of the testing and analysis. While the study highlights the relationship between ash characteristics (in particular, oxide content, element content) and efficacy and safety of the material as a liming agent, only limited comparisons between the materials can be made from this data.

**Methodology**

The experiment was established as a randomized complete block design with one factor, soil amendment, at three levels: calcitic limestone, coal fly ash and pet coke ash. Three test crops were used, beans, beet and sunflower. In each species trial, the three experimental treatments were replicated four times, giving a total of 36 plots.

The limestone and coal fly ash were left-over materials from the Project's 1998 field season that had been stored indoors over winter in sealed barrels at Point Edward. The pet coke ash was a blend of 30% petroleum coke /70% Prince coal fly ash removed from the ash silo at Point Aconi in May, 1999. Limestone analysis of these materials is provided in Table A6.1. Metals analyses (24 elements) on these materials appear in Appendix 3.

A metals analysis was also conducted on plant material from the beans and sunflower. Two separate parts of the bean plant were sampled, immature pods at the edible stage of development, and leaves. For sunflowers, the stems of mature plants were sampled. One sample of plant material was taken from each plot, for a total of 36 samples.

Soil samples were taken for analysis of soil pH and levels of available metals. Soil pH was measured in May of 1999 (pre-amendment) and May of 2000 (one year after application). Initial pH was based on one composite sample of the experimental area, and final soil pH in each treatment was determined on a composite of the four replicates. Soil metals were determined only in the Pet coke ash treatment. One soil sample per trial (bean, beet, sunflower) was taken in Pet coke ash plots for a total of three samples. In the absence of replicated controls, three soil samples were taken outside the experimental plot to provide a comparison with unamended soil. Procedures for analyses of soils, plants and liming materials are provided in Appendix 2.

**Final Research Report****Table A6.1 Limestone analysis of the soil amendments.**

Parameter (%)	Calcitic limestone	Coal fly ash	Pet coke ash
Soluble	92.1	83.2	81.1
Ca	35.5	21.5	31.3
Mg	0.3	0.4	0.4
CCE	90	56	80

The rate of application for the limestone treatment was based on the lime requirement of the field (16 t/ha). The other two treatments were also applied at the lime requirement, adjusted for the lower CCE, or neutralizing value, of the ash materials (Table A6.2).

**Table A6.2 Amendment loading rates equivalent to soil lime requirement (16 t/ha).**

Treatment	Loading rate (t/ha)	CCE
Calcitic limestone	16	90
Coal fly ash	29	56
Pet coke ash	20	80

The range in application rates of the liming materials highlights the inverse relationship between amendment loading required for a given target soil pH (in this case, pH 6.5) and CCE of the liming material (Table A6.2). The higher CCE of the Pet coke ash compared with coal fly ash is attributed to a higher oxide content as a result of the larger amounts of sorbent being utilized in combustion of a high S fuel source<sup>51</sup>. Moisture content appears to have had an influence on CCE of the coal fly ash. The CCE of coal fly ash had dropped from the CCE obtained in 1998 (66%). This may be attributed to hydration of the material (i.e. the unused barrels of ash were outside during application of treatments in 1998, and stored in an unheated building over winter). The fly ash applied in 1999 was reported to be very lumpy, indicating a hydrated condition. Unfortunately, no moisture analysis is available to confirm this observation.

<sup>51</sup>W. Richards, Senior Plant Engineer, Point Aconi Generating Station. Personal communication, June 2000.

**Final Research Report****Results and Discussion****Soil pH**

The results for soil pH in the bean and sunflower plots are generally consistent with those observed throughout the Project. When applied at rates equivalent to the soil lime requirement, all liming treatments dramatically increased soil pH; that is, from a low initial value of 4.8 to values near or above the target soil pH of 6.5 (Table A6.3). While amendment loading rates varied significantly, liming materials were applied on an equivalent CCE basis and therefore similar pH adjustment is expected. Similar values for soil pH were obtained in the coal fly ash and limestone treatments. The reason for a higher soil pH in Pet coke ash plots is not known. Again, the interpretation of the data is limited by the small number of samples on which results are based.

**Table A6.3 Soil pH\* and change in soil pH\*\* in bean and sunflower plots.**

Treatment	Bean		Sunflower	
	Soil pH	<sup>a</sup> pH	Soil pH	<sup>a</sup> pH
Calcitic lime	6.02	1.22	6.22	1.42
Coal fly ash	6.04	1.24	6.62	1.82
Pet coke ash	6.59	1.79	7.06	2.26

\* Final soil pH was measured in May of 2000. Initial soil pH for the field was 4.8.

\*\* Change in soil pH (<sup>a</sup>soil pH) = pH<sub>f</sub>(final soil pH) - pH<sub>i</sub> (initial soil pH).

**Metals in Plants and Soils**

There was a significant effect of soil treatment on metal content of bean plant tissues for Ba, B, Cd, Mn, Mo, Pb, Tl and Zn (Tables A6.4 and A6.5). For sunflower stems, treatment effects were significant for Ba, B and Cd (Table A6.6). With the exception of Ba, levels of metals were consistently higher in plants grown in ash compared with limestone treatments. For all metals except Cd and B in sunflower (Table A6.6) and Mo in bean (Table A6.5), similar results were obtained for the two ash treatments.

