

AN ABSTRACT OF THE THESIS OF

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ON DAYTON SILTY CLAY LOAM SOIL
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Waste products from industry have often been disposed in landfills without regard for any beneficial uses of the product in agricultural production. This research was conducted to determine the effect of a refractory metal processing waste product on (a) soil chemical and physical properties, (b) perennial ryegrass forage quality and seed yield, and (c) percolation water quality.

Refractory metals processing waste was applied either as a slurry or dried to Dayton silty clay loam (sic) at rates of 0, 5, 10, 25, and 50 tons/acre. Ammonium nitrate, concentrated super-phosphate, muriate of potash, calcium sulfate, and lime were added to optimize plant growth. Lime, gypsum, and phosphorus fertilizer variables were incorporated into the study to investigate specific beneficial or problems areas associated with the waste product. The waste and fertilizers were tilled into the soil, and all plots seeded

with perennial ryegrass (var. Linn) and irrigated.

Elements found in the waste in excess of one percent included: Zr, Ca, F, Fe, Al, S, and C (as CO_3). Those elements found in concentrations ranging between 0.1 and 1.0 percent included: Hf, Mg, Na, Pb, P, NH_4 -N, and K. The concentration of Cd, Ci, Co, Cr, Ni, Mn, and Mo were less than 1000 ppm.

Soil pH, soluble salts, extractable Ca, Mg, NH_4 -N, Zn, Ni, S, and F and the total Zr, Hf, and Pb content of the soil increased with waste application, while extractable Fe, Mn, and P levels decreased with waste application. Extractable Na, K, NO_3 -N, Al, and Cu levels were not affected by waste application.

The soluble salt content decreased from greater than 4.0 mmhos/cm in the fall to less than 1.7 mmhos/cm in the spring. The extractable Mg, Na, K, NH_4 , NO_3 , P, S, and Zn also decreased in the spring as compared to the fall levels. Acid extractable P levels were less than the minimum required for optimum crop production, 30 ppm. Iron, Mn, and Ni availability increased with time, due to the wet, reduced soil conditions present between sampling periods.

Water percolation through the Dayton silt soil increased with waste application, but soil moisture retention was not changed.

Perennial ryegrass dry matter yields were not significantly changed by waste product additions, and were similar to yields obtained in commercial farm operations. Mean yields ranged from

2.6 to 3.3 tons/acre on the soils treated with dry waste, and 2.8 to 4.0 tons/acre on soils treated with the waste slurry. Clean seed yields were slightly less than normal, ranging from 754 to 1238 lbs/acre. The subnormal seed yields were probably due to seed loss during harvesting and cleaning. The waste additions did not affect seed viability.

The Ca, Mg, K, P, Fe, Al, Mn, Cr, Zn, Cu, Ni, Co, Mo, F, Zr, Hf, and Pb contents of the perennial ryegrass were not significantly affected by waste application. The S, Na, and N uptake by the ryegrass increased at application rates of 50 ton/acre, compared to control plots, which indicated that the waste product may serve as a N and S fertilizer.

Plant P levels were not significantly depressed by waste application, despite decreases in acid available P levels. Addition of 100 lbs P/acre did not significantly improve P uptake compared to soil treated with 25 lbs P/acre and similar amounts of waste.

Ryegrass grown on soil that received no lime or waste showed significant reductions in uptake of Ca and Mo, compared to control plots. The addition of waste, 25 ton/acre, eliminated these reductions.

The application of the waste product to the soil may pose a threat of fluoride pollution to groundwaters which would require special management practices. No other elemental hazards to groundwater were suggested.

Utilization of refractory metals processing waste on Dayton
sicl appears to be a viable waste disposal alternative, providing that
further study establishes that F does not pose a threat to groundwaters
under field conditions.

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REFRACTORY METALS PROCESSING WASTE UTILIZATION ON DAYTON SILTY CLAY LOAM SOIL

INTRODUCTION

Increased public awareness concerning the nature of the closed ecosystem in which we live has forced society to consider the effects of their wastes on that ecosystem. Heavy industry has been strongly criticized for its effects on air and water quality. Waste products from the production of metals are one source of pollution. In this study, waste from a refractory metals processing plant was examined to determine if it had value as a soil amendment and whether soils could serve as a disposal sink.¹ The waste product results from the refinement of ores into high grade zirconium, hafnium, niobium, and tantalum metals. For many years the slurry-like waste product was lagooned in large settling ponds, and as the solid portion of the waste settled, the effluent flowed into the Willamette River. More recently, the solid fraction of the waste product has been trucked to sanitary landfill sites and buried. Neither practice has been totally satisfactory and another alternative has been sought. Disposal of the refractory metals processing waste on soils of the mid-Willamette Valley was proposed. The waste would be transported to the disposal site,

¹Waste provided by Teledyne Wah Chang Albany Corporation, Albany, Oregon.

applied as a wet slurry, and then the land would be farmed and managed in accordance with good agronomic practice.

Soils of particular interest were those of the Concord-Amity-Dayton Association. These soils form a broad, level terrace on the Willamette Valley floor. The association lies between the poorly drained to excessively well drained river bottom lands and the higher, more well-drained soils of the Woodburn-Willamette association. The Dayton, Concord, and Amity soils are subject to perched water tables, which may surface, for two to six months during the winter, dependent on rainfall duration and amount. These soils are used almost exclusively for the production of ryegrass seed crops.

The Amity soil is a very deep mollisol with a very dark greyish-brown surface horizon. Deep tile drains can be used to improve drainage. The Dayton soil is an alfisol, with a light greyish-brown surface horizon, giving the soil a white coloration when undisturbed. The texture of the surface horizon varies from a silty clay loam to silt loam to a fine silt. An argillic horizon forms a clay pan at a depth of 12 to 18 inches, contributing significantly to the poor drainage characteristics and lack of response to tile drains associated with this soil. Drainage is generally accomplished by surface ditches and bedding. Horizons beneath the clay pan are clay or silty clay loam in texture, massive in structure when wet, prismatic when dry, and distinctly mottled. This soil is considered infertile, with medium to

high surface horizon acidity. Permeability is very slow, and most root growth is limited to the horizons above the clay pan. Available moisture capacity is adequate in the surface horizons (3 to 4.5 inches), but in the late summer the soil is droughty due to the restrictions imposed by the clay pan on root penetration.

The objective of this research project was to determine the effects of waste product additions on the chemical and physical properties of the soil-plant-water system associated with the Dayton soil series. Field and laboratory programs were designed to determine the effect of the waste product on: grass seed yield and viability, plant elemental constituents, ground-water pollution, and changes in soil chemical and physical properties.

LITERATURE REVIEW

The purpose of any waste disposal/recycling system using agricultural soils is to improve conditions for general agricultural production, while minimizing the hazards presented by portions of waste material that may enter the food chain. The waste product must therefore be assayed for chemical and physical properties to determine the possible effects of the material on plants, soil, and groundwater. In this review, the chemical components will be divided as follows:

- 1) Soluble cations which dominate the cation exchange complex of most soils (Ca, K, Mg, NH_4 , Na),
- 2) Cations that are slightly soluble, precipitated or highly complexed in most soils (Al, Fe, Mn, Cu, Zn, Pb, Ni, Zr, Hf, Co, Cr), and
- 3) Constituents present as anions (NO_3 , P, S, F, Mo).

In addition, the effect of pH and oxidation-reduction potential on the behavior of these elements must be considered. Through study of the soil-waste interaction, waste application rates can be established suitable to one's goal.

Exchangeable Bases

The alkali metal and alkaline earth cations (Ca, Mg, Na, K) plus

H, Al, and NH_4 are the principal ions sorbed on the cation exchange sites (Brady, 1974). The distribution of an element between the exchange complex and other chelated or insoluble forms is controlled principally by solubility and the presence of other ionic elements (Lindsay, 1973). Calcium, Mg, Na, and K compounds found in the soil are relatively soluble, thus the predominance of these elements on the exchange sites.

Elemental solubility is related to ionic potential (ionic charge/ionic radius, Table 1), or relative electronegativity (Mason, 1966). The smaller the ionic radius and the larger the charge, the more acidic is the oxide, while the larger the radius and the smaller the charge, as with the exchangeable bases, the more basic is the oxide. Exchangeable bases will hydrate but generally not hydrolyze in solution. The formation of large amounts of hydroxy-precipitates and oxyanions is eliminated. Since the ionic character of the NH_4 ion is similar to that of K, it is included with the exchangeable cations. Exchangeable bases occur in only one oxidation state in the soil solution, and thus are not directly affected by changes in the oxidation-reduction potential of the soil solution.

The basic cations are thus (1) free within the soil solution, (2) absorbed on colloidal materials, (3) fixed within clay crystal lattices, or (4) precipitated as secondary minerals (Tisdale and Nelson, 1966). Four factors govern the distribution of these elements:

- 1) Type of soil colloid
- 2) Soil pH
- 3) Nature of complementary ions on the exchange complex
- 4) Other factors specific for any given cation.

Table 1. Ionic charge, radius and potential for some selected elements (from Mason, 1966).

Element	Charge	Radius (Å)	Potential
K	+1	1.33	0.75
Na	+1	0.97	1.00
Li	+1	0.68	1.5
Sr	+2	1.12	1.8
Ca	+2	0.99	2.0
Mn	+2	0.80	2.5
Fe	+2	0.74	2.7
Co	+2	0.72	2.8
Mg	+2	0.66	3.0
Fe	+3	0.64	4.7
Al	+3	0.51	5.9
Mn	+4	0.60	6.7
Zr	+4	0.79	5.1
Hf	+4	0.78	5.1
P	+5	0.35	14
S	+6	0.30	20
N	+5	0.13	38

Potassium

The soil contains large quantities of K, but 90 to 98 percent of it is unavailable for plants, being lodged in the crystal lattices of primary and secondary minerals. From 1 to 10 percent of the soil K

is slowly available by release from interlayer positions in 2:1 expanding lattice clays. Readily available K makes up only 1 or 2 percent of the total amount, and consists of exchangeable K on the soil colloid and K ions in the soil solution (Brady, 1974). Alternate wetting and drying cycles may release K into readily available forms (Scott, et al., 1960), but contradictory information also exists. Drying field-moist soil samples increased the amount of available K, although the importance of this mechanism in the field has not been determined. The fraction of the exchangeable K lost by leaching has been shown to be inversely proportional to the percent base saturation; thus, a low soil pH promotes K release into the soil solution (Tisdale and Nelson, 1966).

Plant uptake of K is related to the amount of exchangeable K. In the presence of excess available K, plants may take up more K than is required to meet their metabolic needs. With the possible exception of N and Ca, no element is absorbed in larger amounts from the soil than K (Tisdale and Nelson, 1966).

Calcium and Magnesium

Calcium and magnesium are quite similar in their behavior in the soil environment. They weather from feldspathic and mafic rocks, along with secondary minerals. Both ions can be taken up by soil organisms, adsorbed on clay particles, removed from the soil profile

through leaching, or reprecipitated as secondary minerals. The availability of these elements for plant uptake is determined by the exchangeable Ca or Mg present, type of soil colloid, and the nature of the sorbed complementary ions. The amount of Ca used by a plant depends more on the degree of Ca saturation on the exchange complex than on the absolute amount of calcium available. As the calcium saturation decreases, plant uptake decreases. For adequate Ca for growth of some plants, about 70 percent of the exchange capacity of 2:1 clays must be Ca, whereas only 40-50 percent of the exchange capacity of a 1:1 clay need be calcium.

Magnesium deficiencies occur most often in humid climates where soils are coarse-textured and have a low CEC. Such soils have limited Mg-supplying power, and a considerable portion of the Mg present may be lost by leaching. The use of large amounts of potash or lime fertilizers and amendments can also lead to a reduction in Mg availability. King and Morris (1973) showed a reduction in Mg uptake by coastal bermudagrass following application of sewage sludge to Cecil sandy clay loam. The waste had a Ca/Mg ratio of 16:1; despite the availability of Mg, Ca ions were assimilated more readily by the plant.

Sodium

Sodium has not been proven essential for plant growth, although plant uptake can be considerable. Russell (1961) indicated that Na uptake ranged between 0.05 and 0.3 percent for such crops as wheat, red clover, turnips, beans, and potatoes.

Sodium strongly affects soil physical properties. The combination of low salt concentrations and high exchangeable sodium percentage (ESP) is likely to disperse soil colloids and organic matter (McNeal, 1974), resulting in poor soil hydraulic conductivity and/or crust formation. When ESP values exceed 10 percent of the cation exchange capacity of fine textured soils and 20 percent in coarser soils, soil structure is adversely affected. In general, ESP values in excess of 20 can cause reduced plant growth due to both nutritional factors and adverse changes in soil physical conditions. If ESP values exceed 40, crop yield reductions are usually due to adverse soil physical conditions, since soil structure becomes more limiting to plant growth than the Na-induced Ca or Mg deficiencies associated with such soil Na levels (Bernstein, 1974). Pearson, et al. (1958) observed that crop uptake of Na was related to ESP rather than exchangeable sodium content of California loam and clay soils. At ESP = 3, the Na content of fescue was 5 to 15 meq Na/100 g plant material, while at ESP = 36 to 38, the Na content was 107 to 118 meq Na/100 g.

Increases in ESP also resulted in decreases in plant K, Ca, and Mg content, despite adequate available amounts of these elements.

Ammonium-N

The behavior of ammonium in the soil is similar to potassium, with two exceptions. Ammonium fixation by 2:1 expanding lattice clays is relatively insignificant in relation to crop growth or NH_4 availability, and NH_4 -N may be converted to NO_3 -N through biological oxidation (nitrification) (Tisdale and Nelson, 1966). Both NH_4 and NO_3 ions may be used by plants, although in well-aerated soils the NO_3 form dominates. Application of large amounts of NH_4 -N in liquid sewage sludge (containing 500 to 2,000 ppm NH_4 -N) have proven toxic to corn seedlings (Hinesly, et al., 1971). Ammonium toxicities could be eliminated by induced ammonia loss through aeration or aging the sludge material.

Summary

The exchangeable bases constitute the majority of the soils soluble and exchangeable cation suite. All but sodium are essential for plant growth. Plant uptake is dependent principally on the absolute amount available and/or the nature and amount of the complementary ions on the cation exchange sites. Excessive Na may cause both nutritional deficiencies and poor soil physical conditions.

Heavy Metals

The heavy metals (Cu, Zn, Ni, Mn, Fe, Cr, Al, Co, Zr, Hf, and Pb) can be characterized as having: (1) the potential for one or more oxidation states in the soil, (2) the ability to form large hydroxy-complexes (which may polymerize) in water, and (3) the ability to form complexes with anions, particularly organic species (Leeper, 1972).

Redox Potentials

While oxidation-reduction potential/pH relationships have a bearing on many elements in the soil, the most striking and critical examples are Mn and Fe. Theoretical and empirical models have been developed to illustrate the predominant forms of these metals within the bounds of the soil solution (Mason, 1966; Garrels and Christ, 1965; Krauskopf, 1967). While simplified models with strict chemical limitations do not relate well to the myriad of possible chemical reactions that may occur in the soil solution, they can be used as a framework to predict the fate of these elements in the soil. For Fe, the change from generally insoluble ferric to generally soluble ferrous Fe occurs under conditions frequently encountered in the soil. Acidic, reducing conditions favor the formation of the soluble ferrous ion, while oxidizing, basic conditions favor the formation of ferric ions and

relatively insoluble iron oxides. Free Fe is oxidized readily by water to the +2 or +3 valence state. The addition of carbonate, sulfide, or phosphate anions may induce precipitation of ferrous Fe as pyrite or siderite (Krauskopf, 1967).

Manganese is less easily oxidized into insoluble forms such as MnO_2 . In general, the soil environment favors the formation of the manganous ion, although high carbonate concentrations can markedly reduce the conditions under which Mn^{+2} ions predominate. Strong oxidizing agents such as the permanganate (MnO_4^-) cannot exist in the soil solution since they would be reduced by water with the evolution of O_2 .

Hydroxy-Complex and Organic Anion Complexes

Four-fifths of all metals are able to form polymerized sols through hydrolyzation in solution (Leeper, 1972). These sols are not available for plant uptake, even though the sol has a positive charge. These sols may be strongly adsorbed on soil colloids or form complexes with soluble anions (Pokras, 1956).

Many heavy metals complex with organic anions. As much as 99 percent of the copper and 60 percent of the zinc in the soil solution was associated with soluble organic ligands in four loam soils in New York with a pH range from 4.08 to 8.13 (J.F. Hodgson, et al., 1965). Copper and zinc complexes with soluble ligands in calcareous soils of

Colorado increased the total soluble Cu concentration 100-fold, while only a 4-fold increase was seen with Zn. Zinc levels in soil solution were less than 2 ppb, while copper levels ranged between 5 and 16 ppb, explaining the relatively widespread occurrence of Zn deficiencies in western calcareous soils (Hodgson, et al., 1966). Numerous studies on the stability constants of metal-organic matter complexes have been conducted (Table 2). The copper complex with a fulvic acid solution is much stronger than the other metals at both pH 3.5 and 5.0. The strength of copper bonding to adsorptive surfaces has been related to formation of strong covalent bonds (Northmore, cited in Krauskopf, 1972). The amount of extractable copper is dependent on the extractant used, but generally values are less than 5 ppm and often less than 1.0 ppm (Reuther and Labanauskas, 1966).

Table 2. Stability constants for metal-fulvic acid complexes.*

Log K, pH 3.5

Cu	>	Fe	>	Ni	>	Pb	>	Co	>	Ca	>	Zn	>	Mn	>	Mg
5.78		5.06		3.47		3.09		2.20		2.04		1.73		1.47		1.23

Log K, pH 5.0

Cu	>	Pb	>	Fe	>	Ni	>	Mn	>	Co	>	Ca	>	Mn	>	Mg
8.69		6.13		5.77		4.14		3.78		3.69		2.92		2.34		2.09

*Data from Schnitzer and Skinner, as cited in Stevenson and Ardakani (1972).

Organic ligands may contain both aliphatic and amino acids (Geering, 1969). Using dialyzed extracts from the A horizon of a Williamson sil soil, the average metal to ligand ratio was found "equal to unity in complexes of both the dialyzable and non-dialyzable fractions with Zn and Cu." While such anionic complexes are important in solution, the vast majority of the metals added to the soil are fixed in relatively insoluble compounds on the organic and inorganic colloidal structure.

Hodgson (1963) reported that there are at least five ways in which metals can be bound in the soil. These include bonding to organic or inorganic surfaces, occlusion within the development of some new solid phase, precipitation, isomorphic substitution within the crystal lattice, or incorporation into biological systems and their residues. Each metal participates in these reactions to some extent. Factors influencing the relative magnitude of these reactions include the form of the metal added to the soil and soil conditions, such as pH, organic matter content, clay mineralogy, aeration, and the nature of the living biomass.

Aluminum

Aluminum is not an essential element for plant growth, but it can be toxic. Availability of Al is controlled chiefly by soil pH. In soils with a pH above 5.5, essentially no exchangeable Al is normally found. In some

Ohio soils with a pH between 4 and 5, the exchangeable Al content ranged between 1.4 and 8.0 meq/100 g. In North Carolina, exchangeable Al content of the surface horizon of some acid soils (pH 5.3 - 6.3) was between 0.13 and 1.83 meq/100 g, while strongly acid subsoils (pH 4.6 - 4.9) had 5.5 to 17.9 meq/100 g exchangeable Al (Pratt, 1966). Kurtz and Melsted (1973) reviewed chemical movement in soils, and concluded that significant ionic Al can be found only in soils with pH values less than 5.5, while at pH values greater than 6.0, Al forms insoluble polymers and complexes.

Aluminum sensitive barley varieties grown on strongly acid (pH 5.2) Norfolk soil (Long and Foy, 1970) showed severe toxicity symptoms, which were alleviated with a soil pH increase to 5.9. At the low pH, Al was believed to induce a Ca deficiency in the Al-sensitive barley varieties. Foy and Brown (1963) found Al toxicities closely related to reduced uptake of Ca and P by cotton plants grown in nutrient solutions containing 2 to 10 ppm Al. Reduced P uptake resulted from the formation of insoluble aluminum phosphates in the growth medium, on the root surface, or within the root itself. Hunter and Vergnano (1953) observed significant oat yield reductions when the Al concentration in a sand culture exceeded 25 ppm. Likewise, alfalfa yields decreased as Al concentrations were raised from 0 to 20 ppm (Ouellette and Dessureaux, 1958). Alfalfa, grown in a 20 ppm Al solution, was severely damaged and contained from

229-437 ppm Al. Phosphorus uptake was decreased by increased Al concentrations in the nutrient solutions.

Iron and Manganese

Iron and manganese solubility in the soil are strongly affected by soil pH. The manganous ion is the principal soluble manganese species, and decreases 100-fold for each unit increase in pH (Lindsay, 1972). With soil pH greater than 6.5, Mn deficiencies in the soil are often possible (Labanauskas, 1966). The pH effect may be related to soil moisture, since waterlogging and the simultaneous presence of anaerobic bacteria increase the soluble Mn (Leeper, 1972). Soil sterilization has a similar effect, since oxidizing bacteria in the soil are eliminated (Skipper and Westerman, 1973). Such sterilization can occur simply through soil drying (Leeper, 1972). The addition of Mn to the soil is not likely to cause toxicity symptoms in plants unless conditions favoring high solubility of the native soil Mn supply already exist. Under aerobic soil conditions, the vast majority of the added Mn will be oxidized to relatively insoluble MnO_2 .

The ferrous ion is the principal soluble Fe species in poorly drained soils, while in aerated soils, most of the Fe in solution is chelated with organic ions (Leeper, 1972). Addition of soluble Fe compounds to normal aerated soil will result in the transformation of the Fe into an insoluble hydrated oxide (Leeper, 1972). Iron toxicities

are rare, but Fe deficiencies are common, particularly on poorly drained calcareous soils where high HCO_3 concentrations increase P solubility (Tisdale and Nelson, 1966). The phosphates, in turn, precipitate Fe within the root or at the root surface. Plant analyses values of less than 20 ppm Fe are definite indicators of iron deficiency (Wallihan, 1966).

Chromium

Cationic Cr will have little or no effect on plant growth when added to the soil unless it is added at very high application rates (Webber, 1972). Anionic chromates and dichromates can be toxic in nutrient solutions, but in the soil these hexavalent Cr forms would be reduced to trivalent cations. Trivalent Cr forms insoluble oxides or hydroxides under normal aerated soil conditions. Some studies (Soane and Saunder, 1959) on serpentine soils have shown very high plant uptake levels of Cr (250 ppm or more in oats and tobacco in Rhodesia). It has not been established with certainty however, that these toxicity problems were not due to Ni toxicity rather than Cr. Chromium is not believed to be essential for plant growth, although Cr levels in most plants range from 0.2 to 1.0 ppm (Allaway, 1968). Hinesley, et al. (1972) applied 1,150 lbs total Cr/acre over a four year period to acid, poorly drained Illinois cornfields with no significant increase in plant uptake of Cr. In England, sewage sludge applied

for 20 years (1942-1961) resulted in a significant increase in extractable Cr (LeRiche, 1968). About 568 tons of liquid sludge/acre, containing 2.5 to 4.5 ppm Cr, was added to the soil. Soil Cr levels ranged from 0.2 to 0.7 ppm in untreated plots and 2.0 to 3.5 ppm in treated plots in 1959. Six years after waste application ceased, soil Cr levels had not changed. No changes in crop yields were seen.

Copper, Nickel, and Zinc

Copper, Ni, and Zn are not present in the soil in large amounts (total Cu ranges from 2 to 100 ppm; Ni, 10 to 1000 ppm; and Zn, 10 to 300 ppm, Allaway, 1968). The addition of small amounts of these metals to acid soils can be toxic to sensitive plants.

The behavior of Zn in soil is similar to that of Mg. Isomorphous substitution of Zn for Mg occurs in clay crystal lattices. Since plants do not discriminate between Zn and Mg, Zn uptake may be as high as several hundred ppm (Leeper, 1972). Zinc toxicity levels in plants are found when Zn levels are greater than 125 to 200 ppm (Webber, 1972; Allaway, 1968). Zinc deficiencies in calcareous soils have been associated with low Zn solubility in alkaline soil solutions (Hodgson, et al., 1966). Since the solubility of Zn is pH dependent, the maintenance of soil pH values greater than 6.5 should remove the danger of Zn toxicity. Zinc deficiencies were positively correlated to extractable zinc levels of 0.5 to 0.9 ppm, while on soils with no zinc

deficiency, 1.2 to 4.7 ppm extractable Zn was found. Burleson and Page (1967) have shown that phosphorus-induced zinc deficiencies are due to the formation of zinc phosphate in the roots of flax (L. usitis-simum). Corn uptake of zinc was not increased by the application of 1,850 lb. Zn/acre as sewage sludge, even though soil extractable Zn levels significantly increased (Hinesly, 1972). Webber (1972), studying the uptake of metals from sewage sludge-amended soils by red beets and celery, concluded that over a 30 to 50 year period, no more than 250 ppm Zn or Zn-equivalents² should be added to the soil.

Zinc moves slowly through a soil profile. Zinc levels in sewage sludge treated soils in England decreased from 360 and 430 ppm to 210 and 340 ppm, respectively, six years after sludge treatment was stopped. Untreated plots contained less than 45 ppm Zn (LeRiche, 1968).

Copper is an essential plant nutrient and often exists in a chelated form. The normal Cu content in plants ranges between 5 and 15 ppm. A plant containing less than 2 ppm Cu would probably be Cu deficient, while Cu toxicities can occur at levels greater than 20 ppm (Allaway, 1968). Over a 4-year period, Hinesly, et al. (1972) applied 480 lb Cu/acre in anaerobically digested sewage sludge, to successive corn crops. No significant increase in plant Cu levels was seen.

²Zn-equivalent = [Zn] + 2[Cu] + 8[Ni].

Excessive Cu uptake by plants is controlled mainly through proper pH management, although the application of lime does not retard Cu uptake from copper sulfate (Mitchell, 1963).

