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The Use of Unweathered Fly Ash to Improve Select Soil Physical Properties and Barley Growth and Development

by

© Loretta Yvonne Salé

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Science

in

Soil Reclamation

Department of Soil Science

Edmonton, Alberta

Fall 1995

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled The Use of Unweathered Fly Ash to Improve Select Soil Physical Properties and Barley Growth and Development submitted by Loretta Yvonne Salé in partial fulfillment of the requirements for the degree of Master of Science in Soil Reclamation.

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ABSTRACT

Fly ash, a by-product of coal-fired power generation, was added (0 to 100%; v/v) to soil high in clay, to alter soil texture and reduce the potential for surface soil crust and clod formation. During 16 months of exposure to the environment, the fly ash:soil mixtures were periodically analyzed for modulus of rupture, aggregate size distribution, penetration resistance, bulk density and water content. Barley was grown on the mixtures in a greenhouse and monitored for emergence, development, height, leaf length and width, above ground biomass and trace element concentration. Adding up to 12.5% fly ash to this soil reduced mean weight diameter but increased modulus of rupture; adding more fly ash reduced both parameters. Adding 6.25% fly ash increased grain yield; yield decreased linearly to 50% fly ash addition when most plants died. The addition of 25% fly ash reduced plant emergence but not yield because tillering increased.

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1. INTRODUCTION

Ash is a by-product of coal-fired power generating plants and has little current utility. Of the total ash produced, about 70% is fly ash with the remainder being bottom ash. Fly ash (FA) is the portion of ash produced in coal combustion that has a sufficiently small particle size to be carried away from the boiler in the flue gas (El-Mogazi et al. 1988). Bottom ash is composed of fine- and coarse-grained particles (ash and slag) and remains in the boiler (Carlson and Adriano 1993).

Because the market for fly ash in western Canada is relatively small (10% sold to the cement industry), its disposal is an expense for the power generating company. Fly ash that is not sold for commercial use is buried in disposal sites or lagooned. Investigation into possible uses for fly ash is welcomed by both industry and others who would gain. In particular, there is potential to use fly ash as an agricultural soil amendment.

Fly ash is composed of predominantly silt-sized, spherical, amorphous ferro-aluminosilicate minerals (Adriano et al. 1980; Carlson and Adriano 1993). It is generally characterized as having low permeability, low bulk density and high specific surface area (Page et al. 1979). However, the physical, chemical and mineralogical characteristics of fly ash depend on the parent coal source, the method of combustion and the efficiency and type of emission control device (Adriano et al. 1980; Carlson and Adriano 1993).

During the last 20 years the chemical composition of fly ash and its influence on soil chemistry and plant growth has been thoroughly studied (Page et al. 1979; Adriano et al. 1980; Elseewi et al. 1980; Dudas 1981; El-Mogazi et al. 1988; Carlson and Adriano 1993). The influence of fly ash addition on soil physical properties has been reported (Page et al. 1979; Adriano et al. 1980; El-Mogazi et al. 1988; Carlson and Adriano 1993) but a link to plant growth is missing.

Within Alberta, some agricultural soils have intrinsic properties that limit their productivity. Those with a high clay content (6.7 million hectares in Alberta; Brierley et al. 1992) are generally considered difficult to cultivate and, under dry conditions, large, dense and hard clods form (Hadas and Wolf 1983; Shiel et al. 1988). The clods can lead to poor seed-soil contact and reduced germination and pose a mechanical impedance to emerging seedlings (Malik et al. 1985; Wild 1988). In addition, these soils have the potential to form surface crusts that interfere with seedling emergence (Rathore et al. 1981) and can reduce soil infiltration rates and increase soil strength (Moore and Singer 1990). Crusts form when the exposed soil surface is subjected to rain followed by a period of rapid drying (Rathore et al. 1981). The impact from raindrops slake soil aggregates and small particles (clay and silt) are separated from sand particles and disperse at the soil surface. The suspended small particles move into and choke voids between grains forming a thin layer at the surface. The layer densifies during wetting and drying, affecting aeration, mechanically impeding plant growth and reducing water infiltration which increases runoff and erosion (Lemos and Lutz 1957; Awadhwal and Thierstein 1985; Freebairn et al. 1991).

Several methods are available to measure changes in soil physical properties that can be used to infer the potential for surface crust and clod formation. Chepil (1955) found an inverse relationship between modulus of rupture, a method used to quantify soil crusting potential, and soil particle sizes used to form a briquet. Braunack and Dexter (1988) reported that the weakest crusts were those formed by the 1-4 mm aggregate size range for a loam soil. Penetration resistance also quantitatively measures soil surface strength (Braunack and Dexter 1988; Rolston et al. 1991) and can be used to infer the force required by a seedling to emerge.

Fly ash is composed primarily of silt-sized particles, which, when added to a clay, soil could alter its texture (Carlson and Adriano 1993) and in turn the degree to which the soil is susceptible to surface crust and clod formation. Watson (1994) found that the textures of a silty clay and a sandy loam soil could be changed to loam by addition of fly ash. Soil treated with fresh fly ash had reduced bulk density and modulus of rupture and increased water-holding capacity (Chang et al. 1977; Fail and Wochok 1977; Watson 1994). Fail and Wochok (1977) applied 70 tonnes ha^{-1} of fly ash to B horizon material and reported soybean (*Glycine max* L.) yield 11 times higher than that of the control, attributed in part to improved soil texture. Chang and co-workers (1977) significantly reduced modulus of rupture and bulk density of California soils of various textures by the addition of as little as 2.5% v/v fly ash. In studies reviewed by El-Mogazi et al. (1988), for a variety of soils mixed with up to 50% fly ash, the mixtures tended to have lower bulk densities, higher water holding capacities, lower hydraulic conductivities and lower moduli of rupture than soil alone. More recently, Watson (1994) reported that the addition of 5% fly ash to a clay loam soil reduced modulus of rupture strength by 23% (averaged across three fly ashes), while adding 5% fly ash to a sandy loam soil reduced its inherent strength by almost 80%.

Most of the research on changes in soil physical properties after fly ash addition has been conducted using laboratory experiments (Chang et al. 1977; Watson 1994). If fly ash is to be used as an agricultural soil amendment, changes in the soil physical properties should be measured under field conditions. To do this, we need to understand how these properties will change over time when exposed to the environment. For instance, fly ash has pozzolanic (cementing) properties which may influence some parameters.

The purpose of trying to improve the physical characteristics of a problem soil is also to improve crop yield, thus, how fly ash influences plant growth and development must be determined. Fly ash contains trace elements which in certain concentrations are potentially harmful to plants (Plank and Martens 1973; Adriano et al. 1980; Eary et al. 1990) or to animals that consume them (Khattak et al. 1991). Ash amendment can also result in reduced available soil nitrogen and phosphorus, excessive soluble salt concentrations or elemental imbalances due to excessively high pH (Carlson and Adriano 1993).

Aitken and Bell (1985) studied the phytotoxicity of boron from Australian fly ashes on French bean (*Phaseolus vulgaris* L.) and Rhodes grass (*Chloris gayana* Kunth) grown in a glasshouse. They found the addition of 30% or more by weight of unweathered fly ash to silt loam soil significantly reduced the yield of beans (48%) whereas the yield of Rhodes grass was significantly decreased (18%) only at levels of ≥ 70% ash addition. They associated the yield reduction with boron toxicity. In the same experiment, leached fly ash was added to sand and sandy loam soils and crop yield increases were attributed to increased plant available water. For example, a 10% addition of fly ash increased the plant available water of the sand soil by factors of 4.9 and 9.2 for two types of fly ash. Furr et al. (1978) reported that of all elements found in fly ash, arsenic, boron, magnesium and selenium were the ones most consistently elevated in various crops field-grown on fine sandy loam soil amended at rates of 18 tonnes ha^{-1}. The authors reported that arsenic concentration in the plant material was below human and animal toxicologically significant levels according to the U.S. Department of Health, Education and Welfare. The toxicity levels of the other elements were not discussed. In a greenhouse study by Mbagwu (1983), the addition of 5% w/w of unweathered fly ash to calcareous fine-loamy and acidic coarse-loamy soils did not affect crop yields of corn, alfalfa, birdsfoot trefoil or dry beans. Fail (1987) added 70 tonnes ha^{-1} of fly ash (pH 11) to an acidic mine spoil. The average accumulated second year plant biomass increased 30 times for Rhode Island bentgrass (*Agrostis tenuis* Sibth.), 20 times for tall fescue (*Festuca arundinacea* Schreb.) and 5 times for bush clover (*Lespedeza cuneata* "du mont" g. don.) with no adverse effects on the plants. The increased production rates were attributed to the effects of fly ash on soil water holding capacity and improved soil texture although these parameters were not quantified in the study. Carlson and Adriano (1993) reported that the most significant factors limiting establishment of vegetation on ash deposits were excessive concentrations of soluble salts and boron.

The physical and chemical properties of fly ash are dependent upon the geologic origin of the coal, method of combustion, type of emission control devices and age before disposal (Adriano et al. 1980; Carlson and Adriano 1993) and thus are relatively site specific. Results from research in specific geographic locations cannot be extrapolated to all areas and situations. Because of the high variability that exists among fly ashes and soils, the results of mixing the two together will vary among fly ash sources and soil characteristics.

Of the 23.7 million tonnes of coal burned to produce electricity in Alberta during 1992 (Natural Resources Canada 1993), approximately 2.5 million tonnes of fly ash were produced. This amounts to a substantial supply for future use. The purpose of the following two experiments is to determine how much fly ash can be added to a soil high in clay to improve its physical condition but not adversely affect barley growth and development.

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2. TEMPORAL INFLUENCE OF FLY ASH ON SELECT SOIL PHYSICAL PROPERTIES

2.1 INTRODUCTION

Fly ash is a by-product of coal-fired power generation plants that has little current utility (10% of the amount produced is used in the cement industry). Fly ash is the portion of ash produced in coal combustion that has a sufficiently small particle size to be carried away from the boiler in the flue gas (El-Mogazi et al. 1988). Bottom ash is composed of fine- and coarse- grained particles (ash and slag) and remains in the boiler (Carlson and Adriano 1993). Of all the ash produced in Alberta, about 70% is fly ash with the remainder being bottom ash. Fly ash that is not sold for commercial use is buried in disposal sites or lagooned.

The physical, chemical and mineralogical characteristics of fly ash depend on the parent coal source, the method of combustion and the efficiency and type of emission control device (Adriano et al. 1980; Carlson and Adriano 1993). In general, fly ash is composed of predominantly silt-sized, spherical, amorphous ferro-aluminosilicate minerals (Adriano et al. 1980; Carlson and Adriano 1993). Fly ash is generally characterized as having low permeability, low bulk density and high specific surface area (Page et al. 1979).

The aggregate size range for an ideal seedbed is 0.5-1 to 5-6 mm (Russell 1961). Soils with a high clay content are generally considered difficult to cultivate, and under dry soil conditions, large, dense and hard clods form (Hadas and Wolf 1983; Shiel et al. 1988). The clods can lead to poor seed-soil contact and reduced germination and pose a mechanical impedance to emerging seedlings (Malik et al. 1985; Wild 1988).

Germination and seedling emergence can also be influenced by soil surface crusting (Hanks and Thorp 1956; Hanks and Thorp 1957; Awadhwal and Thierstein 1985). Surface crusts are thin, hard layers formed due to dispersive forces in raindrops or irrigation water followed by drying (Awadhwal and Thierstein 1985). The impact from raindrops slake soil aggregates and small particles (clay and silt) are separated from sand particles and disperse at the soil surface. The suspended small particles move into and choke voids between grains, forming a thin layer at the surface. The dense layer formed during wetting and drying reduces aeration, plant growth and water infiltration, thus increasing the potential for runoff and erosion (Lemos and Lutz 1957; Awadhwal and Thierstein 1985; Freebairn et al. 1991). Chepil (1955) found an inverse relationship between modulus of rupture, a method used to quantify soil crusting potential, and soil particle sizes used to form a briquet. Braunack and Dexter (1988) reported that the weakest crusts were those formed by the 1 to 4 mm aggregate size range for a loam soil. Penetration resistance also quantitatively measures soil surface strength (Braunack and Dexter 1988; Rolston et al. 1991) and can be used to infer the force required by a seedling to emerge.

Alberta's agricultural land is a mosaic of soils, including several problem soils with limiting soil physical properties. There are approximately 6.7 million hectares of fine textured soils, 6 million hectares of coarse textured soils and 20 million hectares of Luvisolic soils in Alberta to name a few (Brierley et al. 1992). There is potential to manipulate a problem soil's physical characteristics by the addition of fly ash because of its silt-sized particles and component calcium. Watson (1994) found that the textures of a silty clay and a sandy loam soil could be changed to loam by addition of fly ash. Soil treated with fresh fly ash had reduced bulk density and modulus of rupture and increased water-holding capacity (Chang et al. 1977; Fail and Wochok 1977; Watson 1994). Fail and Wochok (1977) applied 70 tonnes ha^{-1} of fly ash to B horizon material and reported soybean (*Glycine max* L.) yield 11 times that of the control, attributed in part to improved soil texture. Chang and co-workers (1977) significantly reduced modulus of rupture and bulk density of California soils of various textures by the addition of as little as 2.5% v/v fly ash. More recently, Watson (1994) reported that the addition of 5% fly ash to a clay loam soil reduced modulus of rupture strength by 23% (averaged across three fly ashes), while adding 5% fly ash to a sandy loam soil reduced its inherent strength by almost 80%.

