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COMPARISON OF LIME AND FLY ASH AS AMENDMENTS TO ACIDIC COAL MINE REFUSE: GROWTH RESPONSES AND TRACE-ELEMENT UPTAKE OF TWO GRASSES

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COMPARISON OF LIME AND FLY ASH AS AMENDMENTS TO ACIDIC COAL MINE REFUSE: GROWTH RESPONSES AND TRACE-ELEMENT UPTAKE OF TWO GRASSES

by

J.D. Jastrow, C.A. Zimmerman,
A.J. Dvorak, and R.R. Hinchman

Land Reclamation Program

October 1979

Prepared for the U.S. Department of Energy as part of the Argonne Land Reclamation Program, a joint effort of the Energy and Environmental Systems Division and the Division of Environmental Impact Studies.

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PREFACE

This study was performed as a part of the Argonne National Laboratory Land Reclamation Program, which is sponsored by the Department of Energy, Assistant Secretary for Environment, Office of Health and Environmental Research. The program is a joint effort conducted by Argonne's Energy and Environmental Systems Division and the Division of Environmental Impact Studies.

The Land Reclamation Program, as the lead DOE program for reclamation research, conducts basic and applied research into the physical, ecological, and economic problems of land reclamation related to surface mining of coal. This work is aimed at developing energy-efficient and cost-effective techniques for reclaiming and rehabilitating mined land to productive end uses. To achieve this goal, the Program has established integrated research and development projects focused on near- and long-term reclamation problems in all major U.S. coal resource regions. These research sites have been established to address both regional and site-specific problems. The activities of the Land Reclamation Program involve close cooperation with industry and the academic community and focus on establishing a comprehensive field and laboratory effort. At six of its research sites, the Program has developed cooperative working arrangements with the operating coal companies. Close cooperation with related research projects at academic institutions and other agencies, in order to transfer pertinent information and avoid duplication of effort, has been a primary goal of the Program.

The study that is the subject of this report was conducted by the staff of the Program's Revegetation Project. A primary function of this project is to evaluate, through laboratory and field studies, those attributes of candidate revegetation plants that allow them to become established and function in the harsh edaphic environment usually found in minesoils and coal refuse. Data from this study will help in comparing the suitability of lime and fly ash as amendments for coal refuse and will be valuable in determining which potentially toxic trace elements, if any, are taken up by plants from coal refuse in quantities that would indicate the need for further study.

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Land Reclamation Program

Ray R. Hinchman, Deputy Director
for Biological Sciences
Land Reclamation Program

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COMPARISON OF LIME AND FLY ASH AS AMENDMENTS TO ACIDIC COAL MINE REFUSE: GROWTH RESPONSES AND TRACE-ELEMENT UPTAKE OF TWO GRASSES

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ABSTRACT

Two commonly used revegetation species, 'Kentucky 31' tall fescue (Festuca arundinacea Schreb.) and 'Lincoln' smooth brome (Bromus inermis Leyss.) were grown for 60 days in pots containing coarse coal mine refuse (referred to as gob, pH ≐ 3.5) that was amended with lime or alkaline fly ash. Both species were also grown in pots containing a silt-loam surface soil as a control. Morphological growth parameters were measured over time; dry weights and shoot:root ratios were determined at harvest. Concentrations of Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, V, and Zn in the plant shoots were determined by atomic absorption spectrophotometry.

Plant growth of both species was not as good on either lime- or fly ash-amended gob as it was on surface soil. Although plant height and length of the longest leaf were not significantly different ($p > 0.10$) at the end of the experiment for plants grown on the two amended-gob substrates, parameters giving an indication of plant vigor (i.e., number of leaves and stems, width of the longest leaf, and biomass) were significantly greater ($p < 0.01$) for plants grown on lime-amended gob than for those grown on fly ash-amended gob.

Significant ($p < 0.05$) differences in the tissue concentrations of Cd, Co, Fe, Hg, Mn, Pb, V, and Zn were found among the plants grown on the three substrates. Except for Hg and Pb, these elements were higher in plants grown on at least one of the amended-gob substrates than in plants grown on surface soil. Significant substrate differences were not observed for Al, As, Cr, Cu, Ni, and Se. The tissue concentrations of some elements -- notably Al, Cu, Fe, Mn, V, and Zn -- were high enough in plants from one or more of the substrates to either approach or exceed concentrations that have been reported to be associated with toxic effects in some plant species.

INTRODUCTION

Coal mine refuse consists of waste coal, rock, minerals, associated clays, extraction debris, and other waste materials remaining after coal processing or cleaning. There are two types of refuse, commonly referred to as slurry and gob. Slurry is primarily coal fines and other fine material deposited by sedimentation when coal wash water is sluiced into a settling pond; gob consists of the coarser waste materials that either are separated by a screening process or are not suspended in the wash water.

The physical and chemical characteristics of coal mine refuse usually preclude the establishment of natural vegetative cover on this material (37). Oxidation and hydrolyzation of pyritic (FeS_2) material in the refuse causes the formation of strong acids (primarily H_2SO_4), thereby creating extremely low pH conditions. The pH of coal refuse varies considerably, however, and values as low as 1.3 have been reported for abandoned mine sites in Illinois (21). Other characteristics of coal refuse that are unfavorable for vegetative establishment include high surface temperatures (caused by the dark color of the refuse), low water-holding capacity, nutrient deficiencies, high amounts of soluble salts, toxic concentrations of Fe and Al, and perhaps toxic concentrations of certain trace elements such as B, Zn, and Mn (10,37).

Historically, most gob was simply dumped in piles, and the resulting steep, unstable slopes further hampered revegetation. While federal law now requires the proper disposal of coal refuse generated from active mines, many areas of abandoned coal mine refuse still exist, particularly in the Eastern and Central Interior coal provinces. About 3650 ha of exposed coal refuse have been identified in Illinois alone (24). Under current federal regulations for active mines (38), gob is either (a) spread in layers, compacted, and then covered by a minimum of 1.2 m (4 ft) of the best available nontoxic, noncombustible material, or (b) buried in the strip pit or other depressions and covered. In some cases, gob has been disposed of in abandoned or operating deep mines. Slurry ponds are usually dewatered and covered with suitable material.

Previous greenhouse and field studies have determined that amendment of coal refuse with alkaline materials (such as lime or some power-plant fly ashes) and fertilizer can, in some cases, produce a suitable medium for plant growth. Davidson (10), Sorrell (35), and Medvick and Grandt (20) utilized lime as an amendment to coal refuse, whereas Adams et al. (1), Babcock (4), and Capp and Gillmore (7) reported on studies where coal refuse was amended with alkaline fly ash.

The use of fly ash as an amendment for coal refuse is attractive because the adverse nature of one waste may be ameliorated by treatment with another. Besides effecting an increase in pH, the addition of fly ash to coal mine refuse may have some other beneficial effects, such as increased water-holding capacity, improved texture, and increased concentrations of some nutrients (1,8,28). Chang et al. (8), however, reported that (a) although water-holding capacity increased when fly ash was added to five soils, water availability to plants remained unchanged, and

(b) the addition of greater than 10% fly ash (by volume) to acidic soils decreased the hydraulic conductivity of the soils. After adding fly ash to three soils, Jones and Amos (15) reported both increases and no change in plant available water, depending on soil texture. Unfortunately, it is not known if coal refuse amended with fly ash behaves in the same manner as fly ash-amended soils.