Nickel in the soil reacts similar to Zn, but it can also form strong bonds with colloidal surfaces, giving it some similarities with Cu (Leeper, 1972). Halsted, et al. (1969) added nickel chloride salts to four different soils and showed increased Ni uptake in oats and alfalfa with decreased pH and reduced organic matter content. No alfalfa or oat growth occurred when soil of pH 5.8 and <4.1 percent organic matter was treated with 500 ppm Ni. In some cases, as little as 100 ppm Ni would halt plant growth, although lime can be used to reduce Ni toxicity. The addition of P as concentrated super phosphate at rates of 500 ppm P increased the soluble soil Ni and the uptake of Ni in plant tissue, but had no effect on yield. Nickel had a repressive effect on oat growth when the plant Ni concentration was over 600 ppm in the grain and 28 ppm in the straw. Alfalfa was more susceptible to Ni, possibly due to the low Fe/Ni ratio in the plants. Normal Ni levels in plant tissue are about 1.0 ppm, while plant toxicities are generally correlated with Ni levels in excess of 50 ppm (Allaway, 1968).

The application of Ni to the soil in forms other than soluble salts has been studied through the application of sewage sludges to the soil. In England, Ni, applied in sewage sludge over a 20-year period (56.8 lbs Ni/acre), increased soluble soil Ni from 2-6 ppm to 7-18 ppm

(LeRiche, 1968). A two-year application of liquid sewage sludge containing 26 ppm Ni, 0.4 kg/ha/yr, to Georgia soils did not increase the Ni content of coastal bermudagrass (King and Morris, 1972). Application of 116 lb Ni/acre as sewage sludge over a four-year period had no effect on Ni uptake by corn (Hinesly, et al., 1972).

Zirconium and Hafnium

Minimal work has been done on the effect of Zr and Hf on plant growth. Most research was spawned in the 1950's by the concern over waste disposal from nuclear reactors. No evidence of Zr or Hf toxicities at levels normally found in the soil have been detected (Pratt, 1966). Neither element can be extracted from the soil by such inorganic acids as dilute HCl or H_2SO_4 . Zirconium is soluble in citric, oxalic, lactic and tartaric acids excreted by soil microorganisms (Vlamiš and Pearson, 1950). Carrots grown on Yolo silt loam containing radioactive Zr showed that relative large amounts of Zr could be absorbed by the fibrous roots, a moderate amount in the tap root; however, only minimal Zr was translocated to the plant tops. Jacobson and Overstreet (1948) studied radioactive Zr uptake by three week old barley plants grown in montmorillonite clay suspensions dosed with Zr. After a 24-hour treatment, the vast majority of the Zr (98.5%) remained in the suspension, while only 0.003 percent was found in the leaves and stems, the remainder was in the roots. Peas,

grown for three months on sandy soils containing 0.180 $\mu\text{c Zr} + \text{Cb/gm}$ soil, showed poor root growth characterized by substantial Zr uptake. Zirconium translocation to the plant top was minimal. Zirconium found in wheat (T. persicum) grown in nutrient solutions also remained in the roots, with minimal translocation to the plant tops. Translocation tends to increase as the plant reaches maturity (Gulyakin and Yudinseva, 1956).

Lead

The Pb in the soil ranges from 6 to 14 ppm, although levels as high as 200 ppm have been reported (Allaway, 1968). Plant levels are generally between 0.1 and 1.0 ppm. MacLean, et al. (1969) studied the uptake of Pb added to the soil as lead chloride. Couchgrass, brome grass, timothy, alfalfa, and asparagus were grown in four soils treated with Pb, 0 to 1000 ppm, lime, and P. Soils high in organic matter (12%) reduced the soluble Pb considerably as opposed to mineral soils. Lime or P additions also reduced lead extractability. Lead uptake by radishes grown on acid soils contaminated with aerally deposited lead did not increase very much in comparison to the large increases in 1 N HCl extractable soil Pb (Lagerwerff, 1971). The soil Pb content ranged from 29.9 ppm to 299 ppm. In radish roots, the Pb levels ranged from 19.4 to 32.7 ppm, with from 13.3 to 25.1 ppm observed in the leaf tissue. Increasing the soil pH

decreased both yield and Pb content of the radishes. Lead uptake by crops grown on old orchard soils contaminated with lead arsenate sprays increased 2 to 8 times in roots and 1 to 3 times in plant tops, using a wide variety of crops (Jones and Hatch, 1945). The lead content (as total PbO) in untreated soils ranged between 3.2 and 21.3 ppm, while treated soils contained from 127 to 405 ppm.

Cobalt

Cobalt and Ni react similarly in soils although the amount of Co in the average soil is considerably less than Ni (Leeper, 1972). Total soil Co content ranges between 1.0 and 40 ppm (Allaway, 1968). Mitchell (1972) stated that the Co content of the soil correlated with the geology of the parent material, and that the normal plant:soil Co ratio was about 1:200, using 2.5 percent acetic acid as the soil extractant. Plant Co deficiencies are rare, but deficiencies in ruminants grazing on soils low in Co, such as soils developed from acid igneous, arenaceous or calcareous rocks and peat, are common. Sand culture studies using oats as a monitor crop have shown that 15 ppm Co in the solution will reduce yields approximately 50 percent and provoke considerable interveinal chlorosis (Hunter and Vergnano, 1953). Cobalt levels in the control crop were 0.78 ppm, while plants grown in the sand contained an average of 640 ppm Co. More recent studies (Anderson, et al., 1973) on Co uptake by oats from soils developed

from ultrabasic serpentine rocks indicate no Co toxicity until uptake exceeded 50 ppm. Total Co levels in these soils ranged from less than 20 to 778 ppm, while plant uptake ranged from 2.6 to 21.6 ppm. In this case, toxicity symptoms were ascribed to excessive Ni uptake. In general, cobalt uptake by grasses is less than 0.10 ppm (Kubota and Allaway, 1972).

Anions

Nitrate

The production of nitrate in the soil is a biological process involving the conversion of ammonium ions to nitrates by autotrophic nitrobacteria. Nitrification is affected by: soil aeration, supply of ammonium ions, soil reaction, soil moisture, population of nitrifying bacteria, and temperature (Tisdale and Nelson, 1966). Maximum nitrification occurs at about 20 percent oxygen in the soil atmosphere. The nitrobacteria are more sensitive to excessive moisture than to dry soil conditions. Since poor soil aeration is often due to excess moisture, the production of nitrate ions is repressed two ways by excess moisture. Excessively acidic or alkaline soil conditions inhibit nitrification, perhaps by limiting nutrient availability to the bacterial population. Nitrification occurs between the pH values of 5.5 and 10, with optimum value about 8.5. A soil temperature of less than 5°C

reduced nitrification rates 75 percent compared to 27°C in one study (Chandra, from Tisdale and Nelson, 1966). Poorly drained soils warm more slowly because of water evaporation energy requirements. Finally, the size of the nitrobacterial population will affect the time required to completely nitrify an added source of ammonium ions, rather than the total amount of nitrification.

While nitrification is generally a beneficial process, providing plants with a readily available source of nitrogen, it can also pose a pollution problem to groundwaters. The nitrate ion is not sorbed on most soils and moves freely with the soil water.

Nitrate levels in groundwaters in excess of 10 ppm (a limit used by the Public Health Service) may pose a public health hazard, particularly to infants. Drinking water containing excessive nitrate has the same effect on the human body as carbon monoxide--interference with the ability of blood hemoglobin to absorb oxygen. This problem leads to oxygen starvation of body tissues and can be fatal.

Phosphorus

Most soil P is insoluble and is retained in soils by Ca, Fe, and Al (Russell, 1961). Calcium ions in solution, exchangeable Ca, or Ca anchored on calcium carbonate crystals may precipitate with phosphorus. Calcium phosphates are less stable in acid soils. Iron and aluminum which react with phosphate may be present as hydrated

oxides, as exchangeable cations in acid soils, or as hydroxides.

Factors influencing phosphate retention include reaction time, pH, clay kind and amount, particle size, temperature, exchangeable cation suite, soluble salt content, and organic matter content (Pierre and Norman, 1953; Tisdale and Nelson, 1966). Phosphorus fixation increases with time and temperature. Clays with low silica:sesquioxide ratios, particularly kaolinites, adsorb more P per unit weight, due to the relatively large amount of hydroxy-aluminum bonding sites exposed to the soil solution. Increasing the amount of clay (and hence the amount of adsorptive area) also increases P fixation. Phosphorus availability is maximized at pH values between 5.5 and 7.0, since acid conditions promote fixation on Fe and Al compounds, and basic conditions increase fixation on Ca compounds. In acid soils, calcium clays fix more phosphate than NH_4^+ , Na^+ , or K^+ -clays, possibly due to precipitation of calcium phosphates or linkage of phosphate to the soil colloid through Ca (Pierre and Norman, 1953). Increased soluble electrolyte and decreased organic matter content of the soil decreases P solubility, perhaps because of the relatively high solubility of P in carbonic acid and other organic acids, and the coating of inorganic colloidal surfaces with organic materials, reducing their adsorptive capacity. Organic matter also contributes soluble P to the soil solution upon decomposition.

Plants generally take up P as the H_2PO_4^- or $\text{HPO}_4^{=}$ ion. Phosphorus uptake has been found to be fairly constant, with crop removal usually between 4 and 22 pounds P per acre per crop (Pierre and Norman, 1953). Because an equilibrium exists between the phosphorus in the liquid and solid phases of the soil, plant uptake may be many times the soluble orthophosphate level found in the soil (Tisdale and Nelson, 1966). Normal plant P contents can be as low as 0.15 percent, particularly in grasses and cereals.

Excess P in the soil can lead to P-induced micronutrient deficiencies in plants, particularly Zn, Fe, Cu, and Mn (Olsen, 1972). These problems are thought to be due to metal-phosphate interactions occurring at the root surface or within the root. Molybdenum adsorption and translocation is enhanced by increased available P levels in the soil. It has been suggested that this is due to the formation of a phospho-molybdate anion that is absorbed more readily by the plant.

Sulfur

Sulfur occurs in the soil as a part of soil organic matter, as a soluble anion, or adsorbed onto soil colloids. In well drained soils, most of the inorganic sulfur occurs as the sulfate ion. It is found in the soil solution in conjunction with exchangeable cations or precipitated as a salt in arid areas. Sulfates can also be adsorbed by Fe and Al hydroxides, or by 1:1 clays. Leaching losses in cooler, humid areas may be quite large (Tisdale and Nelson, 1966). As a rule, plant S

contents less than 0.1 percent may be regarded as deficient.

Fluoride

Fluoride ions in the soil tend to form only slightly soluble compounds with Ca and Mg, or are tightly held on the clay colloidal complex. Fluoride ions may also form complexes with Fe and Al silicates (Nommik, 1953). In clay soils in Sweden, total soil fluoride contents correlated positively with acid soluble P. In one soil, the fluoride content correlated with the CaCO_3 content of the soil. These results suggest that a major portion of the fluoride compounds in the soil exists as slightly soluble calcium fluoride. Analysis of 31 Swedish soils for water soluble fluoride showed increased fluoride content as the soil texture became finer. Values ranged from 1.0 to 48 ppm F; the average for soils containing more than 15 percent clay was 20.3 ppm.

Plant uptake of fluoride under normal conditions is limited, with normal plant values between 2 and 20 ppm (Allaway, 1968). Plant toxicities due to fluoride are rare and found only on highly acidic soils. Fluoride added as NaF to a sand (pH 7.2) and a "medium clay" soil (pH 6.7) was toxic to spring wheat at 5 g NaF/pot in the sandy soil, with 403 ppm F in the straw as compared with 24 ppm for the control plant. In the clay soil, no fluoride toxicities were seen at the highest application rate (10 g NaF/pot), even though fluoride levels increased

to 80.3 ppm F in the plant straw. The spring wheat was essentially unaffected by the CaF_2 applied. Using another clay soil at pH 5.4, an application of 16 g NaF/pot killed the shoots, while lesser applications seriously reduced yields (Nommik, 1953). Weak acids like HF reduced plant growth in reverse proportion to acid dissociation (Lundgardh, from Nommik, 1953). The undissociated molecules were more easily absorbed than the respective ions.

Fluoride injury to farm animals and humans is due principally to high F levels in groundwaters used for drinking. Accordingly, drinking water should contain no more than 1.8 ppm F when water temperatures are between 50 and 58.3°F, and less as temperatures rise (Am. Water Works Assoc., 1971).

Molybdenum

The total molybdenum content of most soils is quite low, ranging from 0.5 to 2.5 ppm and averaging about 2.0 ppm. Of this supply, a majority is not plant available (Anderson, 1956). Molybdenum is an anion in aerated soils ($\text{MoO}_4^{=}$) and may be present as part of mineral crystal, an adsorbed anion on clay and amorphous material surfaces, as part of soil organic matter, and as a soluble anion in the soil solution (Tisdale and Nelson, 1966). As noted previously, high soil P levels increase Mo availability. Molybdenum availability is depressed in acid soils (Lucas and Knezek, 1972). Acidic pH values

(less than 5.5) favor the formation of relatively insoluble molybdate salts of Mn, Cu, Fe, and Al. Increasing the soil pH increases the solubility of MoO_2 . Sulfate competes with molybdate for adsorption sites on plant roots, since sulfate and molybdate ions are of similar size, charge, and geometry.

Plant uptake of Mo can reach levels as high as 100 ppm without causing plant toxicity, but such high levels cause molybdenosis in ruminant animals (Allaway, 1968).

Soluble Salts

Soluble salts consist mainly of sodium, magnesium, and calcium cations with sulfate and chloride anions (U.S.D. A. Handbook No. 60). The electrical conductivity of a saturated soil paste extract is closely correlated to soil water salinity and osmotic potential, and is used to measure soil salinity (Bernstein, 1974). Plant response to salinity may be due to osmotic potential increases with increasing salinity or may be due to specific ion effects on plant nutrition. Leaf accumulations of more than 0.5 percent chloride and 0.25 percent Na on a dry weight basis have produced reduced yields and leaf burning in most crops. Salt tolerances vary widely among crop species and among varieties within species. Perennial ryegrass (L. perenne) is relatively salt tolerant; with conductivity values near 8 mmhos/cm, yield reductions of only ten percent are reported. Field beans, on the other hand,

experience a 50 percent yield reduction as conductivity approached 3.5 mmhos/cm. Specific ion effects have also been correlated to ionic imbalances in plant tissue, such as excessively high Ca/K ratios or deficiencies of Mg and K in beans or sulfate-induced Ca deficiencies in some lettuce varieties.

Groundwater Contamination

The major mechanisms causing movement of chemicals in the soil are (1) molecular diffusion and (2) convection of chemicals with water as the water moves through the soil (Boast, 1973). The transport of any chemical through the soil profile is controlled by a number of factors, including (1) pore velocity, (2) fluid dispersion, (3) cation and anion exchange capacity, (4) cation and anion exchange equilibrium, (5) kinetic rate of cation and anion exchange, (6) concentration of materials added to the soil, and (7) the soil water content (Tai and Jurinak, 1972).

Because anions such as SO_4 , Cl, and NO_3 are soluble, and because soils generally have low anion fixation capacities, the addition of any anion to the soil may increase the groundwater concentration of that ion (Hill, 1972). The U.S. Public Health Service has set standards that sharply curtail the amount of nitrate, nitrite, sulfate, and chloride permissible in drinking water supplies (Table 3). Crop removal of potential pollutants can play a significant role in reducing

pollution hazards and increase allowable waste application rates (Hill, 1972; Kardos, 1967).

Table 3. U.S. Public Health Service drinking water standards--recommended limits of constituents.¹

	Recommended	Tolerance ²
	- - - - - ppm - - - - -	
Boron	1.0	
Fluoride	-	1.4-2.4
50-58.3°F	1.8	-
58.4-70.6°F	1.5	-
70.7-90.5°F	1.2	-
Nitrogen ($\text{NO}_3^- + \text{NO}_2^-$)	10.0	-
Arsenic	0.01	0.05
Barium	-	1.0
Cadmium	-	0.01
Chlorine	250	-
Chromium (+6)	-	0.05
Copper	1.0	-
Iron	0.3	-
Lead	-	0.05
Manganese	-	0.05
Sulfate	250	-
Zinc	5.0	-

¹From Anonymous. 1971. Water Quality and Treatment - a Handbook of Public Water Supplies. The Amer. Water Works Assoc., Inc. McGraw-Hill, New York.

²Tolerance limits - concentrations higher than those listed constitute grounds for rejection of the supply.

Exchangeable cation movement is related to a number of factors, principally ionic charge, cation exchange capacity, and complementary ions present. In general, relative ionic replacement power follows the order of ionic charge, $M^{+} < M^{+2} < M^{+3}$. Within ion groups of similar charge, replacement power will vary, depending on the type of colloid involved and the ionic concentrations (Wiklander, 1965). Because most heavy metals are insoluble under normal soil conditions, leaching losses and groundwater pollution hazards are minimized. Only under acidic, reducing conditions will these elements pose a hazard to groundwater.

Implications in Waste Disposal Through Soils

If waste disposal on agricultural soils is to be a reasonable waste disposal method, waste application must not pose a direct or indirect threat to the food chain, reduce crop yields significantly, or pose a hazard to groundwater supplies. In the short term, increased soluble salts and high levels of such anions as NO_3 and F may pose problems. The uptake of heavy metals can be high immediately following waste application, particularly on acid soils. Controlling pH such that it is 6.5 or greater in the zone of application and controlling application rates where metals, soluble salts, and/or anions pose a hazard is essential (Chaney, 1973). Long and short term toxicities from metals require that limits be placed on metal application rates. Chaney (1973) and Leeper (1972) recommend that the application of

toxic metals should not exceed 5 percent of the cation exchange capacity of the unamended soil at a pH of 6.5. That corresponds to the application of 653 lbs Zn/acre on a soil with a relatively high CEC = 20 meq/100 g.

MATERIALS AND METHODS

Field Studies

Field trials were initiated in June, 1973 on a site owned by the American Can Company, approximately five miles west of Halsey, Oregon and farmed by Mr. Leroy Nicewood. The plot area was treated with "Roundup," a new experimental glyphosate herbicide designed for postemergence control of a broad spectrum of weeds. Initially, 48 plots were established in a randomized block design, encompassing 12 treatments (Table 4) over four replications (Figure 1). Each plot was eleven feet long and seven feet wide, with an inner eight foot by four foot area to be used for application of the waste material. Two weeks after the herbicide was applied, the plots were staked and the waste product applied. The waste was transported as a wet slurry in a plastic-lined ammunition trailer and applied volumetrically. Since the moisture content of the waste produce varied considerably, the actual dry waste applied was 50 to 100 percent greater than planned (Table 5). In addition, the variability within treatments was sufficiently high that exact treatment replication (in terms of dry weight) no longer existed.

To eliminate the waste application variability, a second set of plots was treated with "Roundup," staked, and the waste applied as a pre-dried solid. The waste material was air dried on a concrete slab,

Table 4. Fertilizer and waste added to Dayton sicl soil.

Treatment number	Waste application (ton/acre)	Nitrogen ²	Fertilizer application (lbs/acre) ¹			
			Phosphorus	Potassium	Sulfur	Lime
1	0	100	25	50	15	5000
2	5	100	25	50	15	5000
3	10	100	25	50	15	5000
4	25	100	25	50	15	5000
5	50	100	25	50	15	5000
6	0	100	25	50	15	0
7	25	100	25	50	15	0
8	0	100	25	50	0	5000
9	10	100	25	50	0	5000
10	0	100	100	50	15	5000
11	10	100	100	50	15	5000
12	50	100	100	50	15	5000

¹ Nitrogen applied as ammonium nitrate; phosphorus, as concentrated super phosphate; potassium, as potassium chloride; sulfur, as gypsum; and calcium carbonate was used as a liming material.

² A second nitrogen application was made in April, 1974, at a rate of 75 lbs N/acre.

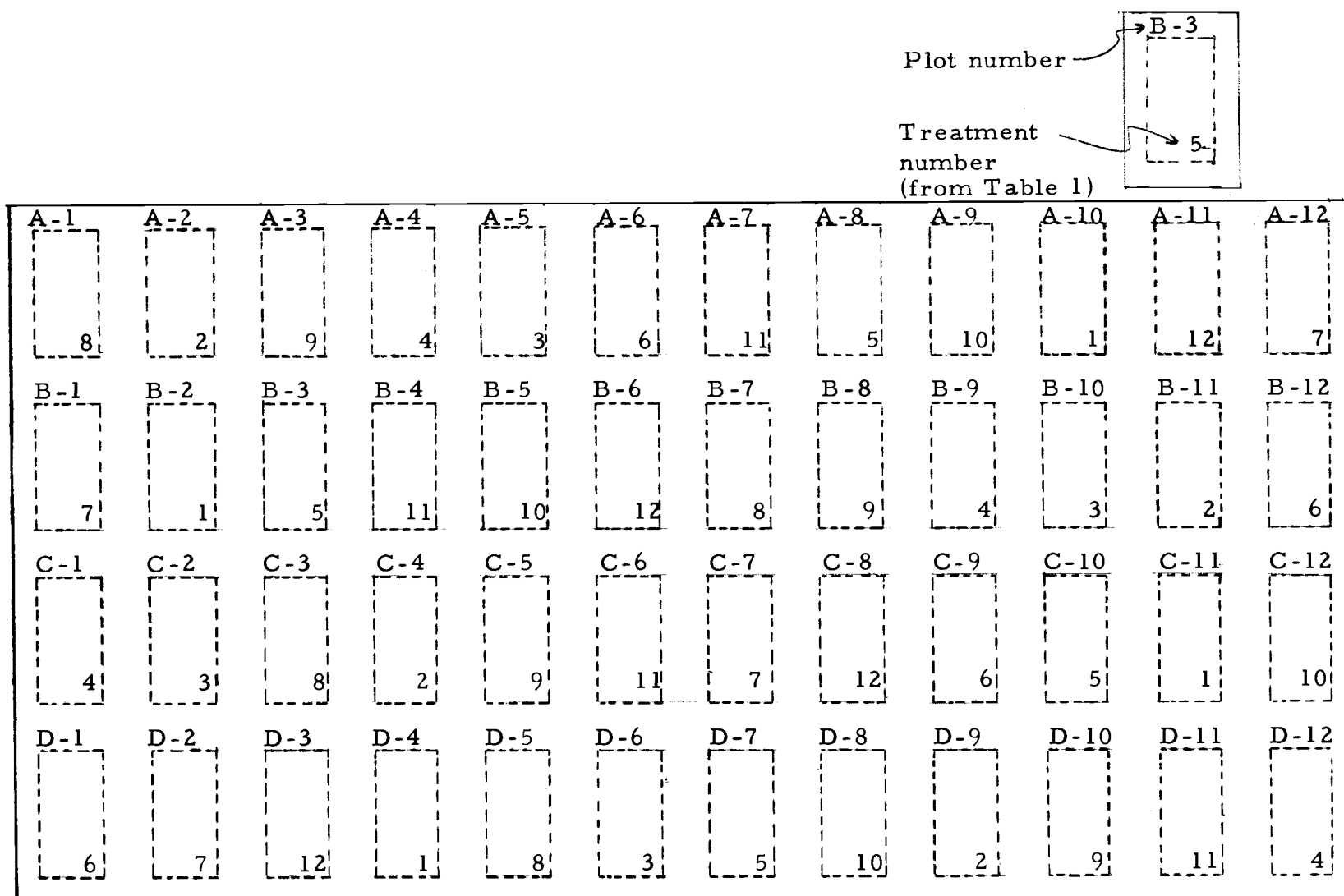


Figure 1. Plot plan for area I.

Table 5. Refractory waste and fertilizer applications to wet waste application area.

Plot	Desired dry waste application ton/acre	Actual dry waste application ton/acre	Fertilizer application				
			Lime ton/ acre	S - - - lb/acre	P - - - lb/acre	N - - - lb/acre	K - - - lb/acre
A-10	0	0	2.5	15	25	100	50
B-2	0	0	2.5	15	25	100	50
C-11	0	0	2.5	15	25	100	50
D-4	0	0	2.5	15	25	100	50
A-2	5	7.50	2.5	15	25	100	50
B-11	5	7.50	2.5	15	25	100	50
C-4	5	9.50	2.5	15	25	100	50
D-9	5	10.19	2.5	15	25	100	50
A-5	10	14.48	2.5	15	25	100	50
B-10	10	14.86	2.5	15	25	100	50
C-2	10	18.92	2.5	15	25	100	50
D-6	10	20.20	2.5	15	25	100	50
A-4	25	36.43	2.5	15	25	100	50
B-9	25	37.08	2.5	15	25	100	50
C-1	25	41.83	2.5	15	25	100	50
D-12	25	41.83	2.5	15	25	100	50
A-8	50	72.41	2.5	15	25	100	50
B-3	50	72.41	2.5	15	25	100	50
C-10	50	99.44	2.5	15	25	100	50
D-7	50	101.04	2.5	15	25	100	50
A-6	0	0	0	15	25	100	50
B-12	0	0	0	15	25	100	50
C-9	0	0	0	15	25	100	50
D-1	0	0	0	15	25	100	50

Table 5. Continued.

Plot	Desired dry waste application ton/acre	Actual dry waste application ton/acre	Fertilizer application				
			Lime ton/ acre	S - - -	P lb/acre	N - - -	K - - -
A-12	25	41.83	0	15	25	100	50
B-1	25	46.04	0	15	25	100	50
C-7	25	47.19	0	15	25	100	50
D-2	25	50.39	0	15	25	100	50
A-1	0	0	2.5	0	25	100	50
B-7	0	0	2.5	0	25	100	50
C-3	0	0	2.5	0	25	100	50
D-5	0	0	2.5	0	25	100	50
A-3	10	14.48	2.5	0	25	100	50
B-8	10	14.86	2.5	0	25	100	50
C-5	10	18.92	2.5	0	25	100	50
D-10	10	20.20	2.5	0	25	100	50
A-9	0	0	2.5	15	100	100	50
B-5	0	0	2.5	15	100	100	50
C-12	0	0	2.5	15	100	100	50
D-8	0	0	2.5	15	100	100	50
A-7	10	14.48	2.5	15	100	100	50
B-4	10	14.48	2.5	15	100	100	50
C-6	10	18.92	2.5	15	100	100	50
D-11	10	20.20	2.5	15	100	100	50
A-11	50	94.62	2.5	15	100	100	50
B-6	50	74.35	2.5	15	100	100	50
C-8	50	94.62	2.5	15	100	100	50
D-3	50	96.03	2.5	15	100	100	50

and the moisture content was measured. The material was crushed, trucked to the field, and applied by weight. Both plot areas were fertilized (Table 4), rototilled to a depth of six to eight inches, and rolled to prepare a firm seed bed. On August 14, 1973, the plots were seeded with perennial ryegrass (L. perennae, var. Linn) at a rate of 14 pounds of seed per acre. The plots were irrigated as necessary by sprinkler, using waste effluent water from the American Can Company, Halsey plant. The irrigation water was high in soluble salts but low in its sodium hazard (SAR = 5.1) (Vomocil, 1974).