Studies on the potential use of fly ash as an amendment for soil physical properties are limited. Within Alberta, the research is even more scarce. Watson (1994) reported from laboratory experiments strength and water retention characteristics of two types of

Alberta fly ashes mixed with two types of soil. There is a need to quantify the influence of fly ash addition on soil physical properties under field conditions.

Information is limited not only on how soil physical properties change after fly ash addition to soil but also on its dynamics. The purpose of this study was to determine the temporal influence of adding fly ash to a problem soil on select soil physical parameters. Fly ash:soil mixtures were analyzed at four time intervals: 1) upon mixing, 2) after one summer, 3) after one summer and a winter, 4) after the second summer following a summer and a winter. Soil parameters used to evaluate a soil's potential to form clods or surface crusts were bulk density, dry aggregate size distribution, penetration resistance and modulus of rupture.

2.2 METHODS

2.2.1 Fly Ash and Soil

Fresh fly ash was collected directly from the electrostatic precipitators (emission control devices that remove particulates discharged to the atmosphere) at the Sundance coal-fired power plant located approximately 100 km west of Edmonton, Alberta. The problem soil used was the surface horizon (15-cm depth) from a reconstructed soil on the Highvale coal mine. The soil was the A horizon of a Dark Gray Luvisol (Mollic Cryoboralf) with a minor contribution from a Gray Solonetz (Natriboralf) with poor tilth prior to mining. The soil was a clay loam with a SAR of 6.4 and organic carbon content of 1.6%. The fly ash was silt loam in texture. The physical and chemical properties of the soil and fly ash are summarized in Tables 2.1 and 2.2.

2.2.2 Fly Ash:Soil Mixtures

The soil sample was air dried, then crumbled to pass a 9.5-mm sieve. Fresh fly ash was mixed with the clay loam soil in rates of 0, 6.25, 12.5, 25, 50, 75 and 100% fly ash on a volume basis. The mixtures were gently poured into plastic pots (ID = 20 cm, volume 553 cm^3) to a depth equal to that of cultivation in the field (15 cm). The bulk densities of the soil (1.15 Mg m^{-3}) and fly ash (1.03 Mg m^{-3}) were determined by dividing the mass of soil and fly ash contained in the pot by the volume of the pot. The bulk densities of the fly ash:soil mixtures were assumed to be the average of the two values (1.09 Mg m^{-3}). Masses of mixtures necessary to fill the pots to 15 cm were determined using this bulk density and the volume of the pots. Holes were punched into the bottom of the pots to allow drainage. The pots were buried on the mine on July 8, 1993 at the same site where the soil was collected so that the mixture within the pot was level with the surrounding soil. The 63 pots were spaced at least 30 cm apart and were arranged in a completely randomized design with seven rows and nine columns. Three replicates of each mixture (3x7) were removed from the ground at different sampling times (October 20, 1993; April 15, 1994; and October 20, 1994), covered with lids, then stored at room temperature for subsequent analysis. Any weeds that grew in the pots were removed manually during the course of the experiment.

2.3 MEASUREMENTS

2.3.1 Bulk Density

A Uhland core sampler (7.6 cm in diameter x 7.6 cm high) was inserted into the center of each pot until the top of the sleeve was level with the soil surface. Bulk densities were determined by using the oven-dried mass of soil collected in the core and the volume (344.8 cm^3) of the core. The bulk densities that were determined for the 0-7.6 cm depth increment were assumed to be the same for the 7.6-15 cm depth. The diameter of the pot restricted the removal of a sample from the lower depth. The samples were saved and later used in the dry sieving analysis.

2.3.2 Soil Water

Three samples per pot were collected at the same time as surface penetration resistance for gravimetric surface soil water (0-2.5 cm) determination. After the surface soil was removed for modulus of rupture analysis, a Backsaver™ soil sampler was used to collect soil samples to the bottom of each pot for gravimetric soil water determination with depth at increments of 2.5-5.0, 5.0-10.0 and 10.0-15.0 cm. Volumetric water content was calculated using the bulk densities explained previously and the gravimetric water results for the four depth increments separately.

2.3.3 Dry Sieving

The soil samples saved from the bulk density determinations were air dried, then placed on a nest of sieves and gently shaken by hand to allow the aggregates to pass through the sieves. The nest was composed of the following sieve sizes: 19.0, 12.5, 9.5, 8.0, 6.3, 4.0, 2.0, 0.500, 0.250, 0.125 mm, and a pan to catch aggregates <0.125 mm. The aggregates that remained on each sieve were weighed. Aggregate size distribution (% of sample) per sieve size and mean weight diameters (MWD) were then calculated as (Kemper and Rosenau 1986):

$$MWD = \sum_{i=1}^{n} \bar{x}_i \, w_i$$

where n = number of sieves, $\bar{x}_i$ = mean diameter and w_i = proportion of the total sample weight.

The aggregates collected on sieves were combined into three groups and their weights (% of sample) added together: Group A for aggregates ≤0.250 mm, Group B for aggregates 0.500 to 4.0 mm, inclusive, and Group C for aggregates 6.3 to 19.0 mm, inclusive.

2.3.4 Penetration Resistance

Surface strength of each fly ash:soil mixture was measured with two types of probes (blunt-end and cone) attached to a hand-held penetrometer (Soil Test, Inc. Cone Penetrometer model #CN-973, Evanston, Illinois, USA). The blunt-end tip was 20 mm in diameter and 20 mm long and consisted of a flat-bottomed cylindrical probe. The dimensions of the 30° cone were 13 mm in diameter at the base and 24 mm long. Resistance was recorded when the base of the cone or blunt-end was level with the surface of the fly ash:soil mixture. Three measurements spaced approximately 2 to 3 cm apart per pot were made for each type of penetrometer.

2.3.5 Modulus of Rupture (MOR)

After the Uhland core was inserted into the center of the pot, the fly ash:soil mixture around the core was collected to a depth of 2.5 cm and air dried. The samples were prepared for measurement of MOR according to Richards (1953) with some modifications. A minimum of three briquets were prepared per replicate giving nine or more briquets for each fly ash:soil mixture for each sampling time. The frame that forms the briquet was lined with petroleum jelly to prevent the mixtures from sticking to the frame. After the briquets were saturated from below, the excess water was aspirated off before oven drying for approximately 24 hours at 50 °C. The method of breaking the briquet followed that of Richards (1953). A caliper was used to measure the width and thickness of each briquet at the point of fracture. The amount of water it took to break the briquet was weighed and used to calculate F using the measured mechanical advantage of 4.376. The modulus of rupture (MOR) of each briquet was calculated using Richards (1953) equation,

$$s = \frac{3FL}{2bd^2} \times \frac{1\text{ bar}}{1\,000\,000\text{ dynes / cm}^2} \times \frac{1000\text{ mbar}}{1\text{ bar}} \times \frac{0.1\text{ kPa}}{1.0\text{ mbar}}$$

where s is the modulus of rupture in kPa, F is the breaking force in dynes (water (g) x 980), L is the distance between the two lower supports, b is the width of the briquet and d is the depth of the briquet, all expressed in centimeters.

2.3.6 Statistical Analyses

Soil water content might change with storing the pots for different lengths of time after field removal. Therefore, soil water and soil physical parameters that are a function of soil water (bulk density and penetration resistance) were compared among rates within each sampling time separately using t-Tests ($p<0.05$) (SAS Institute Inc. 1992). Modulus of rupture, mean weight diameter and grouped dry sieving data are assumed to not be influenced by storage time and were analyzed as both repeated measures over all times and using t-Tests within each sampling time ($p<0.05$) (SAS Institute Inc. 1992).

2.4 RESULTS AND DISCUSSION

2.4.1 Climatic Conditions

From July (date of pot burial) to October 31, 1993 there was 171 mm of rain, with one major single day rainfall event on July 21, 1993 (74 mm). Over the winter, 42.7 cm of snow accumulated in the field (measured March 3, 1994). During summer 1994 (April 1 to October 31), at least 290 mm of rain fell on the site with the largest single precipitation amount on August 17 (31 mm); all other events were < 20 mm. Due to a mechanical problem with the meteorological station used, not all precipitation was measured.

2.4.2 Bulk Density

Bulk density generally increased as percent fly ash increased to 12.5 or 25%, then decreased with additional fly ash (Table 2.3) with the most dramatic increases occurring with as little as 6.25% fly ash (except at Time 3 and 4). Bulk density generally decreased with time. Bulk densities measured at Time 4 were substantially lower than those at Time 2 (both fall measurements) and these effects were consistent across treatments. Over-winter (Time 2 to Time 3) changes in bulk density were greatest for 6.25, 12.5 and 100% fly ash (-0.18, -0.15 and -0.10 Mg m^{-3}, respectively). Other mixtures had little or no change in bulk density over this time period. In addition, growing season changes in bulk density were much greater in 1994 compared to 1993 although the elapsed period was almost twice as long in 1994.

2.4.3 Volumetric Water

Generally, there was a trend of reduced water as percent fly ash increased for all depth increments for sampling Times 2 and 3 but not for 4. Volumetric water content for 6.25% fly ash was not significantly different from the control but 12.5 and 25% fly ash significantly reduced total volumetric water. This trend is expected since percent clay in the fly ash:soil mixture decreased as percent fly ash increased (Table 2.4).

2.4.4 Mean Weight Diameter (MWD)

On a given sampling date MWD generally declined as percent fly ash increased (except 100% fly ash; Figure 2.1). For the 0, 6.25, 12.5 and 25% fly ash treatments, MWD increased over time. In the 50 and 75% fly ash treatments, MWDs increased by Time 3 then declined by Time 4.

Adding fly ash to the soil did not change MWD for the 0 to 25% fly ash treatments until Time 2. Interesting changes in MWD occurred once the mixtures were exposed to the environment. After the first summer, large clods formed in the 100% fly ash treatment, but treatments with soil had dramatically reduced clod formation. The MWDs for the 0 to 12.5% fly ash treatments, however, were still higher at Time 2 than they were at Time 1.

The pattern of increasing MWD over time was consistent for the 6.25, 12.5 and 25% fly ash treatments (Figure 2.1). The average increase in MWD for these three rates of fly ash addition between Time 1 and 2 was 174%, Time 2 and 3 was 139% and Time 3 and 4 was 151%, thus illustrating the influence of freeze-thaw cycles (Time 2 to 3) on reducing aggregate size distribution. Over-winter increases in MWD were consistent for all treatments except 100% fly ash, averaging 187% across the six treatments. Increases in MWD during the summer periods were similar in 1993 and 1994 for the 6.25 and 12.5% fly ash treatments. In contrast, the MWD of the 50% fly ash mixture did not change during these periods, but changed most during the over-winter period.

The low MWD of 100% fly ash at Time 1 was undoubtedly due to fly ash's powdery nature when dry. Its consistent decrease in MWD over Times 2, 3 and 4 was not evidenced in any other treatment (Figure 2.1). The consistent decreases in bulk density for all treatments between Times 2 and 4 were matched with consistent increases in MWD for the same period, with the exception of the 100% fly ash treatment. Decreases in both bulk density (Table 2.3) and MWD (Figure 2.1) between Times 2 and 4 occurred in this latter treatment. The soil's cloddy nature was evidenced by having the highest MWDs on all but one of the sampling dates (Figure 2.1). The lowest MWD was measured in the 75% fly ash treatment on the last three sampling times.

As indicated earlier, the ideal aggregate size distribution to optimize seed-soil contact is 0.5-1 to 5-6 mm (Russell 1961). The 0 and 6.25% fly ash treatments had mean weight diameters that exceeded the ideal range for samples collected at Time 3 and 4. The 100% fly ash treatment was the only other treatment that formed aggregates greater than 6 mm (Time 2). If ≥12.5% fly ash is added to this soil, mean weight diameter of aggregates would be reduced to within the optimal range by 9 months after being exposed to the environment (Time 3) and would remain so by 16 months (Time 4).

If 12.5% fly ash is added to this soil, there would not only be a reduction in MWD but potentially a significant increase in grain yield (Chapter 3.3.1). Adding 25% fly ash would also reduce MWD but maintain grain yield in comparison to the 0% fly ash treatment.