The greater uptake of B and Mo in ash treatments is consistent with the literature, where an increase in these elements in plants grown on fly-ash amended soils is well established (Keefer 1993). Both B and Mo, as well as Mn and Zn, are essential plant nutrients. Concerns with B relate to the low B tolerance of most crops, and high availability of B in fly ash. Molybdenum (like Se) is generally non-toxic to plants, however, uncontrolled accumulation of Mo in plant tissues is a potential hazard to livestock animals (Adriano et al. 1980). Zn can be phytotoxic at high concentrations, however, plant tolerances are higher than for B and excesses of this element following amendment of soils with fly ash are rare. Mn is rarely phytotoxic, except under highly acidic soil conditions.

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In this trial, in no treatments were B, Mn, Mo or Zn present in plant tissues at levels which could be considered toxic<sup>52</sup>. At the highest plant concentrations (i.e., in bean leaves), plant B was at or just below the threshold for B deficiency for most crops (10 mg/kg DW). For the three elements taken up by bean pods as well as leaves (Mn, Mo, and Zn), lower element concentrations were present in the pods, suggesting greater concentrations of most elements in leafy compared with reproductive tissues in the plant. Both Mn and Mo in bean leaves were within ranges considered sufficient for most plants (20-300 mg/kg (DW) for Mn and 0.1-2.0 mg/kg (DW) for Mo) (Stevenson and Cole 1999). Levels of Zn in bean plants, however, are considered deficient (<50 mg/kg DW) (Table A6.5). As a general rule, soil and crop levels of Zn should be monitored following a significant application of any liming material (i.e., greater than 6 t/ha), particularly on sandy, lower capacity soils.

Reasons for the significantly higher plant uptake of Ba in the calcitic limestone treatment compared with the two ash treatments are not clear. From the elemental analysis of the liming materials (Appendix 3), calcitic limestone is only slightly higher in Ba than CFB ash. Dolomitic limestone, however, contains large amounts of this alkaline earth metal. No plant uptake of Ba was noted in other trials, despite the utilization of dolomitic lime in the Limestone treatment in these trials.

**Table A6.4 Effect of liming treatments on metal content in bean pods.**

Element	Limestone	Coal fly ash	Pet coke ash
Mn	7.20a*	10.37b	10.95b
Mo	0.50a	2.10b	1.42ab
Zn	4.17a	5.03b	4.65ab

Units = mg/kg, fresh weight basis.

\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

<sup>52</sup>Plant element concentrations are reported on a fresh weight (FW) basis, and therefore may appear low when compared with ranges reported on a dry weight (DW) basis in the literature.

**Final Research Report****Table A6.5 Effect of liming treatments on metal content in bean leaves.**

Element	Limestone	Coal fly ash	Pet coke ash
Ba	11.37b*	3.35a	3.30a
B	7.60a	9.17ab	10.15b
Cd	0.035a	0.055b	0.052b
Mn	53.65a	71.45ab	84.62b
Mo	0.075a	2.55c	1.62b
Pb	0.082a	0.14b	0.13b
Tl	0.002a	0.041b	0.046b
Zn	9.05a	12.67b	10.32ab

Units = mg/kg, fresh weight basis.

\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

**Table A6.6 Effect of liming treatments on metal content in sunflower stems.**

Element	Limestone	Coal fly ash	Pet coke ash
Ba	7.22b*	1.32a	1.40a
B	6.42a	7.92b	8.92c
Cd	0.035a	0.042ab	0.062b

Units = mg/kg, fresh weight basis.

\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

While present in plant tissues at very low levels, the detection of Cd and Pb in plant tissues is important due to the high toxicity of these metals. Both Cd and Pb were detected in bean leaves in all three liming treatments, however, levels were significantly higher in ash compared with limestone treatments (Table A6.5). Cadmium was also detected in sunflower stems (Table A6.6). Levels of Cd and Pb found in beans and sunflower are similar to concentrations of these metals reported for cabbages and cauliflower grown in the Fraser Valley of British Columbia (0.09-0.57  $\mu\text{g/gm}$  dry weight for Cd, and 0.04-0.15  $\mu\text{g/gm}$  dry weight for Pb) (De Pieri et al. 1996).

While both Cd and Pb are highly undesirable contaminants, Cd in waste materials presents a greater hazard than Pb due to its greater toxicity and bioavailability. Cadmium is readily taken up by plants, however plant species, as well as plant organs, differ widely in terms of ability to absorb this metal. For example, the difference in Cd content of crops grown on the same soil containing 10 ppm Cd exceeded 100-fold: the lowest concentration was in rice, Sudan grass and clover, the highest was in spinach and turnip. The highest concentrations of Cd have been

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reported for roots and leaves, however the metal appears to be excluded from seed pods (Kabata-Pendias and Pendias 1991). Differences in the affinity for metals of various plant parts and plant species indicates the importance of conducting testing on a range of crops. As noted previously, however, while results reported in this trial are potentially significant, the lack of unamended controls and limited testing of the applied materials makes a clear demonstration of a treatment effect difficult.

The other element of potential concern that was taken up by plant tissues was Tl. As with Cd and Pb, although Tl was detected in plants in all liming treatments, levels were significantly higher in ash compared with limestone treatments. The level of Tl present in ash-amended bean leaves (Table A6.5) was low and similar to the levels reported for the rutabaga (Table 4.29).