The neutralizing power of fly ash is variable but generally less than that of lime (18). Therefore, considerably larger quantities of fly ash as compared to lime may be required to raise the pH of coal refuse to the desired level. However, since fly ash is a waste material, its cost can often be less than that of using lime.

One major disadvantage of fly ash as is the variability of its properties, depending on its source and treatment following collection (7,34). Additionally, certain trace elements may be present in some fly ashes at concentrations that either are toxic to plants or, if accumulated by plants, are toxic to plant consumers (1,28,34). The combination of the trace-element concentrations in coal refuse with those in an amending fly ash could seriously restrict the use of at least some fly ashes as a coal-refuse amendment.

Several researchers (12,19,23,34), have shown that plant uptake of essential trace elements -- such as Zn, B, Mo, and Mn -- increased when soils deficient in these elements were amended with fly ash. Boron toxicity has occurred in soils when unweathered fly ash was used, but was greatly reduced by the use of weathered fly ash (19,29); this was probably due to leaching of soluble boron compounds. Although Martens and Beahm (19) demonstrated that weathered fly ash can be added to soil in larger quantities than can unweathered fly ash without adversely affecting plant growth, they cautioned that further research is needed to determine the effects that trace elements in fly ash may have on members of food chains.

Very little information is available on plant uptake and accumulation of trace elements from coal mine refuse. In one study (1), forage plants grown on acidic refuse amended with fly ash were analyzed for a number of elements, including Cu, Fe, Mn, Mo, and Zn; the authors did not consider the elemental tissue concentrations to be abnormally high. High boron tissue concentrations and toxicity were observed, but toxicity symptoms seemed to disappear after several growing seasons, presumably due to loss of the boron through leaching.

A major concern about the establishment of plants on amended refuse is that the vigor of apparently tolerant species may be reduced over time, resulting in a degradation of stand quality that may not be observed during the growing seasons immediately following revegetation. Additionally, plants grown successfully on amended refuse may accumulate trace-element concentrations that are directly toxic to herbivores or that are incorporated into food chains, thus affecting secondary consumers.

The purpose of this experiment was to compare fly ash and lime as amendments for acidic gob obtained from an abandoned underground mine site in southern Illinois. Two commonly used revegetation species, 'Kentucky 31' tall fescue (<u>Festuca arundinacea</u> Schreb.) and 'Lincoln' smooth brome (<u>Bromus</u>

inermis Leyss.), were selected for the experiment because these species are similar in growth form and size. The plants were grown for 60 days on lime- and fly ash-amended gob and on a silt-loam surface soil as a control. Plant growth (morphological parameters and biomass production) and the concentrations of Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, V, and Zn in the above-ground biomass of the test species were compared after 60 days.

MATERIALS AND METHODS

Seeds of 'Kentucky 31' tall fescue and 'Lincoln' smooth brome were sown in 5.7-L plastic pots. In each pot, 48 seeds were planted, equally spaced in a circle, approximately 0.4 cm deep. The radius of the circle was such that the areas inside and outside the circle were equal. After germination, the plants were thinned to 12 evenly spaced individuals in each pot. For each species, three replicate pots were prepared for each of three substrates: silt-loam surface soil (hereafter referred to as topsoil), fly ash-amended gob, and lime-amended gob. Topsoil pots contained 20 cm of topsoil over 2.5 cm of gravel for drainage. Amended-gob pots contained, from the top down: 5 cm of topsoil, 15 cm of amended gob, and 2.5 cm of gravel. The thin (5-cm) layer of topsoil was placed above the amended gob in the latter two substrates to ensure germination and early seedling establishment. Results of preliminary experiments (J. D. Jastrow, unpublished information) indicated that seedling establishment on amended gob (particularly fly ash-amended gob) was enhanced by the application of a thin surface layer of topsoil.

Gob was obtained from an abandoned coal refuse disposal site adjacent to the town of Staunton in southwestern Illinois. (The underground mine that generated the refuse was abandoned in 1921 after mining the Herrin [Illinois No. 6] coal seam for 17 years.) Before the addition of amending materials, the gob was thoroughly mixed to reduce its heterogeneity. Particles (mostly coal) greater than 2 to 3 cm in diameter, were removed from the gob before potting. The pH of the unamended gob after mixing was 3.5.

Fly ash-amended gob was prepared by mixing fly ash (pH = 12.3) with gob at the rate of 80 g fly ash/kg air-dry gob (equivalent to 134 t fly ash/ha).* The fly ash was obtained from an electric generating station in southern Illinois that was burning a blend ($\sim$ 1:1) of pulverized coal from Illinois (No. 6 seam) and Colorado (either the Wadge or the Fish Creek seam) when the fly ash was collected. Lime-amended gob was prepared by mixing lime (85% $CaCO_3$ equivalent; 25% passing a 100-mesh and 90% passing a 10-mesh screen) with gob at the rate of 40 g lime/kg air-dry gob (67 t lime/ha).* Both fly ash- and lime-amended gob had a pH $\sim$ 6 at planting. The topsoil was a silt loam (19% sand, 56% silt, 25% clay) obtained in northern Illinois. Before potting, all plant growth substrates were fertilized with a 10-10-10 fertilizer at a rate equivalent to 134.4 kg N/ha, 58.7 kg P/ha, and 111.6 kg K/ha (120 lbs N, P_2O_5, and K_2O/acre).

The pots were placed in a walk-in controlled-environment chamber with a 16-hour light/8-hour dark photoperiod. Mixed fluorescent/incandescent illumination was 16000 lux at 10 cm above the soil surface. Temperatures were maintained at 27 $\pm$ 2° C during the day and 21 $\pm$ 1° C during the night; relative humidity varied from 50% to 70%. After germination, the pots were watered three times a week to field capacity with distilled water and were rotated around the growth room twice a week to compensate for light-intensity differences.

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*Assumes: (a) a bulk density of 1.0 g/cm^3 for gob rather than 1.33 g/cm^3 which is usually used for an average surface soil, and (b) mixing of the amending material to an average depth of 15 cm in the field.

Morphological measurements were taken at 14, 28 or 29, 39, 49, and 59 days after planting. The following parameters were measured for each plant: height from the soil surface (mm), length of the longest leaf (mm), width of the longest leaf at the widest part (mm), number of live leaves present, and number of stems (minus the main stem) present.

The plants were harvested 60 days after planting. The roots in each pot were carefully washed free of soil and gob over a 2-mm screen. After individual plants were separated, the shoots were cut from the roots and washed in double-distilled water for later trace-element analysis. Shoots and roots were dried to constant weight at 65° C in a forced-air oven, and dry weights were determined. Shoot:root ratios were calculated from the dry weight data.