In the spring of 1974, the plots were fertilized with nitrogen, 75 lb/acre. On July 11, 1974, a 2 1/2 by 8 foot section of each plot was mechanically harvested. The plant material was dried at the Hyslop Experimental Farm and weighed. After yield determination, the dry matter was threshed and the seed collected and stored in plastic bags. The seed was mechanically cleaned and weighed to determine the clean seed yield.

The cleaned seed from plots treated with 0, 10, and 50 tons waste/acre was tested for seed viability by a seed germination test. Triplicate 50 seed samples from each plot were placed on wet blotter paper inside 4 by 4 inch plastic containers. The containers were placed in a growth chamber, where moisture conditions, temperature, and daylength were controlled or monitored. At the end of a two week incubation period, the containers were removed and the germinated

seeds in each container were counted.

Soil Chemical Analysis

In June, 1973, prior to application of waste product or fertilizer, soil samples were collected from each replication in the first set of plots as a function of soil depth (0-3, 3-6, 6-12, 12-24, and 24-36 inches). These samples were analyzed by the Oregon State Soil Testing Laboratory for pH, soluble salts, exchangeable cations (K, Ca, Mg, Na), boron, zinc, nitrate and ammonium nitrogen, sulfur, and SMP buffer capacity. The initial fertilizer recommendations were based on these analyses. The soil on the second set of plots was also sampled prior to treatment, but no soil analyses for fertilizer recommendations were conducted. The soil on the second set of plots was sampled again between August 28 and September 3, 1973, about two to three weeks after planting. These soils were composites of subsamples collected from each replicate for any one treatment. Selected plots, representative of very high waste application rates, were also sampled from the plots which received the waste slurry.

Soil samples were air dried, crushed to pass a 2 mm sieve, and stored in plastic-lined soil sample bags.

Soluble Salts and pH

Soluble salts were determined from saturated extracts of 30 g soil samples, using a RD-26 Solu-Bridge to measure conductivity (Bower and Wilcox, 1965). pH determinations were made on 1:2 soil to solution suspensions using a Corning pH meter and calomel electrode (Jackson, 1958).

Available Phosphorus

Available phosphorus was extracted with a dilute acid-fluoride solution. Ammonium molybdate was added to an aliquot of the extract forming a blue phosphomolybdate complex (Jackson, 1958, after Bray and Kurtz, 1945). The percent transmittance was determined on a Bausch and Lomb Spectronic 20 colorimeter with a wavelength setting of 660 nm.

Exchangeable Cations and Cation Exchange Capacity

Air dried soil (10 g) was extracted with three 25 ml washes of 1N ammonium acetate, pH 7.0, for 20 minutes per wash on a wrist-action shaker. After centrifugation, the supernatant was filtered through Whatman No. 42 filter paper into a 100 ml volumetric flask. After the last wash, the extract was diluted to 100 ml volume with 1N ammonium acetate, and transferred to plastic bottles. Prior to

analysis for calcium and magnesium, the samples and standards were diluted with 1,500 ppm strontium as SrCl_2 to avoid phosphorus interference during atomic absorption analysis. The samples and standards were diluted with a 1,000 ppm Na solution to prevent ionization interference during analysis for potassium. A 1,500 ppm Li solution was used to eliminate ionization interference during the sodium assay. Atomic absorption was also used for the K and Na assays.

Cation exchange capacity (CEC) was determined by saturation of 10 g air dried soil samples with ammonium from 1N ammonium acetate. The ammonium saturated soil was washed once with distilled water and twice with 95% ethanol to remove excess ammonium ions. The exchangeable ammonium was extracted with three 0.1N HCl washes, and the supernatant solution diluted to 250 ml. The ammonium content was determined by a semi-micro Kjeldahl technique (Chapman, 1965) and the CEC calculated.

Extractable Aluminum

Air dry soil samples (10 g) were extracted with three washes of 1N ammonium acetate (pH 4.8) (Rolfe, et al., 1951). Aliquots of the extract were transferred to 50 ml test tubes, and sufficient 6N HCl added to provide an excess of 2.5 to 4.0 milliequivalents HCl. Two mls of thioglycollic acid were added to eliminate iron interference. The tubes were heated in a water bath at 80 to 90°C for 30 minutes,

and cooled to room temperature for at least an hour. The solution was transferred quantitatively to a 50 ml volumetric flask. Ten mls of aluminonacetate buffer were added; the solutions were diluted to 50 ml with distilled water and mixed thoroughly. After at least one hour, the percent transmittance was measured, using a Bausch and Lomb Spectronic 20 colorimeter with a wavelength setting of 530 nm.

Heavy Metals

Iron, zinc, copper, manganese, nickel, and chromium were extracted from the soil samples with an aqueous DTPA (diethylene-triaminepentaacetic acid) solution (Lindsay and Norvell, 1969), and measured by air/acetylene flame atomic absorption.

Nitrate and Ammonium Nitrogen

Air dried soil samples (40 g) were extracted with 200 ml of 2N KCl (Bremner and Keeney, 1966). A 100 ml aliquot of the extractant was steam distilled into a flask containing 10 ml of boric acid. One gram of magnesium oxide was added to the distillation flask to maintain sample basicity such that solution ammonium was converted to ammonia. The distillation process was continued until about 75 ml of the distillate were collected. The distillate was titrated with standardized 0.02N HCl to determine the $\text{NH}_4\text{-N}$ concentration.

The $\text{NO}_3\text{-N}$ remaining in solution was converted to $\text{NH}_4\text{-N}$ by addition of Devarda alloy (1 g) to the sample in the distillation flask. The sample was distilled and the distillate was collected and analyzed in the same manner as the ammonium-N.

Extractable Sulfur

The sulfur procedure used was identical to that recommended by Hoeft, et al. (1973) with the exception that a Hach Model 2100-A turbidimeter was used rather than a nephelometer. Standards were prepared over a range of 0 to 20 ppm sulfur, and readings taken on the 0 to 100 FTU scale.

Extractable Fluoride

Fluoride activity was determined potentiometrically with a specific ion electrode (Harwood, 1969). Aliquots from the exchangeable base extracts were used for the analyses.

A summary of all methods used for soil analysis has been prepared (Table 6).

Plant Analysis

Plant samples were collected on April 25, 1974, prior to the development of seed heads in the perennial ryegrass. Each plot from both the wet and dry waste application areas was sampled. Samples

Table 6. Summary of methods used in soil analysis.

Determination	Method	Reference
Soluble salts	Electrical conductivity	Bower and Wilcox, 1965
pH	2:1 water:soil suspension	Jackson, 1958
Available phosphorus	Dilute acid-fluoride	Jackson, 1958, pp. 160-161; Bray and Kurtz, 1945
Exchangeable bases (Ca, Mg, Na, K)	Ammonium acetate @ pH 7.0, atomic abs.	Pratt, 1965
Cation exchange capacity	Saturation with ammonium acetate, Kjeldahl analysis for ammonium ion	Peech, <u>et al.</u> , 1947; Chapman, 1965
Aluminum	Ammonium acetate extract. @ pH 4.8, colorimetric det. with aluminon	Rolfe, <u>et al.</u> , 1951
Chromium, nickel, zinc, copper, iron, manganese	DTPA at pH 7.3, atomic absorption	Lindsay and Norvell, 1969
Ammonium-, nitrate-N	2N KCl extraction, Kjeldahl steam distill.	Bremner and Keeney, 1966
Sulfur	Extract with 500 ppm P in 2N HOAc, turbidimetric with barium sulfate	Hoeft, <u>et al.</u> , 1973
Fluoride	Potentiometric from 1N ammonium acetate extracts pH 7.0	Harwood, 1969
Lead, hafnium, and zirconium	Arc emission spectroscopy	Courtesy of Teledyne Wah Chang Albany Corporation

were cut 2 to 3 inches above the soil surface. The samples were placed in plastic bags and dried at 65°C. The samples were ground in a Wiley Mill to pass a 20 mesh screen and stored for analysis in coin envelopes.

Two different perchloric acid digestions were performed on all samples. Plant material samples (1.000 g) were digested with six ml of nitric acid in 125 ml Erlenmeyer flasks. Glass beads were added to minimize bumping. The flasks were heated on a hot plate until the organic matter was destroyed. After cooling, perchloric acid, 12 ml, was added to each flask and the samples allowed to boil until the white perchloric fumes disappeared. The solution was filtered and diluted with distilled water to a 100 ml volume. Phosphorus, calcium, magnesium, sodium, potassium, zinc, manganese, iron, sulfur, and aluminum were determined on this digest.

A second set of plant digests were similarly performed, except that 2 g of plant material were used and the perchloric acid was allowed to go to dryness. (Care was taken to insure that all organic matter was destroyed in the nitric acid digest.) The residual material was dissolved 1N HCl, 20 ml, and filtered to eliminate the insoluble silicates. Copper, chromium, molybdenum, nickel, and cobalt were determined by atomic absorption on these digests.

Calcium, magnesium, sodium, potassium, iron, manganese, zinc, and copper were measured by air/acetylene flame atomic

absorption, using a Perkin-Elmer Model 306 spectrophotometer. Interference in the Ca, Na, K, and Mg analyses were eliminated by procedures similar to those used for the soil samples. Aluminum was also determined by atomic absorption, but with a nitrous oxide/acetylene flame. Molybdenum, chromium, and cobalt were determined by flameless atomic absorption, using the Perkin-Elmer HGA 2000 graphite furnace.

Phosphorus was measured through the formation of a yellow vanadomolybdophosphoric complex (Jackson, 1958). The coloring agent was made by combining equal volumes of 0.25% ammonium vanadate and 5% ammonium molybdate solutions. The vanadate solution was prepared by dissolution of 5.0 g of ammonium vanadate in 1,000 ml of boiling water and combining this with 340 ml of concentrated sulfuric acid in 600 ml of water. The molybdate solution was prepared by dissolution of 100 g of ammonium molybdate in 1,000 ml of warm water, cooling the solution, and diluting it to two liters. The percent transmittance for all standards and samples was read at 420 nm on a Bausch and Lomb Spectronic 20.

Plant sulfur was determined turbidimetrically (Hoeft, et al., 1973), using a Hach Model 2100-A turbidimeter in the range of 0 to 100 FTU.

Total nitrogen was determined by a micro-Kjeldahl method (Jackson, 1958).

Plant tissue fluoride content was determined through modification of a potentiometric standard addition technique (Baker, 1972). Plant samples (1 g) were fused in Iconel[®] crucibles with NaOH pellets (6.7 g) over a bunsen burner flame. The melt was cooled and dissolved in 25 ml of distilled water. The solution was quantitatively transferred to a 50 ml volumetric flask and diluted to volume with distilled water. This solution was filtered through Whatman No. 50 filter paper and stored in plastic bottles until analyzed.

Waste Product Analysis

The waste product was analyzed for available elemental constituents and other properties in the same manner as the soil samples. In addition, carbonates were determined by a titrimetric procedure using a carbon dioxide trap (Bundy and Bremner, 1972). Total analysis of the waste product was provided by Teledyne Wah Chang Albany Corporation.

Leaching Column Construction

Columns were constructed from glass tubing, 20.5 cm long and six cm in diameter (Figure 2). A small outlet was attached to each column approximately one cm from the top. The bottom of the column was covered with several layers of cheesecloth, and a piece of Whatman No. 1 filter paper placed inside the column to prevent the

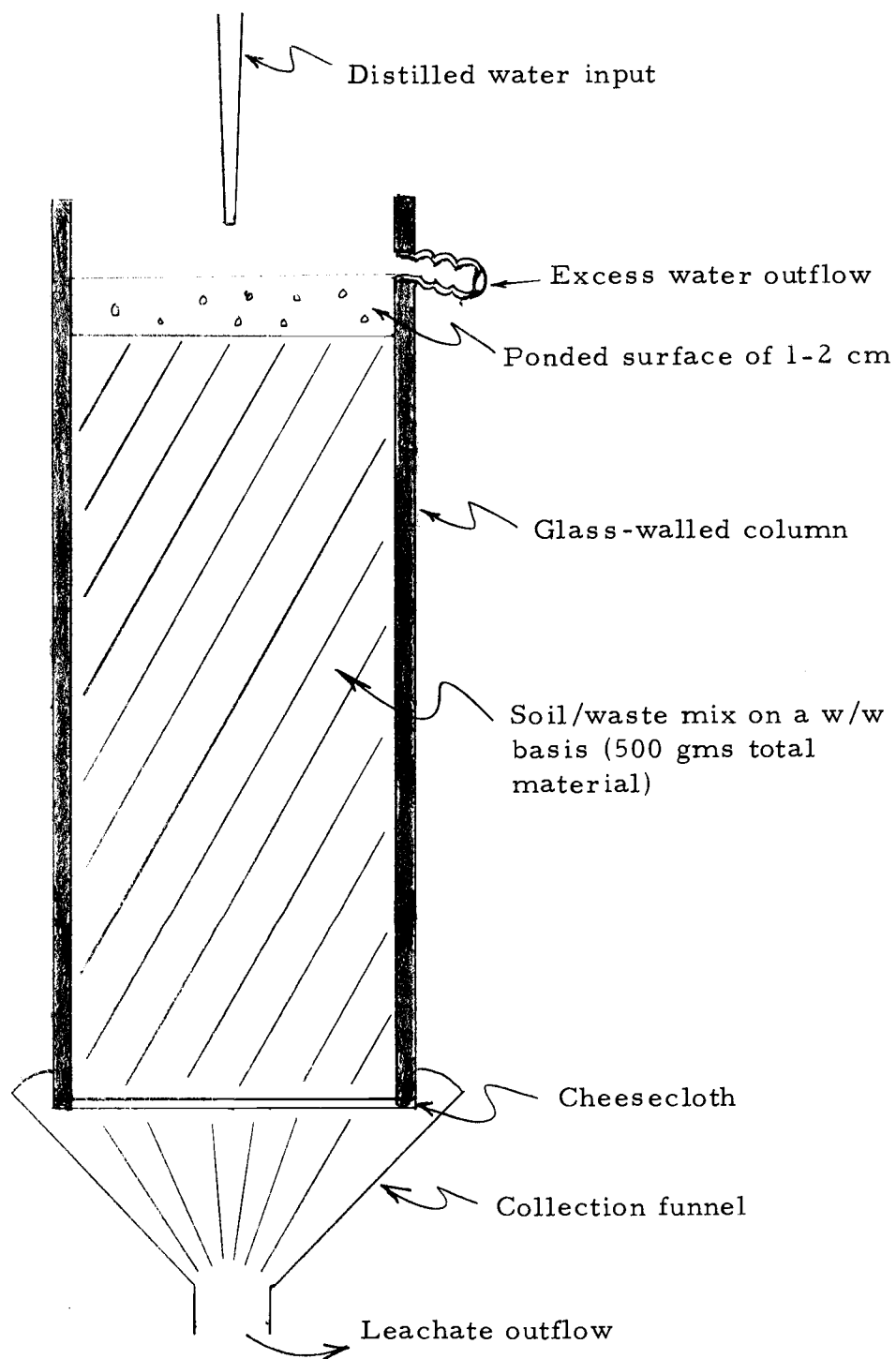


Figure 2. Diagram of leaching column design.

movement of soil particles into the leachate samples. Each column was filled and packed with a 500 g of a soil/waste product mixture, such that the columns contained 0, 2, 4, 6, and 10 percent waste, respectively, on a weight basis. The soil was sieved to less than 2 mm aggregate size, whereas the waste product particle sizes varied in size from more than 5 mm to a very fine powder. The waste product used was the same as that applied to the plots which received the dry waste application.

The columns were leached by ponding distilled water 1 to 2 cm on top of the soil columns. The water in excess of that needed to maintain the head drained through the outlet at the top of the column. The leachate was sampled every few hours during the first day of leaching, every day from the second through the 14th day, every two days from the 16th to the 30th day, and every five days for the remaining 50 days of the study.

Each leachate sample was stored at 4°C in polyethylene "Cubitainers." Between sample collections, the volume of the percolation water was measured, and the percolation rate calculated.

Leachate Analysis

Calcium, sodium, magnesium, manganese, copper, zinc, ammonium and nitrate nitrogen, sulfur, and fluoride were determined directly on the leachate samples by the methods used for the soil

extracts. Soluble orthophosphate was determined colorimetrically of through the formation of a blue antimony-phosphomolybdate complex (EPA Bulletin, 1971). When aliquots of the leachate were concentrated by slow evaporation on a warm hot plate, a precipitate formed, so no attempts were made to measure elements present in very small concentrations (nickel, cobalt, molybdenum, potassium, iron, and aluminum).

Soil Physical Properties

Soil moisture retention as a function of matric potentials and waste application rates was determined by a pressure plate-membrane apparatus (Richards, 1965).

RESULTS AND DISCUSSION

Waste Product Analysis

Only Zr, Ca, F, Fe, Al, C (as CO_3), and S were present in the waste product in amounts of 1 percent or more (Table 7, Appendix I). Those elements found in concentrations ranging from 0.1 to 1.0 percent included Hf, Mg, Na, Pb, P, NH_4 -N, and K. Relatively minor constituents (< 1000 ppm) included Cr, Ni, Cu, Cd, Co, Mn, and Mo. With the exception of fluoride, variation among samples appeared to be 50 percent or less. Fluoride concentrations ranged from 3.29 to 6.28%, for a variance of almost 100% among samples. Other major waste constituents, such as Zr, Hf, Ca, Fe, and Al varied 10 to 30% among samples. Less F, Al, Fe, Ca, Mg, S, Mn, Cu, and Co were present in the samples collected in 1972 than in 1971, while the Zr, K, Pb, Zn, and Ni content increased (Table 7) (Volk, et al., 1971).

The total heavy metal content, with the exception of zirconium and hafnium, is less than 0.3 percent, using Zn, Cu, Ni, Cd, Cr, and Pb as those metals most commonly associated with plant toxicities. According to Leeper (1972), the total amount of toxic metals applied should not exceed 5 percent of the soil cation exchange capacity (CEC). The Dayton silt has an average CEC of 12 meq/100 g or 109×10^6 meq/AFS. The waste contains approximately 5.4×10^4 meq/ton Cu, Zn, Ni, and Pb. Dividing 5 percent of the CEC by the milliequivalents

Table 7. Chemical analysis of refractory metal waste product.

Constituent	Units	1973 ¹	1971 ²
Zr	%	22	7.97 ³
F	%	4.45	16.1
Ca	%	10.8	25.4
Fe	%	2.53	2.79
Al	%	1.38	1.65
Mg	%	0.28	0.39
K	%	0.11	0.06
Na	%	0.39	0.29
S	%	0.99	2.71
P	%	0.32	NA ⁴
Pb	%	0.18	0.029
C (inorganic)	%	1.25	6.18
Hf	ppm	2739	NA
Cr	ppm	831	1100
Zn	ppm	508	<100
Ni	ppm	675	400
Cu	ppm	106	400
Co	ppm	<50	400
Cd	ppm	<50	<100
Mn	ppm	506	3100
NH ₄ -N	ppm	1268	0
NO ₃ -N	ppm	2.1	NA
Sol. salts	mmhos/cm	15.3	NA

¹Mean values for eight air-dried samples.

²Volk, V.V., et al., 1971. Plant Toxicity of Zirconium-Hafnium Rich Solid Wastes. Unpublished report.

³Total Zr + Hf.

⁴NA = not analyzed.

of these metals per ton, waste application rates should not exceed 101 T/A. Leeper's application criteria was based on the application of sewage sludge, which is mainly organic. Because the waste product is inorganic, metal release comes from soluble to slightly soluble salts, rather than the breakdown of organic chelates or direct ingestion of the metals by soil organisms. While the metal sources are indeed different, the net effect on metal availability in the soil may be similar.

For most waste constituents, the amount that was available and/or extractable was considerably less than the total amount present. The greatest amount available in comparison to the total present were found for Ca, Mg, and Na, where values ranged from 8 to 14 percent. Aluminum, F, and Fe were relatively insoluble, with less than 0.5 percent of the total amounts of these elements extracted. DTPA extracts for metals such as Cu, Zn, and Ni were less than 10 percent of the total amount of these metals. The DTPA extract provides a gauge for the total amount of each metal available for plant uptake. No toxic effects on plant growth were expected from these metals (Table 8).

Ammonium acetate extractable F levels averaged 31.3 ppm. The nitrate levels in the waste product averaged 2.1 ppm $\text{NO}_3\text{-N}$, and ranged as high as 5.4 ppm. Since the maximum $\text{NO}_3\text{-N}$ concentration permitted in drinking water is 10 ppm, any nitrate groundwater

pollution problems would be dependent on nitrification rate, water percolation, and plant nitrogen uptake rather than the nitrate content of the waste. The waste contained an average of 1,268 ppm 2N KCl extractable $\text{NH}_4\text{-N}$.

Table 8. Selected extractant chemical analysis of a refractory metal waste product.

Constituent	Unit	Amount ¹	Extractant
pH	$-\log [\text{H}^+]$	7.51	H_2O
Soluble salts	mmhos/cm	15.3	H_2O
$\text{NO}_3\text{-N}$	ppm	2.1	2N KCl
$\text{NH}_4\text{-N}$	ppm	1268	2N KCl
P	ppm	0	Dilute acid-fluoride
S	ppm	885	500 ppm P in 2N HOAc
K	ppm	10.8	NH_4OAc @ pH 7.0
Ca	meq/100 g	76.0	NH_4OAc @ pH 7.0
Mg	meq/100 g	3.55	NH_4OAc @ pH 7.0
Na	meq/100 g	1.49	NH_4OAc @ pH 7.0
Al	ppm	61.1	NH_4OAc @ pH 4.8
Fe	ppm	45.3	NH_4OAc @ pH 4.8
Mn	ppm	57.9	DTPA @ pH 7.3
Zn	ppm	45.3	DTPA @ pH 7.3
Cu	ppm	4.13	DTPA @ pH 7.3
Ni	ppm	10.8	DTPA @ pH 7.3
$\text{CO}_3\text{-C}$	%	1.25	1N HCl
F	ppm	31.3	NH_4OAc @ pH 7.0

¹ Means for no less than 8 samples.

No phosphorus could be extracted from the waste product with a dilute acid-fluoride solution. The waste contained 0.32 percent total P, but none appeared to be plant available. Previous work (Volk, et al., 1971) has shown that increased waste applications decrease available soil phosphorus. A mixture of 25 percent waste to 75 percent Dayton silt contained no available P even when treated with 800 lb P/acre. The waste free soil sample treated similarly contained 140 lbs/acre available P.

Soluble salts were quite high (15.3 mmhos/cm) and may pose a problem to plant species that are not salt tolerant. Crops like beans and tomatoes, whose yields are affected by salt levels of 4 mmhos/cm or less, would possibly suffer yield reductions on waste treated soil. Perennial ryegrass is relatively salt tolerant, and soil soluble salt values as high as 8.0 mmhos/cm did not significantly reduce crop yields (Bernstein, 1974).

Because the waste product contains some available nitrogen, sulfur, calcium, and magnesium, the material may serve as a fertilizer source. The application of waste, 10 T/acre, would supply 16.7 lbs available S, 15.4 lbs $\text{NH}_4\text{-N}$, 304 lbs available Ca, and 8.5 lbs available Mg.

Soil Chemical Analysis

The inherent low fertility of the Dayton soil in the plot area (Table 9) required the addition of N, P, K, and S fertilizers, and lime to ensure optimum plant growth. A strongly acidic soil condition will favor metal uptake by crops while promoting P deficiency. Since the Ca level in the Dayton soil was generally less than 40 percent of the CEC, a possible Ca deficiency could exist. Exchangeable sodium percentages (ESP) approached the 10 to 15 percent level in the surface three inches of the soil, which indicated that Na may adversely affect soil structure through dispersion of soil colloids. No heavy metals were present in the untreated soil in amounts considered hazardous to plant growth.

The addition of the necessary fertilizers increased soil exchangeable Ca, K, N, and P to levels necessary for good perennial ryegrass growth. Soil samples were collected two to three weeks after fertilization. The soil pH was marginally adequate in the surface three inches, but still less than 5.0 at a depth of 3 to 6 inches (Table 10). Those plots with no lime added remained acidic, while those plots with no S fertilizer added contained more extractable S than the unfertilized soil, but less than plots where S fertilizer was applied (Table 14). Application of P (100 lbs/acre) increased the available phosphorus level. At this application rate, 75 lbs extra P was applied.

Of this additional supply, 32 percent was found to be plant available (Table 14). Assuming all of the added P remained in the upper six inches of the soil profile, the addition of 25 lbs P/acre resulted in available P levels of 57 lbs/acre in control plots. Plots treated with 100 lbs P/acre and no waste had 80.9 lbs available P/acre. The additional 23.9 lbs available P was attributed to the additional fertilizer increment of 75 lbs P/acre.

Table 9. Dayton silt chemical analysis prior to waste application, with comparison to suggested nutrient levels.¹

Constituent	Range of values found, surface 6"	Recommended ²
pH	4.5-4.9	> 5.5
Sol. salts	1.50-3.00 mmhos/cm	---
P	7-10 ppm	> 30 ppm
K	68-97 ppm	> 100 ppm
Ca	4.3-5.0 meq/100 g	> 5.0 meq/100 g
Mg	0.8-1.5 meq/100 g	---
Na	0.95-1.80 meq/100 g	---
NO ₃ -N	0.6-20 ppm	Add 80-100 lbs N/A/year
NH ₄ -N	2.6-7.4 ppm	Add 80-100 lbs N/A/year
S	5.3-50 ppm	Add 7-15 lbs S/A/year
Zn	1.1-1.5 ppm	---

¹ Data courtesy of Oregon State University Soil Testing Laboratory, Corvallis Oregon.