**Table A6.7 Metal content in Pet coke ash-amended soil and unamended soils.**

Element	Pet coke ash soil	Unamended Soil
As	3.67b*	2.00a
Ba	73.33b	31.00a
Hg**	0.053b	0.033a
Sr	9.67b	0.00a
U**	0.47b	0.27a
V	42.67b	29.33a

Units = mg/kg, dry weight basis.

\* Values in each row followed by the same letter are not significantly different according to least significant tests ( $p < 0.05$ ).

\*\* Significantly different at  $p = 0.07$ .

Metals that increased in the Pet coke ash amended soils were As, Ba, Hg, Sr, U and V (Table A6.7). While no comparisons with the other treatments in the trial are possible (metals analysis was limited to Pet coke ash amended soils), it may be noted that element loading in the Pet coke ash plots reflects the element content of the ash and amendment loading rate. While levels of several metals are higher in Pet coke ash compared with the other ash utilized in the Project (Appendix A3.1), amendment loading rates were lower due to the higher neutralizing value of the material. Consequently, soil levels of most elements are consistent with those found in other ash amended soils in the Project. The main difference noted in the Pet coke ash amended soils is a greater increase in V and lack of increase in Pb when compared with ash amended soils in the other trials. The fact that other elements (As, Ba, Hg, Sr, and U) were present at the lower end of the range reported previously for ash-amended soils (Tables 4.41, 4.42), may be attributed to the slightly lower amendment loading of the Pet Coke ash. For unknown reasons, background values for several metals (As, Ba, and V) are slightly higher in this analysis compared with the replicated controls in the other trials (Tables 4.41, 4.42).

**Final Research Report****Conclusions**

When applied at rates equivalent to the soil lime requirement, both Pet coke ash and coal fly ash were effective at increasing low soil pH to values near or above the target soil pH of 6.5. Similar values for final soil pH were obtained for Coal fly ash and Limestone treatments despite a large difference in amendment loading rates. This result is consistent with other data from the Project as well as the literature, and indicates that similar soil pH adjustment can be expected when liming materials are applied on an equivalent CCE basis. The reason for persistence of a higher soil pH in Pet coke ash plots one year after the application of liming treatments is not clear.

There was no excessive uptake of metals by bean and sunflowers grown in ash amended soils. A number of potentially toxic elements (Cd, Pb, Tl), however, were present at low but detectable levels in plant tissues. While these elements were present in plants in both limestone and ash treatments, levels were significantly higher in plants from the ash treatments. As in other trials in the Project, element loading in Pet coke ash-amended soils reflected the element content in the ash and the amendment loading rate. The main difference in soil loading with the Pet coke ash compared with Prince coal fly ash appeared to be a greater increase in V and lesser increase in Pb. While the results on plant and soil metal content are potentially significant, the lack of unamended controls and limited testing of the Pet coke ash limits the conclusions that can be drawn from the data.

The Pet coke ash trial lends further support to the supposition that varying the fuel source used in CFB combustion has an effect on both neutralizing value and trace element content of the ash. This highlights the need to develop ash quality standards for both liming efficacy as well as metal content. Short-term (2-4 week) bioassays, or growth experiments, may be required to determine the bioavailability of elements which are not commonly reported (i.e. V, Tl) yet are frequently present at elevated concentrations in the ash.

**Final Research Report****APPENDIX 7 SOIL ACIDITY AND SOIL LIMING RESPONSE****Importance of Soil Acidity and Liming**

Soil reaction, commonly defined as the degree of acidity or alkalinity, is a master variable that affects all soil properties—chemical, physical, and biological. Expressed as soil pH, this variable largely controls plant nutrient availability and biological activity in soils. It affects which vegetation will dominate the natural landscape, and which cultivated crops will grow well or grow at all in a given field site. Soil reaction also affects the fate of environmental pollutants, such as pesticides, organic contaminants and heavy metals, affecting their breakdown and mobility in the soil (Brady and Weil 1999).

Soil pH may be defined as the negative logarithm of the hydrogen ion activity ( $\text{pH} = -\log(\text{H}^+)$  where  $(\text{H}^+) = (\gamma [\text{H}^+])$ , ( $\gamma$  is the activity of coefficient of  $\text{H}^+$  and  $[\text{H}^+]$  is the concentration of the ion in solution in moles per litre). The range of pH values found in soil solutions is between 2 and 10.5, i.e., the activity of hydrogen ions ranges between  $10^{-2}$  and  $3 \times 10^{-11} \text{ mol l}^{-1}$  (Rowell 1988). Acid soils (which typically range between pH 4-6) result from the leaching of exchangeable bases, and are characteristic of humid climatic regions. Alkaline and salt-affected soils (pH 7 to about 8.5 for alkaline and saline soils, and  $> 8.5$  for sodic soils), formed by the accumulation of bases and soluble salts, dominate in arid and semi-arid regions (Tisdale et al. 1999). Soil acidity, and the attendant low base saturation, is the major limiting factor to agricultural productivity of soils from the order Spodosols. Spodosols, which comprise the majority of soils of eastern Canada and the northeastern United States, are coarse-textured mineral soils formed under forest vegetation through a process of intensive acid leaching. They are characterized by having a spodic horizon, or sub-surface accumulation of illuviated organic matter, and an accumulation of Al oxides with or without Fe oxides (Brady and Weil 1999).