The dried plant shoots were ground in a Wiley mill to pass through a 20-mesh screen. Plant shoots from the same pot were combined to give a total dry weight of 2.1 g for each sample. For each species, two samples from each pot of topsoil and lime-amended gob were digested. Due to low shoot-biomass production, only one sample from each pot of fly ash-amended gob was digested. Each sample was digested with 20 mL of concentrated, ultrapure nitric acid for 4.5 hours in an 80°C shaker bath; reflux conditions were maintained for the first 3.5 hours. During the last hour, the evolution of nitrogen dioxide fumes was not restricted. All samples were filtered and brought to a final volume of 100 mL with double-distilled water. Trace-element concentrations in the digested plant samples were determined with a Perkin-Elmer 306 atomic absorption spectrophotometer equipped with a Perkin-Elmer HGA 2100 flameless graphite furnace.

Table 1. Mean pH (± standard error) of Topsoil, Fly Ash-Amended Gob, and Lime-Amended Gob at Harvest

Substrate	Smooth Brome	Tall Fescue
	pH	
Topsoil	5.61 ± 0.04[a*]	5.33 ± 0.08[a]
Fly ash-amended gob		
Topsoil layer	5.34 ± 0.04[ab]	5.31 ± 0.14[a]
Amended-gob layer	4.79 ± 0.15[ab]	4.19 ± 0.25[b]
Lime-amended gob		
Topsoil layer	5.49 ± 0.09[ab]	5.36 ± 0.04[a]
Amended-gob layer	4.53 ± 0.63[b]	3.80 ± 0.44[b]

*Means in each column followed by the same superscript are not significantly different at the 5% level of probability based on Duncan's multiple range test. n = 3.

Soil and/or gob samples were taken from each pot prior to root washing. In the lime- and fly ash-amended gob treatments, samples were taken from both the topsoil layer and the gob layer. Samples were allowed to air dry and then ground to pass a 2-mm sieve. The pH was determined for three replicate 1:1 (sample to distilled water) extracts of each sample (Table 1).

Statistical analyses of the morphological growth measurements, biomass production, and trace-element accumulation data included means and standard errors, one- and two-way analyses of variance, and Student-Newman-Keuls or Duncan's multiple range tests. Plant tissue concentrations of each element were also tested for linear correlation with substrate pH (at harvest) and plant dry weights. Analysis of variance and multiple range tests of the number of leaves and the number of stems were performed after square root transformation of the raw data (36).

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RESULTS AND DISCUSSION

GROWTH RESPONSES

Changes in mean plant height over time are illustrated in Figures 1 and 2 for 'Lincoln' smooth brome and 'Kentucky 31' tall fescue, respectively. Changes in the other morphological parameters (i.e., length and width of the longest leaf, number of live leaves, and number of stems) are reported in Tables 2 and 3. During the first stages of growth, plant metabolism is probably maintained primarily by endosperm reserves; this could account for the lack of significant between-substrate differences ($p > 0.05$) in some parameters at the first measurement (14 days). The most important pattern of substrate and species differences occurred at the end of the experiment (49 to 59 days), the time period representing the longest exposure of the plants to the substrate conditions (see Figures 1 and 2, Tables 2 and 3).

At the end of the experiment, no significant differences ($p > 0.10$) between lime- and fly ash-amended gob were observed in shoot elongation as measured by plant height and length of the longest leaf. Shoot elongation of plants grown on both amended gobs was found to be significantly less ($p < 0.01$) than shoot elongation of plants grown on the topsoil control.

Those parameters giving an indication of plant vigor (number of leaves and stems, width of the longest leaf, and biomass) showed significant differences ($p < 0.01$) between all three substrates by the end of the experiment, and generally followed the order: topsoil > lime-amended gob > fly ash-amended gob (Tables 2 and 3, Figure 3). If plant vigor during early growth can be considered an indication of potential long-term plant survival and stand development, then the experimental results indicate that amending gob with lime rather than fly ash may increase the chances for successful long-term revegetation.

It must be pointed out, however, that the extrapolation of relatively short (60-day) growth-chamber experiments, where moisture and temperature conditions are ideal, to potential field results must be made with caution. Field studies investigating the use of either lime or fly ash as amendments to gob have been conducted at several sites (1,4,7,10,20,35), although no reports have been found of studies where lime and fly ash were tested and compared at the same site. This is unfortunate because the extremely variable natures of gob and fly ash, site-to-site variations in environmental conditions, and even differences in the method of incorporating lime or fly ash require that meaningful field comparisons of lime and fly ash as amendments to gob be conducted at the same site. The chemical and physical properties of gob can vary as a function of coal type, coal seam, overburden type, mining method, coal processing method, and, with abandoned gob, the degree of weathering. Fly ash properties can vary as a function of coal type, coal seam, coal processing method, powerplant boiler type, method of ash collection, and degree of weathering of the ash before use.

Both 'Kentucky 31' tall fescue and 'Lincoln' smooth brome have been utilized with some success in the revegetation of amended gob (1,10,20,35),

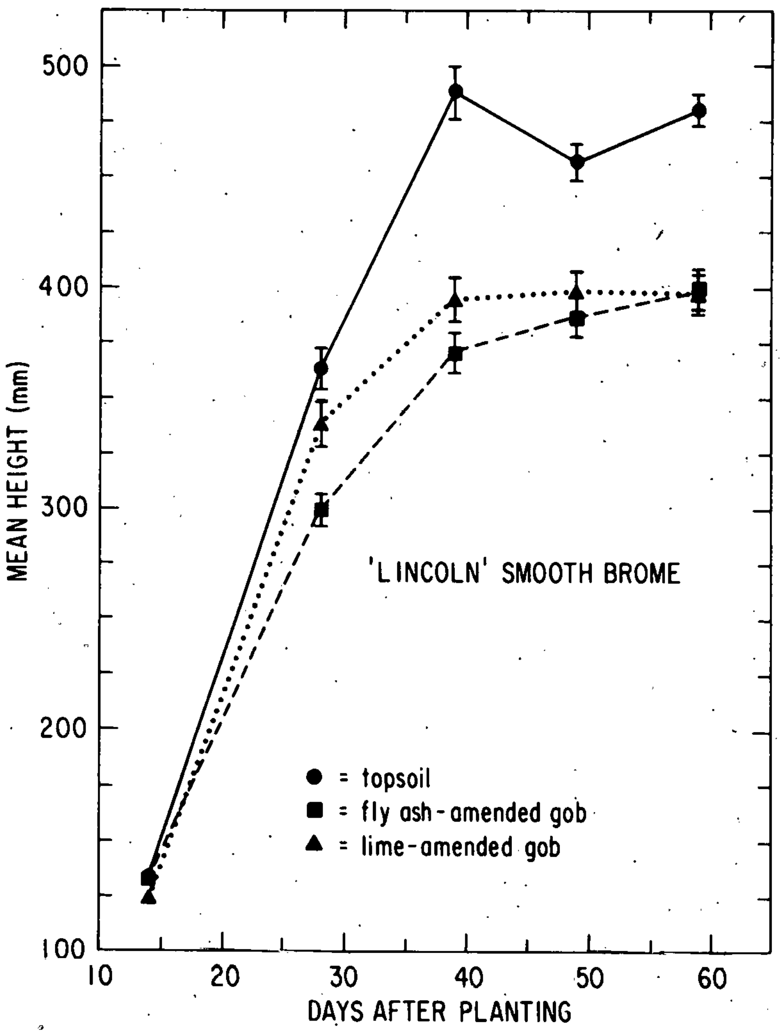

Fig. 1. Mean Heights (± standard errors) of 'Lincoln' Smooth Brome Grown on Topsoil, Fly Ash-Amended Gob, and Lime-Amended Gob (n = 36, Except n = 35 for Topsoil After First Measurement)

although few studies have quantitatively evaluated either the quality of plant growth or the species' success on lime- or fly ash-amended gob. Medvick and Grandt (20) reported that 'Lincoln' smooth brome and 'Kentucky 31' tall fescue grown on lime-amended gob at two field sites had achieved similar plant cover percentages at the end of the first growing season, but that after four seasons, smooth brome appeared to be "doing better" than fescue. Using 'Kentucky 31' tall fescue and lime-amended gob, Davidson (10) reported only green matter production data from pot studies and percent cover data from field plots.