² From O.S.U. Fertilizer Guide Sheet (FG-46) for perennial ryegrass seed, west of the Cascades; Revised November 1969.

Effect of Waste Application on Soil Chemical Properties

Soil chemical analyses data was collected principally on samples collected from the plot area where the waste was applied dry. The only soil data from the plots where the waste was applied as a wet slurry is that shown for the 100 ton/acre waste application rate. These data represent soil samples collected from two plots, C-10 and D-7. The lack of control over the wet waste application rates increased application rate variability between replicate plots.

Soil pH

Soil pH values in samples collected in the fall of 1973 and spring of 1974 increased with waste application (Table 10). The surface soil pH in the fall sample for those plots with no waste applied ranged between 4.3 and 5.5, with the most acid conditions found on the unlimed plots. The pH changes in the waste treated soils were the greatest in the surface three inches, with less marked trends at the 3 to 6 inch depth. Below a depth of 6 inches, the soil pH was not changed by the lime or waste application. In the spring of 1974 the pH in the surface 6 inches of soil was generally higher than those found in the fall of 1973. This may have been due to the relatively short time span in 1973 between waste and fertilizer application and the fall soil sampling.

Soluble Salts

Soluble salt levels in the fall of 1973 as measured by conductivity increased with waste application for the upper 6 inches of the soil profile (Table 10). Values exceeded 5.0 only when the waste application rate exceeded 50 ton/acre. Values in excess of 4.0, at which point the soil is considered saline, occurred when application rates exceeded 25 ton/acre. The addition of the waste product appeared to have no effect on soluble salt levels greater than 6 inches below the soil surface, where values were generally less than 2.0 mmhos/cm. Because of the high conductivity in the surface 6 inches of soil, salt sensitive crops such as beans and tomatoes should not be planted directly after waste application.

The soluble salt levels in the spring of 1974 were less than 1.70 mmhos/cm in all cases and generally less than 1.0 mmhos/cm throughout the soil profile (Table 11). Heavy winter rains removed most of the salts through leaching and surface runoff. Conductivity values such as those shown for spring soil samples would pose no hazard to crop growth. At most soil depths, the soluble salts increase positively correlated with waste application.

Calcium

Exchangeable Ca levels in the surface 6 inches of soil increased with waste application. In the surface 3 inches, the application of lime on waste increased the exchangeable Ca to levels equal to or exceeding the soil CEC (which ranged from 10 to 14 meq/100 g), indicating the presence of free Ca salts (Table 10). Because the waste product contained approximately 10.8 percent Ca, the high soil Ca content was not unexpected. While little of the Ca added in the waste was recovered as extractable Ca at low application rates, at application rates >25 ton/acre, 68 to 80 percent of the added Ca was extracted by the ammonium acetate. The limited Ca recovery at low waste application rates appears to relate to the soil sampling error. On the average, a waste application of 5 ton/acre could increase extractable Ca a maximum of 5 meq/100 g, assuming complete homogeneous mixing of the waste in the upper 6 inches of the soil, total Ca solubility, and no leaching losses. Calcium levels below a soil depth of 6 inches were not affected by waste application.

Exchangeable Ca levels in the upper six inches of the spring soil samples decreased only slightly from fall levels. This slight reduction is probably due to plant uptake, although surface runoff may play a minor role. Only in those plots where no lime or waste was applied did Ca approach deficiency levels suggested for perennial ryegrass.

For fall samples, the exchangeable Ca levels in the upper six inches of the soil profile were greater in plots that received 25 T/A waste and no lime than in plots that received lime but not waste (13.8

vs. 15.5 meq/ 100 g in the surface 3 inches; 8.2 vs. 11.3 meq/100 g at the 3 to 6 inch depth). The waste product can thus supply Ca for plant growth.

Magnesium

Exchangeable magnesium levels in the surface 6 inches of soil increased slightly with waste application for both spring and fall soil samples (Tables 10 and 11). No significant changes in exchangeable Mg were seen at soil depths greater than 6 inches, due in part to the relatively high level of Mg already present at those depths. No perennial ryegrass response to added magnesium fertilizers in the area west of the Cascades has been demonstrated (Gardner, et al., 1969).

Potassium

The addition of the waste product did not significantly alter the exchangeable potassium levels found in the soil (Tables 10 and 11). Potassium levels in the upper 3 inches of the soil were considered adequate for plant growth, but exchangeable K levels at a depth of 3 to 6 inches were less than adequate.

The exchangeable K in the upper 6 inches of soil sampled in the spring of 1974 was less than that found in the fall of 1973, and less than that considered necessary for optimum perennial ryegrass production. The reduction in K levels with time probably resulted from K fixation

by clay minerals and plant uptake.

Sodium

Exchangeable sodium levels in the soil did not change significantly with waste application. While Na levels were elevated in comparison with samples collected before waste or fertilizer was applied, the effect did not appear to be caused by the waste application. The increase was due to the application of Na through the irrigation system, since the pulp mill effluent contained 9.7 meq Na/l (Vomocil, 1974).

The exchangeable Na in the soil in the spring was generally less than in the fall for the upper 12 inches of the soil profile, and generally less than 0.8 meq/100 g throughout the profile. The Na was probably lost by leaching and runoff, since Na is usually the most weakly held cation on the exchange complex. Sodium uptake by plants could also reduce exchangeable Na levels.

Nitrogen

Soil extractable ammonium-N levels in the fall increased in the upper 24 inches of the profile with waste application (Table 10). In the upper 3 inches of the profile, the NH_4 -N levels at application rates of 50 ton/acre were approximately 6 to 10 times those levels found on plots not treated with waste, but fertilized with nitrogen at 100 lbs/acre.

Table 10. Exchangeable bases, pH, and soluble salt content of soil profile samples collected in August and September, 1973.

Waste application (T/A)	Fertilizer application			Soil depth (inches)	pH	Soluble salts (mmhos/cm)	Ca	Mg	Na	K	NH ₄ N
	Lime (T/A)	P (lbs/A)	S (lbs/A)				- - -meq/100 g - - -	- - -	- - -	- - ppm - -	- -
0	2.5	25	15	0-3	5.4	3.90	13.8	0.8	2.43	114	6.2
				3-6	4.7	2.60	8.2	0.9	1.22	82	5.7
				6-12	4.9	2.10	7.5	2.5	1.06	72	3.0
				12-24	4.7	0.95	16.8	11.3	0.87	158	0.8
				24-36	5.5	0.90	19.6	13.4	0.83	144	0.0
5	2.5	25	15	0-3	5.5	3.05	13.8	0.9	1.74	112	11.1
				3-6	4.7	2.00	8.2	1.1	1.26	60	2.2
				6-12	4.5	1.00	7.5	3.4	0.83	64	1.4
				12-24	4.8	0.62	17.5	11.8	0.75	140	2.4
				24-36	5.2	0.53	19.6	12.6	0.72	130	5.7
10	2.5	25	15	0-3	6.0	3.20	14.6	0.9	1.78	106	6.2
				3-6	5.2	3.30	10.0	1.2	1.43	72	5.4
				6-12	4.3	1.40	8.6	3.8	0.56	70	3.0
				12-24	5.2	NA	17.5	11.8	0.76	150	0.0
				24-36	5.5	NA	20.3	13.0	0.75	154	0.5
25	2.5	25	15	0-3	6.1	4.50	20.3	0.9	1.48	112	26.0
				3-6	4.8	3.50	11.8	1.3	1.48	66	8.7
				6-12	4.8	1.70	8.8	3.4	0.60	68	7.3
				12-24	4.7	NA	18.9	12.6	0.83	160	4.1
				24-36	5.2	NA	20.3	13.4	0.71	130	1.6
50	2.5	25	15	0-3	6.4	4.60	26.6	1.0	1.39	122	62.7
				3-6	5.3	4.60	13.4	1.2	1.35	66	34.5
				6-12	4.6	1.80	7.7	2.9	0.55	60	8.7
				12-24	4.8	NA	18.2	11.3	0.80	140	5.7
				24-36	5.3	NA	21.0	13.4	0.74	174	4.1

Table 10. Continued.

Waste application (T/A)	Fertilizer application			Soil depth (inches)	pH	Soluble salts (mmhos/cm)	Ca	Mg	Na	K	NH ₄ -N
	Lime (T/A)	P (lbs/A)	S (lbs/A)								
							- - - meq/100 g - - -			- - ppm - -	
100	2.5	25	15	0-3	6.8	7.00	27.3	1.1	2.13	104	23.9
				3-6	6.2	7.50	21.7	1.1	1.74	78	11.4
				6-12	5.0	3.80	14.5	2.9	1.20	58	9.5
				12-24	4.9	1.20	15.4	10.1	0.81	128	6.8
				24-36	5.4	1.10	19.6	12.6	0.68	138	2.7
0	0	25	15	0-3	4.6	3.60	6.4	0.8	1.87	116	34.7
				3-6	4.3	2.10	5.7	1.0	1.22	78	15.2
				6-12	4.6	1.50	7.1	3.4	1.10	72	4.9
				12-24	4.7	1.00	17.5	11.8	0.83	158	3.0
				24-36	5.2	0.55	19.6	12.6	0.76	140	2.2
25	0	25	15	0-3	6.1	4.50	15.5	0.9	1.43	120	39.3
				3-6	5.4	3.60	11.3	1.1	1.09	76	19.8
				6-12	4.6	2.20	7.7	2.1	1.18	64	8.1
				12-24	4.6	1.10	17.5	11.8	0.81	142	3.0
				24-36	5.7	0.70	19.6	12.5	0.68	110	2.7
0	2.5	25	0	0-3	5.0	4.50	10.4	0.9	1.78	114	10.9
				3-6	4.7	2.30	7.5	1.1	1.35	78	5.2
				6-12	4.5	1.80	7.9	4.2	0.97	78	4.9
				12-24	4.9	NA	18.2	13.0	0.77	156	6.8
				24-36	5.2	NA	20.3	13.4	0.77	140	1.6
10	2.5	25	0	0-3	6.0	4.70	16.3	1.0	1.96	110	9.8
				3-6	4.9	3.00	9.6	1.3	1.30	72	7.9
				6-12	4.6	1.50	7.1	2.9	0.94	66	7.1
				12-24	4.8	NA	18.9	11.3	0.90	152	4.1
				24-36	5.1	NA	21.0	12.2	0.87	126	1.9

Table 10. Continued.

Waste application (T/A)	Fertilizer application			Soil depth (inches)	pH	Soluble salts (mmhos/cm)	Ca	Mg	Na	K	NH ₄ -N
	Lime (T/A)	P (lbs/A)	S (lbs/A)				- - - meq/100 g - - -	- - - meq/100 g - - -	- - - meq/100 g - - -	- - ppm - -	- -
0	2.5	100	15	0-3	5.5	3.60	11.1	0.9	0.91	110	10.9
				3-6	5.0	2.20	7.1	0.9	2.00	78	8.4
				6-12	4.5	1.60	6.8	2.1	0.94	62	5.2
				12-24	4.9	NA	17.5	11.8	0.93	152	3.3
				24-36	5.3	NA	19.6	12.2	0.90	130	3.5
10	2.5	100	15	0-3	6.1	5.00	16.4	0.9	1.91	104	9.8
				3-6	5.1	2.70	9.3	1.2	1.22	66	5.4
				6-12	4.6	1.60	7.3	2.9	0.94	66	4.6
				12-24	5.4	NA	18.9	11.3	0.80	146	1.9
				24-36	5.6	NA	NA	NA	0.81	NA	1.1
50	2.5	100	15	0-3	6.6	5.00	26.6	1.0	1.70	124	67.0
				3-6	5.7	4.50	15.9	1.2	1.26	74	23.6
				6-12	4.8	1.70	8.6	2.5	1.06	62	6.2
				12-24	4.7	NA	18.2	12.6	0.84	170	1.6
				24-36	5.5	NA	18.2	11.3	0.77	136	1.9
0	0	0	0	0-3	4.3	2.77	4.7	1.0	1.82	68	5.5
				3-6	4.4	1.80	4.7	1.2	0.78	53	3.6
				6-12	4.6	1.03	6.4	3.0	0.85	77	2.8
				12-24	5.0	0.76	17.3	11.9	0.67	146	2.8
				24-36	5.5	0.54	21.2	13.8	0.73	118	2.1

NA = not analyzed.

Table 11. Exchangeable bases, pH, and soluble salt content of soil profile samples collected in May, 1974.

Waste application (T/A)	Fertilizer application			Soil depth (inches)	pH	Soluble salts (mmhos/cm)	Ca - - -meq/100 g-	Mg - - -	Na - - -	K - - -	NH ₄ -N ppm - -
	Lime (T/A)	P (lbs/A)	S (lbs/A)								
0	2.5	25	15	0-3	6.0	1.10	10.5	0.8	0.60	58	13.0
				3-6	5.5	0.85	6.4	1.1	0.70	42	7.1
				6-12	4.9	0.65	7.9	4.6	0.77	66	3.3
				12-24	5.2	0.60	20.3	12.6	0.77	96	1.1
				24-36	5.5	0.70	18.9	12.6	0.63	86	3.0
5	2.5	25	15	0-3	6.0	0.40	14.3	0.7	0.59	64	9.7
				3-6	5.2	0.30	6.6	0.9	0.65	46	5.7
				6-12	4.8	0.55	6.6	4.6	0.69	48	6.2
				12-24	5.1	0.70	16.8	13.0	0.69	96	7.1
				24-36	5.5	0.60	18.9	14.3	0.57	92	3.8
10	2.5	25	15	0-3	6.2	0.50	12.3	0.7	0.43	72	18.4
				3-6	5.6	0.43	8.6	0.9	0.56	56	11.1
				6-12	4.9	0.40	8.4	3.8	0.72	64	6.2
				12-24	5.2	0.50	18.9	12.2	0.82	114	7.6
				24-36	5.5	0.70	19.6	13.0	0.64	70	5.2
25	2.5	25	15	0-3	6.4	0.70	14.3	0.7	0.53	54	4.6
				3-6	5.8	0.72	9.8	1.5	0.64	58	3.3
				6-12	5.0	0.49	8.9	3.4	0.75	76	2.4
				12-24	5.1	1.00	18.9	12.2	0.87	148	4.3
				24-36	5.5	0.75	21.0	13.4	0.64	140	1.6
50	2.5	25	15	0-3	6.8	1.10	23.1	0.9	0.61	78	5.2
				3-6	6.0	0.82	12.0	0.8	0.61	62	0.8
				6-12	4.9	0.80	9.3	3.8	0.72	78	0.0
				12-24	5.1	0.80	21.0	12.2	0.70	150	0.0
				24-36	5.6	0.65	21.7	13.9	0.63	150	0.0

Table 11. Continued.

Waste application (T/A)	Fertilizer application			Soil depth (inches)	pH	Soluble salts (mmhos/cm)	Ca	Mg	Na	K	NH ₄ -N
	Lime (T/A)	P (lbs/A)	S (lbs/A)				- - -meq/100 g-	- - -	- - -	- - ppm	- -
0	0	25	15	0-3	5.1	0.55	5.7	0.8	0.58	60	18.2
				3-6	5.1	0.50	5.4	1.5	0.70	56	4.1
				6-12	4.9	0.70	7.5	4.2	0.77	72	3.5
				12-24	5.2	0.75	17.5	12.2	0.82	142	3.8
				24-36	5.6	0.70	19.6	13.0	0.70	122	2.4
25	0	25	15	0-3	6.4	0.90	12.7	0.8	0.58	66	11.0
				3-6	5.6	0.65	8.8	1.1	0.69	68	4.6
				6-12	5.0	0.70	9.3	4.6	0.76	82	2.4
				12-24	5.2	0.80	16.8	12.2	0.85	92	2.2
				24-36	5.5	0.80	19.6	12.6	0.63	126	2.4
0	2.5	25	0	0-3	6.0	0.55	10.7	0.8	0.58	70	4.9
				3-6	5.5	0.50	6.8	1.0	0.69	60	2.2
				6-12	4.9	0.75	8.2	4.2	0.76	82	4.6
				12-24	5.3	0.75	18.9	13.0	0.83	158	2.7
				24-36	5.7	0.75	21.7	13.0	0.64	128	1.1
10	2.5	25	0	0-3	6.3	0.60	14.3	0.7	0.50	68	5.4
				3-6	5.6	0.50	7.7	1.0	0.62	54	0.0
				6-12	5.0	0.70	7.5	2.9	0.75	72	0.0
				12-24	5.1	0.95	17.0	11.3	0.83	148	0.0
				24-36	5.6	0.90	19.6	12.2	0.65	136	0.0
0	2.5	100	15	0-3	5.8	0.60	10.5	0.7	0.50	168	5.7
				3-6	5.3	0.40	6.6	0.8	0.50	46	3.8
				6-12	5.0	0.45	8.2	3.4	0.70	74	0.8
				12-24	5.3	0.65	18.2	12.2	0.71	92	0.3
				24-36	5.6	0.60	19.6	12.6	0.58	132	0.8

Table 11. Continued.

Waste application (T/A)	Fertilizer application			Soil depth (inches)	pH	Soluble salts (mmhos/cm)	Ca	Mg	Na	K	NH ₄ -N
	Lime (T/A)	P (lbs/A)	S (lbs/A)				- - -meq/100 g-	- - -	- - -	- - ppm	- -
10	2.5	100	15	0-3	6.2	0.70	13.6	0.8	0.59	68	2.7
				3-6	5.5	0.70	8.4	1.1	0.64	58	1.4
				6-12	4.9	0.75	7.7	3.4	0.74	74	0.3
				12-24	5.2	0.80	18.2	12.2	0.82	156	0.0
				24-36	5.5	0.65	18.9	12.6	0.64	88	0.0
50	2.5	100	15	0-3	6.8	1.70	21.7	0.8	0.70	58	5.4
				3-6	6.0	1.50	12.3	1.3	0.73	52	2.7
				6-12	5.1	1.45	8.9	3.4	0.80	54	2.4
				12-24	5.2	1.35	18.2	11.8	0.84	138	0.5
				24-36	5.6	1.10	19.6	13.0	0.68	122	0.0
100	2.5	25	15	0-3	6.5	0.70	14.8	0.7	0.54	50	3.8
				3-6	5.9	0.70	9.1	0.7	0.57	46	2.7
				6-12	5.2	0.47	5.9	2.1	0.57	34	6.5
				12-24	5.2	0.80	16.1	10.5	0.81	74	1.9
				24-36	5.5	0.80	19.6	12.6	0.65	82	1.1

The increase in the $\text{NH}_4\text{-N}$ content of the soil with waste application was less pronounced below the 6 inch depth. The $\text{NH}_4\text{-N}$ extracted by KCl did not correlate well with the amount of $\text{NH}_4\text{-N}$ with the waste product applied, suggesting that the ammonium applied: was not readily extractable, had been nitrified and leached out of the profile, or had been volatilized. For example, if 10 tons of the waste product, containing 1200 ppm extractable $\text{NH}_4\text{-N}$, were added per acre, the $\text{NH}_4\text{-N}$ concentration in the soil should increase 48 ppm, assuming no $\text{NH}_4\text{-N}$ loss. Since in no case did such $\text{NH}_4\text{-N}$ concentration increases occur, N losses did occur.

Soil samples collected in the spring showed no definite correlation between waste product application rate and extractable $\text{NH}_4\text{-N}$ (Table 11). Ammonium-N levels appeared to be low throughout the profile, suggesting a possible nitrogen deficiency.

Nitrate nitrogen levels did not correlate with waste application rates in either the spring or fall soil samples, although $\text{NO}_3\text{-N}$ levels were much higher in the fall than in the following spring (Tables 14 and 15). Nitrate-nitrogen could be easily leached, denitrified, or used by the ryegrass crop. The $\text{NO}_3\text{-N}$ level in the soil appeared to decrease with increased waste application. An increase in the soil ammonium level and pH is usually associated with increased $\text{NO}_3\text{-N}$ levels. One possible explanation is that the waste product reduced growth of the

Nitrosomonas or Nitrobacter bacteria required to convert NH_4^- to NO_3^- -N.

Iron

Extractable iron levels (Tables 12 and 13) decreased with waste application rates in the upper 6 inches of soils collected in the spring and fall. Control plots in the fall contained 92 ppm extractable Fe in the surface 3 inches of soil, while the plots receiving 50 tons/acre waste contained 62 ppm available Fe. The decrease in the extractable Fe content of the soil in the spring was not pronounced until 50 ton/acre waste were applied, dropping from 234 ppm in the control plots to 98 ppm. This trend correlated with the pH increase which decreases iron solubility. The spring soil samples contained about 2 to 2.5 times more DTPA-extractable iron than the fall samples in the upper 6 inches of the soil profile. This increase occurred despite the increase in pH with time, suggesting that the reducing conditions imposed by the perched water table present during the winter increased Fe availability. Reducing conditions favor the production of soluble ferrous ions.

Aluminum

Ammonium acetate (pH 4.8) extractable Al (Table 12) was not significantly affected by waste application rates in the soils sampled in the fall. Extractable Al levels ranged from 50 to 122 ppm through

the upper 6 inches of the soil profile, without regard to treatment. Similar disparities were seen at soil depths greater than six inches, although extractable Al levels decreased with soil depth.

Manganese

The DTPA-extractable Mn in the upper 6 inches of the soil profile decreased with waste application in soils sampled in the spring and fall, ranging from 135 to 32 ppm in the upper 3 inches of fall samples (Tables 12 and 13). As with Fe, the Mn decrease correlated with an increase in soil pH. The spring soil samples contained considerably more extractable Mn than the fall samples (levels ranged from 265 to 74 ppm in the upper 3 inches), in spite of the pH increase. Again, it appeared that the reducing conditions imposed by the perched winter groundwater converted some insoluble tetravalent and trivalent Mn compounds to soluble divalent Mn ions. The waste product did not significantly affect the extractable Mn levels below a soil depth of 6 inches.

Chromium

The DTPA extractable Cr content of the soil was below the sensitivity of the atomic absorption spectrophotometer for both the waste and soil samples, indicating an extractable Cr concentration less than 1.0 ppm. This may have been due to actual low levels of extractable Cr, or to the inability of DTPA to complex Cr. Because Cr is generally found as an insoluble hydroxide in the soil, extractable

Cr levels should be low.

Zinc

The DTPA-extractable Zn levels in the upper six inches of the soil increased with waste application for both the fall and spring soil samples (Tables 12 and 13). The Zn levels in the fall were generally greater than those found in the spring. Zinc levels observed in the surface 6 inches of the soil (0.94 to 8.45 ppm) would not cause a Zn deficiency (<0.5 ppm) nor were the levels sufficiently high to induce Zn toxicity. Extractable Zn levels were independent of waste treatment at soil depths greater than 6 inches.

Nickel

In the soils sampled in the fall, DTPA-extractable Ni increased with waste application for the surface 6 inches of the soil profile, ranging from 0.20 to 2.38 ppm (Table 12). At depths greater than 6 inches, no discernible correlation existed between waste application and extractable Ni. For the spring soil samples, similar, but less distinct trends were shown (Table 13); however, the extractable Ni was generally higher than in the fall. The extractable Ni level did not exceed levels toxic to crops even with the largest waste application.

Table 12. Metal content of soil profile samples collected in August and September, 1973.

Waste application (T/A)	Fertilizer application			Soil depth (inches)	Ni	Zr	Hf	Pt	Al	Fe	Mn	Zn	Cu
	Lime (T/A)	P (lbs/A)	S (lbs/A)										
0	2.5	25	15	0-3	0.48	1130	<100	<10	107.5	94	95	2.50	0.80
				3-6	0.54	1320	<100	23	122.5	142	123	1.87	0.90
				6-12	0.44	610	<100	19	121.3	104	135	1.38	0.85
				12-24	0.50	550	<100	21	122.5	41	47	0.78	0.60
				24-36	1.04	420	<100	15	82.5	35	37.5	1.10	0.45
5	2.5	25	15	0-3	0.54	2290	<100	18	77.5	89	105	1.70	0.80
				3-6	0.50	1180	<100	19	102.5	103	147	1.58	1.10
				6-12	0.56	710	<100	17	108.5	90	111	1.02	1.05
				12-24	0.56	1040	<100	15	90.0	33	20.5	0.74	1.10
				24-36	0.98	720	<100	18	62.5	28	34.5	0.95	0.85
10	2.5	25	15	0-3	0.60	3160	<100	27	92.5	71	77	1.46	0.95
				3-6	0.52	2440	150	17	97.5	121	100	1.45	1.15
				6-12	0.48	1270	<100	17	90.0	83	84.5	0.81	1.30
				12-24	0.54	790	<100	13	97.5	35	15	0.38	0.90
				24-36	1.34	430	<100	14	65.0	NA	22.5	0.45	0.65
25	2.5	25	15	0-3	0.82	6100	150	35	110.0	78	51	2.40	0.90
				3-6	0.54	5200	<100	50	95.0	114	125	1.96	1.10
				6-12	0.44	1780	340	18	77.5	78	100	0.79	1.15
				12-24	0.62	1380	<100	18	47.5	34	33	0.54	0.95
				24-36	1.34	580	<100	13	85.0	28	34	0.68	0.80
50	2.5	25	15	0-3	1.72	10200	260	75	107.5	62	42	4.90	1.15
				3-6	0.88	3500	<100	36	95.0	130	124	2.90	1.00
				6-12	0.60	1010	<100	21	80.0	84	98	0.89	1.10
				12-24	0.70	880	<100	15	47.5	31	21.5	0.40	0.75
				24-36	1.58	630	150	12	52.5	29	29	0.58	0.70

Table 12. Continued.