While soil acidity has wide-ranging effects on the physio-chemical environment of soils, the main reason for recommending lime to increase the pH of acid soils is to improve crop yield. The soil pH at which optimum yields are obtained has been the subject of some controversy, and varies to some extent with the crop species being grown and the soil type. Usually the optimum pH is 6.5, but may be as low as 5.0-5.5 for acid-tolerance crops such as blueberries and cranberries and as high as 6.8 for alfalfa (APASCC 1986). There is some indication that highly weathered soils (i.e. Oxisols, Ultisols) may be adversely affected by liming to neutrality. Hence, the optimum pH ranges for crops may vary with intensity of soil weathering (McLean 1973). Yields of most crops are greatly reduced below pH 5.7, and data from more than 1,500 plant species indicate that relative crop yields at pH 4.7 are only 32% compared to 98% at pH 6.8 (Foth and Ellis 1996). Within the pH range of 4 to 10, the primary effect of soil pH on plant growth is not the  $\text{H}^+$  activities *per se* but the associated chemical environments. In general, the major influence of pH is on ion activities that affect the toxicity of elements like Al and Mn and availability of essential plant nutrients (in particular, Ca, Mg, P, K, S, B, Mo and Zn). On strongly acid soils (pH 5.1-5.5), root growth is restricted due to Al toxicity and a deficiency of Ca and/or Mg. Legume crops are particularly intolerant of soil acidity, due to the sensitivity of



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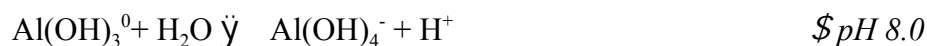
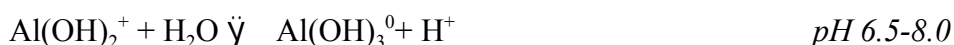
their associated N-fixing *Rhizobium* bacteria and the generally higher requirements of legumes for elements such as Mo and Ca (Kamprath 1970).

Another reason why acid soils require lime to be productive is to maintain the capacity to supply and hold base-forming cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ . The base cations are critical elements in plant and animal nutrition, and play an important role in maintaining the physical and biological integrity of soils. As a source of Ca and sometimes Mg, liming materials can directly and significantly increase soil Ca and Mg base saturation. As described below, raising soil pH through liming also influences the ability of soils to retain and supply these and other nutrient cations (i.e.,  $\text{K}^+$ ,  $\text{NH}_4^+$ ) by increasing the soil cation exchange capacity.

### Sources of Soil Acidity

Neutral soils become acid when acidic inputs in time exceed neutralizing inputs (i.e., mineral weathering, return of basic cations through nutrient cycling or additions) (Foth and Ellis 1996). Consequently, acid soils tend to occur in humid regions where the acidic inputs from precipitation and associated biological activity are high, and where leaching is effective in removing the soils neutralizing components. The acids that are constantly added to neutral soils in humid regions are a source of  $\text{H}^+$ , which gradually replaces exchangeable base cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ). Thus, the increasing saturation of soil colloids with  $\text{H}^+$  and corresponding loss of base cations results in a decrease in soil pH (Foth and Ellis 1996). Natural sources of acidity include humus or organic matter, aluminosilicate clays, hydrous oxides of Fe and Al, exchangeable Al, soluble salts and  $\text{CO}_2$ . In addition to natural sources of acidity, soils may also be subject to man-induced acidity. Anthropogenic sources of acidity include decomposing crop residues, acid-producing N and S fertilizers, and acidic inputs from the atmosphere (acid rain) (Tisdale et al. 1999).

Advances in soil science within the last 50 years demonstrate that the chemistry of acid soils is intimately linked to the solution chemistry of Al. The role of Al in acidification of soils is primarily in the form of hydroxy-Al cations, which serve as both a source and a sink for  $\text{H}^+$ . That is, hydrolysis of  $\text{Al}^{3+}$  liberates lower valence hydroxy-Al species and  $\text{H}^+$  and lowers pH, unless there is a source of  $\text{OH}^-$  to neutralize  $\text{H}^+$ , as illustrated by the following sequence (Bohn et al. 1985; Tisdale et al. 1999):



Each reaction is driven to the right by the consumption of  $\text{H}^+$  through reaction with added or indigenous  $\text{OH}^-$ . Thus, successive hydrolysis reactions are associated with solutions of

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successively higher pH, since the sink for  $H^+$  increases with increasing pH. Above pH 6.5, solid-phase gibbsite ( $Al(OH)_3$ ) will precipitate out whenever the solubility product of this mineral is exceeded (Bohn et al. 1985). Apart from releasing hydrogen ions, monomeric hydroxy-Al ions ( $Al(OH)^{2+}$ ,  $Al(OH)_2^+$ ) behave essentially as exchangeable cations, and at progressively lower pH, begin to dominate the cation exchange complex. Polymerization of hydroxy-Al, however, produces large cations of variable charge. Because of their high positive charge, hydroxy-Al polymers are strongly retained by soil colloid surfaces and are virtually non-exchangeable (Tisdale et al. 1999). Below pH 5.5, trivalent Al and Al polymers dominate adsorption sites on the colloid surfaces, thereby lowering the soil cation exchange capacity.