In this study, plant heights and lengths of the longest leaf of both species were equal ($p > 0.40$) at the end of the experiment. However, shoot elongation rates of smooth brome had reached a plateau by 39 days (Figure 1 and Table 2), whereas they had just begun to level off for tall

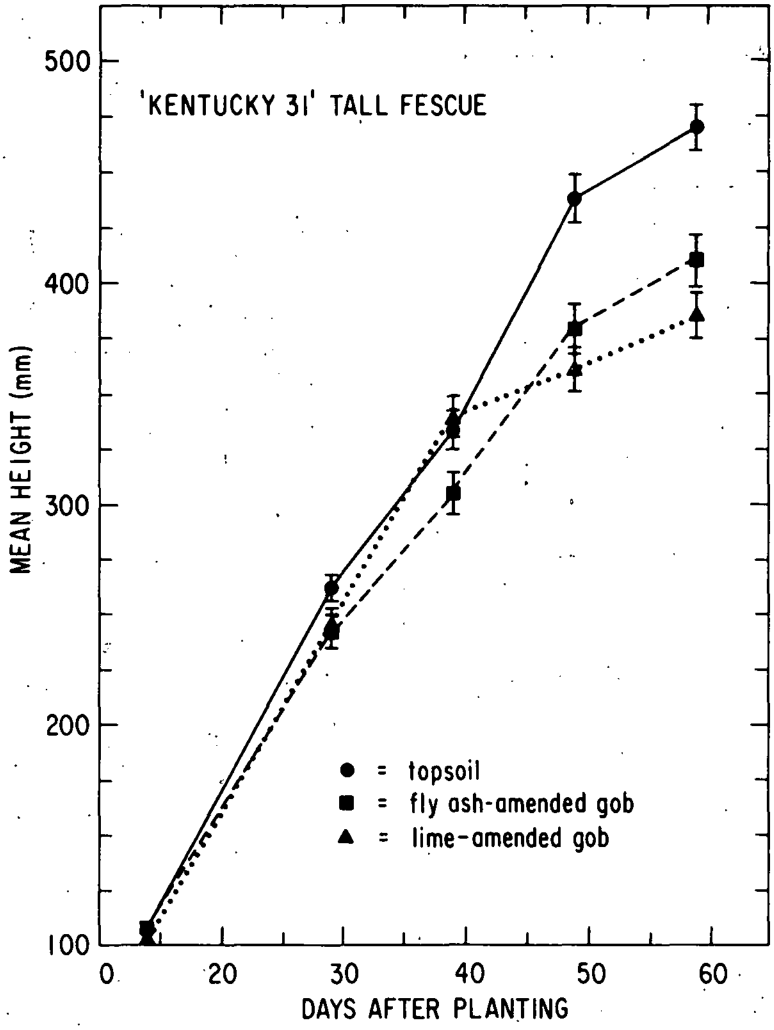

Fig. 2. Mean Heights (± standard errors) of 'Kentucky 31' Tall Fescue Grown on Topsoil, Fly Ash-Amended Gob, and Lime-Amended Gob (n = 36, Except n = 35 for Topsoil at First Measurement)

fescue at the end of the experiment (Figure 2 and Table 3). Thus, if the plants had grown for a longer time, tall fescue might have achieved greater height and leaf elongation than did smooth brome, for all substrates.

Although significant ($p < 0.001$) at the earlier measurement periods, the differences in leaf width between the two species were probably not large enough to afford any advantage to either species. Conversely, the larger number of leaves and stems, earlier development of stems, and greater shoot biomass produced by tall fescue ($p < 0.001$) (Tables 2 and 3 and Figure 3) may indicate the potential for more rapid establishment of plant cover by tall fescue as compared to smooth brome. Early development of plant cover is important to the reclamation of gob areas because plant interception of rainfall helps reduce surface erosion.

Table 2. Mean Values (± standard errors) of Length and Width of the Longest Leaf, Number of Leaves, and Number of Stems at Each Measurement Period for 'Lincoln' Smooth Brome Grown on Topsoil, Fly Ash-Amended Gob, and Lime-Amended Gob

Substrate	Days after Planting 14	28	39	49	59
	Length of Longest Leaf (mm)				
Topsoil	114 ± 3[a*]	302 ± 8[a]	372 ± 8[a]	375 ± 7[a]	392 ± 6[a]
Fly ash-amended gob	113 ± 2[a]	248 ± 6[b]	303 ± 7[b]	328 ± 8[b]	331 ± 8[b]
Lime-amended gob	107 ± 2[a]	281 ± 8[a]	326 ± 8[b]	330 ± 8[b]	328 ± 8[b]
	Width of Longest Leaf (mm)				
Topsoil	1.6 ± 0.1[a]	5.9 ± 0.1[a]	8.4 ± 0.2[a]	8.6 ± 0.2[a]	8.3 ± 0.2[a]
Fly ash-amended gob	1.4 ± 0.1[a]	3.9 ± 0.1[c]	4.9 ± 0.1[c]	4.8 ± 0.1[c]	5.1 ± 0.1[c]
Lime-amended gob	1.4 ± 0.1[a]	5.1 ± 0.2[b]	6.6 ± 0.2[b]	6.2 ± 0.2[b]	6.5 ± 0.2[b]
	Number of Leaves				
Topsoil	2.0 ± 0.03[a]	4.9 ± 0.05[a]	10.1 ± 0.4[a]	11.1 ± 0.4[a]	16.1 ± 0.8[a]
Fly ash-amended gob	2.0 ± 0.0[a]	4.0 ± 0.04[b]	4.9 ± 0.1[c]	6.0 ± 0.2[c]	7.1 ± 0.3[c]
Lime-amended gob	2.0 ± 0.03[a]	4.2 ± 0.1[b]	7.1 ± 0.3[b]	9.3 ± 0.4[b]	11.2 ± 0.5[b]
	Number of Stems**				
Topsoil	0.0 ± 0.0[a]	0.1 ± 0.05[a]	1.7 ± 0.1[a]	2.5 ± 0.3[a]	3.4 ± 0.2[a]
Fly ash-amended gob	0.0 ± 0.0[a]	0.0 ± 0.0[a]	0.0 ± 0.0[c]	0.2 ± 0.1[c]	0.9 ± 0.1[c]
Lime-amended gob	0.0 ± 0.0[a]	0.1 ± 0.05[a]	0.8 ± 0.1[b]	1.4 ± 0.1[b]	1.7 ± 0.1[b]

*Within each parameter, means at each age followed by the same superscript are not significantly different at the 1% level of probability based on one-way analysis of variance, and the Student-Newman-Keuls multiple range test when analysis of variance indicated significant differences between substrates. n = 36, except n = 35 for topsoil after first measurement.