2.4.5 Grouped Dry Sieving

After the soil was crushed to pass a 9.5-mm sieve, it had the highest percentage of aggregates within the ideal range (Group B: 0.5 to 4 mm) for seedbed preparation (Russell 1961) as well as in Group C (6.3 to 19 mm) (Table 2.5). However, once the soil had been exposed to the environment, its percentage within Group B decreased and within Group C increased (Group C contains the large clods that lead to poor tilth). This trend of decreasing percent in Group B over time was generally characteristic of all fly ash:soil mixtures. The 12.5% fly ash treatment maintained the highest percentage of aggregates within Group B after being subjected to the environment although the differences among the 0 to 50% fly ash treatments were not significantly different. In general, as percent fly ash in the mixture increased, the percent of aggregates within Group C decreased (except 100% fly ash which formed large clods over time likely due to pozzolanic properties; note the dramatic increase in Group C percent for 100% fly ash between Times 1 and 2). The Group C percent also increased markedly for the 0% fly ash treatment over time, a reflection of the cloddy nature of the soil. At least 25% fly ash had to be added before the increase in Group C percent over time was small. The 50% fly ash treatment was the most stable (unchanging proportions for a given group) over time.

2.4.6 Penetration Resistance

Different results were obtained from the two types of penetrometers used to measure resistance. This illustrates the need for careful consideration of methods chosen to measure a particular parameter.

2.4.6.1 Blunt-end Penetrometer

Consistent trends in soil surface strength using the blunt-end penetrometer among fly ash treatments occurred within each sampling time (Table 2.6). Adding 6.25, 12.5 and

25% fly ash to this soil significantly increased surface strength for all sampling times with one exception: 0 and 6.25% fly ash treatments at Time 4. The 6.25, 12.5 and 25% fly ash treatments appeared to respond similarly with behavior analogous to the pattern observed for changes in MWD over time (Figure 2.1): the measured parameters decreased over the winter followed by an increase. Generally, adding ≥50% fly ash reduced surface strength to levels that were not significantly different from the 0% fly ash treatment. Magnitudes of penetration resistance for a given type of penetrometer were remarkably stable across time for almost all treatments, with the 50% fly ash being most stable (Table 2.6).

2.4.6.2 Cone Penetrometer

There were generally no significant differences in cone penetration resistance among treatments for any of the three sampling times (Table 2.6). Similar to the trends observed for the blunt-end penetrometer, penetration resistance for a given treatment changed very little over time. When making comparisons within each sampling time, smaller differences in penetration resistance among fly ash treatments were detected with the blunt-end penetrometer than with the cone penetrometer.

The generally accepted threshold for penetration resistance that may impede root penetration is 2000 kPa (Graecen 1986). Penetration resistance measured by either blunt-end or cone penetrometers did not approach this level, thus fly ash addition to this soil probably would not interfere with root penetration. However, it must be noted that the penetration resistances measured were only near-surface, and not in the root zone. Penetration resistance would be expected to increase with depth.

2.4.7 Modulus of Rupture (MOR)

At Time 1, MOR was highest for the 0 and 6.25% fly ash treatments (Figure 2.2). At this time, there was a significant reduction in MOR when 12.5% fly ash was added to the soil and a dramatic reduction to zero strength for 25 and 50% fly ash treatments. MOR values increased again slightly for 75 and 100% fly ash treatments, a result similar to that found by Watson (1994).

There was approximately a three and five fold increase in MOR at Time 2 and Time 3 as compared to Time 1 for the 6.25 and 12.5% fly ash treatments. By Time 4, however, MOR for all treatments declined to levels similar to those at Time 1. The lowest MOR values were recorded for the 50 to 100% fly ash treatments for Times 2, 3 and 4.

Adding fly ash to soil and exposing the mixtures to the environment generally increased MOR initially, but over longer periods of time MOR decreased for 6.25, 12.5 and 25% fly ash treatments. There were less consistent trends, with fluctuating MOR values over time, for the 50, 75 and 100% fly ash treatments. Minor decreases in MOR occurred between Times 2 and 3 (over-winter).

The slight increase in MOR as percent fly ash increased from 50 to 100% were generally not supported by the penetrometer measurements (Table 2.6). A noteworthy difference in trends in MOR (Figure 2.2) and penetration resistance (Table 2.6) occurred for the 25% fly ash treatment. The dramatic decrease in MOR from the 12.5 to 25% fly ash treatment was not reflected in penetration resistance with either penetrometer.

Soil crusts create a physical barrier that emerging seedlings may not have the strength to penetrate. Factors that add to the difficulty in establishing critical crust strength include crop species, variety, seed size, soil temperature and soil water content (Awadhwal and Thierstein 1985). Richards (1953) reported a complete failure of emergence of bean seedlings when modulus of rupture values reached 273 mbar (27.3 kPa) for one soil. Hanks and Thorp (1956) suggested that wheat seedling emergence was limited by modulus of rupture values that ranged from 200 to 500 mbar (20 to 50 kPa) for soils of fine sandy loam to silty clay loam texture.

Modulus of rupture measured for the 6.25 to 25% fly ash treatments at Time 2 and the 6.25 and 12.5% fly ash treatments at Time 3 exceeded the 20 to 50 kPa that is considered limiting to wheat seedling emergence. Since barley seeds are similar in size and vigor as wheat seeds, cross-referencing is possible. After 16 months of exposure to the environment (Time 4), MOR was reduced to less than 50 kPa but greater than 20 kPa for the 0 to 25% fly ash treatments. Adding $\geq 50\%$ fly ash reduced MOR to less than 20 kPa for most sampling times.

Given that the addition of ≥ 50% fly ash to this soil substantially reduced above ground barley biomass (Chapter 3.3.1), this rate of fly ash addition is not recommended to reduce MOR. However, once the fly ash:soil mixtures are exposed to the environment for approximately 16 months and MOR is less than 50 kPa, there is potential for significant increases (6.25 and 12.5% fly ash) or no change (25% fly ash) in grain yield from that of the control.

2.4.8 Temporal Changes

The addition of fly ash to soil influenced soil physical characteristics, particularly modulus of rupture, mean weight diameter and grouped dry sieving.

When considering the general pattern of temporal changes in MOR analyzed as a repeated measure (SAS Institute Inc. 1992), there were significant differences among all treatments except 0% and 25% fly ash. This can be interpreted as 25% fly ash being the only treatment that responded to temporal influences the way 0% fly ash did. Comparable to this, temporal trends in MWD were similar between 25 and 50% fly ash and 12.5 and 100% fly ash but different among the remaining fly ash treatments. The portion of aggregates between 0.5 and 4 mm (Group B) was not significantly different among 6.25, 12.5 and 25% fly ash and 75 and 100% fly ash but was different from the 0% fly ash treatment over the duration of the experiment.

2.5 CONCLUSIONS

Adding up to 25% fly ash increased bulk density; adding more decreased it. In general, bulk densities declined over time for most of the treatments to levels below 1.0 Mg m^{-3}. Fly ash decreased volumetric water content for all depth increments for all but the final sampling time, a result of decreasing clay content. From a practical, seedbed preparation perspective, adding 12.5 or 25% fly ash to this soil produced the highest percentage of aggregates within the ideal range. Penetration resistance (blunt-end) and MWD for the 6.25, 12.5 and 25% fly ash treatments decreased over-winter, demonstrating the influence of freeze-thaw cycles on these parameters, then these parameters increased slightly by the following autumn. When considering the physical changes that occurred in the fly ash:soil mixtures, adding 25% fly ash resulted in lower MOR values while maintaining a desirable level of aggregation, thus reducing this soil's cloddy nature.

Table 2.1. Physical and chemical characteristics of the fly ash and soil prior to the experiment.

	Water Extractable Conc. (mg kg^{-1})		Total Conc. (mg kg^{-1})	
Elements	Fly Ash	Soil	Fly Ash	Soil
Ag	<0.1	–	<1	<1
Al	112	0.73	72000	45200
As	0.024	<0.004	12	5
B	30	<1	160	<10
Ba	84	0.56	3000	320
Be	<0.1	–	5	<1
Ca	5400	306	70000	4000
Cd	<0.1	–	<1	<1
Co	<0.1	–	11	7
Cr	1.7	<0.1	25	24
Cu	<0.1	<0.02	22	18
Fe	<0.1	–	18000	19800
Hg	0.0044	–	0.37	0.11
K	4	–	690	4200
Mg	2	7.66	3900	3100
Mn	<0.1	–	250	200
Mo	4.2	<0.1	19	<4
Na	220	16.37	10000	890
Ni	<0.1	–	16	15
P	<4	<1	320	340
Pb	<0.4	<0.1	74	18
Se	0.4	<0.004	4	0.5
Si	42	–	–	–
Sr	76	0.39	660	60
Ti	<0.1	–	1700	550
V	<1.0	–	46	48
W	1.1	–	5	<4
Zn	<0.1	–	34	44

Available Nutrients (mg kg^{-1})		
N	0.3	11
P	30	9
K	2	251
S	24	24

Other Characteristics		
pH	9.5	6.8
EC (dS m^{-1})	12.5	0.2
Org-C (%)	–	1.6
SAR	–	6.4
CEC (cmol kg^{-1})	–	15.8
% Sand	37	23
% Silt	54	38
% Clay	9	39

Table 2.2. Particle size distribution of fly ash:soil mixtures by hydrometer method.

% Fly Ash	Size Fraction (%)			Classification (ACESS 1987)
	Clay	Silt	Sand	
0	39.0	38.2	22.8	clay loam
6.25	39.0	39.2	21.8	clay loam
12.5	35.5	39.6	24.9	clay loam
25	33.8	41.7	24.5	clay loam
50	30.0	44.2	25.8	clay loam
75	18.3	50.9	30.8	silt loam
100	9.1	54.3	36.6	silt loam

Table 2.3. Bulk density ($Mg\ m^{-3}$) of seven fly ash:soil mixtures at four sampling times.

% Fly Ash	Time			
	1	2	3	4
0	1.05 c	1.00 c	0.95 c	0.85 bc
6.25	1.17 b	1.16 a	0.98 bc	0.94 abc
12.5	1.20 ab	1.18 a	1.03 abc	0.93 abc
25	1.23 a	1.16 a	1.16 a	0.92 abc
50	1.21 ab	1.16 a	1.12 ab	0.97 a
75	1.03 c	1.13 ab	1.14 a	0.95 ab
100	0.91 d	1.04 bc	0.94 c	0.83 c

Means within each column followed by the same letter are not significantly different (LSD, $p<0.05$).
Time 1 = July 8, 1993; Date of mixing
Time 2 = October 20, 1993; 3.5 months after mixing
Time 3 = April 15, 1994; 9 months after mixing
Time 4 = October 20, 1994; 15.5 months after mixing

Table 2.4. Volumetric water content (mm) among seven fly ash:soil mixtures at four depth intervals.

% Fly Ash	Depth Interval (cm) 0.0-2.5	2.5-5.0	5.0-10.0	10.0-15.0	Total
	Time 2				
0	4.1 a	4.9 a	10.5 a	10.6 a	30.1 a
6.25	3.8 a	4.6 ab	9.7 ab	9.5 b	27.6 ab
12.5	3.8 a	4.4 bc	9.1 b	9.2 b	26.5 b
25	3.9 a	4.1 bc	9.0 b	8.8 bc	25.8 b
50	2.8 b	3.8 c	7.4 c	8.1 c	22.1 c
75	2.4 b	2.6 d	5.8 d	5.8 d	16.6 d
100	1.2 c	1.8 e	4.6 e	4.9 d	12.5 e
	Time 3				
0	4.9 a	6.2 a	12.8 a	13.1 a	37.0 a
6.25	4.5 ab	5.5 ab	11.4 ab	11.4 b	32.8 ab
12.5	4.2 bc	4.9 bc	10.5 bc	10.6 b	30.2 bc
25	3.9 bc	5.0 bc	10.2 bc	10.3 bc	29.4 bc
50	3.7 c	4.6 c	9.0 cd	9.0 cd	26.3 cd
75	3.6 c	4.1 cd	8.1 ed	8.3 d	24.1 de
100	2.4 d	3.4 d	7.4 e	7.7 d	20.9 e
	Time 4				
0	2.7 c	5.1 a	11.0 a	11.8 a	30.6 a
6.25	3.1 c	5.1 a	11.4 a	11.5 a	31.1 a
12.5	3.4 c	5.0 a	10.6 a	10.7 a	29.7 a
25	5.2 ab	5.1 a	10.5 a	10.7 a	31.5 a
50	5.7 a	5.3 a	10.8 a	11.0 a	32.8 a
75	4.7 b	4.6 a	10.0 a	9.9 a	29.2 a
100	4.5 b	4.8 a	11.3 a	11.9 a	32.5 a

Means within each column followed by the same letter for each sampling time are not significantly different (LSD, $p<0.05$).
Time 2 = October 20, 1993; 3.5 months after mixing
Time 3 = April 15, 1994; 9 months after mixing
Time 4 = October 20, 1994; 15.5 months after mixing

Table 2.5. Comparison of grouped dry sieving data (%) of seven fly ash:soil mixtures within each sampling time.