Waste application (T/A)	Fertilizer application			Soil depth (inches)	Ni	Zr	Hf	Pb	Al	Fe	Mn	Zn	Cu
	Lime (T/A)	P (lbs/A)	S (lbs/A)										
100	2.5	25	15	0-3	2.38	NA	NA	NA	90.0	52	32	8.45	1.50
				3-6	1.58	NA	NA	NA	72.5	66	53	5.30	1.30
				6-12	0.74	NA	NA	NA	90.0	90	107.5	1.64	0.90
				12-24	0.64	NA	NA	NA	82.5	38	40	0.50	0.60
				24-36	1.20	NA	NA	NA	67.5	34	27	0.54	0.45
0	0	25	15	0-3	0.22	760	<100	14	85.0	74	135	1.50	0.90
				3-6	NA	610	<100	15	97.5	132	169	1.32	1.25
				6-12	0.32	620	<100	14	85.0	88	99.5	0.74	0.80
				12-24	0.44	500	<100	15	62.5	23	30.5	0.53	1.00
				24-36	0.72	460	<100	15	42.5	19	32.5	0.54	0.70
25	0	25	15	0-3	0.64	4440	<100	70	75.0	62	76	3.50	1.05
				3-6	0.74	2520	<100	32	87.5	128	60	2.80	0.90
				6-12	0.50	590	<100	14	80.0	84	103.5	1.23	0.75
				12-24	0.60	960	<100	17	60.0	25	29.5	0.67	0.95
				24-36	1.54	1620	160	17	42.5	30	25	0.58	0.45
0	2.5	25	0	0-3	0.20	NA	NA	NA	52.5	68	101	0.95	1.00
				3-6	0.30	NA	NA	NA	67.5	104	142	1.33	1.30
				6-12	0.42	NA	NA	NA	72.5	44	69	0.90	1.35
				12-24	0.38	NA	NA	NA	70.0	25	23.5	0.50	0.90
				24-36	0.80	NA	NA	NA	42.5	22	33.5	0.55	0.70
10	2.5	25	0	0-3	0.32	NA	NA	NA	72.5	62	75	1.68	1.00
				3-6	0.34	NA	NA	NA	80.0	112	125	1.48	1.15
				6-12	0.34	NA	NA	NA	85.0	67	93	0.69	1.25
				12-24	0.50	NA	NA	NA	72.5	28	23	0.48	1.10
				24-36	1.24	NA	NA	NA	42.5	21	30.5	0.65	0.90

Table 12. Continued.

Waste application (T/A)	Fertilizer application			Soil depth (inches)	Ni	Zr	Hf	Pb	Al ppm	Fe	Mn	Zn	Cu
	Lime (T/A)	P (lbs/A)	S (lbs/A)										
0	2.5	100	15	0-3	0.26	NA	NA	NA	50.0	84	110	1.05	1.00
				3-6	0.34	NA	NA	NA	67.5	126	48	1.20	1.25
				6-12	0.42	NA	NA	NA	85.0	84	78	0.66	1.20
				12-24	0.54	NA	NA	NA	70.0	30	24.5	0.37	0.80
				24-36	1.30	NA	NA	NA	47.5	25	34	0.60	0.85
10	2.5	100	15	0-3	0.52	NA	NA	NA	70.0	80	74	1.69	0.90
				3-6	0.48	NA	NA	NA	77.5	113	130	1.33	1.10
				6-12	0.36	NA	NA	NA	87.5	68	97	0.81	0.75
				12-24	0.52	NA	NA	NA	65.0	24	24	0.45	0.75
				24-36	0.88	NA	NA	NA	50.0	18	29	0.54	1.10
50	2.5	100	15	0-3	1.22	NA	NA	NA	72.5	41	52	4.90	1.10
				3-6	0.80	NA	NA	NA	75.0	91	152	3.30	1.10
				6-12	0.56	NA	NA	NA	72.5	84	108.5	1.22	0.80
				12-24	0.70	NA	NA	NA	70.0	29	37.5	0.35	0.55
				24-36	1.08	NA	NA	NA	45.0	27	41.5	0.54	0.55
0	0	0	0	0-3	NA	885	<100	14	120.3	NA	161	2.09	1.05
				3-6	NA	910	<100	13	119.3	NA	150	1.76	1.18
				6-12	NA	1130	<100	17	108.3	NA	76.6	0.79	0.98
				12-24	NA	935	<100	15	89.2	NA	32.6	0.64	0.71
				24-36	NA	605	<100	12	63.3	NA	36.4	0.78	0.72

NA = not analyzed.

Table 13. Metal content of soil profile samples collected in May, 1974.

Waste application (T/A)	Fertilizer application			Soil depth (inches)	Ni	Zr	Hf	Pb	Fe	Mn	Zn	Cu
	Lime (T/A)	P (lbs/A)	S (lbs/A)									
0	2.5	25	15	0-3	2.00	530	< 100	15	234.0	282	0.88	1.0
				3-6	1.20	460	< 100	14	286.0	234	0.88	0.7
				6-12	1.20	790	< 100	22	188.0	156	0.60	1.0
				12-24	NA	880	< 100	20	39.6	39	0.72	0.7
				24-36	1.10	870	< 100	15	33.0	36	0.46	0.6
5	2.5	25	15	0-3	NA	2190	< 100	18	265.0	252	1.28	1.0
				3-6	0.64	880	< 100	16	275.0	222	1.02	1.0
				6-12	NA	580	< 100	15	146.0	144	0.62	1.0
				12-24	0.44	510	< 100	17	40.2	30	0.34	0.5
				24-36	1.32	470	< 100	14	32.4	45	0.64	0.4
10	2.5	25	15	0-3	NA	2700	< 100	32	214.0	270	1.76	1.3
				3-6	0.70	910	< 100	10	214.0	234	1.04	0.9
				6-12	0.98	500	< 100	20	186.0	162	1.26	1.3
				12-24	0.66	440	< 100	15	36.6	27	0.88	0.6
				24-36	1.14	420	< 100	15	28.8	33	0.90	0.6
25	2.5	25	15	0-3	2.06	4540	140	33	204.0	264	3.60	1.0
				3-6	0.90	1620	< 100	24	150.0	162	1.66	1.0
				6-12	0.58	640	< 100	18	96.0	132	0.86	0.9
				12-24	0.56	450	< 100	14	34.8	33	0.34	0.7
				24-36	1.18	490	< 100	15	29.4	33	0.46	0.6
50	2.5	25	15	0-3	1.90	14000	290	72	98.0	78	3.96	1.3
				3-6	1.00	7200	490	40	148.0	150	1.62	1.0
				6-12	0.52	930	< 100	20	86.0	132	0.82	0.8
				12-24	0.54	950	< 100	15	29.4	18	1.98	0.4
				24-36	1.14	950	< 100	14	24.6	21	0.64	0.5

Table 13. Continued.

Waste application (T/A)	Fertilizer application			Soil depth (inches)	Ni	Zr	Hf	Pb	Fe	Mn	Zn	Cu
	Lime	P	S									
	(T/A)	(lbs/A)	(lbs/A)									
----- ppm -----												
100	2.5	25	15	0-3	0.82	NA	NA	NA	90.0	84	1.54	1.1
				3-6	0.64	NA	NA	NA	150.0	144	1.28	1.1
				6-12	0.38	NA	NA	NA	80.0	126	0.82	0.6
				12-24	0.78	NA	NA	NA	23.4	27	0.74	0.6
				24-36	1.00	NA	NA	NA	22.2	30	0.68	0.5
0	0	25	15	0-3	0.92	690	<100	14	198.0	174	1.16	0.9
				3-6	1.18	490	<100	13	204.0	204	1.52	1.0
				6-12	1.16	810	<100	17	152.0	132	0.92	0.9
				12-24	0.90	430	<100	19	51.0	45	0.72	0.6
				24-36	1.38	610	<100	13	40.8	39	0.70	0.6
25	0	25	15	0-3	1.12	7800	550	53	94.0	120	2.52	1.0
				3-6	1.40	1760	110	18	170.0	204	1.86	1.0
				6-12	1.20	710	110	26	80.0	120	0.90	0.8
				12-24	2.08	590	<100	16	48.8	48	0.74	0.5
				24-36	1.70	470	<100	18	48.0	54	0.96	0.7
0	2.5	25	0	0-3	0.28	NA	NA	NA	136.0	162	0.92	1.0
				3-6	0.32	NA	NA	NA	194.0	204	1.16	1.0
				6-12	0.68	NA	NA	NA	92.0	120	1.08	0.9
				12-24	0.68	NA	NA	NA	37.8	30	0.68	0.6
				24-36	1.02	NA	NA	NA	36.0	39	0.72	0.6
10	2.5	25	0	0-3	0.50	NA	NA	NA	126.0	138	1.74	1.1
				3-6	0.56	NA	NA	NA	158.0	198	1.10	1.0
				6-12	0.44	NA	NA	NA	90.0	108	1.08	0.8
				12-24	0.56	NA	NA	NA	38.4	27	1.22	0.6
				24-36	1.50	NA	NA	NA	29.4	27	1.14	0.6

Table 13. Continued.

Waste application (T/A)	Fertilizer application			Soil depth (inches)	Ni	Zr	Hf	Pb	Fe	Mn	Zn	Cu
	Lime (T/A)	P (lbs/A)	S (lbs/A)									
0	2.5	100	15	0-3	NA	NA	NA	NA	176.0	120	0.96	1.0
				3-6	0.52	NA	NA	NA	196.0	144	1.42	1.0
				6-12	0.42	NA	NA	NA	80.0	96	0.84	0.8
				12-24	0.54	NA	NA	NA	30.0	24	0.90	0.6
				24-36	0.98	NA	NA	NA	33.0	27	1.32	0.6
10	2.5	100	15	0-3	0.74	NA	NA	NA	166.0	144	1.36	1.2
				3-6	0.56	NA	NA	NA	367.0	186	1.36	1.0
				6-12	0.60	NA	NA	NA	136.0	126	0.84	0.8
				12-24	0.60	NA	NA	NA	48.0	36	0.70	0.5
				24-36	1.00	NA	NA	NA	34.8	39	1.06	0.5
50	2.5	100	15	0-3	1.84	NA	NA	NA	104.0	108	3.96	1.5
				3-6	0.76	NA	NA	NA	144.0	102	1.76	1.1
				6-12	0.52	NA	NA	NA	118.0	138	1.16	0.9
				12-24	0.74	NA	NA	NA	47.4	21	0.82	0.5
				24-36	0.96	NA	NA	NA	28.8	24	1.36	0.6

NA = not analyzed.

Copper

Extractable Cu levels were not affected by waste application ranging from 0.8 to 1.5 ppm (Table 12 and 13). Copper levels did not vary significantly between sample periods. At no time did Cu levels approach values that could be considered toxic. While reliable soil tests correlating Cu levels to deficiency symptoms have not been developed (Cox and Kamprath, 1972), no evidence of Cu deficiency in the soil was found.

Zirconium, Hafnium and Lead

Total Zr and Hf levels increased in the upper 6 inches of the soil profile with waste application, ranging from 760 to 10,200 ppm in the upper 3 inches of the soil profile for Zr and from <100 to 260 ppm for Hf (Tables 12 and 13). Because the waste contained 22 percent Zr and less than 0.3 percent Hf, the rate of increase for Zr was considerably greater than for Hf. Both elements are essentially insoluble in the soil solution, so extractable Zr and Hf levels would be low. No reliable test for plant availability of these metals now exists, and no analysis for the "extractable" portion of these metals was performed. There was no apparent difference in Zr or Hf contents of the soil samples tested over time.

Total Pb levels in the soil increased with waste application, ranging from <10 to 75 ppm in the upper 6 inches of the soil profile, but did not appear to pose a toxicity problem to plants (Tables 12 and 13).

No change in total soil Pb levels was seen between samples collected in the spring and fall.

Phosphorus

The available P levels in the soils sampled in the fall decreased in the upper 6 inches of the soil profile with increasing waste application (Table 14). While control plots (treated with 25 lb P/acre) contained 33.5 ppm available P in the upper 3 inches, plots treated with the same amount of P and 25 ton/acre waste contained only 15 to 24 ppm P. With waste added at 50 ton/acre rate the available P levels were 5.0 ppm, or less than the unfertilized soil. Soil available P levels were not affected below the 6 inch soil depth, where available P contents were generally less than 12 ppm. The additional phosphorus fertilizer ameliorated this problem to some extent, but at waste application rates in excess of 10 ton/acre, P levels indicative of possible plant deficiency (i. e., less than 30 ppm P) appeared. Previous research (Volk, 1971) indicated that the waste product fixed P as a calcium fluoroapatite or calcium hydroxyphosphate compound. The possible P deficiency observed in this project was only reduced in severity rather than eliminated by addition of the phosphorus fertilizers. To reduce the P fixation, the fertilizer P could be banded beside the seed row at planting, rather than broadcast and tilled into the soil during seed-bed preparation. Banding should reduce the surface area of the fertilizer in contact with the waste, reduce fertilizer application rates, and increase the readily available soil P supply. Without proper

Table 14. Anion content of soil profile samples collected in August and September, 1973.

Waste application (T/A)	Fertilizer application			Soil depth (inches)	P	S	F	NC ₃ -N
	Lime (T/A)	P (lbs/A)	S (lbs/A)		- - - - -	- - - - - ppm	- - - - -	- - - - -
0	2.5	25	15	0-3	33.5	86.3	19.7	103.6
				3-6	23.5	45.6	9.4	103.9
				6-12	8.8	38.7	3.2	30.7
				12-24	0	33.4	2.7	10.9
				24-36	0	26.5	3.4	4.6
5	2.5	25	15	0-3	38.0	105.9	13.9	81.4
				3-6	18.0	81.5	3.8	6.5
				6-12	6.0	34.7	1.8	5.4
				12-24	0	31.2	2.5	11.7
				24-36	0	37.1	3.6	4.3
10	2.5	25	15	0-3	23.8	135.3	3.4	96.6
				3-6	18.5	96.1	8.6	60.5
				6-12	10.5	38.8	< 2.0	19.0
				12-24	0	37.6	1.8	6.2
				24-36	1.0	31.8	3.1	2.4
25	2.5	25	15	0-3	15.5	314.7	32.0	70.5
				3-6	24.2	140.0	19.0	54.0
				6-12	3.5	37.1	2.2	16.3
				12-24	1.0	37.1	2.2	3.0
				24-36	0	30.0	3.2	3.0
50	2.5	25	15	0-3	5.0	343.4	33.3	62.1
				3-6	18.0	274.3	25.5	48.0
				6-12	8.5	47.1	3.0	14.9
				12-24	1.0	40.0	3.4	6.0
				24-36	0	34.7	3.4	3.8
100	2.5	25	15	0-3	NA	442.9	40.0	176.1
				3-6	NA	356.6	48.0	133.2
				6-12	NA	131.3	27.2	38.0
				12-24	NA	87.4	6.6	10.9
				24-36	NA	70.9	8.6	8.7
0	0	25	15	0-3	22.5	65.7	1.8	45.0
				3-6	11.7	49.2	< 1.7	34.5
				6-12	13.5	24.7	< 1.7	19.8
				12-24	1.0	28.5	2.0	12.5
				24-36	1.5	27.4	3.1	7.1

Table 14. Continued.

Waste application (T/A)	Fertilizer application			Soil depth (inches)	P	S	F	NO ₃ -N
	Lime (T/A)	P (lbs/A)	S (lbs/A)		- - - - -	- - - - - ppm	- - - - -	- - - - -
25	0	25	15	0-3	23.7	203.4	34.0	52.4
				3-6	20.5	186.6	19.0	49.9
				6-12	12.3	54.6	2.9	18.5
				12-24	3.0	37.3	3.3	9.0
				24-36	4.0	31.8	3.7	3.3
0	2.5	25	0	0-3	35.5	61.8	2.4	75.7
				3-6	30.5	48.8	< 1.7	48.3
				6-12	11.0	32.9	< 1.7	19.3
				12-24	2.5	37.6	2.0	4.1
				24-36	0	34.1	3.3	1.9
10	2.5	25	0	0-3	29.0	129.4	2.3	95.2
				3-6	23.7	81.5	5.6	59.7
				6-12	10.0	35.3	< 1.7	16.3
				12-24	4.0	35.3	2.0	2.7
				24-36	4.0	30.6	3.1	0.5
0	2.5	100	15	0-3	46.5	80.5	4.0	79.0
				3-6	34.4	42.4	< 1.7	48.3
				6-12	4.5	31.8	< 1.7	21.7
				12-24	0	37.1	2.2	11.7
				24-36	0	37.6	3.3	8.1
10	2.5	100	15	0-3	39.0	142.4	24.0	98.8
				3-6	22.5	83.9	9.2	57.2
				6-12	4.5	37.6	< 1.7	20.6
				12-24	0	35.3	2.3	11.1
				24-36	0	35.3	3.0	5.7
50	2.5	100	15	0-3	10.2	166.2	35.0	61.6
				3-6	25.8	134.4	26.0	49.1
				6-12	12.5	80.5	3.0	16.3
				12-24	1.0	31.8	2.7	13.6
				24-36	0	31.8	3.6	7.3
0	0	0	0	0-3	14.0	46.4	NA	0.6
				3-6	10.3	27.0	NA	2.4
				6-12	3.7	28.7	NA	5.3
				12-24	0.5	31.2	NA	6.0
				24-36	1.5	23.8	NA	3.4

fertilizer management, waste application rates to soils intended for general agricultural use should not exceed 10 tons per acre.

The available P levels in the soil sampled in the spring were similar to those found in unfertilized, untreated soil, with the exception of those plots which received the high P fertilizer application (Table 15). In that case, soil P levels were somewhat higher, but still considerably less than those levels found in the fall soil samples. Available soil P levels appeared to move rapidly toward equilibrium with fixed P at available P levels near those found in undisturbed soil unless high waste applications (> 25 ton/acre) were made.

Sulfur

Extractable S levels in the upper 12 inches of the soil profile increased with waste application (Table 14). A five-fold increase in extractable S was observed between plots with no waste applied and plots with a 50 ton/acre waste application. At the 100 ton/acre application rate, the extractable S content increased throughout the soil profile. In the spring the extractable S content was generally less than half of that found in the preceding fall (Table 15). Elevated S levels were found throughout the lower soil profile at the 100 ton/acre waste application rate, although levels in the surface 6 inches had dropped to 71 ppm S or less. The reduced soil S content was expected, since the sulfate ion is subject to leaching, runoff losses, and plant uptake. The

Table 15. Anion content of soil profile samples collected in May, 1974.

Waste application (T/A)	Fertilizer application			Soil depth (inches)	P	S	F	NO ₃ -N
	Lime (T/A)	P (lbs/A)	S (lbs/A)		ppm			
0	2.5	25	15	0-3	14.7	23.5	2.0	10.9
				3-6	17.6	22.9	< 2.0	3.5
				6-12	5.8	31.8	< 2.0	2.7
				12-24	0.3	40.0	2.2	2.4
				24-36	1.5	27.1	3.2	1.4
5	2.5	25	15	0-3	14.5	26.5	15.5	9.5
				3-6	15.0	26.5	3.2	3.0
				6-12	6.8	35.3	< 2.0	2.2
				12-24	0.5	30.0	1.8	3.5
				24-36	1.3	27.1	2.6	4.1
10	2.5	25	15	0-3	12.6	26.5	17.3	27.1
				3-6	11.9	19.4	14.1	6.8
				6-12	4.4	42.9	< 2.0	3.0
				12-24	0.9	42.9	1.9	4.3
				24-36	1.5	38.1	2.2	2.7
25	2.5	25	15	0-3	13.9	55.9	25.5	3.0
				3-6	16.7	44.7	14.2	1.4
				6-12	9.9	57.1	2.0	1.9
				12-24	0.7	52.2	1.9	4.6
				24-36	1.3	38.8	2.9	5.7
50	2.5	25	15	0-3	3.0	132.4	34.0	19.5
				3-6	16.2	81.5	29.4	4.1
				6-12	7.9	91.2	3.2	1.4
				12-24	1.2	39.4	2.4	0.8
				24-36	0.2	35.3	3.5	1.0
100	2.5	25	15	0-3	16.7	70.9	29.3	4.6
				3-6	15.9	54.4	24.5	1.9
				6-12	7.2	76.4	1.8	4.9
				12-24	0.5	65.4	2.3	3.3
				24-36	0.5	59.9	3.6	3.5
0	0	25	15	0-3	19.0	19.0	2.8	11.4
				3-6	15.8	20.3	< 1.7	3.8
				6-12	7.0	28.0	< 1.7	2.2
				12-24	0	32.4	2.2	3.5
				24-36	0	22.5	3.4	3.0

Table 15. Continued.

Waste application (T/A)	Fertilizer application			Soil depth (inches)	P	S	F	NO ₃ -N
	Lime (T/A)	P (lbs/A)	S (lbs/A)		- - - -	- - - - ppm	- - - -	- - - -
25	0	25	15	0-3	11.4	54.7	40.0	9.8
				3-6	18.9	57.1	31.0	2.4
				6-12	4.8	52.2	2.9	1.1
				12-24	1.2	33.5	2.9	1.9
				24-36	1.0	36.8	4.4	1.4
0	2.5	25	0	0-3	11.3	32.4	1.8	8.7
				3-6	6.8	16.5	< 1.7	1.6
				6-12	4.0	28.2	< 1.7	2.7
				12-24	0.8	34.7	1.8	1.1
				24-36	1.0	25.9	3.1	1.6
10	2.5	25	0	0-3	13.5	23.5	20.0	5.4
				3-6	13.2	24.9	10.0	3.3
				6-12	7.0	42.9	< 1.7	0.0
				12-24	1.2	38.8	2.0	1.1
				24-36	1.5	30.6	3.3	0.0
0	2.5	100	15	0-3	32.8	23.5	3.1	9.0
				3-6	23.5	14.1	1.7	3.3
				6-12	5.2	28.5	< 1.7	1.6
				12-24	0	37.1	2.0	1.9
				24-36	1.5	29.4	3.0	1.6
10	2.5	100	15	0-3	20.5	55.9	26.0	1.6
				3-6	15.8	29.4	11.0	1.6
				6-12	8.6	41.2	1.8	0.5
				12-24	1.0	35.3	2.6	0.3
				24-36	1.5	29.4	NA	0.0
50	2.5	100	15	0-3	13.4	164.3	39.0	13.0
				3-6	14.9	101.4	39.0	0.0
				6-12	12.8	74.1	5.1	0.0
				12-24	0.8	54.6	3.4	1.4
				24-36	1.0	32.4	5.1	3.8

application of 10 ton/acre waste increased extractable S levels as high or higher than those levels attained by adding 15 lbs S/acre as CaSO_4 . In the upper 3 inches of the control plots, the extractable S was 86 ppm, while similar plots lacking S fertilizer contained 62 ppm extractable S. Following application of 10 tons of waste and no CaSO_4 , extractable S measured 129 ppm.

Fluoride

Soil ammonium acetate (pH 7.0) extractable fluoride content increased with waste application in both the spring and fall soil samples (Tables 14 and 15). In the fall, the fluoride increase was seen throughout the soil profile in plots which received a 100 ton/acre waste application. Extractable fluoride levels were generally less than 2.0 ppm for soils which received no waste. The addition of 50 ton/acre waste product increased the extractable fluoride level to 40 to 50 ppm, while lesser applications resulted in intermediate increases. No appreciable decrease in fluoride levels occurred from fall to spring. The soil fluoride levels appeared to be within the normal range for soils, despite the wide disparity between the values observed. Extractable fluoride levels in the untreated Dayton soil appeared quite low when compared with data on other fine-textured soils (Hommik, 1953). Since plant toxicities from fluoride in the soil are rare and occur only on highly acidic soils, the levels of extractable

fluoride obtained do not appear to pose a threat to general crop production.

Summary

Addition of the waste product increased the pH, soluble salts, extractable Ca, Mg, NH_4 -N, Zn, Ni, S, and F of the Dayton silt soil. The waste product served as a fertilizer source for Ca, N, and S. The extractable Fe, Mn, and P in the soil decreased with increased waste application. The decrease in P availability could be significant for sensitive crops. Extractable Na, K, NO_3 -N, Al, and Cu levels were not affected by waste applications.

Extractable Mg, Na, K, NH_4 , NO_3 , P, S, and Zn and soluble salts levels decreased over time while exchangeable Fe, Mn, and Ni increased. Total Zr, Hf, and Pb levels in the soil increased with waste application.

Soil Physical Properties and Waste Application

Water percolation rates increased with waste application, as measured in leaching columns (Figures 3 and 4). All columns were maintained in a ponded state, simulating soil conditions found in the Dayton soil during the winter rainy season. Over the first 10 to 12 days of leaching, no definite correlation between percolation rate and waste application was seen (Figure 3). (Percolation rates were measured in terms of leachate output, rather than the amount of water entering the soil body.) The variation indicated here appeared to be

a function of soil column preparation techniques more than any other factor. After a relatively stable leaching rate was attained (Figure 4), leaching rates increased with increased waste application. In the control column (containing no waste), leaching rates averaged about 10 ml/hr, or about 0.15 inches/hr. In the 10 percent waste column, leaching rates were about 31 ml/hr, or 0.45 inches/hr. The increase in percolation rates associated with increasing waste applications may be due to the increase in exchangeable Ca associated with increased waste applications. Increased exchangeable Ca contents would tend to improve soil structure through increased aggregation of colloidal soil particles. Such aggregation would lead to increased soil pore sizes and thus to increased percolation rates.

Soil moisture retention capacity was not affected by waste application (Figure 5). As measured from soil samples collected from the surface 6 inches of the profile, at 1/3 bar, the soil moisture content ranged between 32 and 37.5 percent; at 1.0 bars, 21 and 22 percent, and at 15 bars, 9 to 10 percent.

Plant Dry Matter and Clean Seed Yields

Because of the irregularities in waste application when the waste was applied as a wet slurry, data on plant yield and elemental content was not analyzed for differences between treatments, since true replication of treatments did not exist. Data has been analyzed from those plots where the waste was applied dry, with the data from the wet application location presented in the Appendix and only used to illustrate trends.