**Does not include the main stem.

The calculation of shoot:root ratios for each plant species and substrate produced some unexpected results (see Figure 3). For both species, the shoot:root ratios of plants grown on lime-amended gob were significantly less ($p < 0.01$) than those of plants grown on either topsoil or fly ash-amended gob. Thus, for lime-amended gob there was relatively more root growth and/or less shoot growth than for the other two substrates. Without further experimentation, the cause of this phenomenon is only a matter of speculation. Yet, given the environmental conditions and the stage of plant development, if the shoot:root ratios of the plants grown on topsoil can be considered normal for each species, then a proportional increase in root growth for plants grown on lime-amended gob may have been caused by one or a combination of factors such as (a) elevated calcium ion concentrations due to the added lime, (b) moisture stress resulting from low (increasingly negative) osmotic potentials caused by high levels of soluble salts, or (c) either the availability or lack of availability of nutrient ions such as

Table 3. Mean Values (± standard errors) of Length and Width of the Longest Leaf, Number of Leaves, and Number of Stems at Each Measurement Period for 'Kentucky 31' Tall Fescue Grown on Topsoil, Fly Ash-Amended Gob, and Lime-Amended Gob

Substrate	Days after Planting				
	14	29	39	49	59
	Length of Longest Leaf				
	mm				
Topsoil	98 ± 2[a*]	220 ± 5[a]	275 ± 8[ab]	355 ± 9[a]	381 ± 9[a]
Fly ash-amended gob	94 ± 3[ab]	208 ± 7[a]	255 ± 7[b]	318 ± 10[b]	338 ± 11[b]
Lime-amended gob	86 ± 2[b]	208 ± 7[a]	290 ± 8[a]	298 ± 9[b]	317 ± 8[b]
	Width of Longest Leaf				
	mm				
Topsoil	1.1 ± 0.03[a]	3.9 ± 0.1[a]	5.8 ± 0.1[a]	6.5 ± 0.2[a]	7.0 ± 0.2[a]
Fly ash-amended gob	1.1 ± 0.03[a]	4.1 ± 0.1[a]	5.2 ± 0.1[b]	5.8 ± 0.2[b]	6.5 ± 0.1[ab]
Lime-amended gob	1.0 ± 0.0[a]	3.9 ± 0.1[a]	5.4 ± 0.1[ab]	5.9 ± 0.1[b]	6.0 ± 0.1[b]
	Number of Leaves				
Topsoil	2.0 ± 0.0[a]	5.7 ± 0.2[a]	9.1 ± 0.3[a]	14.5 ± 0.5[a]	18.8 ± 0.6[a]
Fly ash-amended gob	2.0 ± 0.0[a]	4.4 ± 0.1[c]	6.1 ± 0.3[b]	7.7 ± 0.4[c]	9.8 ± 0.5[c]
Lime-amended gob	2.0 ± 0.0[a]	5.1 ± 0.1[b]	8.7 ± 0.4[a]	11.2 ± 0.5[b]	12.4 ± 0.6[b]
	Number of Stems**				
Topsoil	0.0 ± 0.0[a]	1.2 ± 0.1[a]	2.2 ± 0.1[a]	3.2 ± 0.1[a]	4.3 ± 0.2[a]
Fly ash-amended gob	0.0 ± 0.0[a]	0.4 ± 0.1[c]	0.8 ± 0.1[b]	1.1 ± 0.1[c]	1.7 ± 0.1[c]
Lime-amended gob	0.0 ± 0.0[a]	0.8 ± 0.1[b]	1.8 ± 0.1[a]	2.3 ± 0.2[b]	2.3 ± 0.2[b]

*Within each parameter, means at each age followed by the same superscript are not significantly different at the 1% level of probability based on one-way analysis of variance, and the Student-Newman-Keuls multiple range test when analysis of variance indicated significant differences between substrates. n = 36, except n = 35 for topsoil at first measurement.

**Does not include the main stem.

nitrate or phosphate (3,22). Some of the same conditions (e.g., low osmotic potentials) probably existed in the fly ash-amended gob; yet the shoot:root ratios of plants grown on this substrate were either significantly greater than or equal to the shoot: root ratios of plants grown on topsoil and, of course, significantly greater than the shoot:root ratios for lime-amended gob. Since total biomass production was lower for fly ash-amended gob than lime-amended gob (Figure 3), it is likely that toxic factors in the fly ash-amended gob may have affected root growth more severely than shoot growth, resulting in higher shoot:root ratios than those observed for lime-amended gob.

Although species differences in total biomass production for each substrate were not significant ($p > 0.30$), the allocation of more energy for root development by smooth brome (Figure 3) may be advantageous for nutrient uptake or under conditions of low available soil moisture. Early