	Time											
	1			2			3			4		
% Fly Ash	A	B	C	A	B	C	A	B	C	A	B	C
0	31.4 f	62.3 a	6.3 ab	18.1 g	49.2 ab	32.7 b	4.7 f	26.8 de	68.4 a	7.3 d	32.0 ac	60.6 a
6.25	35.8 e	59.7 a	4.4 bcd	28.3 e	54.7 a	17.0 c	16.5 e	36.4 cd	47.1 b	12.7 cd	41.0 ad	46.3 ab
12.5	37.8 e	56.4 b	5.8 ab	33.9 d	56.5 a	9.6 cd	26.7 d	51.1 a	22.2 c	22.2 bc	43.4 a	34.3 ac
25	43.8 d	49.4 c	6.8 a	42.0 c	52.0 a	6.0 d	42.3 c	47.2 abc	10.5 d	30.7 b	42.7 abd	26.6 bc
50	52.6 c	41.9 d	5.5 ac	56.2 b	38.8 b	5.0 d	51.3 b	33.5 ce	15.2 cd	54.5 a	30.2 ac	15.4 c
75	78.6 b	18.5 e	2.9 d	72.2 a	23.8 c	4.0 d	60.9 a	28.3 de	10.9 d	63.6 a	17.5 c	18.9 c
100	99.7 a	0.3 f	0.0 e	23.9 f	27.1 c	49.0 a	38.9 f	40.1 bc	21.0 c	56.9 a	28.5 bcd	14.7 c

Means within each column followed by the same letter are not significantly different (t-Test, $p<0.05$).
Time 1 = July 1993; Date of mixing
Time 2 = October 1993; 3.5 months after mixing
Time 3 = April 1994; 9 months after mixing
Time 4 = October 1994; 15.5 months after mixing
Group A = 0.250 mm - pan, Group B = 0.500 - 4.0 mm and Group C = 6.3 - 19.0 mm.

Table 2.6. Comparison of surface penetration resistance (kPa) of the seven fly ash:soil mixtures.

% Fly Ash	Type of Penetrometer					
	Blunt End			Cone		
	Time 2	Time 3	Time 4	Time 2	Time 3	Time 4
0	885 b	719 c	706 b	169 a	186 bc	173 ab
6.25	1232 a	1043 ab	1079 ab	226 a	269 ab	251 ab
12.5	1324 a	1166 a	1282 a	229 a	233 abc	293 a
25	1310 a	1137 a	1213 a	228 a	279 a	291 a
50	933 b	984 b	911 ab	164 a	215 abc	165 ab
75	922 b	787 c	786 b	171 a	150 c	153 b
100	1273 aA	718 cB	898 abB	246 aA	162 cAB	142 bB

Means within each column followed by the same lowercase letter are not significantly different (LSD, $p<0.05$). Means within a row within a penetrometer type followed by the same uppercase letters are not significantly different (t-Test, $p<0.05$). Comparisons without any uppercase letters are not significantly different (t-Test, $p<0.05$).
Time 2 = October 20, 1993; 3.5 months after mixing
Time 3 = April 15, 1994; 9 months after mixing
Time 4 = October 20, 1994; 15.5 months after mixing

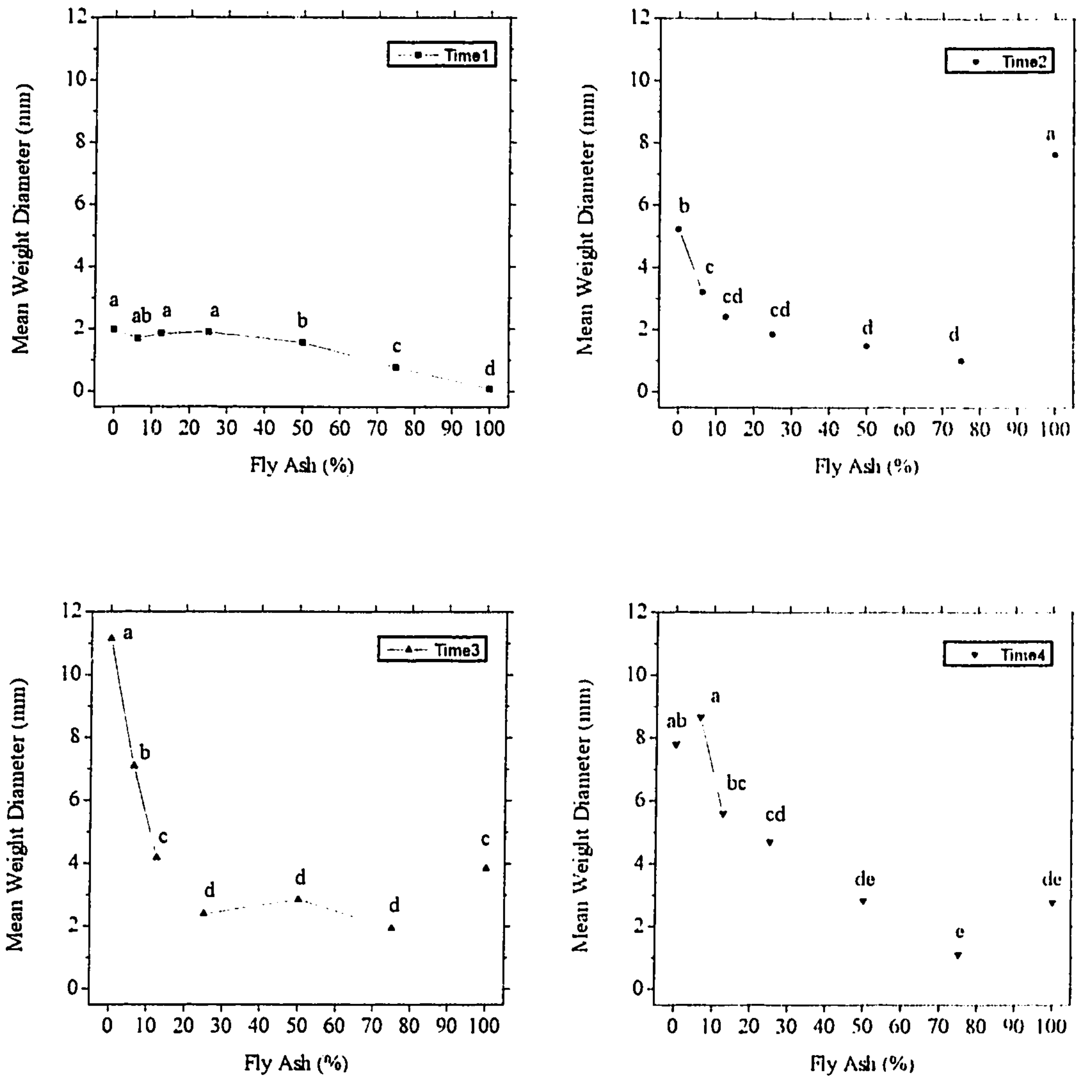

Figure 2.1 Mean weight diameter (mm) of aggregates among fly ash:soil mixtures sampled at four times. Means with the same letters within each sampling time are not significantly different (t-Test, $p<0.05$).
Time 1 = July 8, 1993; Date of mixing
Time 2 = October 20, 1993; 3.5 months after mixing
Time 3 = April 15, 1994; 9 months after mixing
Time 4 = October 20, 1994; 15.5 months after mixing

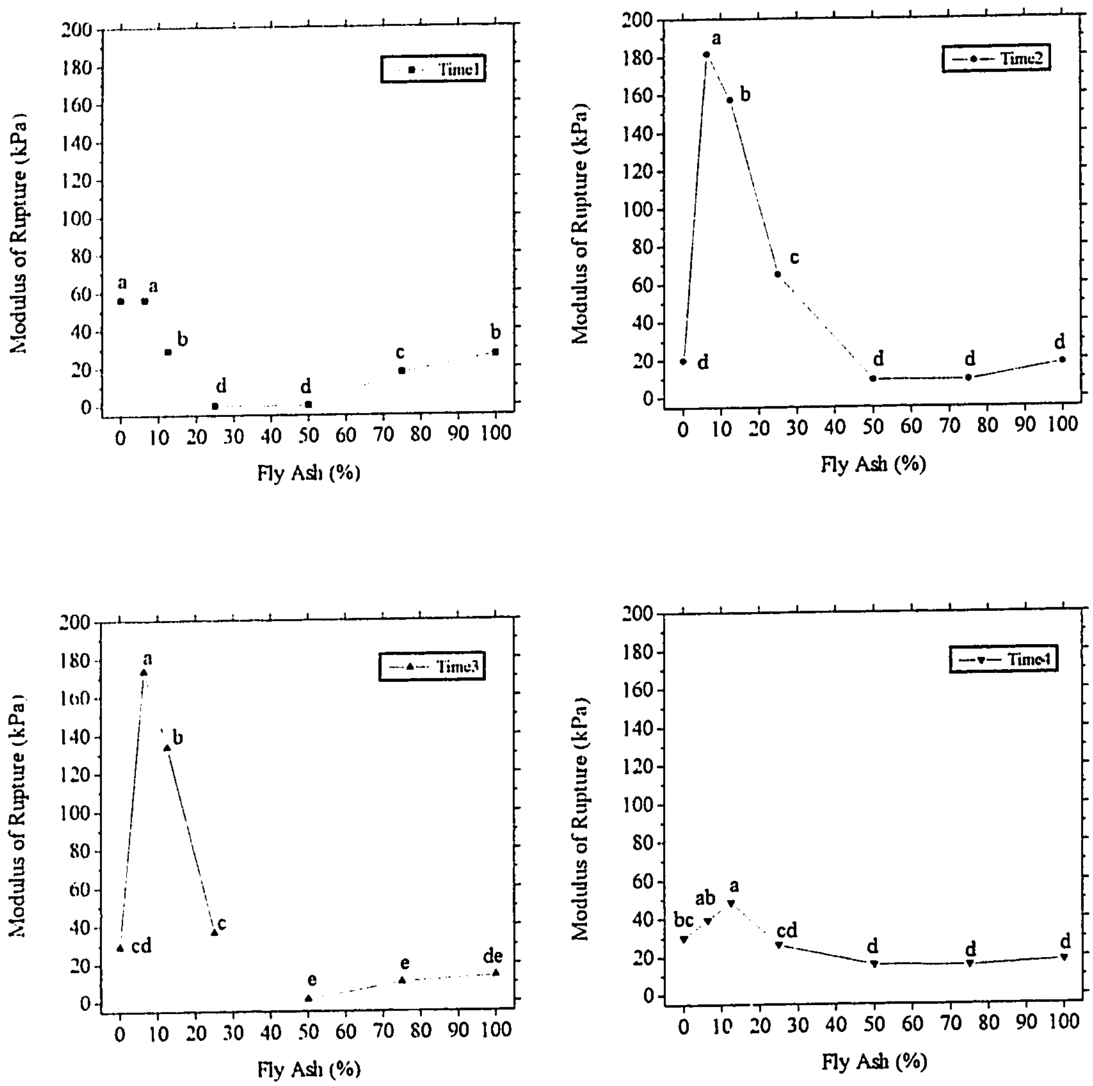

Figure 2.2 Modulus of rupture (kPa) of the soil surface (0-2.5 cm) among fly ash:soil mixtures sampled at four times. Means with the same letters within each sampling time are not significantly different (t-Test, $p<0.05$).
Time 1 = July 8, 1993; Date of mixing
Time 2 = October 20, 1993; 3.5 months after mixing
Time 3 = April 15, 1994; 9 months after mixing
Time 4 = October 20, 1994; 15.5 months after mixing

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3. GROWTH RESPONSE OF BARLEY ON UNWEATHERED FLY ASH AMENDED SOIL[1]

3.1 INTRODUCTION

Strip coal mines provide coal for electrical power generation. Of the 23.7 million tonnes of coal burned in 1992 for this purpose in Alberta (Natural Resources Canada 1993), approximately 2.5 million tonnes of fly ash were produced. Approximately 70% of the total ash produced in Alberta is fly ash; that portion of ash produced in coal combustion that has a sufficiently small particle size to be carried away from the boiler in the flue gas (El-Mogazi et al. 1988). Bottom ash is composed of fine and coarse grained particles (ash and slag) and remains in the boiler (Carlson and Adriano 1993). Most of the ash produced is buried in disposal sites within the mines.

Within Alberta agroecosystems there are a variety of problem soils whose productivity is mainly limited by intrinsic physical and/or chemical properties (Izaurralde 1992). The most abundant problem soils in Alberta are fine textured, coarse textured, Solonetzic, Luvisolic, acidic or saline (Brierley et al. 1992; Izaurralde 1992). Soils high in clay have the potential to form surface crusts; a result of compaction, structural breakdown and deposition of fine particles at the surface. This occurs when the exposed soil surface is subjected to rain followed by a period of rapid drying (Rathore et al. 1981). Soil crusts can reduce soil infiltration rates and increase soil strength (Moore and Singer 1990) and subsequently impede seedling emergence (Rathore et al. 1981). Fly ash, because of its texture and calcium content, has potential as a soil amendment to alleviate these problems. Fly ash is composed primarily of silt-sized particles which, when applied to soil, can alter its texture (Carlson and Adriano 1993). In studies reviewed by El-Mogazi et al. (1988), for a variety of soils mixed with up to 50% fly ash, the mixtures tended to have lower bulk densities, higher water holding capacities, lower hydraulic conductivities and lower moduli of rupture than soil alone.