### Soil pH, CEC and Cation Associations

Soil pH has a pronounced effect on both the cation exchange capacity (CEC) (the amount of exchangeable cations that a soil can adsorb) as well as the cation dominance on the exchange complex. As indicated above, a predominance of non-exchangeable forms of Al and H on the exchange complex of acid soils reduces the number of available cation adsorption sites, thereby lowering the CEC. Conversely, the neutralization of soil acidity releases some of the covalently bound H as well as strongly adsorbed exchangeable Al. This frees up negatively charged sites on the soil colloids resulting in an increased capacity for cation adsorption, or increased CEC. As one moves from very acid soils to moderate acidity, and to neutrality and above, there is a steady replacement of exchangeable hydrogen and aluminum with base-forming cations ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ ,  $Na^+$ ), which increases the percentage base saturation of the soil (i.e., percentage of the total exchange capacity saturated with exchangeable cations other than hydrogen and aluminum) (Brady and Weil 1999).

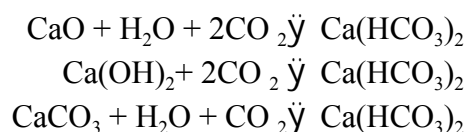
The relationship between pH and CEC is strongly affected by the kind and amount of soil colloids (clay and humus particles), which are the source of negative charge. There are two types of charge associated with soil colloids, variable or pH dependant charge, and permanent or constant charge. The pH dependant charge of soils results from the protonation and deprotonation of surface exposed hydroxyls and other functional groups on the surfaces of the colloidal particles. All colloids, organic or inorganic, exhibit surface charges that are largely pH dependant. Most of the charges associated with the soil organic matter, 1:1 type clays (e.g. kaolinite), and Fe and Al oxide clay minerals are of this type (Foth and Ellis 1996). In the case of layer silicate clays, however, these surface charges are complemented by a much larger number of charges emanating from ionic substitutions, the source of what is termed permanent charge. Permanent charge results from a charge imbalance brought about by the isomorphous substitution in the clay crystal structure of one cation by another of similar size but differing in charge (Brady and Weil 1999). Thus, there is a dominance of permanent charge in mineral soils with significant amounts of 2:1 type clay minerals, whereas pH dependant charge prevail in organic soils or soils containing appreciable amounts of 1:1 type clays or Fe and Al oxide clays.

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Colloidal materials also differ in terms of CEC. For example, the CEC of humus in neutral soils is approximately 100 cmol/kg, whereas the CEC of clays ranges from virtually nil in sesquioxide minerals (gibbsite, goethite and hematite) to 10 cmol/kg for 1:1 clays such as Kaolinite, and up to 250 cmol/kg for 2:1 clays such as Smectite, Vermiculite or Illite (Rowell 1994). Sandy soils are generally low in all colloidal materials and therefore generally have very low CEC (2-4 cmol/kg for sands and 2-12 cmol/kg for sandy loams) compared with silt loams (9-26 cmol/kg) and clay loams (4-60 cmol/kg) (Rowell 1994).

### Reactions of Liming Materials in the Soil

The acid neutralizing reaction which takes place in soils is essentially the same for all liming materials (oxides, hydroxides, carbonates). First, there is a reaction of the liming material with carbon dioxide and water to yield the bicarbonate form, followed by a reaction with the colloidal complex of acid soils which results in the replacement of hydrogen and aluminum with calcium and magnesium (Brady and Weil 1999). The reaction sequence may be summarized as follows:



The insolubility of  $\text{Al}(\text{OH})_3$  and the release of  $\text{CO}_2$  to the atmosphere pulls the reaction to the right. The adsorption of the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions raises the percent base saturation of the colloidal complex. There is a corresponding decrease in Al saturation, and increase in the pH of the soil solution (Brady and Weil, 1999).

### Forms of Soil Acidity

There are three main forms of soil acidity: (1) *active acidity*, (2) *exchangeable (salt-replaceable) acidity*, and (3) *residual (potential) acidity*. These types of acidity all add up to the *total acidity* of a soil (Brady and Weil 1999). *Active acidity* is a measure of the  $\text{H}^+$  ion activity in the soil solution that is attributed largely to the hydrolysis of aluminum. It is very small compared to the acidity which exists in exchangeable or residual forms. *Exchangeable acidity* is associated with the exchangeable aluminum and hydrogen ions that are present in largest quantities in very acid soils. These ions can be released into the soil solution by cation exchange with an unbuffered salt, such as KCl. In moderately acid soils, the limestone needed to neutralize exchangeable acidity is commonly more than 100 times that needed to neutralize the soil solution (active acidity). In strongly acid soils, the amount may be several thousand times greater. *Residual acidity* is represented by hydrogen and aluminum which is bound in non-exchangeable forms by organic matter and silicate clays. Residual acidity may be neutralized by limestone or other alkaline materials but cannot be detected by the salt-replaceable technique. Residual acidity is usually far greater than either active or exchangeable acidity. It may be 1000 times greater than

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active acidity in a sandy soil, and 50,000-100,000 times greater in a clay soil high in organic matter (Brady and Weil 1999).