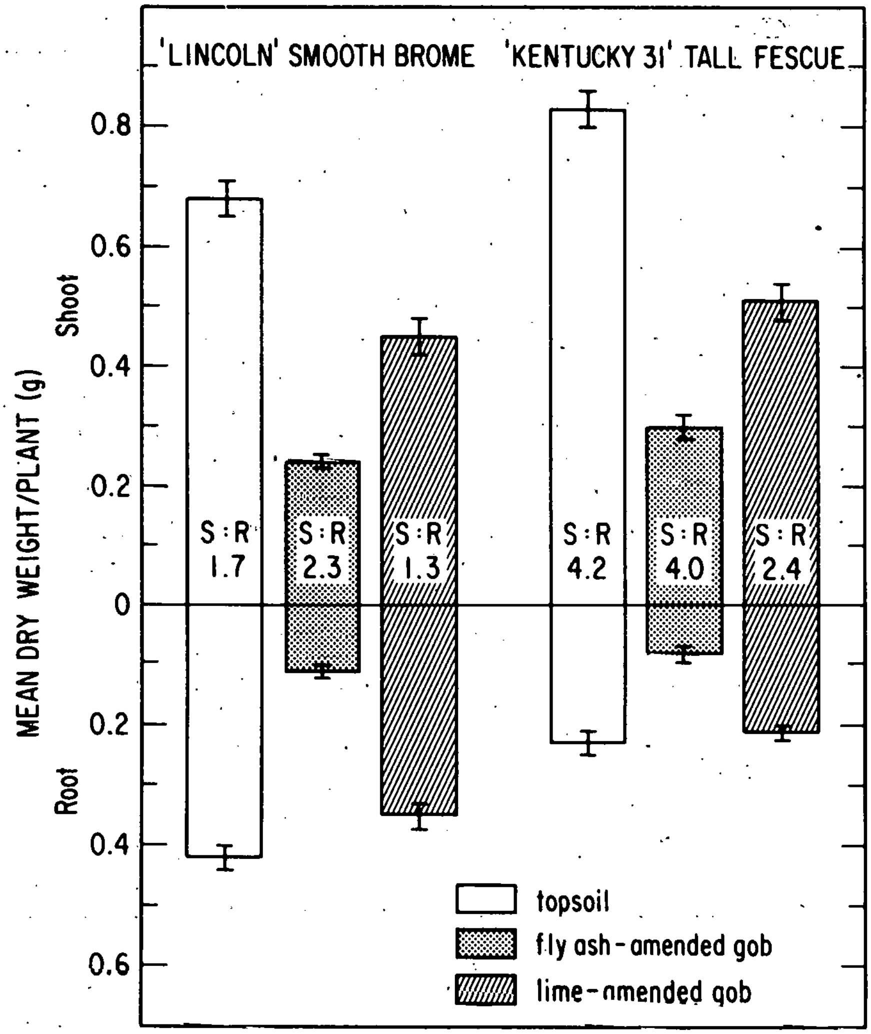

Fig. 3. Mean Biomass (g dry wt/plant) Accumulations (± standard errors) in Shoots and Roots and Mean Shoot:Root Ratios (S:R) of 'Lincoln' Smooth Brome and 'Kentucky 31' Tall Fescue after 60 days Growth on Topsoil, Fly Ash-Amended Gob, and Lime-Amended Gob (n = 36, Except n = 35 for Smooth Brome on Topsoil)

establishment of an extensive root system could potentially support a better stand over a growing season or several years.

TRACE ELEMENT UPTAKE

The mean tissue concentrations of Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, V, and Zn in the shoots of 'Lincoln' smooth brome and 'Kentucky 31' tall fescue grown on topsoil, fly ash-amended gob, and lime-amended gob are presented in Tables 4 and 5. The As, Co, and Se concentrations in some samples and the V concentrations in all tall fescue and some smooth brome samples were found to be below detectable limits (i.e., 0.3-0.5 μg As or

Se/g dry wt, 0.2-0.4 µg Co/g dry weight, and 0.2 µg V/g dry wt). In order to facilitate statistical analyses of the data, all samples with elemental concentrations below detectable limits were assigned the concentration of 0.1 µg/g dry wt.

The statistical information in Tables 4 and 5 represent separate analyses of the data for smooth brome and tall fescue; however, data for both species were also analyzed in combination. For most elements, analysis of the combined data gave the same results as the separate analyses by species, although in some cases (notably Fe), the pattern of substrate differences in plant uptake differed for the two species. Therefore, both the separate and combined analyses of the data were used and reported, as necessary, to interpret the data.

Tissue concentrations in tall fescue and smooth brome were significantly different ($p < 0.04$, from two-way analysis of variance) over all substrates for 8 of the 14 elements analyzed. For each substrate, Cd, Co, and Zn concentrations in tall fescue shoots were greater than those in smooth brome (with the exception of Zn concentrations in plants grown on topsoil). Copper, Fe, Hg, Pb, and V concentrations were generally higher in smooth brome than in tall fescue, although a substrate x species interaction effect occurred with Cu and Pb because, in fly ash-amended gob, tall fescue accumulated more Cu and Pb than did smooth brome.

No significant differences ($p > 0.11$) between growth substrates were found in the Al, As, Cr, Cu, Ni, and Se concentrations of the plant shoots. The lack of significant differences for Al, As, and Cr was not surprising, since these elements are not readily translocated and are generally accumulated to a greater extent in plant roots than in shoots (2,14, 40). For example, Pratt (30) cites several cases in which Cr concentrations in the tops of plants exhibiting Cr toxicity symptoms differed little from Cr concentrations in healthy plant tops. However, for all six elements, the absence of significant substrate effects on differences in plant tissue concentration may simply indicate little difference among the three substrates in the available concentrations of these elements.

The mean Al concentrations reported in Tables 4 and 5 (38 to 122 µg Al/g dry wt) are in the same general range as those (25 to 90 µg Al/g dry wt) reported for the tops of 'Kenblue' Kentucky bluegrass (*Poa pratensis* L.) and 'Manhattan' perennial ryegrass (*Lolium perenne* L.) grown on a sandy loam soil adjusted to numerous acidic pH levels (26). As soil pH decreased, the reduced growth of Kentucky bluegrass and perennial ryegrass compared to the growth of 'Pennlawn' red fescue (*Festuca rubra* L.), which accumulated from less than 1 to 15 µg Al/g dry wt, was related at least partially to the higher Al concentrations in the tops of the first two species (26). Thus, the Al concentrations accumulated from all substrates in this experiment may have adversely affected the growth of tall fescue and smooth brome. Mean Cu concentrations in plants from all substrates were close or equal to the "upper critical level" (20 µg Cu/g dry wt) determined by Davis et al. (11) for spring barley (*Hordeum vulgare* L.) shoots at the five-leaf stage. (The "upper critical level" is defined as the minimum concentration in actively growing plant tissues at which plant yield is reduced.) Other workers (16,32) have also suggested that leaf Cu concentrations in excess of 20 µg/g dry wt may be toxic. In contrast, the As, Cr, Ni, and Se concentrations

Table 4. Mean Trace-Element Concentrations (± standard errors) in 'Lincoln' Smooth Brome Shoots Grown on Topsoil, Fly Ash-Amended Gob, and Lime-Amended Gob

Substrate	Al	As	Cd	Co	Cr	Cu	Fe
	μg/g dry wt						
Topsoil	81 ± 28[a*]	1.6 ± 0.6[a]	1.7 ± 0.3[b]	0.1 ± 0.0[c**]	0.6 ± 0.1[a]	20 ± 1[a]	390 ± 102[ab]
Fly ash-amended gob	38 ± 7[a]	0.1 ± 0.0[a**]	1.4 ± 0.1[b]	0.9 ± 0.1[a]	0.6 ± 0.1[a]	16 ± 0.2[a]	649 ± 39[a]
Lime-amended gob	119 ± 34[a]	0.3 ± 0.1[a]	5.9 ± 0.9[a]	0.4 ± 0.1[b]	0.5 ± 0.1[a]	17 ± 1[a]	314 ± 30[b]
	Hg	**Mn**	**Ni**	**Pb**	**Se**	**V**	**Zn**
	μg/g dry wt						
Topsoil	1.5 ± 0.1[a]	169 ± 9[b]	6 ± 3[a]	60 ± 22[a]	0.4 ± 0.2[a]	0.5 ± 0.2[b]	132 ± 32[b]
Fly ash-amended gob	1.1 ± 0.03[b]	215 ± 3[b]	6 ± 1[a]	2 ± 0.1[b]	0.1 ± 0.0[a**]	1.4 ± 0.3[a]	223 ± 4[a]
Lime-amended gob	0.9 ± 0.1[b]	323 ± 25[a]	4 ± 1[a]	4 ± 1[b]	0.5 ± 0.1[a]	0.5 ± 0.1[b]	210 ± 14[a]

*For each element, means followed by the same superscript are not significantly different at the 5% level of probability based on one-way analysis of variance, and Duncan's multiple range test when analysis of variance indicated significant differences between substrates. For topsoil and lime-amended gob, n = 6; for fly ash-amended gob, n = 3.

**Concentrations in all samples were below detectable limits. A concentration of 0.1 μg/g dry wt was assigned to all samples below detectable limits to facilitate statistical analyses.