If fly ash is used as a physical amendment for soil, its effect on plant growth must be determined. Fly ash contains trace elements which in sufficient concentrations can be

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harmful to plants (Plank and Martens 1973; Adriano et al. 1980; Eary et al. 1990) or to animals that consume it (Khattak et al. 1991). Ash amendment can also result in reduced available soil nitrogen and phosphorus, excessive soluble salt concentrations or elemental imbalances due to high pH (Carlson and Adriano 1993).

Aitken and Bell (1985) studied the phytotoxicity of boron from Australian fly ashes on French bean (*Phaseolus vulgaris* L.) and Rhodes grass (*Chloris gayana* Kunth) grown in a glasshouse. The addition of ≥ 30% by weight of unweathered fly ash to silt loam soil significantly reduced the yield of beans (48%) whereas the yield of Rhodes grass was significantly decreased (18%) only at levels of ≥70% ash addition. Yield reduction was associated with boron toxicity. In the same experiment, leached fly ash was added to sand and sandy loam soils and crop yield increases were attributed to increased plant available water. For example, a 10% addition of fly ash increased the plant available water of the sand soil by factors of 4.9 and 9.2 for two types of fly ash. Furr et al. (1978) reported that of all elements found in fly ash, arsenic, boron, magnesium and selenium were most consistently elevated in various field-grown crops on fine sandy loam soil amended with about 18 tonnes ha^{-1}. The authors reported that arsenic concentration in the plant material was below human and animal toxicologically significant levels according to the U.S. Department of Health, Education and Welfare. In a greenhouse study by Mbagwu (1983), the addition of 5% w/w of unweathered fly ash to calcareous fine-loamy and acidic coarse-loamy soils did not affect crop yields of corn, alfalfa, birdsfoot trefoil or dry beans. Fail (1987) added 70 tonnes ha^{-1} of fly ash (pH 11) to acidic mine spoil in a field experiment. The average accumulated second year plant biomass increased 30 times for Rhode Island bentgrass (*Agrostis tenuis* Sibth.), 20 times for tall fescue (*Festuca arundinacea* Schreb.) and 5 times for bush clover (*Lespedeza cuneata* "du mont" g. don.) with no adverse effects on the plants. He attributed the increased production rates to the effects of fly ash on soil water holding capacity and improved soil texture although these parameters were not quantified in the study. Carlson and Adriano (1993) reported that the most significant factors limiting establishment of vegetation on ash deposits were excessive concentrations of soluble salts and boron.

The physical and chemical properties of fly ash are dependent upon the geologic origin of the coal, method of combustion, type of emission control devices and age before disposal (Adriano et al. 1980; Carlson and Adriano 1993) and thus are relatively site specific. Results from research in specific geographic locations cannot be extrapolated to all areas and situations. Research on fly ash from coal mined and burned in Alberta is sparse. Fullerton (1987) determined that 30 cm of bottom ash incorporated into sodic spoil with a subsoiler improved soil chemistry (pH, sodium adsorption ratio, percent saturation), soil strength and plant yield compared to 20 and 10 cm of bottom ash. In another study (Leskiw 1989), a layer of bottom ash between subsoil and underlying sodic spoil was used as a capillary barrier to upward movement of sodium salts. The ash layer improved leaching of the sodic spoil resulting in reduced electrical conductivity and sodium adsorption ratio, increased depth of rooting zone and forage yield and improved plant available water. We used fly ash from the Sundance power generating plant located 100 km west of Edmonton, Alberta and owned by TransAlta Utilities Corporation. The Sundance plant is the largest producer of ash in Alberta. Barley (*Hordeum vulgare* L. var. Leduc), commonly grown on agricultural land surrounding the Highvale coal mine, which supplies coal to the Sundance power plant, was used as the study crop. Most of the research conducted with fly ash amended soil in greenhouse and field experiments has been at rates of less than 250 tonnes ha^{-1} (approximately 20% v/v fly ash) (Furr et al. 1978; Elseewi et al. 1980; Gutenmann et al. 1981). The present study includes fly ash application to soil ranging from 0 to 100% v/v to determine the upper limit for fly ash application to soil without detrimental effects on barley growth and development. The specific objectives were:

1. To determine if plant emergence, stages of development, plant height, length and width of the first, third and fifth leaves and above-ground plant biomass (grain, straw and silage) are influenced by addition of fly ash to soil.
2. To determine if trace element uptake by barley and concentrations in the soil are influenced by addition of fly ash to soil.
3. To determine if the above parameters vary with different ratios of fly ash to soil.

3.2 METHODS

3.2.1 Fly Ash

Fly ash is "unweathered" when it is taken from the electrostatic precipitators (emission control devices that remove particulates discharged to the atmosphere) directly and not allowed to age and weather in storage piles. Unweathered fly ash can be used to demonstrate the "worst case scenario" of the effects of elements from fly ash on barley. The unweathered fly ash used in this study is characterized in Table 3.1.

3.2.2 Soil

The problem soil used was the A horizon of a Dark Gray Luvisol (Mollic Cryoboralf) with a minor contribution from a Gray Solonetz (Natriboralf) prior to mining. The soil was fine-textured, low in organic carbon and had poor tilth as indicated by the formation of large clods in the field. The physical and chemical characteristics of the soil are summarized in Table 3.1. Given these properties, this soil is susceptible to surface crusting.

3.2.3 Fly Ash:Soil Mixtures

Soil from the upper 15 cm (A horizon prior to mining) of a reclaimed field on the Highvale coal mine was air dried, then crumbled to pass a 9.5-mm sieve. Unweathered fly ash from the Sundance coal-fired power plant was mixed with the clay loam soil at rates of 0, 6.25, 12.5, 25, 50, 75 and 100 % on a volume basis. Each fly ash:soil mixture was analyzed for N, P, K and S. Fertilizer was applied to each mixture to obtain nutrient concentrations at 1.5 times the average level considered adequate for available soil nutrients for cereal production by the Alberta Soil and Feed Testing Laboratory. The nutrient sources were ammonium nitrate, triple superphosphate, potassium chloride and ammonium sulfate which were dissolved in deionized water and applied uniformly to the mixtures. The mixtures were poured without compaction into plastic pots (ID = 20 cm, volume 553 cm^3) to a depth equal to the depth of cultivation in the field (15 cm). The bulk densities of the soil (1.15 Mg m^{-3}) and fly ash (1.03 Mg m^{-3}) were determined by measuring the mass of soil and fly ash contained in the pot. The bulk densities of the fly ash:soil mixtures were assumed to be the average of the two values (1.09 Mg m^{-3}). Masses of mixtures necessary to fill the pots to 15 cm were determined using this bulk density and the volume of the pots. The pots had closed bottoms to prevent leaching of water and subsequent loss of elements.

The pots were arranged in the greenhouse in a randomized complete block design, with seven ratios of fly ash to soil, two plant treatments (silage and grain) and one set of control pots with no plants, resulting in 21 pots (7x3) within each of five blocks. The greenhouse had natural lighting and photoperiod with a diurnal temperature range of 15 to 28 °C. The experiment began May 28, 1993 and was completed September 13, 1993.

3.2.4 Plant Preparation and Growth

Twelve barley seeds treated with the fungicide Vitavax (5,6-Dihydro-2-methyl-1, 4-oxathiin-3-carboxanilide) were placed 2 cm deep in the fly ash:soil mixture. Pots were supplied with sufficient deionized water (approximately 100 to 200 mL day^{-1}) to eliminate water stress; symptoms of water deficiency or excess were visually monitored. When the plants reached the fifth leaf stage, six randomly selected plants per pot were maintained and the remainder were removed to reduce competition for resources. If fewer than six seeds germinated, no plants were removed.

3.2.5 Plant Measurements

General observations for toxicity and deficiency symptoms were recorded weekly for each pot according to descriptions by Kabata-Pendias and Pendias (1992). The fifth leaf on each plant was examined in detail.

The primary stages of development were recorded for each plant using Zadoks growth stages (Zadoks et al. 1974) of seedling growth, tillering, booting, emergence of inflorescence, anthesis, milk development, dough development and ripening. Plant height and the width and length of the first, third and fifth leaves were recorded.

Barley for silage was harvested between Zadoks stages 83 and 85 to simulate silage production (Berkenkamp and Meeres 1987; McLelland 1989) while that for grain was harvested at maturity. The plants in each pot were cut at the soil surface and combined to form a composite sample. This above ground plant biomass was washed in 2% phosphate-free soap solution to remove dust, then rinsed with tap water three times. The final rinse was with deionized water. The plant material was placed in paper bags and air dried in the greenhouse to constant weight and the weight recorded. Silage samples included all above ground plant biomass. The mature grain heads harvested were hand separated from the straw, then the awns were removed and included with the straw. The straw and grain were weighed separately.

3.2.6 Plant and Soil Chemical Analyses

Plant and soil chemical analyses were completed by a commercial laboratory. Plant material was digested on a block digester using two parts concentrated HNO_3 and one part $HClO_4$ to white fumes of $HClO_4$ (Bock 1979). Metal analyses were by ICP according to EPA 6010A except for arsenic and selenium which were by hydride using EPA 7061A for arsenic and EPA 7741A for selenium (EPA - SW 846, test methods for evaluating solid waste, physical and chemical methods).

Soil elements were determined through strong acid digestion using Aqua Regia/Perchloric acid (Bock 1979). Soil elements were determined by analyzing solid soil extracts obtained according to CGSB leachate extraction procedure with the modification that only ultra pure water was used as the extractant (CGSB 164 CP - IMP, February 1987). Exceptions to this were calcium, magnesium, sodium, potassium, iron and aluminum which were saturation extracts according to McKeague (1978) but analyzed by the same method, ICP (EPA 6010A).

3.2.7 Statistical Analyses

Plant emergence data on Day 5 and 19 were analyzed with general linear models on each day separately. Non-linear regression was used to analyze plant emergence over time. Regression analyses can be used as a tool to help predict the effect on plant emergence at other rates of fly ash addition to soil (i.e. 20%). To determine significance, fly ash treatments were compared to one another by pooling the raw data of two treatments at a time and analyzing it with non-linear regression; the sum of squares and degrees of freedom were recorded. The individual rates of fly ash were then analyzed with non-linear regression and the sum of squares and degrees of freedom from the separate two rates of fly ash were added together. These two sets of sum of squares and degrees of freedom were used to calculate the F-value. If the pooled raw data had similar sum of squares to that of the combined sum of squares of the same two rates of fly ash, then the F-value would be small and there would be no significant difference ($p<0.05$).

Plant height data on Day 13 and 69 were analyzed on each day with T-tests because not all pots in the 75 and 100% fly ash treatments grew plants. To evaluate the change in plant height throughout the experiment, the data from all days were analyzed by non-linear regression. The plant height measured for the 100% fly ash treatment followed a linear growth pattern and was, therefore, analyzed with a linear regression model. Comparisons among rates of fly ash were completed in the same manner as for plant emergence above.

The Zadoks growth stage scale is not quantitative, therefore, the data were ranked using the RANK procedure in the SAS statistical program (SAS Institute Inc. 1992). Zadoks growth stages and the ranked data were highly correlated ($R^2 = 0.979$). It was not possible to obtain data from all experimental units on all sampling days because either some plants had not reached the Zadoks growth stage when recording began or plants died during the experiment. Thus, the ranked data were analyzed as a split plot with time as the split (least significant difference, $p<0.05$). Plant chemical composition and biomass and soil pH and SAR were analyzed with general linear models.

3.3 RESULTS AND DISCUSSION

3.3.1 Plant Growth and Development

Adding ≥12.5% fly ash to soil initially delayed plant emergence (Day 5 in Table 3.2) but by Day 19, plant emergence for the 0 to 12.5% fly ash treatments was not significantly different. Adding ≥25% fly ash significantly reduced plant emergence (Table 3.2). Three patterns of plant emergence developed among the seven fly ash treatments (Figure 3.1). On Day 5, in the 0 and 6.25% treatments, plant emergence was high and almost the same as their maximum emergence. In contrast, in the 12.5 to 50% fly ash treatments, far fewer plants emerged by Day 5 followed by sharp increases in emergence. In 75 and 100% fly ash treatments there were dramatically fewer plants emerging after a long delay.

Non-linear regression models are presented in Table 3.3. Fly ash addition resulted in significant differences in patterns of plant emergence over time for all rates of fly ash except 75 and 100%. The models predicted maximum number of plants to emerge from each rate of fly ash (Table 3.3) was similar to the actual number of plants on Day 19 (Table 3.2). Although the pattern of plant emergence is significantly different among the 0, 6.25 and 12.5% fly ash treatments, the maximum number of plants to emerge for each treatment are the same.