### Lime Requirement of Soils

An important practical procedure in the management of acid soils is the determination of soil lime requirement. The lime requirement may be defined as the amount of liming material required to change the soil to a specified state with respect to pH or soluble Al content (Foth and Ellis 1996). Normally, the 'specified state' is the pH associated with optimum crop yield. Other criteria, such as the elimination of Al toxicity, a given 'ideal' base saturation, or economics, may also be used (McLean 1973; Webber et al 1977; Liebhardt 1981).

Two soils may have the same soil pH, but differ markedly in the amount of acidity which is adsorbed or held by the soil colloidal complex. For example, a group of soils all measuring pH 4.5, but varying in CEC, had lime requirements to pH 6.5 ranging from 6.7 to more than 33.5 metric tons  $\text{CaCO}_3$  per ha (McLean 1978). Soil pH (or  $\text{H}^+$  ion activity in the soil solution) is an intensity factor, whereas adsorbed acidity (sum of exchangeable and reserve acidity) is a quantity factor, determined largely by the buffer capacity of the soil (McLean 1973). Soil buffer capacity (BC) can be described by the ratio of the concentrations of adsorbed ions ( $^aQ$ , change in quantity) and solution ions ( $^aI$ , change in intensity), i.e.,  $\text{BC} = ^aQ/^aI$  (Tisdale 1999). In the context of soil acidity, buffer capacity confers on soils the ability to resist changes in pH. Thus, a strongly buffered soil is more able to resist the acidifying effects of leaching than a weakly buffered soil. Once it becomes acid, however, such a soil contains much more exchangeable and reserve acidity which must be neutralized before there is an increase in pH. Buffering therefore has a great influence on the amount of liming material required to affect a desired change in pH, i.e. soil lime requirement. Soils vary widely in terms of buffer capacity. Thus, factors which increase soil CEC (layer silicate clay and/or organic content) will tend to increase soil buffering, hence, soil lime requirement (Brady and Weil 1999). In the interpretation soil tests, it is important to remember that lime requirement has little relationship to the pH of the soil. The fact that total acidity may be thousands of times in excess of the active acidity, and varies in soils according to buffer capacity, explains why soil pH (while a useful indicator of active acidity) can not be used to determine soil lime requirement.

Various approaches have been used to estimate the soil lime requirement. Most routine or batch analyses utilize buffered solutions as a means to estimate a proportion of the total acidity. Samples of soils are equilibrated with a buffered solution that contains a small quantity of a neutral salt. The greater the total acidity of the soil, the more the solution buffering is overcome and the solution pH reduced, the degree of reduction being proportional to the acidity released from the soil (Brady and Weil 1999). The soil lime requirement (i.e. the amount of  $\text{CaCO}_3$  required to achieve the target soil pH) is then obtained by calibrating the pH of the soil-buffer mixtures against the lime requirement established by titrating soils with  $\text{Ca}(\text{OH})_2$  or incubating them with various amounts  $\text{CaCO}_3$  (Tran and Lierop 1981). Different buffering solutions are used for soils with different cation exchange capacities. Because of its speed and simplicity, the SMP test has been the most widely used buffer lime requirement test in soil test labs in Canada

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and the United States. The method is best suited to soils with appreciable buffer acidity and appreciable exchangeable Al. Another method, the Adams and Evans buffer method, is utilized in the southeastern US and is recommended for soils with low effective CEC and low lime requirement (Foth and Ellis 1996). Other methods of determining soil lime requirement are based on CEC and soil pH-base saturation relationships (i.e. calculating lime needs to produce a desired Ca base saturation (50-70%), or percentage base saturation which, for a given clay type, is correlated with the target soil pH (e.g. 90% base saturation for pH 6.8) (Brady and Weil 1999; McLean 1973). In humid tropical soils, where soil acidity is often associated with high levels of soluble Al, lime requirement may be based solely on the amount of lime needed to lower the solubility of Al. Lime requirement based on the 0.02 M CaCl<sub>2</sub>-soluble Al results in a more economical use of lime, and has been recommended in Canada for regions (i.e. northern Alberta, northeastern British Columbia) where limestone transportation distances may be prohibitive (Webber et al 1977).

There are, in addition to soil buffer capacity, two other important factors which influence the soil lime requirement. These include the change in pH required, and the characteristics of the liming material to be used. These factors are discussed below, in the general context of the response of soils to liming.

**Soil Liming Response**

The soil response to liming, as indicated by the extent and rate of the acid neutralizing reaction and persistence of liming effects, is a function of the characteristics of both the liming material and the soil.

Characteristics of liming materials

Commonly used liming materials include Ca and Mg oxides, hydroxides, carbonates and silicates. Ground calcite (CaCO<sub>3</sub>) or dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>), from mined deposits of natural calcium and magnesium carbonates, are the predominant agricultural liming materials. Other traditional liming materials include marl, shells and other sources of natural carbonates, and wood ashes (Tisdale 1999). There are in addition, a wide range of manufacturing or industrial by-products (e.g. slag, cement kiln dust, coal combustion by-products, alkaline sludges, and refuse limes from diverse manufacturing processes) which exhibit liming activity by virtue of the calcium and magnesium compounds they contain (Barber 1984). Due to the generally higher applications involved, use of such materials is importantly related to nearness to source (Foth and Ellis 1996).