Table 5. Mean Trace-Element Concentrations (± standard errors) in 'Kentucky 31' Tall Fescue Shoots Grown on Topsoil, Fly Ash-Amended Gob, and Lime-Amended Gob

Substrate	Al	As	Cd	Co	Cr	Cu	Fe
	µg/g dry wt						
Topsoil	80 ± 13^{a*}	0.4 ± 0.2^{a}	2.7 ± 0.5^{b}	0.2 ± 0.1^{c}	0.6 ± 0.1^{a}	12 ± 2^{a}	187 ± 15^{b}
Fly ash-amended gob	76 ± 11^{a}	0.4 ± 0.2^{a}	6.6 ± 1.1^{a}	1.9 ± 0.4^{a}	0.5 ± 0.2^{a}	20 ± 4^{a}	154 ± 18^{b}
Lime-amended gob	122 ± 33^{a}	0.8 ± 0.4^{a}	9.1 ± 0.8^{a}	1.3 ± 0.1^{b}	0.4 ± 0.1^{a}	12 ± 1^{a}	296 ± 42^{a}

	Hg	Mn	Ni	Pb	Se	V	Zn
	µg/g dry wt						
Topsoil	1.2 ± 0.1^{a}	138 ± 9^{b}	7 ± 3^{a}	11 ± 1^{a}	0.2 ± 0.04^{a}	0.1 ± 0.0**	115 ± 9^{c}
Fly ash-amended gob	0.5 ± 0.2^{b}	275 ± 21^{a}	6 ± 1^{a}	5 ± 1^{b}	0.4 ± 0.1^{a}	0.1 ± 0.0**	522 ± 37^{a}
Lime-amended gob	0.7 ± 0.1^{b}	317 ± 13^{a}	9 ± 2^{a}	3 ± 1^{b}	0.3 ± 0.1^{a}	0.1 ± 0.0**	335 ± 12^{b}

*For each element, means followed by the same superscript are not significantly different at the 5% level of probability based on one-way analysis of variance, and Duncan's multiple range test when analysis of variance indicated significant differences between substrates. For topsoil and lime-amended gob, n = 6; for fly ash-amended gob, n = 3.

**Concentrations in all samples were below detectable limits. A concentration of 0.1 µg/g dry wt was assigned to all samples below detectable limits to facilitate statistical analyses.

accumulated in the shoots of both species grown on all three substrates were well below the "upper critical levels" (20 μg As/g, 10 μg Cr/g, 26 μg Ni/g, and 30 μg Se/g dry wt) for young spring barley (11).

For both species, only Hg and Pb were found to have significantly higher ($p < 0.05$) concentrations in the plants grown on topsoil as compared to those grown on lime- or fly ash-amended gob (Tables 4 and 5). The mean Hg and Pb concentrations reported here were below the "upper critical levels" (3 μg Hg/g and 35 μg Pb/g dry wt) reported for spring barley (11), with the exception of Pb in smooth brome grown on topsoil (60 μg Pb/g dry wt).

Although substrate differences in Fe tissue concentrations were significant when data for smooth brome and tall fescue were analyzed separately (Tables 4 and 5), differences between substrates were not significant ($p > 0.22$) when the data for the two species were combined. Thus, any general trend in Fe uptake from the three substrates was not obvious, due to the dissimilar patterns of substrate differences observed for smooth brome and tall fescue. The patterns may reflect actual species differences in Fe uptake from the various substrates. However, Etherington and Davies (13) have reported that plant digestion with concentrated nitric acid yields Fe recoveries of high variability, probably as a result of the formation and volatilization of iron carbonyl. The Fe concentrations reported for tall fescue (Table 5) were probably not abnormally high; Fe concentrations of 50 to 250 μg/g dry wt are generally considered to be in the sufficiency range (16). In contrast, Fe concentrations were generally higher in smooth brome (Table 4) and may have had toxic effects, at least in plants grown on fly ash-amended gob. Wallace et al. (41) reported growth reductions in the range of 60 to 80% associated with Fe concentrations of approximately 400 to 600 μg/g dry wt in the leaves of bush beans (Phaseolis vulgaris L.).

When data for both species were combined, plants grown on fly ash-amended gob had significantly higher ($p < 0.05$) tissue concentrations of Co, V, and Zn than did plants grown on the other two substrates. Cobalt and Zn concentrations were also significantly higher ($p < 0.05$) in plants grown on lime-amended gob than in plants grown on topsoil. Results from separate analyses of the Co, V, and Zn concentrations in smooth brome and tall fescue (Tables 4 and 5) were similar to the combined analyses, except V concentrations in tall fescue were below detectable limits for all substrates.

Mean Co concentrations in plants from all three substrates were no more than one-third of the "upper critical level" of Co (6 μg Co/g dry wt) in barley (11). Vanselow (39) reported that most plants contain less than 1 μg Co/g dry wt and that citrus (Citrus spp.) and sudangrass (Sorghum sudanense [Piper] Stapf) plants showing toxicity symptoms had Co concentrations in the range of 10-30 μg Co/g dry wt. In contrast, the mean V concentration in smooth brome grown on fly ash-amended gob (1.4 μg V/g dry wt) approached the "upper critical level" of V (2 μg V/g dry wt) in barley (11). Vanadium concentrations as low as 2 μg V/g dry wt in the tops of soybean (Glycine max [L.] Merr.) and pea (Pisum sativum L.) plants have been reported to reduce dry weight production (31).

Mean Zn concentrations in tall fescue plants grown on both lime- and fly ash-amended gobs (335 and 522 μg Zn/g dry wt) exceeded the "upper critical level" determined for Zn (290 μg Zn/g dry wt) in spring barley (11); mean Zn concentrations in smooth brome grown on both lime- and fly ash-amended gobs (210 and 223 μg Zn/g dry wt) approached the "upper critical level." Tissue concentrations of 200 μg Zn/g dry wt were associated with a 10% reduction in the growth of cotton (Gossypium hirsutum L.) plants (25). More conservatively, Chapman (9) indicated that tissue concentrations of 300-400 μg Zn/g dry wt may have toxic effects for some plants.

When data for tall fescue and smooth brome were analyzed together, plant tissue concentrations of Cd and Mn were significantly different ($p < 0.01$) for all substrates and followed the order: lime-amended gob > fly ash-amended gob > topsoil. Although separate analyses for each species (Table 4 and 5) showed a slightly different pattern among substrates, mean tissue concentrations of Cd and Mn were always highest in plants grown on lime-amended gob.

Mean Cd concentrations were highest in tall fescue shoots grown on lime-amended gob (9 μg Cd/g dry wt), but even these concentrations were only three-fifths of the "upper critical level" of Cd (15 μg Cd/g dry wt) in barley (11). Bingham et al. (5) compared several forage species and reported that fescue was relatively tolerant of Cd, with 37 μg Cd/g dry wt in the shoots associated with a 25% decrease in yield. Sudangrass was the most sensitive species tested; a 25% reduction in yield was associated with 9 μg Cd/g dry wt.