Delays and reductions in emergence are likely a result of excessive concentrations of soluble salts and boron (Carlson and Adriano 1993). For most plants, growth is adversely affected by EC $\geq$4 dS m^{-1} (Bernstein 1975). Prior to the experiment, the mixing of soil and fly ash produced ECs that reflected the relative contribution from each material (Table 3.4). In theory, after adding water to the mixtures, the calcium oxide in the fly ash changed to calcium hydroxide and then precipitated out of solution as calcium carbonate resulting in reduced ECs in the alkaline mixtures at the end of the experiment. The time it would take to lower the ECs was not studied, therefore, it is speculated that the ECs of the mixtures were initially sufficiently high to reduce germination and emergence. Bresler et al. (1982) commented that barley was more sensitive to EC during the emergence and early seedling growth stages than during either germination or the later growth stages, including grain development. Mbagwu (1983) found that the addition of 5% w/w fly ash to fine-loamy and coarse-loamy soil did not affect germination of corn, alfalfa, birdsfoot trefoil or dry beans. This is consistent with our study, in which the addition of up to 12.5% v/v did not affect the maximum number of plants to emerge by Day 19.

Plant height for the 0 to 12.5% fly ash treatments was not significantly different on Day 13 (Table 3.5). However, by Day 69, adding 6.25 and 12.5% fly ash significantly increased plant heights compared to plants on 0% fly ash. There were two general patterns of plant height growth (Figure 3.2). Plants on the 0 to 25% fly ash treatments followed similar height trends. With 50 to 100% fly ash, plant height growth was dramatically delayed and maximum heights were reduced.

Regression model results are presented in Table 3.6. Based on the pattern of plant height growth, each fly ash treatment responded differently. Of particular interest, adding 6.25 to 25% fly ash to soil improved barley height growth compared to the 0% fly ash treatment (Figure 3.2).

As ash increased, leaf length and width of the first and third leaves decreased (data not shown). A different trend developed for the fifth leaves. Generally, the plants grown on 6.25, 12.5 and 25% fly ash had longer fifth leaves than the plants in 0% fly ash. By the 53rd day, the fifth leaves from the 6.25 and 12.5% fly ash treatments were 25 cm long while the leaves on 25% fly ash were 29 cm long and those in 0% fly ash were 22 cm long. In the 50 and 75% fly ash treatments, the fifth leaves were much smaller than those of the ≤25% fly ash. No plants survived to the fifth leaf stage in the 100% fly ash treatment.

Applications of ≥ 50% fly ash produced significantly less silage than 0% fly ash (Figure 3.3). However, the addition of 6.25 and 12.5% fly ash increased grain yield by 75 and 53%, respectively, above the 0% fly ash treatment. Similarly, straw yield was increased by 76% for 6.25, 61% for 12.5 and 54% for 25% fly ash treatments compared to the 0% treatment. Grain yield was higher because the plants on 6.25 and 12.5% fly ash grew bigger heads and more tillers headed out. However, the harvest index for these two treatments (0.57 and 0.56 respectively) and the 25% fly ash treatment (0.41) were lower than that for the 0% fly ash treatment (0.61). This indicates that plants grown on fly ash amended soil do not partition energy as efficiently as plants grown on 0% fly ash. Both grain and straw yield were reduced significantly when 50% or more fly ash was added to soil.

Tillers first emerged 14 days after seeding for 0% fly ash treatments, 15 days for 6.25%, 16 days for 12.5% and 21 days for 25% fly ash. Tillers began to emerge for 50% fly ash on Day 76 but did not grow and form seeds. No tillering occurred for 75 and 100% fly ash. Tillers in the 0% fly ash treatment began to turn chlorotic and weak on Day 42. By the 47th day after seeding, all but one of the 25 tillers were dead. On the 53rd day after seeding there were 54 tillers for the 6.25% fly ash, 50 for 12.5%, and 43 for 25%.

Some of these tillers died but most advanced to form seeds as evidenced by the greater grain yield for these treatments (Figure 3.3). The addition of up to 25% fly ash to soil promoted growth and maturation of tillers to a level beyond that which the clay loam soil used in this experiment was capable of supporting alone. The unsuccessful tillering in the 0% fly ash treatment was attributed to soil texture and the resulting increased bulk density and poor tilth as discussed below.

Plant development was similar for 0, 6.25, 12.5 and 25% fly ash treatments but only the 6.25% fly ash was not significantly different from 0% fly ash (Figure 3.4). For instance, barley development on the 12.5% fly ash treatment was about ten days delayed in reaching maturity compared to the 0% fly ash treatment. Plant development was more noticeably delayed for 50% fly ash and dramatically reduced for the 75% fly ash. Plants that grew in the 100% fly ash treatments did not develop far beyond the boot stage.

3.3.2 Toxicity Symptoms

Boron toxicity symptoms on plants were first observed 10 days after seeding for the 6.25, 12.5 and 25% fly ash treatments, 12 days for 50% fly ash and 18 days for 75 and 100% fly ash. The plants grown on 75 and 100% fly ash were always at earlier development stages than the other treatments, thus, symptoms took longer to manifest. Symptoms began as a white leaf tip bordered by a necrotic edge on the second youngest leaf. The necrosis enlarged and advanced down the leaf margins. Random areas on the leaf veins became necrotic then enlarged to form spots that overlapped into the interveinal areas. The necrotic lesions were generally surrounded by chlorosis. By the 32nd day after seeding, the necrotic and chlorotic damage on the youngest two leaves covered 5% of leaf area for 6.25% fly ash, 7% for 12.5% fly ash, 15% for 25% fly ash, 18% for 50% fly ash, 40% for 75% fly ash and 34% for 100% fly ash. Small necrotic spots on the young and old leaf tips of the plants grown on 0% fly ash appeared approximately 18 days after seeding. By the 32nd day after seeding, the plants had some necrotic spots on the leaf margins and veins on the youngest two leaves (<1% leaf area), but most of the necrosis was on the older leaves as spots on leaf tips, margins and veins (4% leaf area). The older leaves on plants growing on 0% fly ash slowly turned chlorotic then started to die approximately 55 days after seeding.

The first leaves on the plants died more rapidly as percent fly ash increased, with the exception of the 0 and 6.25% treatments. The rapid senescence could be a plant response to element toxicity or deficiency induced by the addition of fly ash to soil. First leaves in the 6.25% treatment had slightly less affected leaf area and stayed green longer than leaves in other treatments. The absence of rapid senescence in this treatment could be explained by the reduced necrosis having less impact on leaf metabolism and growth as a result of the lower rate of fly ash addition. The plants in the 0% treatment underwent more rapid senescence of older leaves than fly ash treatments; a result of inherent properties of the soil.

3.3.3 Deficiency Symptoms

The soil in this experiment may have been deficient in copper and/or boron for healthy plant growth (Lindsay and Norvell 1978; Kabata-Pendias and Pendias 1992). On copper deficient soils in Alberta, crops respond to copper fertilization when the soil contains 0.4 to 0.8 mg kg^{-1} of copper (Penney et al. 1991). Adding ≥6.25% fly ash to the soil increased plant concentration of these elements to those considered normal for copper but toxic for boron (Kabata-Pendias and Pendias 1992). The young leaf tips of the plants grown on all fly ash treatments, including 0% fly ash, turned white. The effect was minimal (<1% leaf area) and is believed to be a copper deficiency symptom (Graham and Nambier 1981).

When ≥6.25% fly ash was added to the soil, plant growth was improved even though there were toxic levels of boron. Thus, the improvements in plant growth are further attributed to changes in soil physical properties. Water was amply supplied to meet plant needs, thus changes to available water cannot explain the increased yields. The physical properties of the different mixtures of fly ash and soil were not investigated during this experiment but some generalizations can be made. At the end of the experiment, there was a noticeable reduction in soil volume in the 0% fly ash treatment compared to the 6.25 to 50% treatments. Although bulk density was not measured, it can be surmised that there was an increase in bulk density for the 0% fly ash treatment and that it impeded root development, and thus affected above ground plant growth. The 75 and 100% fly ash treatments also had reduced volumes by the end of the experiment. We suggest that the addition of fly ash to soil in intermediate amounts changes the texture to a more optimal distribution of sand, silt and clay that prevents the natural settling that increases bulk density and restricts root development for this fine-textured soil.

3.3.4 Plant Chemical Composition

Plant chemical composition uptake of two elements that are of environmental and toxicological concern was determined (Table 3.7). Plant requirements and sensitivities to trace elements are species specific. Barley showed boron toxicity symptoms with addition of 6.25% (and greater) fly ash and boron accumulated in the silage (170 mg kg^{-1}) and straw (384 mg kg^{-1}) in excess of the amount considered adequate (20 - 100 mg kg^{-1}) and toxic (>200 mg kg^{-1}) for most plant species (Gupta et al. 1985). This was not accompanied by reductions in silage, straw or grain yield for fly ash treatments ≤25%. The advantage of increasing plant yield by adding up to 25% fly ash exceeded the disadvantage of reduced photosynthetic area caused by necrotic and chlorotic lesions. Few other boron toxicity studies have been with cereal or grass crops. Davis et al. (1978) reported that 80 mg kg^{-1} boron reduced leaf and stem biomass of barley. Ryegrass grown in fly ash amended soil contained up to 430 mg kg^{-1} (DW) boron and did not show toxicity symptoms (Kabata-Pendias and Pendias 1992). The National Research Council (1980) provides a general guideline for the maximum tolerable level of boron in cattle diets to be 150 mg kg^{-1}. Puls (1988) reports >200 mg B kg^{-1} in cattle diets as toxic and 50 to 150 mg B kg^{-1} as high. Given this, silage grown on ≥6.25% fly ash may be a health concern for cattle, however, grain harvested from ≤50% fly ash amended soil (<46 mg kg^{-1}) would not be a health concern.

Selenium is an essential element in animal diets, however, the acceptable range in concentrations to avoid deficiency or toxicity to animals is narrow (Carlson and Adriano 1993). Gissel-Nielsen et al. (1984) reported that animal diets with concentrations less than 0.05 - 0.1 mg kg^{-1} of selenium can result in deficiency, whereas concentrations greater than 2-5 mg kg^{-1} can result in toxicity. We found selenium concentrations in the grain, straw and silage biomass between 0.01 and 0.73 mg kg^{-1} for 0 to 25% fly ash treatments. The addition of up to 25% fly ash to soil in this study improved selenium levels in the 0% treatment which reached toxic levels at higher rates of fly ash addition.

3.3.5 Chemical Ratios

Molybdenosis in livestock is a result of high levels of dietary molybdenum having antagonistic effects on copper metabolism and inducing copper deficiency (Miller et al. 1991). The suggested ratio of Cu:Mo in animal diets is 2.0 (Miltimore and Mason 1971). The addition of fly ash to soil increased plant uptake of both copper and molybdenum but the increase in molybdenum was greater than that of copper (Table 3.8). As a result, Cu:Mo ratios generally decreased with increasing levels of fly ash. The 0% treatment had ratios of >2.0 for silage and grain (straw is generally not used as livestock feed), however, adding 6.25% fly ash reduced the ratio to 1.4 for silage. Grain accumulated less molybdenum than silage and straw, thus adding 6.25 and 12.5% fly ash resulted in ratios of >2.0. The 25% treatment for grain had a ratio of 1.6. Given these results, feeding livestock grain grown on ≤12.5% fly ash would probably not cause molybdenosis, however, copper supplementation would likely be required when 25% fly ash is added to soil for grain production. When growing silage, copper supplementation would be required for all levels of fly ash addition to soil.

3.3.6 Soil Chemical Composition

Soil pH was determined post-harvest and was significantly different among all fly ash treatments, ranging from 5.6 for 0% fly ash to 11.3 for 100% fly ash (Table 3.9). Adding up to 25% fly ash changed the moderately acidic soil to moderately basic. Soil treatments with ≥50% fly ash produced strongly basic pHs. Soil ECs varied widely among treatments (Table 3.9), however, all treatments had ECs of less than 0.83 dS m^{-1} which is below the level which adversely affects plant growth (≥4 dS m^{-1}; Bernstein 1975). Calcium oxide in the fly ash presumably precipitated out of solution as calcium carbonate, thus lowering EC. Fly ash was a source of calcium to the soil and as a result lowered

SARs to below 5 with the exception of the 100% fly ash which had SARs that averaged between 7.2 and 8.6 (Table 3.9).

3.4 CONCLUSIONS

The addition of ≤25% fly ash to soil improved barley growth on a fine textured problem soil. Adding this amount of fly ash to a problem soil reduced barley plant emergence but either increased or had no influence on straw, grain and silage biomass. The trace element composition of the plant biomass was within acceptable levels for animal health when ≤25% fly ash was added. Exceptions to this are molybdenum in which case copper supplementation may be required when the animals are fed silage grown on fly ash amended soil and boron in silage which may lead to animal health concerns.