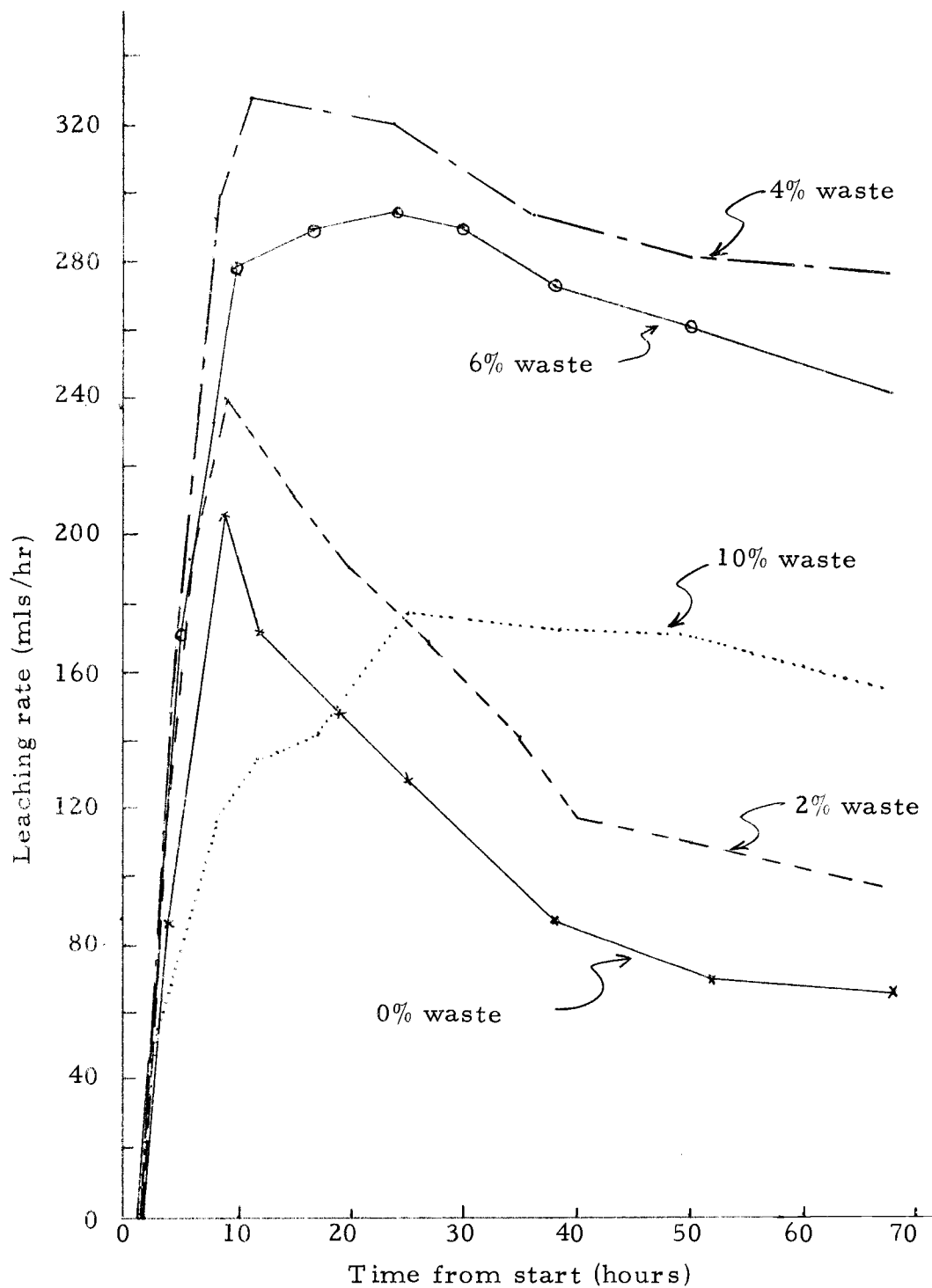


Figure 3. Water percolation in waste-treated Dayton silt soil columns, 0-72 hours.

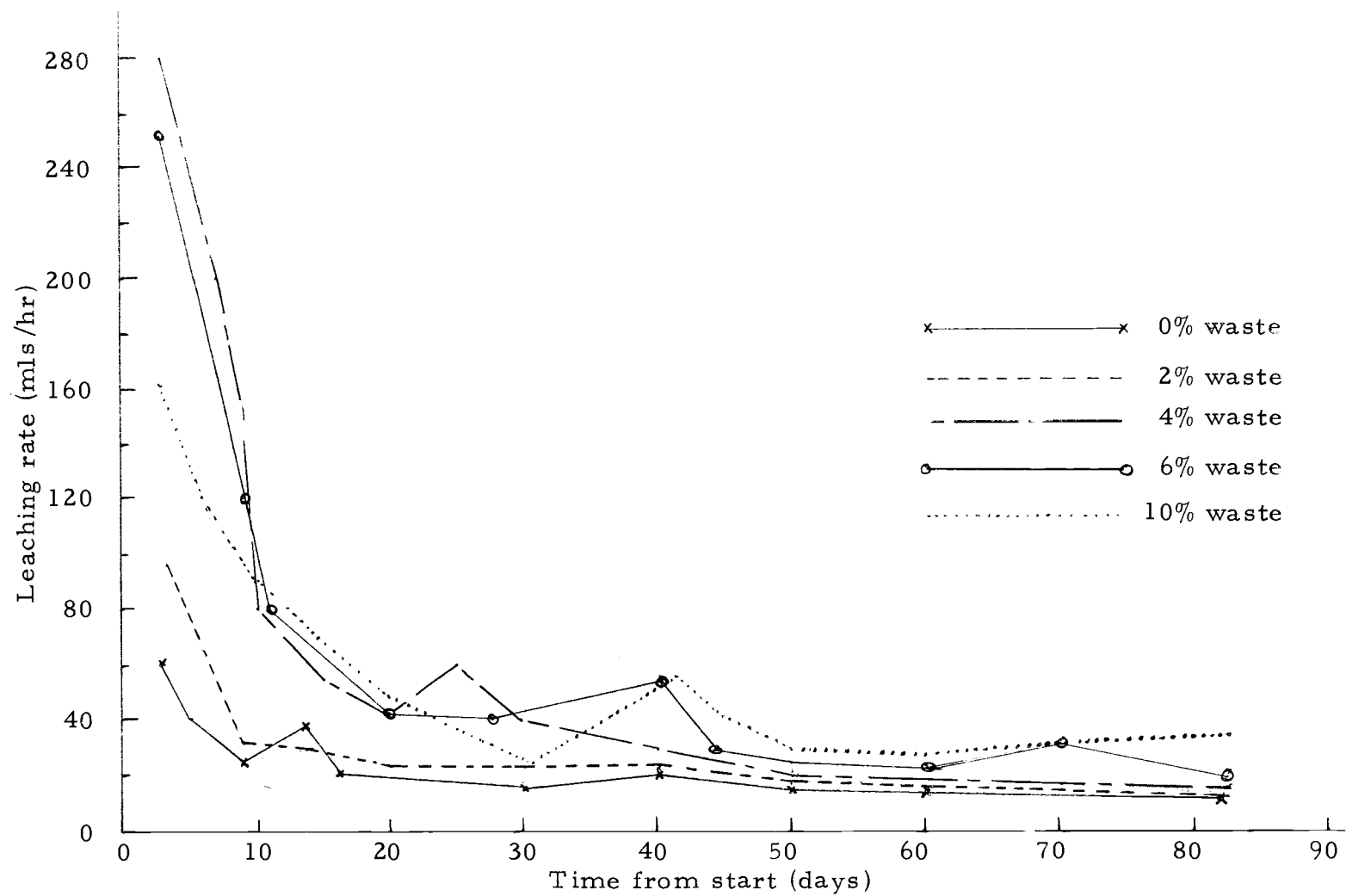


Figure 4. Water percolation in waste-treated Dayton sil soil columns, 3 to 83 days.

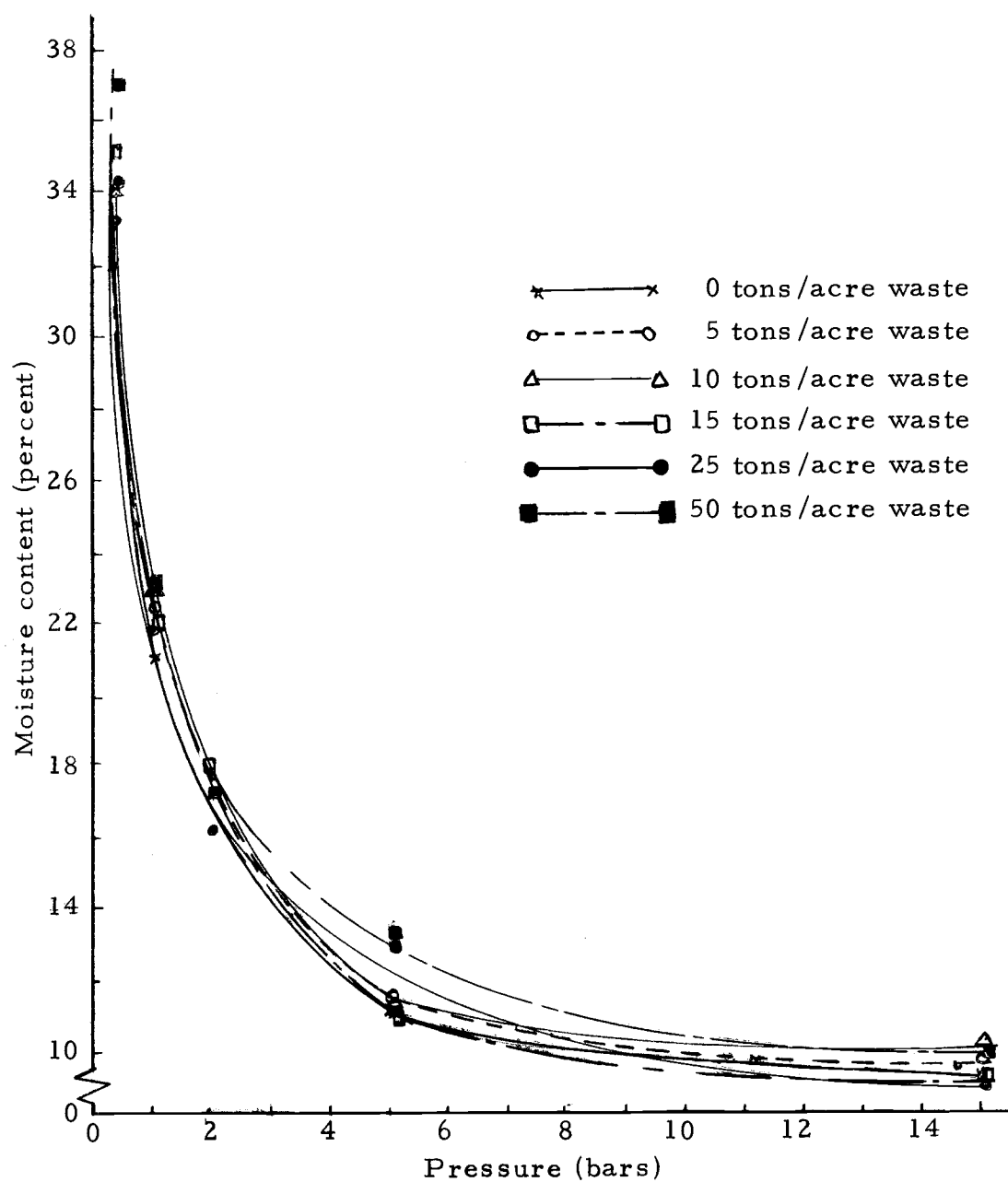


Figure 5. Soil moisture retention in waste-treated Dayton silt soil.

Dry Matter Yield

Mean dry matter yields as a function of waste application were not significantly different (at the 5 percent probability level), nor were they significantly different between locations, ignoring differences in treatments (Table 16). Mean perennial ryegrass yields ranged from 2.56 to 4.01 ton/acre, yields considered normal for this crop. Comparison of yields for control plots versus those treated with no sulfur, no lime, or higher levels of P fertilizers showed no significant differences at the 5 percent probability level.

Clean Seed Yield

Mean clean seed yields as a function of waste application were not significantly different at the 5 percent level of probability in either location (wet and dry waste application areas) (Table 16). Seed yield comparisons for control plots versus those treated with no lime, no sulfur, or extra phosphorus also showed no significant difference at the 5 percent level of probability. No attempt was made to separate annual from perennial ryegrass seeds during the cleaning operation. Yields were slightly less than normal for perennial ryegrass, ranging from 754 to 1238 lbs/acre. This is probably due to seed loss during the seed cleaning and harvesting process rather than an actual seed yield reduction.

Ryegrass Seed Viability

Seed germination in grass seed grown on soil treated with 0, 25, and 50 tons waste/acre showed no significant difference between

Table 16. Mean perennial ryegrass dry matter yield and clean seed yield on waste treated Dayton sici (harvested July, 1974).

Waste application (T/A)	Fertilizer application			Dry matter yield (T/A)		Clean seed yield (lbs/A)	
	Lime	P	S				
	(T/A)	(lbs/A)	(lbs/A)	Location 1 ^a	Location 2 ^b	Location 1 ^a	Location 2 ^b
0	2.5	25	15	3.76	2.65	1186	1036
5				2.86	2.70	754	993
10				3.43	3.16	1096	1083
25				3.14	2.94	967	1020
50				4.01	3.16	1315	1238
0	0	25	15	3.38	2.56	1048	873
25				3.65	3.25	1126	1184
0	2.5	25	0	2.89	2.69	895	903
10				3.38	3.03	1005	1090
0	2.5	100	15	3.48	2.61	812	822
10				2.92	2.76	961	998
50				2.76	2.56	938	1020

^aLocation 1 - Waste applied as a wet slurry; waste application rates theoretical; yields are means of 4 replications.

^bLocation 2 - Waste applied dry; yields are means of 4 replications, LSD (0.05); dry matter = 1.40 T/A; LSD (0.05), seed yield = 74 lbs/A.

treatment means (Table 17). After 15 days of incubation, germination percentages were never lower than 90 percent, with a mean germination percentage of 97.2 percent. Every attempt was made to eliminate annual ryegrass seeds from the germination trial.

Table 17. Germination of perennial ryegrass seed grown on waste amended Dayton soil.

Waste application (T/A)	Germination (%)
0	96.5
25	98.2
50	97.1

Plant Tissue Analysis

Calcium

The Ca content of the ryegrass was not significantly changed by increasing waste application (Table 18). The plants grown on plots which had no lime or waste applied, however, contained significantly lower Ca content. The application of 25 ton/acre of the waste product effectively replaced the lime as a source of plant Ca. No significant differences in plant Ca content were found between plants grown in control plots and those plots receiving no lime but 25 ton/acre of the waste product. The combination of a high P fertilizer application and 50 ton/acre waste product application resulted in a significant increase

in plant Ca uptake. No evidence of a serious Ca deficiency was found. Plant Ca levels in wet and dry waste application areas were similar.

Magnesium

The mean ryegrass Mg content varied significantly when all treatments were considered, and also varied significantly when only waste application rates were considered (Table 18). The lack of S fertilizer and large amounts of Ca depressed plant Mg uptake; however, data analysis appeared to be affected by the unusually high Mg content for one control plot. No definite correlation was seen between waste application and Mg content. With wet waste applications, the Mg levels in the ryegrass increased with application rate. Decreased Mg uptake by plants was observed on plants grown in soil lacking the S fertilizer and those fertilized heavily (100 lb/acre) with P. Even though the waste product had a Ca/Mg ratio of near 39, Mg uptake was not reduced. Plant Mg contents were well within normal levels for grasses.

Sodium

No significant differences in plant Na content were seen between treatment means for all treatments, but there were significant differences as a function of waste application only (Table 18). The plant Na content ranged between 0.3 and 0.7 percent, and while sodium content

increased with waste applications, the increase was not statistically significant until 50 tons/acre waste was applied. Sodium from the irrigation water may have contributed some Na to the plant, but since the water was applied evenly, its effect should have been uniform throughout the plots.

Potassium

No significant variation in plant K content among the treatments was found, nor did plant K vary significantly with waste application (Table 18). The ryegrass K content ranged between 0.97 and 1.93 percent, and was not significantly affected by the lack of S fertilizers, lime, or by relatively high amounts of P fertilizer.

Nitrogen

The N content of the plants grown on the control plots averaged 0.93 percent, while plants grown on plots receiving 50 ton/acre waste product average 1.07 percent N (Appendix II). Lesser N content increases were found at lower waste application rates, and only at the 50 ton/acre applications was the increase significant. This data agrees with Volk, et al. (1971), concerning nitrogen uptake by wheat from waste treated Dayton silt soil. In that study, waste application of 100 ton/acre increased total N from 1.37 to 1.54 percent.

Phosphorus

Plant P content did not significantly change with increasing waste application rates (Table 18), despite reduced available soil P. Comparison of plots treated with 100 lbs P/acre with those receiving 25 lbs P/acre at similar waste applications (0, 10, and 50 ton/acre) showed a significant increase in plant P content only at the 10 T/A waste application rate. The added P evidently did not directly contribute to plant P content. For control plots, the P content of the ryegrass averaged 0.23%, while plants grown on soil which received no waste and 100 lbs P fertilizer/acre contained an average of 0.24% P. Plants grown on soil treated with 10 ton/acre waste and 25 lbs P/acre, contained an average of 0.19% P, but after application of P, 100 lbs/acre, and the same amount of waste, the plant P content increased to 0.23%. For plots treated with 50 ton/acre waste and 25 lbs P/acre the plant P content averaged 0.20%, while on plots treated with 50 ton/acre waste and 100 lbs P/acre, the plant P content averaged 0.22%. Similar trends were observed with the P content of plants grown in the wet waste application area. Plants grown on plots treated with no waste and extra P in the wet waste area appeared to have significantly higher P contents than the control plants (Table 19). Plant P contents were consistent with normal P levels found in some grass and cereal crops; no deficiencies or P-induced yield reduction were observed.

Table 18. Perennial ryegrass chemical analysis; dry application area.

Waste application (T/A)	Fertilizer application			K	Ca	Mg %	P	Na	Al	Fe	Mn ppm	Cr	Zn
	Lime (T/A)	P (lbs/A)	S (lbs/A)										
0	2.5	25	15	1.35	.39	.14	.23	.42	1613	1283	207	.74	29
5				1.40	.40	.11	.20	.50	1633	1263	215	.91	14
10				1.26	.42	.13	.19	.51	1810	1440	209	1.0	20
25				1.18	.41	.10	.18	.49	1195	1000	168	.76	13
50				1.19	.44	.13	.20	.56	1618	1275	183	1.0	22
0	0	25	15	1.39	.31	.10	.19	.47	1505	1063	227	.84	25
25				1.42	.38	.09	.20	.43	1065	815	184	1.0	14
0	2.5	25	0	1.33	.39	.08	.19	.45	1505	1200	183	.84	13
10				1.32	.39	.08	.20	.51	1351	1088	190	1.03	15
0	2.5	100	15	1.50	.39	.09	.24	.46	1495	1212	214	.94	13
10				1.34	.42	.09	.23	.53	1395	1188	195	1.05	16
50				1.27	.50	.09	.22	.60	1500	1209	177	.63	30
LSD (.05) ¹				.18	.04	.02	.04	.08	487	361	29	.31	3.1

Table 18. Continued.

Waste application (T/A)	Fertilizer application			Cu	Ni	Co	S	Mo ppm	F	Zr	Hf	Pb
	Lime (T/A)	P (lbs/A)	S (lbs/A)									
0	2.5	25	15	4.1	3.0	1.18	846	.32	46.0	<50	<50	<1
5				3.4	1.5	.81	746	.30	31.9	<50	<50	<1
10				3.5	1.8	.93	1230	.47	31.7	<50	<50	1
25				2.8	1.8	.72	1111	.40	25.0	<50	<50	1
50				3.8	1.8	.73	1183	.28	41.6	<50	<50	<1
0	0	25	15	3.2	1.8	.91	1086	.09	18.8	<50	<50	<1
25				3.6	2.1	.90	1030	.54	40.7	<50	<50	<1
0	25	25	0	3.5	2.3	.50	836	.27	36.7	NA ²	NA	NA
10				3.7	1.2	.49	921	.23	41.9	NA	NA	NA
0	25	100	15	4.0	1.7	.81	1114	.17	34.4	NA	NA	NA
10				3.6	1.4	.84	1143	.27	43.2	NA	NA	NA
50				3.5	1.9	.60	1314	.21	24.8	NA	NA	NA
LSD (.05)				0.8	0.3	.28	217	.21	NC ³	NC	NC	NC

¹LSD values were calculated at the 5% probability level as a function of waste application, with identical lime, P, and S treatments.

²NA = not analyzed.

³NC = not calculated.

Table 19. Perennial ryegrass chemical analysis, wet application area.¹

Waste application (T/A)	Fertilizer application			K	Ca	Mg %	P	Na	Al	Fe	Mn ppm	Cr	Zn
	Lime (T/A)	P (lbs/A)	S (lbs/A)										
0	2.5	25	15	1.66	1.54	.09	.18	.36	125	148	159	.47	11
5				1.68	1.69	.09	.22	.35	225	175	151	.48	10
10				1.56	1.59	.09	.19	.36	123	130	121	.51	10
25				1.70	1.91	.10	.19	.31	153	170	142	.86	14
50				1.60	1.92	.11	.16	.56	135	134	109	.59	15
0	0	25	15	1.77	1.40	.10	.22	.35	150	173	222	.50	17
25				1.64	1.87	.10	.20	.39	223	170	137	.53	16
0	2.5	25	0	1.59	1.56	.07	.21	.38	108	138	154	.58	11
10				1.46	1.63	.07	.21	.47	123	133	128	.55	11
50	2.5	100	15	1.67	1.57	.08	.25	.47	118	138	166	.79	13
10				1.58	2.04	.08	.22	.44	140	158	148	.64	13
50				1.73	2.08	.09	.22	.38	183	168	127	.61	26

Table 19. Continued.

Waste application (T/A)	Fertilizer application			Cu	Ni	Co	S	Mo ppm	F	Zr	Hf	Pb
	Lime (T/A)	P (lbs/A)	S (lbs/A)									
0	25	25	15	3.5	1.6	.69	1026	.46	6.7	<50	<50	<1
5				3.7	1.6	.78	1097	.84	4.5	<50	<50	<1
10				3.7	1.7	.66	982	.77	3.9	<50	<50	1
25				4.3	2.7	.74	1273	.91	7.6	<50	<50	1
50				4.4	2.4	.69	1416	.54	2.9	<50	<50	<1
0	0	25	15	3.5	1.5	1.01	1092	.22	9.4	<50	<50	<1
25				3.5	2.0	.71	1457	.86	7.5	<50	<50	<1
0	25	25	0	3.3	0.8	.84	850	.33	4.4	NA ²	NA	NA
10				3.9	1.5	.62	941	.59	6.1	NA	NA	NA
0	25	100	15	3.9	1.3	.88	1138	.44	6.3	NA	NA	NA
10				3.7	1.6	.75	1159	.76	5.3	NA	NA	NA
50				4.4	2.3	.76	1542	.66	5.8	NA	NA	NA

¹ Figures are mean values for 4 replicates, except for F, where figures are means for 2 replicates.

² NA = not analyzed.

Sulfur

Significant variation between the mean plant S contents was seen as a function of waste application (Table 18). The plant S content appeared to increase with waste, but no consistent pattern developed. On those plots which received no waste or S fertilizer, plant S level was not reduced compared to control plots, nor was there a significant increase in S content over control plots when 10 ton/acre waste was applied to plots with no S fertilizer. Among those plots which received no waste but were fertilized with S the mean plant S content varied significantly, ranging from 846 to 1114 ppm S, making comparisons to waste treated plots difficult. The lack of lime or the addition of high levels of P fertilizer did not significantly affect S uptake. The waste product does serve as a plant S source, but conclusive evidence as to the amount of S supplied to the crops by the waste was lacking. Additional plant analysis data on succeeding crops may provide better quantitative relationships between plant S and waste application.

Aluminum and Iron

Plant Al and Fe contents did not vary significantly as a function of waste application only, nor did they vary significantly in response to fertilizer treatments (Table 18). The plant Al or Fe uptake was not

reduced on limed plots when compared to unlimed plots at similar waste application rates. The plant Al and Fe contents in the wet waste application plots were, however, 8 to 10 times lower than those found in plants grown on the dry waste application site. Since the plant samples were not washed, and the dry waste application site was closer to the highway than the wet site, the higher plant Fe and Al content could have resulted from road dust collected on plant leaves. The plant Fe content ranged from 80 to 250 ppm on the wet site while plant Al content ranged between 40 and 360 ppm. No evidence of Fe chlorosis or Al toxicity was observed.

Manganese

The mean plant Mn content did not significantly change among fertilizer and waste treatments, nor did it significantly vary with waste application rates alone (Table 18). No evidence of a Mn deficiency (< 20 ppm Mn) or toxicity (> 500-600 ppm Mn, Labanauskas, 1966) occurred. Manganese levels were not elevated in the plants grown on the unlimed plots as compared to the limed plots, treated similarly. The addition of 25 ton/acre of waste did not significantly reduce plant Mn uptake compared to plots which received no waste or lime. Thus, despite reduced extractable soil Mn with increasing waste and lime applications, the plant Mn contents did not change.

Plant Mn levels were generally lower on the wet waste application site than on the dry site.

Chromium

The plant Cr content did not significantly vary as a function of waste application or fertilizer treatments (Table 18). Chromium contents were within the normal range for most crops, and well below levels that might be considered toxic (5-10 ppm, Pratt, 1966).

Zinc

The plant Zn content varied significantly across all treatments and across waste application rates; however, no distinct positive or negative correlation was established between waste application and plant Zn content (Table 18). The Zn content of the ryegrass was generally low (< 25 ppm), since Zn deficiencies occur at levels of less than 20-25 ppm in many crops (Chapman, 1966). No visual symptoms of Zn deficiency such as mottled chlorosis, reduced plant height, or leaf burn were seen.