The ability of a given liming material to neutralize soil acidity depends primarily on the neutralizing value of the material. Pure calcium carbonate (CaCO<sub>3</sub>) is the standard against which liming materials are measured, and acid-neutralizing capacity is expressed as a weight percentage of calcium carbonate, or calcium carbonate equivalent (CCE). The rate at which the material reacts (effective CCE) is related to both the physical size of the lime particles and chemical purity of the material. Moisture content and impurities reduce CCE by replacing an

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equivalent weight of potentially reactive agricultural lime (PPIC 1996). The CCE of agricultural limestone (high-grade calcitic or dolomitic limestone), is between 90-108%. A high CCE (up to 180%) in pure oxides and hydroxides of Ca and Mg (i.e., CaO, Ca(OH)<sub>2</sub>) results in highly alkaline materials which are caustic to handle, reactive in soils, and produce a higher pH following application compared to carbonate limestones (Brady and Weil 1999). Oxides are inherently unstable, however, and when applied to soils, readily undergo carbonation<sup>53</sup> (McCarty et al. 1994; Carlson and Adriano 1993). Thus, in terms of acid neutralization, when applied on a CCE basis the net effect of oxide materials on soil pH is similar to carbonate limestones. Lime-based by-products are usually complex mixtures of alkaline and inert compounds, which include oxides, carbonates, silicates and sulfates of Ca, Mg, Fe, Al, as well as trace amounts of a wide range of other elements (BNQ 1997; Barber 1984; Elrashidi et al 1999). For liming materials derived from industrial processes, 25% is the minimum CCE for the by-product to be considered an effective liming material (BNQ 1997).

In addition to chemical composition, the other main factor affecting the rate of the acid neutralizing reaction is particle size. Carbonate limestones must be finely ground in order to react with the soil, whereas liming materials comprised of oxides/hydroxides are by nature powdery and therefore require no particle size reduction. Crushing procedures used on carbonate limestones result in a range of particle sizes. The liming efficiency of different size fractions increases with decreasing particle size; that is, 0% efficiency for > 2 mm (9-mesh Tyler sieve); 60% between 0.150 mm and 2 mm; and 100% for < 0.150 mm (100-mesh Tyler sieve) (BNQ 1997). Most agricultural grade carbonate limestones are ground so that all of the material passes a 2.00 mm screen and 60% of the material passes a 0.150 mm screen (APASCC 1986). Such a size distribution provides enough fine particles for some neutralization of acidity immediately following application, as well as some coarse particles for continued liming effect one to four years after application (A&L 1992).

While residual activity is in part a function of particle size (i.e. large particles take longer to dissolve than small particles), chemistry of the liming material and the soil is also a factor. More specifically, factors which lower the solubility of the liming material, and therefore reduce the rate of reaction with soil particles (i.e. increased soil pH, increased concentration of precipitating ions, surface application (not soil incorporated), high amendment application rates) will tend to prolong the liming effect. Carbonates of Ca are more soluble than carbonates of Mg. Thus, for any given particle size fraction, calcitic limestone will react more quickly than dolomitic limestone, however the residual activity will be about half that of dolomitic lime. As noted above, the fine particle size of oxides compared with carbonates initially allows a more rapid neutralization of soil acidity. The reactivity of oxides is soon reduced in soils by hydration and carbonation reactions, and the subsequent formation of hardened granules of CaCO<sub>3</sub> which may remain in the soil for long periods of time. Thus, for all intents and purposes, the liming persistence of oxides is similar to that of calcitic lime (Tisdale 1999).

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<sup>53</sup>Following hydrolysis of the oxide, carbon dioxide from the atmosphere and/or biological respiration combines with Ca<sup>2+</sup> or Mg<sup>2+</sup>, forming more stable calcium or magnesium carbonate compounds (Ca (HCO<sub>3</sub>)<sub>2</sub>, Mg(HCO<sub>3</sub>)<sub>2</sub>) of near neutral pH.

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It is noted that high alkalinity due to the reactivity of a correctly dosed oxide or other reactive liming material differs importantly from alkalinity caused by overliming. While alkalinity in excess of the lime requirement from oxides is short-lived (due to hydration and carbonation reactions which cause a reduction in soil pH), overliming effects may persist for years. The main reason for a highly persistent liming effect on overlimed soils is that at alkaline pH values (7.0), and in the absence of any appreciable reserve acidity in the soil, dissolution of the excess liming material is exceedingly slow<sup>54</sup>. Both overliming and under-liming will result in a soil pH which is not optimum, however, of these two, overliming is the more costly and difficult to correct. Overliming injury to crops results primarily from changes in the availability of micronutrients; e.g., deficiencies of B, Cu, Mn, Fe, and Zn, reduced availability of P, or Mo toxicity (Foth and Ellis 1996). Regardless of the type of liming material used, the rate and frequency of liming applications should always be based on soil tests and crop requirements.

### Characteristics of the soil

The main soil characteristics which have the greatest influence on soil liming response are soil buffer capacity and colloid characteristics. The role of soil pH relates primarily to effects on the solubility of liming materials as well as precipitating ions.