Table 3.1. Physical and chemical characteristics of the fly ash and soil prior to the experiment.

	Water Extractable Conc. (mg kg^{-1})		Total Conc. (mg kg^{-1})	
Elements	Fly Ash	Soil	Fly Ash	Soil
Ag	<0.1	–	<1	<1
Al	112	0.73	72000	45200
As	0.024	<0.004	12	5
B	30	<1	160	<10
Ba	84	0.56	3000	320
Be	<0.1	–	5	<1
Ca	5400	306	70000	4000
Cd	<0.1	–	<1	<1
Co	<0.1	–	11	7
Cr	1.7	<0.1	25	24
Cu	<0.1	<0.02	22	18
Fe	<0.1	–	18000	19800
Hg	0.0044	–	0.37	0.11
K	4	–	690	4200
Mg	2	7.66	3900	3100
Mn	<0.1	–	250	200
Mo	4.2	<0.1	19	<4
Na	220	16.37	10000	890
Ni	<0.1	–	16	15
P	<4	<1	320	340
Pb	<0.4	<0.1	74	18
Se	0.4	<0.004	4	0.5
Si	42	–	–	–
Sr	76	0.39	660	60
Ti	<0.1	–	1700	550
V	<1.0	–	46	48
W	1.1	–	5	<4
Zn	<0.1	–	34	44

Available Nutrients (mg kg^{-1})		
N	0.3	11
P	30	9
K	2	251
S	24	24

Other Characteristics		
pH	9.5	6.8
EC (dS m^{-1})	12.5	0.2
Org-C (%)	–	1.6
SAR	–	6.4
CEC (cmol kg^{-1})	–	15.8
% Sand	37	23
% Silt	54	38
% Clay	9	39

Table 3.2. Plant emergence 5 and 19 days after seeding fly ash treated soil.

% Fly Ash	# Plants (Day 5)	# Plants (Day 19)
0	10.3 a	11.3 a
6.25	9.3 a	11.1 a
12.5	5.7 b	11.3 a
25	1.7 c	9.8 b
50	0 d	7.2 c
75	0 d	1.1 d
100	0 d	0.7 d

Means (n=5) within a column followed by the same letter are not significantly different (LSD, $p<0.05$).

Table 3.3. Regression models relating plant emergence to time after seeding fly ash treated soil.

	Coefficients					Predicted	
% Fly Ash	Intercept	Linear	Quadratic	Range (days)	R^2	Maximum Plants	Day Max. Emergence Reached
0 a	5.51	1.31	-0.074	$5 \leq x \leq 19$	0.996	11.3	9
6.25 b	1.01	2.36	-0.139	$5 \leq x \leq 19$	0.996	11.1	9
12.5 c	-64.45	22.06	-1.605	$5 \leq x \leq 19$	0.995	11.3	7
25 d	-37.40	10.92	-0.631	$5 \leq x \leq 19$	0.981	9.9	9
50 e	-46.82	10.91	-0.551	$5 \leq x \leq 19$	0.989	7.2	10
75 f	-1.01	0.19	-0.004	$5 \leq x \leq 27$	0.435	1.2	24
100 f	-0.50	0.10	-0.002	$5 \leq x \leq 27$	0.584	0.7	24

Treatments followed by the same letter are not significantly different (non-linear regression, $p<0.05$).

Table 3.4. Electrical conductivity (EC, dS m^{-1}) and pH of fly ash:soil mixtures prior to the experiment.

% Fly Ash	EC	pH
0	0.2	6.8
6.25	0.4	8.2
12.5	0.6	9.8
25	1.3	11.2
50	3.6	12.0
75	6.3	12.3
100	9.5	12.5

Table 3.5. Plant height (cm) on Day 13 and 69.

% Fly Ash	Height (Day 13)	Height (Day 69)
0	17.5 a	68.4 b
6.25	17.1 a	76.6 a
12.5	16.0 a	75.2 a
25	13.5 b	69.9 b
50	7.8 c	38.5 c
75	5.4 d	21.7 d
100	6.2 cd	--

Means (n=5) within a column followed by the same letter are not significantly different (t-Test, $p<0.05$).

Table 3.6. Regression models relating plant height (cm) to time after seeding fly ash treated soil.

	Coefficients					Predicted	
% Fly Ash	Intercept	Linear	Quadratic	Range (days)	R^2	Maximum Height	Day Max. Height Reached
0 a	-14.78	2.67	-0.021	$13 \leq x \leq 69$	0.995	69.7	63
6.25 b	-21.40	3.15	-0.025	$13 \leq x \leq 69$	0.996	77.5	63
12.5 c	-16.35	2.61	-0.018	$13 \leq x \leq 69$	0.993	76.5	71
25 d	-19.80	2.76	-0.021	$13 \leq x \leq 69$	0.998	70.1	65
50 e	-5.87	0.92	-0.004	$13 \leq x \leq 95$	0.987	44.4	109
75 f	0.96	0.47	-0.002	$13 \leq x \leq 95$	0.967	27.8	116
100 g	4.54	0.08	—	$13 \leq x \leq 53$	0.219	—	—

Treatments followed by the same letter are not significantly different (non-linear regression, except 100% fly ash - linear regression, $p<0.05$).

Table 3.7. Boron and selenium concentration in barley (pot basis) grown on fly ash treated soil.

Fly Ash %	Boron $\mu g\ pot^{-1}$			Selenium $\mu g\ pot^{-1}$		
	Silage	Grain	Straw	Silage	Grain	Straw
0	78 e	15 a	56 e	0.16 d	0.11 c	0.05 c
6.25	2077 c	33 a	3060 c	1.14 d	2.19 b	1.04 bc
12.5	3032 b	74 a	3981 b	4.06 b	4.33 a	2.33 b
25	4377 a	69 a	7470 a	6.56 a	3.99 a	4.95 a
50	844 d	20 a	1389 d	2.59 c	1.71 b	1.44 b

Means (n=3) within a column followed by the same letter are not significantly different (t-Test, $p<0.05$).

Table 3.8. Copper, molybdenum and Cu:Mo in barley grown on fly ash treated soil.

Fly Ash %	Copper $mg\ kg^{-1}$		Molybdenum $mg\ kg^{-1}$		Cu:Mo	
	Silage	Grain	Silage	Grain	Silage	Grain
0	4.3 (0.4)	3.7 (0.2)	0.0 (0.0)	0.0 (0.0)	216.5	186.5
6.25	7.5 (0.3)	4.8 (0.5)	3.7 (2.0)	0.0 (0.0)	2.0	238.5
12.5	8.3 (0.3)	8.8 (2.0)	7.3 (0.3)	3.3 (0.9)	1.1	2.7
25	7.9 (0.9)	6.2 (0.8)	12.3 (0.3)	4.0 (0.0)	0.6	1.6

Means (n=3) did not conform to normality tests, therefore, comparisons were not made between treatments. Values in brackets are standard errors.

Table 3.9. Mean pH, electrical conductivity (EC, dS m^{-1}) and sodium adsorption ratio (SAR) of soil treatmen s after harvest.

	Control (no plants)			Silage			Grain/Straw		
% Fly Ash	pH	EC	SAR	pH	EC	SAR	pH	EC	SAR
0	5.6 a	0.33 d	5.4 b	5.7 a	0.20 d	5.7 b	6.0 a	0.23 d	4.4 b
6.25	6.9 b	0.47 c	4.7 c	7.2 b	0.27 d	4.8 c	7.1 b	0.33 d	4.3 b
12.5	7.7 c	0.77 ab	4.2 cd	7.7 c	0.47 c	4.3 cd	8.0 c	0.53 c	3.9 c
25	8.2 d	0.70 ab	4.3 cd	8.2 d	0.67 b	4.1 de	8.3 d	0.70 b	3.6 cd
50	8.9 e	0.60 b	3.6 e	9.0 e	0.80 a	3.8 de	9.0 e	0.83 a	3.1 e
75	10.4 f	0.57 bc	4.1de	10.7 f	0.77 ab	3.6 e	10.6 f	0.70 b	3.3 de
100	11.0 g	0.57 bc	8.6 a	11.3 g	0.70 ab	7.5 a	11.1 g	0.57 c	7.2 a

Means (n=3) within a column followed by the same letter are not significantly different (pH and EC: t-Test, $p<0.05$; SAR: LSD, $p<0.05$).