A wide range of toxic Mn concentrations has been reported in the literature, indicating a large variability in species tolerances of Mn. Plant growth is usually affected when tissue concentrations of Mn are in excess of 1000 μg/g dry wt, although some species may be affected by concentrations in excess of 500 μg Mn/g dry wt (16) or by even lower concentrations in the range of 200-500 μg Mn/g dry wt (17). Manganese concentrations ranging from 300 to 600 μg/g dry wt in rye (Secale cereale L.), oats (Avena sativa L.), and barley tops were not considered "markedly high" by Pinkerton and Simpson (27); however, White (42) reported toxicity symptoms for barley plants with tissue concentrations of 200 μg Mn/g dry wt. Thus the Mn concentrations reported here, particularly for plants grown on lime-amended gob (> 300 μg Mn/g dry wt), may have adversely affected the growth of smooth brome or tall fescue, depending on their tolerances of Mn.

Soil (or substrate) pH is known to affect the availability and uptake of both nutrient and unessential elements. Trace-element cations are generally more available in acidic soils due to a number of factors including their increased solubility and replacement on cation exchange sites by hydrogen (6). Trace-element anions are generally more soluble and available in neutral to alkaline soils. Since at the end of the experiment pH levels of both amended gobs were significantly lower ($p < 0.05$) than the pH of the topsoil (Table 1), correlations of substrate pH at harvest with the tissue concentrations of each trace element (both species combined) were calculated (Table 6). For the amended-gob treatments, only the pH of the amended-gob layer was used in calculating correlations. Root development was relatively

Table 6. Correlations (r) of Plant Shoot Concentrations with Substrate pH for Each Element

Element	r†
Al	-0.09
As	0.24
Cd	-0.56**
Co	-0.58***
Cr	0.51**
Cu	0.23
Fe	0.15
Hg	0.58***
Mn	-0.55**
Ni	-0.06
Pb	0.40*
Se	0.01
V	0.11
Zn	-0.61***

*Significant at the 5% level of probability.
**Significant at the 1% level of probability.
***Significant at the 0.1% level of probability.
†Tall fescue and smooth brome combined, n = 30.

good in both lime- and fly ash-amended gob and was not disproportionately high or overdeveloped in the thin topsoil layer. Therefore, it was assumed that the pH of the amended-gob layer would have the greatest effect on the plants. Of the five elements (Cd, Co, Mn, V, and Zn) having significantly higher concentrations in plants grown on amended gob compared to topsoil, all but V were negatively correlated with substrate pH ($p < 0.01$). On the other hand, without analysis of substrate concentrations it is impossible to know if the correlations in Table 6 are reflecting only pH differences, rather than actual concentration differences between substrates. For example, Pb tissue concentrations were positively correlated ($p < 0.05$) with pH even though Pb availability is usually decreased by increasing soil pH (43). Thus, Pb concentrations were probably higher in the topsoil than in the amended gobs.

Of the four elements negatively correlated with pH, the concentrations of Cd, Co, and Zn were higher in tall fescue than in smooth brome, whereas Mn concentrations in the two species were not significantly different. Substrate pH in tall fescue pots was consistently lower than in smooth brome pots (Table 1); the lower pH conditions may have resulted in increased availability of Cd, Co, and Zn cations and, thus, increased uptake by tall fescue. However, inherent species differences in the uptake mechanisms and in translocation of each element from root to shoot are additional and, perhaps, overriding factors which could have caused the observed differences in elemental concentrations. Conversely, it is also possible that tall fescue, which is more acid-tolerant than smooth brome (33), may have in some manner (e.g., exudation of organic acids) actually reduced the substrate pH in each pot.

One important factor to remember when working with gob is the very heterogeneous nature of the material. Small pockets of clay and sulfurous materials are often visible even after thorough mixing. It is likely that some trace elements may also occur in pockets, and this could explain some of the variability in the uptake data.

Although the greatest accumulation of trace elements would be expected in the plants grown on fly ash-amended gob due to additional trace elements present in fly ash, this was not always the case (e.g., Cd and Mn). Since internal standards and background corrections were used in the atomic absorption analyses, the lower accumulation of some elements by plants grown on fly ash-amended gob was most likely related to the stunted growth of these plants (Figure 3). Under such adverse conditions, both direct and indirect effects on uptake and translocation mechanisms as well as other plant functions could result in lower accumulations than under less severe conditions.

The trace-element concentrations reported for smooth brome and tall fescue (Tables 4 and 5) were generally higher than the concentrations reported for forage plants (seeding mixtures included tall fescue) grown on fly ash-amended acidic coal mine refuse at field sites in West Virginia and Pennsylvania (1). This was not surprising due to differences in plant species, plant age, substrate pH, environmental conditions, and site-to-site variations in the composition of the gob and amending materials.

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CONCLUSIONS

By amending gob with alkaline material such as lime or fly ash, and by adding fertilizer, it is possible to turn a substance previously unable to support vegetation into a growth medium that plants can tolerate. However, plant growth on either lime- or fly ash-amended gob was not as good as on the topsoil used as the experimental control. Although the results of this experiment indicate that more vigorous growth of the test species may be achieved on lime-amended gob than on fly ash-amended gob, further field studies will be needed to determine the long-term effects of each amendment. Furthermore, the variable nature of both gob and fly ash is such that certain fly ashes may be unsuitable for reclaiming some coal refuse sites.

Although this study indicates that tall fescue may be superior to smooth brome for early plant establishment, the lower shoot:root ratios of smooth brome may favor long-term plant viability and stand quality. Since there was no statistically significant difference in the total biomass production of the two species in this experiment, field studies are needed to determine the long-term superiority of either species.

Although plant species vary in their tolerance to different elements, tall fescue and smooth brome grown on amended gob did accumulate concentrations of some elements (notably Mn, V, and Zn) that approached or exceeded concentrations reported in the literature to be associated with toxic effects in some plant species. Additionally, Al, Cu, and Fe were accumulated from both the amended gobs and the topsoil in concentrations approaching toxic levels for some species. Of course, other species may accumulate higher or lower trace element concentrations than tall fescue or smooth brome, and they may be more or less tolerant of these elements.

Although the Co, Mn, V, and Zn concentrations in the shoots of both species were inversely correlated ($p < 0.05$) with shoot, root, and/or total dry weight production, cause-and-effect relations cannot be implied from correlations. Therefore, when planning the reclamation and potential land uses of coal refuse areas, the possibility of elevated concentrations of elements -- such as Cd, Co, Mn, V, and Zn -- in plants grown on amended refuse being consumed by grazing animals and incorporated into local food webs should not be overlooked. This is particularly important when it is considered that the reserve acidity of some coal refuse materials may make it impossible, in some cases, to maintain optimum pH conditions for minimizing trace-element availability without repeated application of amending materials. Further study into trace-element uptake and accumulation by plants grown on amended refuse is certainly warranted.

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The Land Reclamation Program is addressing the need for coordinated applied and basic research into the physical and ecological problems of land reclamation, and is advancing the development of cost-effective techniques for reclaiming land mined for coal. This program is conducting integrated research and development projects focused on near- and long-term reclamation problems in all major U.S. coal resource regions, and is evaluating and disseminating the results of related studies conducted at other research insitutions. These activities involve close cooperation with the mining industry. Regional and site-specific reclamation problems are being addressed at research demonstration sites throughout the country, and through laboratory and greenhouse experiments.

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