As indicated above, soil buffering is of great practical significance in soil liming. Not only is it a key factor in determining soil lime requirement, it also influences the rate and extent of pH adjustment as well as the persistence of liming effects. For example, soils of low buffering capacity (low CEC soils) require less lime for a given required change in soil pH compared with more highly buffered soils. Because of a low amount of reserve and exchangeable acidity, neutralization of total acidity on these soils is likely to be more rapid than on highly buffered soils. Correspondingly, fluctuations in soil pH (active acidity) due to the effects of leaching or crop removal of basic cations, acidifying fertilizers, or applied liming materials, are greater. Thus, on low buffer capacity soils there is a much greater risk of overliming. Transient increases in soil pH following the application of oxides or other highly reactive liming materials will also be more pronounced on these soils. Some authors report more lasting pH effects from the application of alkaline fly ash to poorly buffered soils (Petruzzelli et al. 1987). More commonly, the consensus is that greater leaching on low capacity soils reduces the duration of liming effects so that such soils require lime more often than highly buffered soils (Brady and Weil 1999). The response of soils to liming according to the amount of buffering affects the liming strategy. On weakly buffered soils, frequent light applications are recommended, whereas on more strongly buffered soils, larger amounts may be applied less often (Tisdale 1999).

Soil buffer capacity and nutrient holding capacity are both a function of soil charge, which in turn, is determined by the type and amount of colloids present. Because charge in soils plays a key role in many soil processes (e.g., cation and anion exchange, acidity and basicity, fixation/adsorption of metal and other ions), soils have been placed into four major groups based on charge and colloid characteristics (Foth and Ellis 1996):

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<sup>54</sup>Petra Loro, Manager, Soil and Analytical Services Section, New Brunswick Dept. of Agriculture and Rural Development. Personal communication, August, 2000.

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- Mineral soils with moderate to high constant charge from 2:1 layer silicate clay minerals. Most of these soils are in the orders Alfisols, Aridisols, Entisols, Inceptisols, Mollisols, and Vertisols.
- Mineral soils with low variable charge from low activity crystalline clay minerals (1:1 layer silicate and oxide clay minerals) that are characteristics of Oxisols and Ultisols. Entisols and Inceptisols that occur in association with Ultisols and Oxisols will likely have variable charge characteristics.
- Mineral soils with low to high variable charge from short range-order and amorphous aluminosilicate minerals and organic matter; the Andisols and Spodosols.
- Organic soils (Histosols) with high variable negative charge from humus.

Each group of soils has unique properties and kinds of response to management practices, and therefore requires a different kind of soil fertility management program to make and keep the soils productive. For example, the predominance of variable (pH dependant) charge in Spodosols, means that liming can produce significant increases in the CEC, thereby greatly increasing the nutrient holding capacity of these soils. Liming of Mollisols and Vertisols (permanent charge soils), on the other hand, may improve nutrient availability but will not significantly affect the CEC (Brady and Weil 1999). Furthermore, Spodosols have much lower clay content but higher organic C content than other soils with comparable CEC (e.g., Entisols, Alfisols, Spodosols and Inceptisols all have CEC in the range of 14-16 cmol/kg). Consequently, maintaining soil organic matter in these soils is critical to maintaining the ability of the soils to resist acidification and to hold and supply nutrients.

While buffer capacity and kind and amount of colloids are the soil characteristics which largely determine liming response, other soil conditions, such as moisture content and initial pH, may also be important. The effect of the latter two is mostly in terms of influencing the reactivity and rates of dissolution of liming materials. On a moderately well buffered Caribou loam soil (pH 5.3), a soil moisture content of 25% invariably resulted in a more rapid and extensive change in pH than did 10% soil moisture content. The lower soil moisture content reduced the efficacy of a 6.7 t/ha liming application to that of a 3.4 t/ha application. The higher pH initially associated with the 6.7 t/ha rate was restored in this treatment within 2-3 days of increasing soil moisture to 25% (Nielsen 1958). The rates of dissolution of most liming materials is greater at soil pH below 5.0, however, there is little effect of pH on limestone reactivity between pH 5 and 7 (Bailey 1989; Warfvinge and Sverdrup 1989). Within the pH range of 4.5-7.5, sequential increases of lime cause a linear increase in soil pH, indicating that the rate of acid neutralization is essentially constant within this range (McLean 1973; 1978).



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## APPENDIX 8 RESIDUAL LIMING EFFECTS IN YEAR 2000

## Soil pH\* and change in soil pH\*\* in cabbage, rutabaga and forage plots in 2000.

Treatment	Cabbage		Rutabaga		Forage	
	Soil pH	<sup>a</sup> pH	Soil pH	<sup>a</sup> pH	Soil pH	<sup>a</sup> pH
			2000			
Control	4.6	-0.4	4.7	-0.1	5.0	-0.1
Limestone	7.2	2.2	6.4	1.6	6.9	1.8
Low-Ash	5.9	1.0	6.0	1.2	7.1	2.0
Split-Ash	7.1	2.2	7.0	2.3	7.6	2.5
High-Ash	7.4	2.4	7.2	2.5	7.5	2.4

\* Values are based on July 2000 soil samples, averages of four replicates.

\*\* Change in soil pH (<sup>a</sup> soil pH) = pH<sub>f</sub> (final soil pH, July 2000) - pH<sub>i</sub> (initial soil pH (June '97, pre-amendment))