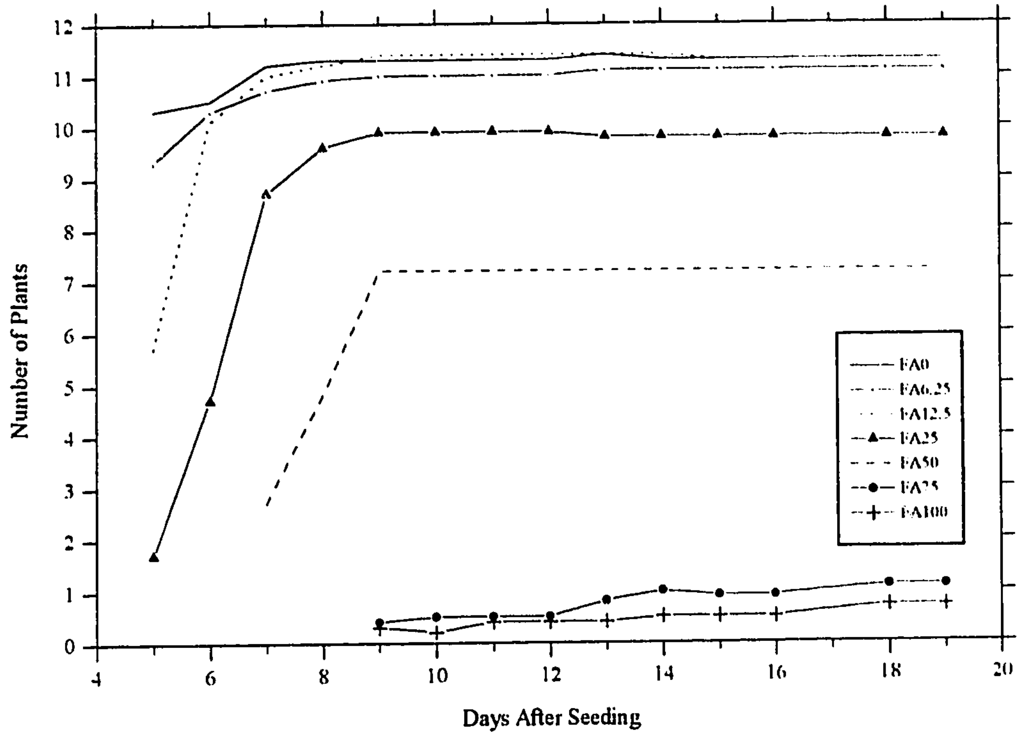

Figure 3.1 Average number of plants that emerged from 12 seeds

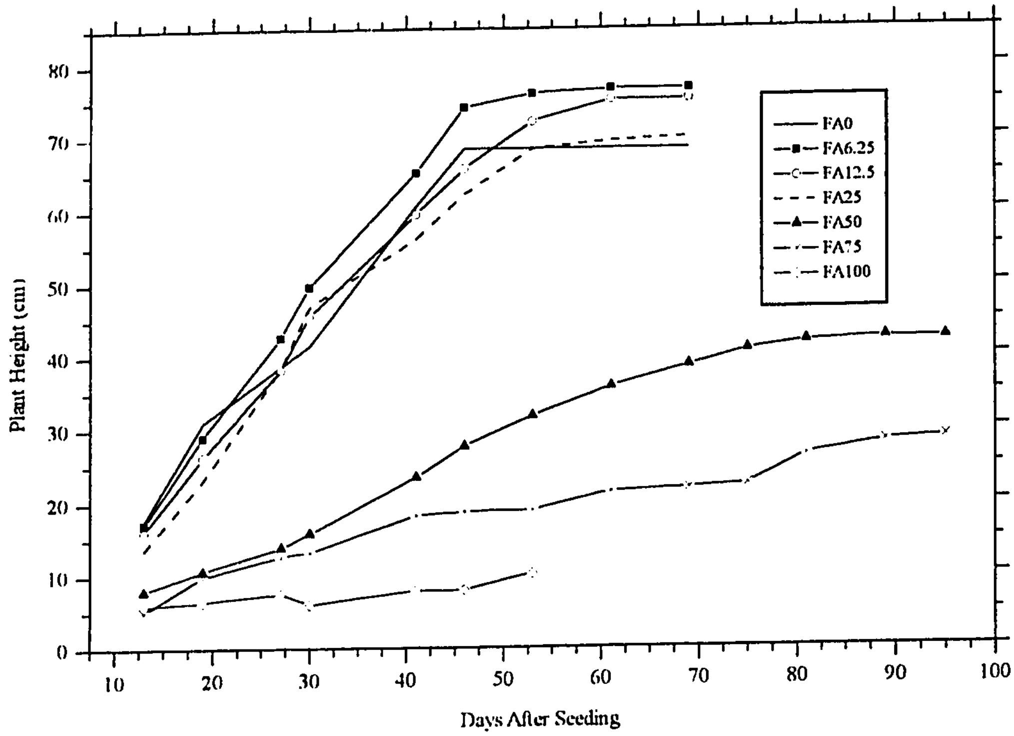

Figure 3.2 Temporal variation in plant height

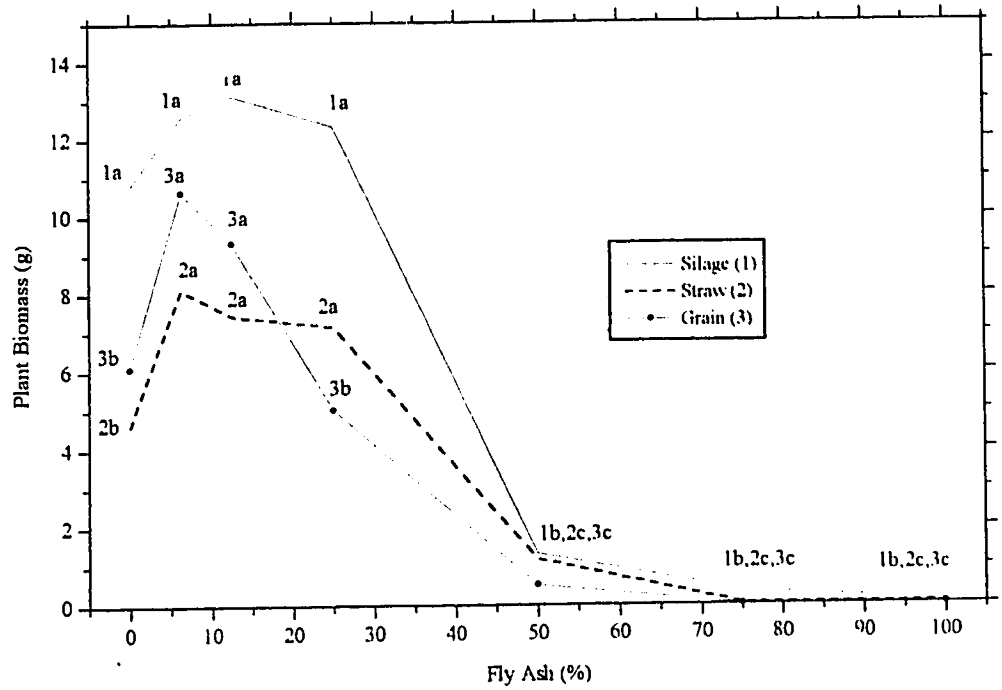

Figure 3.3 Biomass of silage, straw, and grain harvested. Numbers (used to differentiate plant material) followed by the same letter are not significantly different (LSD, $p<0.05$).

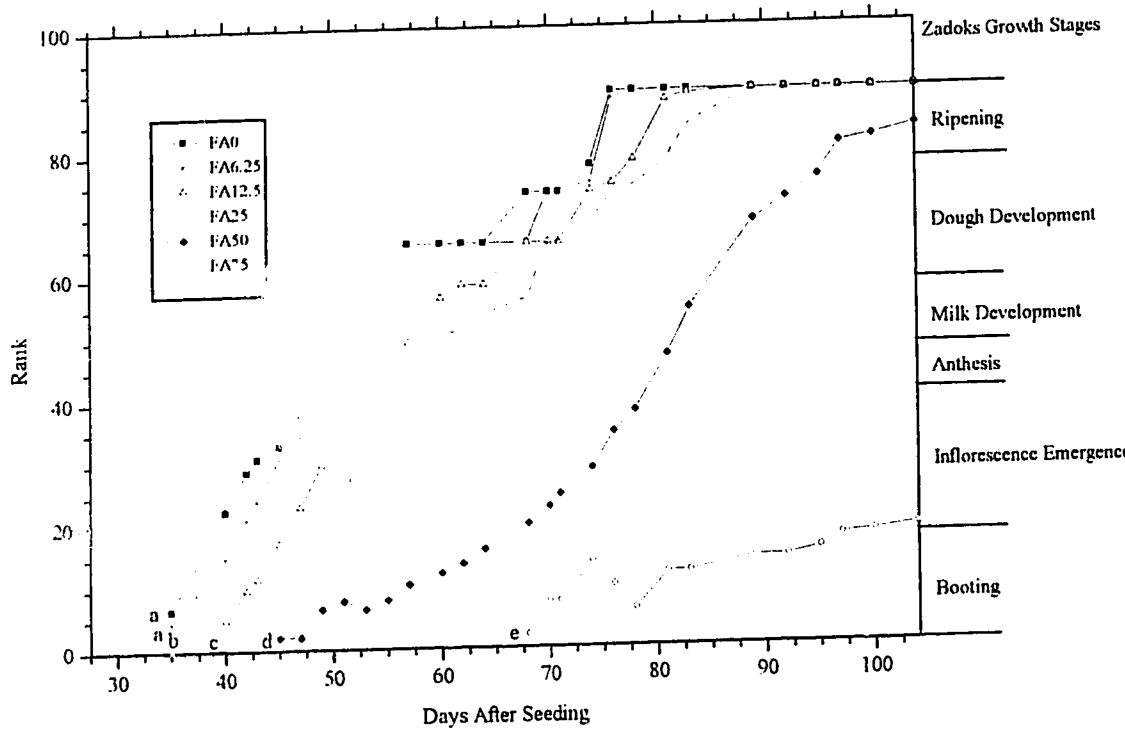

Figure 3.4 Barley development as ranked data and Zadoks growth stages. Plots preceded by the same letter are not significantly different (LSD, $p<0.05$).

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4. SYNTHESIS

There is abundant information in the literature on the effects of fly ash on soil chemical properties but little research reported on the effects of fly ash on soil physical properties. Furthermore, both soil chemical and physical parameters should be related to plant growth if fly ash is used in reclaiming a problem soil. In the two studies presented here, changes in soil physical properties and barley growth as a result of adding fly ash to a problem soil were researched. The two issues were addressed separately (soil and plants), but the same fly ash treatments were used in each, thus allowing for integration.

In the study of soil physical properties, two aspects were explored: the influence of adding increasing amounts of fly ash to soil on select soil physical parameters and how these select soil physical parameters changed over time. Barley was grown in a greenhouse on fly ash amended soil to determine the effect fly ash would have on growth and development.

Mixing up to 12.5% fly ash with this soil reduced mean weight diameter but increased modulus of rupture. Both mean weight diameter and modulus of rupture are reduced when more fly ash is added. Adding 6.25% fly ash dramatically increased grain yield then yield decreased linearly to 50% fly ash addition when most plants died.

The addition of 25% fly ash reduced soil crusting and cloddiness after 16 months as measured by modulus of rupture and mean weight diameter. The same rate of fly ash addition did not change barley grain yield nor plant height. However, 25% fly ash delayed plant emergence by approximately three days and reduced total emergence. This may be important when considering the length of the growing season for a particular area and the chosen barley cultivar. Early maturing barley varieties should be considered on land amended with 25% fly ash.

Time played a significant role on the influence of fly ash addition on some soil physical properties but not others. While mean weight diameter for most fly ash:soil mixtures generally increased over time, bulk densities decreased. Adding fly ash to this soil initially increased modulus of rupture, but over time, values decreased to levels that were similar among most treatments. When penetration resistance was measured with a cone penetrometer, there was little variation among fly ash treatments or over time.

However, with the blunt-end penetrometer, smaller differences in penetration resistance were detected.

The concern that fly ash will increase soil strength through pozzolanic reactions appears to be unwarranted because after the first winter, penetration resistance and modulus of rupture were reduced. We surmise that freeze/thaw cycles assisted in reducing soil strength.

Adding 12.5% fly ash to this problem soil delayed barley emergence by one day but did not change total plant emergence. The greatest benefit to adding 12.5% fly ash to this soil was an increase in plant height and grain yield. Exposing the fly ash:soil mixture to the environment for 16 months would result in the highest percent aggregation in the ideal range for seedbed preparation, however, modulus of rupture would be 1.6 times higher than for the soil alone.

Fly ash addition to this soil changed both the chemical and physical properties of the soil. Since the soil did not initially have detrimental chemical characteristics with respect to plant growth, the resulting improvement in barley growth is attributed to improvements in soil physical properties. The high clay content makes the soil dense and thus hinders plant root development. Fly ash reduced the relative clay content and created a more optimal rooting medium. This in turn improved the movement and distribution of water within the mixture for plant use.

Silage grown on fly ash amended soil may have boron concentrations that are potentially harmful to cattle, however, the grain would not be harmful. Adding fly ash to this soil improved selenium concentrations in grain with respect to ruminant health but adding ≥25% may lead to molybdenosis in ruminants, thus copper supplementation may be required.

The greenhouse component of this study was designed to determine the influence of fly ash addition to soil on barley under controlled conditions. In a field experiment, barley may respond differently when variables such as water limitations and competition for resources are factors.

The most effective parameters to measure the success of improving soil tilth by adding fly ash were aggregate size distribution and modulus of rupture. Of the plant parameters measured, development, yield and chemical composition were the most useful in understanding the influence of fly ash on barley growth.

To reduce the cloddy nature of this soil and develop a more desirable level of aggregation, we recommend that 25% fly ash be used as an amendment. From a plant perspective, if barley is grown on this soil amended with 25% fly ash, a delay in plant emergence may be expected but likely no reduction in grain yield. Copper supplementation in ruminant diets fed grain grown on 25% fly ash amended soil would likely be required. If the slightly higher modulus of rupture values that result from adding 12.5% fly ash are not a hindrance to plant growth or are not persistent beyond the time frame of this experiment, then 12.5% fly ash could be used instead.

To gain a better understanding of the influence of fly ash addition on soil physical properties and barley growth and development the previous experiments should be combined into one and conducted in the field to evaluate plant growth response to changing soil physical properties. A greenhouse environment removes stresses that may influence plant growth. For instance, the results obtained here may change if barley plants were grown in the field and were required to withstand periods of water deficits or compete with weeds for nutrients. The application of fly ash to soil should be conducted on a field scale to test the ability to incorporate fly ash using standard agricultural implements. The changes in soil physical properties would better reflect what plants would be exposed to when large scale applications are made. Further research into the reasons for and substantiation of reduced harvest indices of barley grown on fly ash amended soils in required. Because there were significant reductions in plant growth on the ≥50% fly ash treatments, treatments exceeding this value would not provide insight into the potential use of fly ash as a problem soil amendment and are not recommended.

APPENIDIX

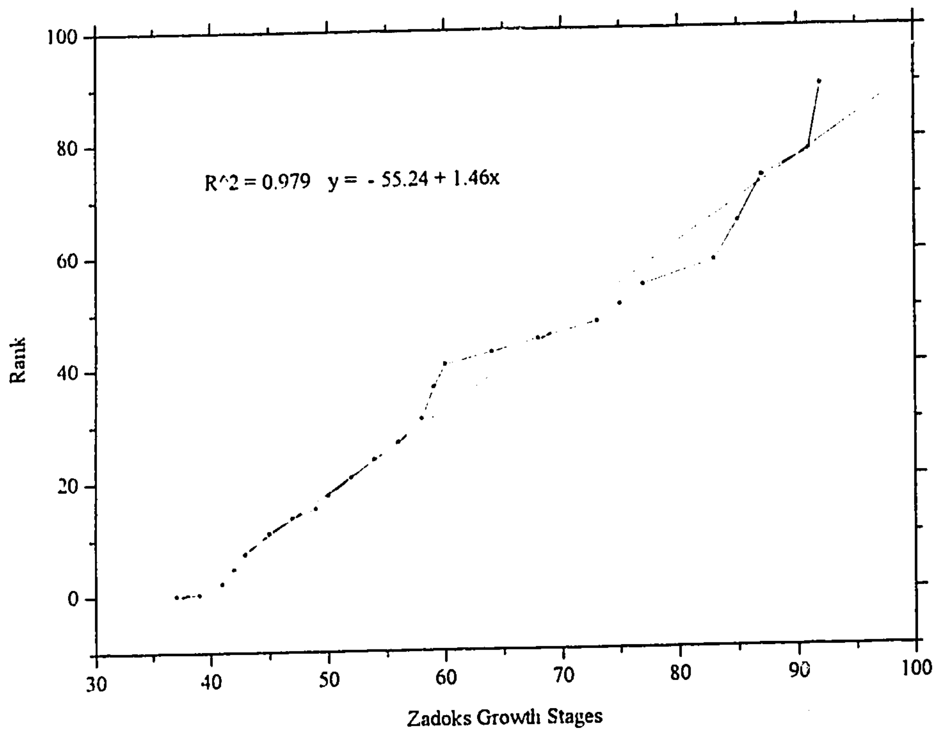

Figure A: Comparison of ranked data and Zadoks growth stages.