Copper

The plant Cu content did not vary significantly as a function of waste application rates or fertilizer treatment (Table 18). No difference was observed between limed and unlimed plots treated with no

waste, but plots treated with 25 ton/acre waste, but without lime contained significantly higher plant Cu contents than plants grown on soil treated with the same amount of waste and lime. The plant Cu contents from the wet and dry areas were very similar. The Cu concentration did not exceed 6.0 ppm and averaged about 3.5, levels that border deficiencies on many crops (Reuther and Labanauskas, 1966). Levels in excess of 20 ppm Cu are generally thought to be toxic.

Nickel

Plant Ni contents were low, with most values ranging between 1 and 3 ppm in both the dry and wet waste application areas (Tables 18 and 19). No significant variation in mean plant Ni content was seen across waste and fertilizer treatments. The normal Ni level in plant tissue is about 1.0 ppm, while toxicities occur at levels in excess of 50 ppm (Allaway, 1968). Thus, no evidence of nickel toxicity following waste product application was found.

Cobalt

Cobalt uptake by the ryegrass (0.5 to 1.18 ppm) grown on all plots was considerably higher than that found in most grasses (0.1 ppm), but also considerably lower than the levels normally associated with cobalt toxicities (50 ppm). Plant Co levels were not significantly affected by waste product application (Table 18). The lack of S

fertilizer appeared to reduce the Co content of plant grown in the dry waste application area. This decrease may have been due to experimental error.

Molybdenum

The plant Mo levels were not significantly affected by waste application, but were significantly depressed by the lack of lime and/or waste, dropping from 0.32 ppm in control plots to 0.09 ppm in plots lacking lime or waste. Molybdenum solubility increases with soil pH, explaining the depressed Mo content in the acid soil. Normal plant Mo contents range from 1 to 10 ppm, and less than 0.10 ppm is considered a sign of deficiency.

Fluoride

No correlation was found between waste treatment and plant F content. Large variances were seen within treatments, with some plant F contents 100 percent larger than others for the same treatment. This large variation was also seen between the two plot area, with plant F levels in the dry application area 6 to 8 times larger than those which occurred in plants grown on the wet application area (Tables 18 and 19). Mean plant F contents in the dry area ranged from 25 to 46 ppm, and 3 to 8 in the wet area. Normal plant F concentrations range from 2 to 20 ppm in areas where F air pollution is minimal

or non-existent. The disparity between the two plot areas may have been due to the proximity of the dry area to the highway and pollution from it, or the influence of somewhat better drainage in the wet application site.

Zirconium and Hafnium

With one exception, plant Zr and Hf contents were below 50 ppm in all samples tested. Levels less than 50 ppm exceeded analytical sensitivity, and no conclusions were drawn on Zr and Hf uptake by plants. It seems reasonable, however, to predict that Zr and Hf levels were quite low in the plant tissue, since the oxides of these metals are quite insoluble.

Lead

Lead levels in all but one plant sample tested were equal to or less than 1.0 ppm, which is consistent with lead levels found in most plants. No evidence of plant lead toxicity was found.

Summary

Of all elements assayed, only N, S, and Na content in the plant tissue increased with waste application, and those increases were significant only at the 50 ton/acre waste application rate. No heavy metals were taken up by the ryegrass in amounts that could be considered toxic,

and with the possible exception of Zn, no elemental deficiencies in the plants were found due to waste product application.

Percolation Water Quality

Five Dayton sicl soil columns treated with the refractory waste product were leached with distilled water to determine which waste constituents in the percolate might pose a health hazard to man or animals (Table 3). Since this study was completed in the laboratory, several factors of importance in determining the amount of any element that reached the groundwater were eliminated. No crop was grown on the soil, native soil structure was destroyed, the entire soil profile was not represented, and soil temperatures were elevated above normal field conditions. With the above limitations only a qualitative or semi-quantitative approach to interpretation of results may be made. However, with the conditions imposed, one would probably find the maximum elemental movement.

Waste constituents not found in measurable amounts in any leachate samples included K, Fe, Cu, Ni, Cr and water soluble P. No attempt was made to measure Al, Pb, Co, Zr, Hf, or Mo which also would be present only in very low concentration. Those ions found at detectable levels in the leachate were Ca, Mg, Na, Mn, Zn, $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, F, and S. At the termination of the sample collecting period (75 days of continuous leaching), the Na, Zn, $\text{NO}_3\text{-N}$, and

$\text{NH}_4\text{-N}$ concentration were below detection or insignificant. Manganese levels dropped below detection during the study, but Mn was detected again in water samples collected near the end of the study. Fluoride levels were less than 2.0 ppm for all but the initial sample from the 100% soil column.

Calcium

Calcium is not considered a health hazard in water, although it contributes to water "hardness," which makes the water difficult to use for some purposes, most notably, laundry cleaning. Calcium concentrations were quite high over the first six to twelve hours of leaching, exceeding 800 ppm in the percolate from the column containing 10 percent waste (Table 25). The Ca concentration in the percolate from the Dayton soil never exceeded 67 ppm. The Ca concentration declined rapidly after the first 4-6 pore volumes of water had passed through the columns (Tables 21-25). The Ca concentration in the water from the control column stabilized at levels less than 1.0 ppm, while the Ca concentration in the 10 percent waste treated column leachate stabilized between 13 and 30 ppm. The Ca content of the 2, 4, and 6 percent waste treated column leachates were proportionately less.

Calcium leached from the 4, 6, and 10 percent waste treated columns exceeded the amount of readily exchangeable calcium in the

soil plus added waste (Table 20), which suggested considerable low solubility Ca in the waste product. The total Ca output was roughly proportional to total waste input (Table 20).

Magnesium

Magnesium is not considered a health hazard in water, but it also contributes to water hardness. Like Ca, the Mg concentrations were high (Tables 21-25); 800 ppm in the first 4 to 6 pore volumes of percolate from the high waste treated columns in comparison to the check column (120 ppm). The Mg concentration in the first pore volume may have even exceeded 800 ppm. The Mg concentration in the percolation water declined rapidly after the first 4 to 6 pore volumes passed through the columns, with concentrations stabilizing at 0 to 2 ppm in water from the control column, and at 2 to 5 ppm from the waste treated columns. The Mg concentration in the percolate was independent of waste application rate, but the total Mg output was proportional to the waste applied. The Mg leached from the waste treated soil exceeded the amount of exchangeable Mg in the soil and waste and the total Mg content of the waste. No reason for this discrepancy was found.

Table 20. Elemental constituents added to and leached from waste treated Dayton sil soil.

Constituent	Inputs		Output ¹ (mg)
	Extractable waste & soil (mg)	Total in waste (mg)	
<u>0 Percent Waste</u>			
Ca	544.0	0	64.0
Mg	66.0	0	133.6
Na	209.5	0	209.7
Mn	80.5	0	11.9
Zn	1.0	0	6.4
NO ₃ ⁻ -N	3.1	0	6.6
NH ₄ ⁺ -N	2.3	0	2.8
F	7.2	0	ND
S	18.4	0	159.5
<u>2 Percent Waste</u>			
Ca	685.1	1070.0	565.6
Mg	69.0	26.0	473.5
Na	205.6	32.0	248.2
Mn	79.5	4.3	47.5
Zn	1.7	5.0	10.4
NO ₃ ⁻ -N	3.0	ND ²	6.6
NH ₄ ⁺ -N	14.9	ND	13.0
F	7.3	331.0	205.0
S	26.8	103.0	178.6
<u>4 Percent Waste</u>			
Ca	826.2	2140.0	1320.3
Mg	71.9	52.0	832.6
Na	201.8	64.0	254.7
Mn	78.5	8.6	44.4
Zn	1.9	10.0	5.8
NO ₃ ⁻ -N	3.0	ND	9.9
NH ₄ ⁺ -N	27.5	ND	25.2
F	7.5	662.0	437.0
S	35.3	206.0	262.5

Table 20. Continued.

Constituent	Inputs		Output ¹ (mg)
	Extractable waste & soil (mg)	Total in waste (mg)	
<u>6 Percent Waste</u>			
Ca	967.4	3210.0	2264.0
Mg	74.8	78.0	1271.4
Na	198.0	96.0	388.6
Mn	77.4	12.9	52.5
Zn	2.4	15.0	6.7
NO ₃ ⁻ -N	3.0	ND	12.6
NH ₄ ⁺ -N	40.2	ND	62.8
F	7.7	993.0	653.9
S	43.8	309.0	559.3
<u>10 Percent Waste</u>			
Ca	1249.6	5350.0	3175.0
Mg	80.7	130.0	1707.3
Na	190.3	160.0	473.9
Mn	75.4	21.5	48.9
Zn	3.2	20.0	4.2
NO ₃ ⁻ -N	2.9	ND	13.2
NH ₄ ⁺ -N	65.4	ND	88.4
F	8.0	1655.0	844.2
S	60.8	515.0	1009.4

¹ All columns leached for 75 days.

² No data.

Table 21. Elemental content of percolate from Dayton silt soil.

Elapsed time	Cumulative pore volumes	Soluble salts (mmhos/cm)	Ca	Mg	Na	NH ₄ -N	NO ₃ -N	Zn	Mn	F	S
			ppm								
0 hr	2.0	1.35	67	120	196	0.8	4.4	8	13	0.3	244
6 hr	5.8	0.2	6.2	10.3	32	0.3	0.3	0.7	1.0	<0.2	7.9
12 hr	7.7	<0.1	2.7	3.6	12.8	0.2	0.1	0.3	0.2	<0.2	5.5
18 hr	12.6	<0.1	1.5	3.1	9.0	0.3	0.1	0.2	0.2	<0.2	2.5
24 hr	14.5	<0.1	1.1	3.6	7.0	0	0.2	0.2	0.1	<0.2	
2 day	20.0	<0.1	0.4	2.0	4.0	0	0.1	0.1	0	<0.2	0.7
3 day	25.1	<0.1	0	1.7	3.0	0.1	0	0.1	0	<0.2	0.7
4 day	29.7	<0.1	0	0.4	3.0	0.1	0.1	0	0	<0.2	0.5
5 day	33.3	<0.1	0	1.5	3.4	0	0.2	0.1	0	<0.2	0.5
6 day	36.2	<0.1	0	1.1	3.6	0	0.1	0	0	<0.2	0.3
7 day	38.7	<0.1	0	0.6	2.4	0	0.1	0	0	<0.2	0.1
8 day	41.0	<0.1	0	0.6	2.2	0	0	0	0	<0.2	0
9 day	43.5	<0.1	0	0.5	2.2	0	0.1	0	0	<0.2	0.1
10 day	46.0	<0.1	0	2.1	2.0	0	0.2	0	0	<0.2	0
11 day	48.5	<0.1	0.3	0.3	1.5	0.1	0	0	0	<0.2	NA ¹
12 day	50.9	<0.1	0.2	0.1	1.4	0	0	0	0	<0.2	NA
13 day	53.3	<0.1	0.4	1.5	0.6	0.1	0	0	0	<0.2	NA
14 day	55.6	<0.1	0.2	0.7	0.4	0	0.2	0	0	<0.2	NA
16 day	59.4	<0.1	0.4	0.8	0.3	0	0	0	0	<0.2	NA
18 day	62.8	<0.1	8.5	5.3	0	0	0.1	0	0.5	<0.2	NA
20 day	66.0	<0.1	0.8	1.6	0	0.2	0.1	0	0.1	<0.2	0
22 day	70.6	<0.1	0.9	2.6	0	0.1	0.2	0	0.1	<0.2	NA
26 day	75.0	<0.1	0.7	1.9	0	0.1	0.1	0	0.2	<0.2	NA
28 day	77.8	<0.1	0.5	1.2	0	0	0.2	0	0.1	<0.2	NA
30 day	80.4	<0.1	0.7	1.6	0	0	0.1	0	0.1	<0.2	0
35 day	88.8	<0.1	0.9	1.8	0	0.1	0.1	0	0.1	<0.2	NA
40 day	96.3	<0.1	0.3	0.9	0	0.2	0.1	0	0.1	<0.2	0
45 day	103.2	<0.1	0.4	0.7	0	0	0.3	0	0.1	<0.2	NA
50 day	109.2	<0.1	0.3	1.6	0	0.1	0	0	0.1	<0.2	0
55 day	114.6	<0.1	0.5	1.0	0	0.2	0.1	0	0.1	<0.2	NA
60 day	119.6	<0.1	0.7	1.7	0	0	0.1	0	0.1	<0.2	0
65 day	126.6	<0.1	0.5	1.0	0	0	0.2	0	0.1	<0.2	NA
75 day	135.2	<0.1	0.4	1.0	0	0	0.1	0	0.1	<0.2	0

¹ NA = not analyzed.

Table 22. Elemental content of percolate from 2% waste-treated Dayton silt soil.

Elapsed time	Cumulative pore volumes	Soluble salts (mmhos/cm)	Ca	Mg	Na	NH ₄ -N	NO ₃ -N	Zn	Mn	F	S
			- - -	- - -	- - -	- - -	- - -	- - -	- - -	- - -	- - -
						ppm					
0 hr	2.4	2.13	178	220	224	5.8	5.0	8	22	2.2	101
6 hr	8.0	< 0.1	48	33	40	1.8	0.3	0.7	2.8	2.8	42
12 hr	12.5	0.15	26	13	11.4	0.7	0	0.3	1.2	3.7	11
18 hr	15.9	0.11	22	8.8	5.4	0.4	0.1	0.2	0.8	4.0	6.2
23 hr	28.4	< 0.1	20	7.3	3.8	0.5	0.1	0.2	0.6	4.2	5.1
2 day	36.4	< 0.1	17	6.8	1.2	0.4	0.1	0.1	0.4	5.0	2.1
3 day	43.6	< 0.1	17	5.4	0.8	0.2	0.1	0.1	0.4	5.0	1.3
4 day	50.2	< 0.1	16	5.3	1.0	0.2	0.2	0	0.4	5.2	0.1
5 day	55.6	< 0.1	17	5.6	0.6	0.1	0	0.1	0.4	5.0	0.5
6 day	60.1	< 0.1	16	5.9	0	0.1	0	0	0.4	4.8	0.3
7 day	63.9	< 0.1	17	5.0	0	0.3	0	0	0.4	5.0	0.7
8 day	67.3	< 0.1	16	5.0	0	1.1	0.1	0	0.4	5.0	0.5
9 day	70.5	< 0.1	17	4.8	0	0.1	0.3	0	0.4	4.6	0.1
10 day	73.6	< 0.1	17	5.1	0	0	0	0	0.4	4.8	0.7
11 day	76.4	< 0.1	9	9.6	0	0	0	0	0.4	NA	NA ¹
12 day	79.1	< 0.1	9	5.8	0	0.1	0.1	0	0.5	NA	NA
13 day	81.7	< 0.1	9	5.7	0	0	0	0	0.5	NA	NA
14 day	84.3	< 0.1	9	0.6	0	0	0.1	0	0.5	NA	NA
16 day	89.0	< 0.1	9	5.3	0	0	0.1	0	0.5	NA	NA
18 day	93.3	< 0.1	9	1.6	0	0	0	0	0.1	NA	NA
20 day	97.1	< 0.1	8	6.4	0	0.1	0.1	0	0.6	5.2	0.2
22 day	102.7	< 0.1	8	8.4	0	0	0	0	0.7	NA	NA
26 day	108.2	< 0.1	10	5.7	0	0	0	0	0.7	NA	NA
28 day	111.8	< 0.1	9	8.0	0	0.9	0.2	0	0.7	NA	NA
30 day	115.3	< 0.1	8	7.8	0	0.1	0.1	0	0.6	4.8	0.7
35 day	126.1	< 0.1	9	1.0	0	0	0.2	0	0.7	NA	NA
40 day	134.3	< 0.1	8	6.8	0	0	0	0	0.7	4.8	0.5
45 day	141.5	< 0.1	8	5.0	0	0.1	0.1	0	0.7	NA	NA
50 day	147.8	< 0.1	8	5.0	0	0	0	0	0.8	3.6	0.5
55 day	153.1	< 0.1	9	4.8	0	0	0	0	0.9	NA	NA
60 day	157.9	< 0.1	9	5.1	0	0	0.1	0	1.0	2.7	0.5
65 day	164.5	< 0.1	9	8.2	0	0.1	0	0	1.0	NA	NA
75 day	171.9	< 0.1	10	11	0	0	0.1	0	1.2	2.7	0

¹ NA = not analyzed.

Table 23. Elemental content of percolate from 4% waste-treated Dayton silt soil.

Elapsed time	Cumulative pore volumes	Soluble salts (mmhos/cm)	Ca	Mg	Na	NH ₄ -N	NO ₃ -N	Zn	Mn	F	S
			ppm								
0 hr	2.8	2.60	331	312	200	9.0	5.4	5.6	24.5	NA	157
6 hr	8.7	0.41	51	48	36	2.3	0.3	0.5	2.5	5.0	46
12 hr	15.7	< 0.1	30	25	9.8	1.1	0.1	0.1	1.2	5.9	12
18 hr	21.5	< 0.1	21	25	3.8	1.1	0.2	0.1	0.8	7.2	5.6
23 hr	48.6	< 0.1	19	13	2.2	0.8	0	0	0.7	6.8	3.8
2 day	73.0	< 0.1	10	6.0	0	0.1	0	0	0.3	5.4	0
3 day	95.1	< 0.1	9.3	5.5	0	0.3	0.1	0	0.1	5.0	0.4
4 day	115.3	< 0.1	8.8	3.8	0	0	0	0	0.1	4.6	0.2
5 day	133.9	< 0.1	8.5	3.3	0	0	0	0	0.1	4.4	0
6 day	150.6	< 0.1	9.0	3.8	0	0	0.1	0	0.1	4.1	0
7 day	163.9	< 0.1	7.5	3.8	0	0	0	0	0.1	3.9	0.2
8 day	173.5	< 0.1	7.5	2.8	0	0	0	0	0.1	3.7	0
9 day	180.9	< 0.1	7.8	3.3	0	0	0	0	0.1	4.0	0.4
10 day	187.0	< 0.1	8.3	4.5	0	0	0.2	0	0.2	3.9	0 ¹
11 day	192.6	< 0.1	8.4	4.0	0	0	0.1	0	0.1	NA	NA
12 day	197.7	< 0.1	9.0	3.8	0	0.2	0.1	0	0.1	NA	NA
13 day	202.6	< 0.1	9.0	3.4	0	0	0	0	0.1	NA	NA
14 day	207.4	< 0.1	8.9	4.0	0	0	0.1	0	0.1	NA	NA
16 day	216.2	< 0.1	8.6	4.1	0	0	0	0	0.1	NA	NA
18 day	224.3	< 0.1	8.2	3.4	0	0	0.1	0	0.1	NA	NA
20 day	231.7	< 0.1	9.0	4.0	0	0.1	0.1	0	0.1	4.6	0.9
22 day	246.4	< 0.1	9.0	4.8	0	0	0	0	0.1	NA	NA
26 day	260.2	< 0.1	8.1	4.0	0	0.1	0.1	0	0.1	NA	NA
28 day	269.6	< 0.1	8.0	3.4	0	0.2	0	0	0.1	NA	NA
30 day	277.1	< 0.1	7.4	5.0	0	0	0.1	0	NA	4.0	0.2
35 day	295.5	< 0.1	8.5	3.0	0	0.1	0.3	0	0.2	NA	NA
40 day	309.6	< 0.1	6.8	4.1	0	0	0.1	0	0.1	4.0	0
45 day	318.0	< 0.1	7.1	2.7	0	0.1	0.2	0	0.2	NA	NA
50 day	327.2	< 0.1	7.6	3.2	0	0.1	0.1	0	0.3	3.3	0
55 day	334.8	< 0.1	8.7	3.0	0	0	0.1	0	0.4	NA	NA
60 day	342.0	< 0.1	9.3	3.4	0	0	0	0	0.5	3.2	0
65 day	348.0	< 0.1	9.8	4.0	0	0.1	0.1	0	0.6	NA	NA
75 day	354.0	< 0.1	9.6	3.7	0	0	0.1	0	0.6	3.6	0.5

¹ NA = not analyzed.

Table 24. Elemental content of percolate from 6% waste-treated Dayton sici soils.

Elapsed time	Cumulative pore volumes	Soluble salts (mmhos/cm)	Ca	Mg	Na	NH ₄ -N	NO ₃ -N	Zn	Mn	F	S
			- - -	- - -	- - -	- - -	- - -	- - -	- - -	- - -	- - -
			ppm								
0 hr	5.4	2.65	423	344	204	12.4	4.1	3.9	21	3.6	208
10 hr	13.5	0.46	48	70	30	3.4	0.3	0.3	2.7	6.4	60
18 hr	18.8	0.22	38	28	4.8	1.8	0.4	0.1	0.9	9.0	9.2
24 hr	44.0	0.16	31	18	1.8	3.7	0	0	0.6	7.8	7.1
2 day	66.8	0.13	19	9.0	0.1	0.3	0.1	0	0.1	7.8	2.5
3 day	87.1	0.10	16	6.0	0	0	0.1	0	0.1	7.5	0.2
4 day	105.5	0.10	15	5.8	0	0.2	0.2	0	0.1	7.2	1.5
5 day	122.5	0.10	17	5.5	0	0.3	0	0	0.2	7.5	2.1
6 day	137.2	0.10	14	4.5	0	0	0.1	0	0.1	6.8	2.1
7 day	149.5	0.10	13	4.0	0	0.2	0.1	0	0	6.0	1.7
8 day	159.7	< 0.1	12	3.8	0	0	0.1	0	0	6.0	1.5
9 day	168.3	< 0.1	13	4.8	0	0	0.1	0	0	6.2	1.5
10 day	175.2	< 0.1	15	5.8	0	0	0.1	0	0	6.2	1.6
11 day	181.2	< 0.1	14	4.2	0	0.1	0	0	0	NA	NA ¹
12 day	186.7	< 0.1	14	4.5	0	0.1	0	0	0	NA	NA
13 day	192.0	< 0.1	13	3.8	0	0.2	0.2	0	0	NA	NA
14 day	196.8	< 0.1	13	4.6	0	0.1	0	0	0	NA	NA
16 day	205.4	< 0.1	13	3.5	0	0	0	0	0	NA	NA
18 day	213.3	< 0.1	12	3.0	0	0	0.1	0	0	NA	NA
20 day	220.6	< 0.1	14	4.0	0	0.1	0	0	0	6.2	1.6
22 day	231.3	< 0.1	12	3.2	0	0.1	0	0	0	NA	NA
26 day	241.7	< 0.1	17	4.6	0	0.1	0.2	0	0	NA	NA
28 day	247.3	< 0.1	13	3.7	0	0	0.1	0	0.1	NA	NA
30 day	253.1	< 0.1	13	3.4	0	0	0	0	0.1	5.8	0.9
35 day	272.5	< 0.1	14	4.5	0	0	0.1	0	0.1	NA	NA
40 day	294.5	< 0.1	16	5.0	0	0.2	0	0	0.2	8.4	1.2
45 day	305.5	< 0.1	12	5.1	0	0.1	0.1	0	0.2	NA	NA
50 day	315.5	< 0.1	12	3.8	0	0.1	0	0	0.2	5.8	1.6
55 day	324.8	< 0.1	13	4.1	0	0	0	0	0.3	NA	NA
60 day	334.3	< 0.1	12	7.6	0	0.1	0.1	0	0.2	5.6	0
65 day	351.1	< 0.1	12	4.9	0	0.1	0.1	0	0.3	NA	NA
75 day	369.4	< 0.1	12	4.4	0	0	0.2	0	0.4	5.8	0.2

¹ NA = not analyzed.

Table 25. Elemental content of percolate from 10% waste-treated Dayton sil soil.

Elapsed time	Cumulative pore volumes	Soluble salts (mmhos/cm)	Ca	Mg	Na	NH ₄ -N	NO ₃ -N	Zn	Mn	F	S
			----- ppm -----								
0 hr	3.9	5.5	819	813	364	28.8	6.6	2.9	27	3.7	415
12 hr	9.7	1.3	195	128	32	7.5	0.3	0.3	4.5	6.8	162
23 hr	24.9	0.4	38	43	7.4	4.4	0.1	0.1	1.5	9.0	51
2 day	38.8	0.2	41	15	0.95	1.7	0.1	0.1	0.4	11.0	9.0
3 day	51.4	0.2	34	13	0.45	1.1	0	0	0.3	11	4.6
4 day	61.8	0.2	32	12	0	0.9	0	0	0.2	11	4.6
5 day	72.5	0.1	30	13	0	NA ¹	0	0	0.1	12	3.1
6 day	82.3	0.1	28	8.3	0	0.5	0	0	0.1	12	3.1
7 day	91.0	0.1	26	6.8	0	0.4	0	0	0.1	11	1.5
8 day	99.3	0.1	25	6.5	0	0.4	0.1	0	0.1	11	2.3
9 day	107.3	0.1	25	7.3	0	0.2	0	0	0.1	11	2.5
10 day	114.7	0.1	26	6.5	0	0.3	0	0	0.1	12	3.0
11 day	121.7	0.2	24	6.0	0	0.1	0.1	0	0.1	NA	NA
12 day	128.3	0.1	22	5.2	0	0.1	0	0	0.1	NA	4.6
13 day	134.5	0.1	21	5.2	0	0.1	0.1	0	0.1	NA	NA
14 day	140.3	0.1	22	7.6	0	0.5	0.2	0	0	NA	2.8
16 day	150.8	0.1	21	5.0	0	0.1	0.1	0	0	NA	3.0
18 day	160.0	0.1	20	4.6	0	0.2	0.1	0	0	NA	1.6
20 day	167.8	0.1	22	5.5	0	0.4	0	0	0	10	3.0
22 day	178.0	0.1	20	4.5	0	0.4	0.1	0	0	NA	NA
26 day	187.3	0.1	22	4.6	0	0	0.1	0	0	NA	NA
28 day	194.4	0.1	20	3.7	0	0.1	0.1	0	0	NA	NA
30 day	201.3	0.1	18	4.4	0	0.2	0.1	0	0	9.4	2.5
35 day	226.6	0.1	19	3.4	0	0.2	0.2	0	0	NA	NA
40 day	250.7	0.1	13	2.4	0	0	0.1	0	0	6.8	0
45 day	264.2	0.1	14	2.2	0	0.1	0	0	0	NA	NA
50 day	276.1	< 0.1	16	2.1	0	0	0	0	0	7.0	1.4
55 day	286.9	< 0.1	16	2.1	0	0	0.1	0	0	NA	NA
60 day	299.2	< 0.1	15	2.6	0	0.1	0.1	0	0	7.2	1.8
65 day	319.5	< 0.1	14	2.0	0	0	0.2	0	0.1	NA	NA
75 day	343.8	< 0.1	14	2.8	0	0.2	0	0	0.2	6.2	NA

¹ NA = not analyzed.

Sodium

Sodium is not considered to be a water toxin, other than its contribution to water saltiness. Unlike Ca and Mg, Na levels in the leachate decreased below detection limits shortly after leaching was initiated (Tables 21-25). With increased waste application, less time was required for Na disappearance. For the waste treated columns, the Na level dropped below detection in 2 to 6 days, while 16 days were required for the column which received no waste. The rate of Na leached from the columns was not proportional to the number of pore volumes passing through the column. This evidence suggested that Ca added with the waste rapidly displaced Na on the colloidal exchange sites allowing the Na to move through the column. For the control, 2 percent and 4 percent waste treated columns, the total Na output closely paralleled the calculated total Na input. With 6 and 10 percent waste added to the column, the Na output exceeded input by approximately 30 percent (Table 20).

Manganese

Manganese concentrations should not exceed 0.05 ppm (Table 3) in drinking water. In almost all leachate samples analyzed, the Mn levels exceeded this maximum, including those from the untreated Dayton silt soil. Manganese concentrations in the leachate from the

waste-treated columns ranged from 21 to 27 ppm during the first 2 to 6 pore volumes, while averaging 13 ppm in the leachate from the control column over the first 2 pore volumes. Manganese concentrations decreased eventually to levels less than 1.0 ppm in all columns, and in some cases below 0.1 ppm. After extended periods of anaerobic conditions in all columns, the Mn concentrations rose slowly to as much as 1.2 ppm (Tables 21-25).

Manganese outputs from the leaching columns were not correlated to the waste added to the column. Output from the control column was 11.9 mg, while waste-treated columns had outputs between 44 and 52 mg. Since anaerobic soil conditions promote Mn solubility, it appeared that the Mn total output and concentration in the leachate were higher than might occur under field conditions. In all cases the Mn leached was less than the total Mn extracted by DTPA from the soil and waste.

Zinc

Drinking water should not contain more than 5.0 ppm Zn. In the first 4 pore volumes from all columns, the Zn concentrations were in the leachate well within the allowable standards (Tables 21-25). Zinc output exceeded the estimated DTPA-extractable Zn input in the control and 2 percent waste-treated columns. They may have been due to an underestimate of the DTPA-extractable Zn in the soil.

The Zn concentration in the percolate decreased with increasing waste added (Tables 21-25). This effect may be attributable to the increased soil pH associated with waste applications. Like Na, the Zn concentration in the leachate decreased to below the detectable level (0.01 ppm) by the fourth day of leaching for columns treated with 4 percent or more waste.

Nitrate-N

The NO_3 -N concentration in the leachate increased slightly with waste application (Tables 21-25). At no time, however, did the NO_3 -N levels exceed the concentration recommended for drinking water (10 ppm) (Table 3). With 10 percent waste added, the NO_3 -N concentration averaged 6.6 ppm in the initial leachate, while leachate from the control column averaged 4.4 ppm NO_3 -N in the first 2 pore volumes. After leaching for 24 hours, the NO_3 -N levels decreased to zero. The NO_3 -N output was greater than the extractable NO_3 -N in the soil and waste. This discrepancy resulted from conversion of ammonium-N to NO_3 -N, decomposition of soil organic N, or under-estimation of soil NO_3 -N. Nitrate-nitrogen does not pose a threat to groundwater contamination at waste application rates up to 100 T/A.

Ammonium-N

Ammonium nitrogen is not considered a hazard in drinking water, although excessive NH_4 -N may be toxic to young plants. Ammonium nitrogen does serve as a nutrient source in the eutrophication process. The NH_4 -N concentration in the leachates increased with waste application (Tables 21-25). The leachate from the untreated Dayton silt soil never contained more than 0.8 ppm NH_4 -N, while the NH_4 -N concentration in the first 3 pore volumes from the 10 percent waste treated column averaged 28.8 ppm. The NH_4 -N outputs were reasonably close to the extractable NH_4 -N inputs, indicating that the NH_4 ion was not strongly held by the clay colloid.

Fluoride

Fluoride levels permitted in drinking water should not exceed 1.4 to 2.4 ppm F, depending on water temperature (Table 3). Leachate samples contained maximums of 2.6 to 11.5 ppm F at waste application rates of 2 percent or more, thus presenting a distinct fluorosis problem. Leachates from the control column contained less than 0.2 ppm F. The F content of the leachate from all columns was maximal after one to two days of leaching, followed by a subsequent reduction and stabilization after 6 to 40 days (Tables 21-25). The initial F leached may have come from the dissolution of readily soluble

compounds such as sodium fluoride, with less soluble compounds, such as calcium fluoride, establishing the longer term equilibrium in the percolation water. This hypothesis may be corroborated by the loss of Ca from waste treated soil over time. A 2:1 Ca:F ratio was observed in the percolate after the first 6 days of leaching. Since the atomic weight of Ca is approximately double that of F, a molecular ratio of approximately 1:1 exists in the leachate. If the Ca and F in the leachate came from the dissolution of Ca-F compounds, then that compound would have the formula $\text{CaF}(x)$, where x represents a hydroxy ion or other singly charged negative species. The presence of CaSO_4 and CaCO_3 compounds in the waste, however, complicates a comparison of the Ca:F release.

The question remains, however, whether waste application rates must be limited to less than 20 T/A (the equivalent of the 2 percent waste column) to avoid groundwater F pollution. Soil sample analysis from the field plots did not show appreciable downward F movement. However, the ammonium acetate extraction solution may have removed only the freely soluble F, and left some F in the soil. The restrictive nature of the B horizon of the Dayton soil profile limits downward water flow to the permanent water table, so most soil water movement would be lateral. Localized pollution of small creeks and streams near the application area would be possible, and could present a hazard to livestock, if sufficient F dilution does not occur. The

surface runoff water from field application areas must also be diluted.

Further research and analysis on this subject is recommended.

Sulfur

Drinking water should not contain over 250 ppm SO_4 , or about 83 ppm S. Sulfur from the waste product did not appear to pose a long term threat to groundwaters, even though the initial S levels in the leachate from the 10 percent waste-treated column were as high as 400 ppm S. The S concentration in the leachate increased with waste application in the initial leachate water collected. Leachate from the 2 percent waste treated soil contained about 100 ppm S over the same period. After the passage of 2 to 9 pore volumes through the waste treated soil, the S concentrations were below the maximum drinking water standards (Tables 21-25). Sulfur levels in the percolates stabilized between 0 and 3 ppm S after 3 or 4 days.

Sulfur output exceeded total waste and extractable soil S added in all columns (Table 20). Since the S output increased rapidly with waste application, the waste must contribute considerable mobile SO_4 -S. If the total waste S analysis is accurate, the error must lie with the low estimate of the soil leachable S, which may be plausible since the S from the control column also exceeded S input.

Soluble Salts and pH

With a few minor exceptions, the pH of the leachate from all columns was near 7.0. Soluble salt levels were high during the first 6 to 12 hours of leaching, but fell to less than 1.0 mmhos/cm (Tables 21-25). Only the leachate from the 10 percent waste treated soil column had a saline reading; 5.5 mmhos/cm conductivity during the first 4 pore volumes. Soluble salts do not appear to present a serious long term hazard to groundwaters.

Summary

With the exception of F and Mn, the elemental constituents measured in the leachate waters do not appear to pose any long-term problem to groundwaters. The Ca, Mg, and Na concentrations in the leachate from the waste treated soil were initially relatively high but posed no pollution threat and decreased markedly with leaching time. The NO_3^- -N and NH_4^- -N levels were low (less than 6 ppm for NO_3^- -N, less than 29 for NH_4^- -N) in all leachate water samples, and would not be the limiting factor in determining waste application rates.

The F levels in the leachate may present a hazard to drinking water unless it is adsorbed by the soil or diluted before it enters a water supply, either runoff or groundwater. Zinc levels were well

within drinking water standards, but Mn levels appeared high, perhaps due to the anaerobic conditions created in the soil columns. Sulfur does not appear to pose a long term pollution threat.

SUMMARY AND CONCLUSIONS

Disposal of refractory metals processing waste on Dayton silt soil appears feasible provided that information can be obtained to demonstrate that no F problems occur in ground or surface runoff water.

Crop Production

Perennial ryegrass, var. Linn, yields were not decreased by the application of up to 100 T/A waste product. No statistically significant yield increases were seen, although some indications of yield increases with increased waste application were observed. The ryegrass showed no visual symptoms of nutrient deficiency or toxicity.

The levels of such toxic heavy metals as Zn, Cu, Ni, and Pb were low in the plant tissue. Copper and Zn concentration in the plant tissue were near deficiency levels generally associated with most crops. Phosphorus levels in plant tissue did not decrease with increased waste application, despite a reduction in available soil P. Since perennial ryegrass is tolerant to low P levels, it cannot be inferred that other crops will be equally tolerant of the reduced available soil P. Plant S contents increased with waste applications of 50 T/A or more, compared to control plots. Plant nitrogen levels increased with waste application rates over 25 T/A. The Mg contents

of the ryegrass decreased with increasing waste applications, although that decrease may have been more apparent than real, due to an unusually high Mg content for one control plot. If in fact such decreases were real, the cause of this decrease is the high Ca/Mg ratio of the waste product. Despite these apparent reductions in Mg content, no Mg deficiencies occurred.

Waste Disposal

One principle purpose of any soil waste disposal system is to dispose of toxic heavy metals safely and permanently. Increased waste application to the Dayton s1cl soil did not increase Cu, Zn, Ni, Fe, Al, or Mn availability. In fact, less of most metals was extracted with increased waste application, since the waste material increased the soil pH. Metal constituents in the waste did not appear to be a limiting factor in determining the maximum waste application rates.

The waste product reduced the acid-fluoride extractable P in the Dayton s1cl soil to levels below that amount considered necessary for normal plant growth. However, with ryegrass, no P deficiency symptoms appeared, nor were plant P contents affected. The addition of high rates of P fertilizer (100 lbs P/A) increased plant P content in some cases, but did not increase forage or seed yields.

Increased waste applications appeared to increase the available S content in the soil, although wide variations between treatments did

occur. Plants grown on plots which received no S fertilizer or waste, contained low S levels. The addition of S, either through the waste product or as CaSO_4 fertilizer, increased plant S uptake.

Total soil Zr and Hf contents increased with waste applications. No evidence of plant uptake at any serious level was seen. Most Zr and Hf added to the soil was insoluble and thus not available for plant uptake.

Some of the exchangeable bases in the soil, notably Ca, increased only slightly soon after the waste application in the fall but the ESP value decreased considerably over time, due to leaching and plant uptake. Exchangeable K levels in the soil were not affected by waste application.

The addition of the waste increased the soil pH, a very beneficial effect on strongly acid soils. The need to lime fields for ryegrass production could be eliminated by waste applications of 25 T/A.

Water percolation rates through the waste treated soil increased with waste application in laboratory leaching columns, but the net effect of this phenomena in the field may be minimal in the short run, since the restrictive claypan was not affected by the waste additions. Long term effects of waste product additions on soil water percolation rates were not determined. Chances for increases in soil water percolation rates would depend on the effect of Ca and Mg ions leached into the soil profile. These ions would tend to increase soil aggregation, and thus increase percolation rates. Soil moisture retention was not affected by waste application.

Groundwater and runoff water quality would be affected by waste application but F appeared to be the only element which could present a problem.

Future Research Needs

The successful utilization of this waste material on Dayton sicl soil depends upon development of more specific data on possible F contamination of groundwater and reducing the impact of the waste on P availability. No definite maximums for waste application can be established until field studies are conducted on the movement of F in the Dayton profile and its concentration in leachate samples. The use of the Dayton sicl for crops other than those tolerant to high soluble salts and low available P may be resolved by leaching the soil over the winter before planting and banding P fertilizers, respectively, but specific research should be completed to assure that these remedies will eliminate the problem. Since this study was conducted over only one growing season, information should also be gathered over longer time periods to see whether there are any long term deleterious effects on perennial ryegrass crop growth.

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APPENDICES

APPENDIX I

Table I. Chemical analysis of refractory metal waste product.¹

Sample Number ²	F	Zr	Fe	Al	Ca	Mg	Na	Pb	P	K	S
	%										
2/1	4.29	22	2.82	1.66	10.5	0.33	0.47	0.12	0.35	0.14	0.91
2/2	4.56	21	2.77	1.68	10.2	0.34	0.46	0.14	0.34	0.14	0.86
5/1	6.28	22	2.60	1.44	11.1	0.29	0.45	0.14	0.38	0.11	0.95
5/2	5.93	22	2.58	1.41	10.9	0.28	0.41	0.16	0.34	0.11	0.94
6/1	3.92	24	2.35	1.14	11.0	0.26	0.33	0.17	0.29	0.10	1.07
6/3	4.03	22	2.33	1.14	11.0	0.26	0.34	0.19	0.30	0.10	1.14
8/1	3.29	24	2.39	1.30	10.5	0.26	0.33	0.24	0.29	0.10	1.01
8/2	3.32	22	2.38	1.26	10.8	0.26	0.31	0.25	0.30	0.10	1.04
	Hf	Cr	Ni	Cu	Cd	Co	Mn	Mo	Zn		
	ppm										
2/1	3250	1030	600	110	<50	< 50	610	< 20	490		
2/2	2980	1000	700	120	<50	< 50	600	< 20	510		
5/1	2760	890	700	110	<50	< 50	500	< 20	520		
5/2	3020	900	600	110	<50	< 50	500	< 20	500		
6/1	2280	690	750	100	<50	< 50	490	< 20	510		
6/3	2080	660	900	100	<50	< 50	490	< 20	530		
8/1	2870	720	600	100	<50	< 50	430	< 20	500		
8/2	2670	760	550	100	<50	< 50	430	< 20	500		

¹ Data courtesy of Teledyne Wah Chang Albany Corporation.

² Samples are subsamples of waste product collected at four times during the summer of 1973 from Teledyne Wah Chang Albany Corporation.

APPENDIX II

Table II. Plant constituent analysis--ryegrass harvested July, 1974.

1 Treatment	N	P	K	S	Ca	Mg	Na	Al	Fe	Mn	Zn	Cu	Ni	Cr	Mo	Co	F	Zr	Hf	Pb
	%				ppm															
0-2.5-25-15																				
A ²	1.05	0.18	1.55	820	0.43	0.09	0.45	130	150	184	12	3.8	1.7	0.39	0.37	0.87	NA	<50	<50	<1
B	0.91	0.17	1.73	1060	0.35	0.09	0.24	80	115	130	8	3.4	1.7	0.38	0.40	0.62	6.4	<50	<50	<1
C	0.87	0.19	1.65	1120	0.39	0.09	0.44	200	220	175	13	3.5	1.9	0.55	0.49	0.66	NA	<50	<50	<1
D	NA	0.18	1.69	1100	0.37	0.09	0.31	90	105	148	10	3.3	0.9	0.54	0.58	0.62	6.9	<50	<50	<1
F	NA	0.26	1.09	760	0.41	0.12	0.46	1700	1330	237	30	3.7	2.6	0.80	0.21	1.33	NA	<50	<50	<1
G	1.03	0.26	1.24	1120	0.37	0.12	0.50	1670	1290	242	24	3.1	2.1	0.72	0.30	0.91	48.4	<50	<50	1
H	0.81	0.19	1.63	930	0.36	0.13	0.35	1240	980	197	26	3.6	2.2	0.75	0.27	1.39	43.7	NA	NA	<1
I	0.91	0.19	1.46	570	0.42	0.19	0.38	1840	1540	153	34	5.9	5.2	0.69 ³	0.49	1.10	NA	NA	NA	NA
5-2.5-25-15																				
A	NA	0.18	1.67	1120	0.38	0.08	0.24	150	120	151	10	3.2	1.1	0.68	0.65	0.83	5.6	<50	<50	<1
B	1.08	0.25	1.80	1160	0.52	0.11	0.56	310	250	202	11	4.3	1.7	0.37	1.0	1.08	NA	<50	<50	<1
C	1.01	0.23	1.69	1060	0.40	0.08	0.24	120	100	126	8	3.7	2.2	0.42	1.0	0.58	3.3	<50	<50	<1
D	0.90	0.21	1.56	1050	0.39	0.09	0.34	320	230	124	10	3.6	1.4	0.45	0.71	0.61	NA	<50	<50	<1
F	0.96	0.21	1.50	670	0.37	0.11	0.42	1770	1450	233	13	3.6	1.2	1.32	0.33	0.77	30.6	<50	<50	<1
G	1.04	0.17	1.28	800	0.43	0.10	0.50	1050	800	210	12	3.4	2.5	0.78	0.36	1.11	NA	<50	<50	<1
H	NA	0.20	1.38	550	0.40	0.11	0.55	1460	1150	203	15	3.3	1.1	0.76	0.38	0.77	NA	<50	<50	1
I	0.97	0.20	1.44	970	0.40	0.11	0.52	2250	1650	212	16	3.4	1.3	0.78	0.14	0.60	33.2	<50	<50	<1
10-2.5-25-15																				
A	0.96	0.19	1.57	860	0.39	0.09	0.37	100	125	121	9	3.7	0.9	0.63	0.71	0.68	NA	<50	<50	<1
B	0.97	0.20	1.41	890	0.42	0.09	0.50	130	135	130	11	3.8	1.6	0.56	0.59	0.74	3.0	<50	<50	1
C	NA	0.18	1.87	1220	0.41	0.09	0.22	100	100	121	9	3.8	0.9	0.45	0.94	0.58	NA	<50	<50	<1
D	1.08	0.18	1.40	970	0.37	0.09	0.33	160	160	110	12	3.5	3.3	0.40	0.85	0.63	4.8	<50	<50	<1
F	0.99	0.18	1.33	1290	0.42	0.13	0.50	2090	1550	231	18	4.0	1.6	0.87	0.70	0.72	NA	<50	<50	<1
G	0.96	0.18	1.04	1160	0.40	0.12	0.53	1080	890	195	18	3.2	2.6	0.65	0.16	0.79	19.6	<50	<50	1
H	1.01	0.19	1.29	1290	0.42	0.13	0.54	2000	1570	201	20	3.4	1.4	1.32	0.47	0.95	43.7	<50	<50	2
I	NA	0.19	1.37	1180	0.42	0.14	0.45	2070	1760	207	24	3.3	1.7	1.14	0.56	1.28	NA	<50	<50	1

Table II. Continued.

Treatment	N	P	K	S	Ca	Mg	Na	Al	Fe	Mn	Zn	Cu	Ni	Cr	Mo	Co	F	Zr	Hr	Pb
	-%				ppm															
<u>25-2.5-25-15</u>																				
A	1.03	0.17	1.50	1100	0.47	0.10	NA	180	160	117	13	3.7	4.4	1.98	0.83	0.63	12.8	<50	< 50	1
B	0.74	0.19	1.85	1250	0.46	0.11	0.33	180	190	159	17	5.6	2.6	0.46	0.91	0.83	NA	<50	< 50	1
C	NA	0.21	1.84	1220	0.51	0.10	0.28	40	100	129	13	4.1	2.3	0.43	>1.0	0.76	2.3	<50	< 50	<1
D	1.00	0.19	1.60	1520	0.47	0.09	0.32	210	230	164	13	3.6	1.6	0.55	0.90	0.75	NA	<50	< 50	<1
F	NA	0.17	1.14	1080	0.38	0.09	0.46	1040	850	162	14	3.0	1.2	0.66	0.63	0.88	31.9	<50	< 50	1
G	0.93	0.18	1.06	1220	0.40	0.10	0.57	1300	1100	179	13	2.9	2.2	0.84	0.44	0.76	NA	NA	NA	NA
H	0.91	0.19	1.13	1120	0.40	0.10	0.51	1540	1300	179	13	2.8	1.8	0.86	0.28	0.60	NA	<50	< 50	1
I	0.83	0.19	1.39	1030	0.44	0.09	0.43	900	750	150	12	2.7	2.0	0.66	0.23	0.63	18.2	<50	< 50	<1
<u>50-2.5-25-15</u>																				
A	1.09	0.17	1.81	1350	0.44	0.11	0.48	120	140	94	13	5.0	2.3	0.89	0.74	0.85	NA	<50	< 50	<1
B	1.12	0.16	1.58	1410	0.46	0.11	NA	40	90	105	14	3.3	2.8	0.70	NA	0.66	2.8	<50	< 50	<1
C	1.22	0.18	1.61	1670	0.57	0.11	0.64	160	180	135	20	5.5	3.0	0.38	0.84	0.68	NA	<50	< 50	<1
D	NA	0.14	1.41	1240	0.45	0.10	NA	90	130	102	12	3.8	1.6	0.40	0.56	0.55	3.0	<50	< 50	<1
F	1.07	0.17	0.97	1120	0.37	0.12	0.69	1590	1170	173	24	3.4	1.7	0.72	0.18	0.58	NA	62	< 50	<1
G	0.92	0.17	1.27	990	0.43	0.12	0.52	1800	1330	168	21	3.9	2.1	1.24	0.40	0.62	43.9	<50	< 50	<1
H	NA	0.23	1.31	1330	0.46	0.13	0.53	1750	1330	192	24	4.2	1.8	1.32	0.34	0.92	39.2	<50	< 50	<1
I	0.99	0.23	1.19	1290	0.51	0.13	0.49	1330	1210	198	20	3.8	1.7	0.70	0.19	0.80	NA	<50	< 50	<1
<u>0-0-25-15</u>																				
A	NA	0.20	1.60	980	0.35	0.08	0.35	120	160	190	18	3.6	1.0	0.40	0.28	1.06	NA	<50	< 50	<1
B	NA	0.26	2.10	1270	0.42	0.13	0.34	210	250	288	17	3.7	2.2	0.63	0.18	0.87	8.9	<50	< 50	<1
C	NA	0.20	1.80	1090	0.35	0.09	0.34	110	130	170	18	3.9	1.4	0.45	0.32	0.78	7.7	<50	< 50	<1
D	NA	0.20	1.58	1020	0.28	0.08	0.38	160	150	238	14	2.8	1.3	0.53	0.08	1.33	NA	<50	< 50	<1
F	NA	0.17	1.20	1050	0.32	0.10	0.56	2240	1450	207	50	3.5	1.8	0.96	0.0	0.76	NA	<50	< 50	<1
G	NA	0.18	1.29	1230	0.29	0.10	0.50	1310	1000	294	16	3.0	1.6	0.78	0.16	1.11	NA	<50	< 50	<1
H	NA	0.20	1.53	930	0.32	0.10	0.40	1450	1100	221	19	3.1	1.5	0.85	0.10	0.74	16.6	<50	< 50	<1
I	NA	0.19	1.55	1140	0.31	0.10	0.40	1020	700	187	16	3.3	2.4	0.76	0.10	1.03	21.0	<50	< 50	<1

Table II. Continued.

	N	P	K	S	Ca	Mg	Na	Al	Fe	Mn	Zn	Cu	Ni	Cr	Mo	Co	F	Zr	Hf	Pb	
Treatment	--%--				--ppm--																
<u>25-0-25-15</u>																					
A	NA	0.23	1.77	1150	0.50	0.11	0.40	360	280	157	16	3.8	2.8	0.62	0.89	0.87	NA	<50	<50	<1	
B	NA	0.20	1.58	1650	0.45	0.09	0.47	130	100	111	16	3.3	2.3	0.50	0.61	0.51	NA	<50	<50	<1	
C	NA	0.20	1.62	1560	0.48	0.10	0.36	200	140	160	17	3.1	1.6	0.57	0.89	0.59	7.2	<50	<50	<1	
D	NA	0.18	1.57	1160	0.44	0.09	0.32	200	160	121	16	3.9	1.2	0.44	1.0	0.85	6.7	<50	<50	<1	
F	NA	0.19	1.44	1110	0.41	0.09	0.40	1050	850	217	17	3.4	1.3	0.84	0.50	0.91	NA	<50	<50	<1	
G	NA	0.19	1.23	960	0.33	0.09	0.48	1430	1100	172	13	3.8	3.8	1.30	0.54 ³	1.00	55.7	<50	<50	<1	
H	NA	0.22	1.52	1050	0.37	0.10	0.40	740	750	167	13	3.3	1.6	1.00	0.55	0.88	25.7	<50	<50	1	
I	NA	0.19	1.50	1000	0.40	0.09	0.45	1040	560	179	13	3.7	1.6	0.84	0.55	0.80	NA	<50	<50	<1	
<u>0-2.5-25-0</u>																					
A	NA	0.20	1.57	720	0.34	0.07	0.43	110	190	180	10	3.1	0.7	0.64	0.21	1.05	4.4	NA	NA	NA	
B	NA	0.21	1.55	990	0.43	0.08	0.48	160	160	167	12	3.2	1.4	0.60	0.38	0.93	NA	NA	NA	NA	
C	NA	0.22	1.64	860	0.41	0.07	0.31	110	120	130	11	3.3	1.0	0.52	0.40	0.69	4.3	NA	NA	NA	
D	NA	0.20	1.60	840	0.38	0.06	0.29	50	80	137	9	3.1	0	0.56	0.34	0.68	NA	NA	NA	NA	
F	NA	0.19	1.47	740	0.31	0.07	0.30	1060	900	154	13	3.4	0.8	0.92	0.12	0.53	21.9	NA	NA	NA	
G	NA	0.19	1.17	860	0.41	0.08	0.59	1070	900	212	12	3.6	4.8	0.84	0.10	0.43	NA	NA	NA	NA	
H	NA	0.16	1.19	990	0.41	0.08	0.57	2040	1600	154	15	3.6	2.5	0.64	0.32	0.63	NA	NA	NA	NA	
I	NA	0.20	1.48	760	0.42	0.10	0.33	1850	1400	212	13	3.4	1.2	0.95	0.53	0.41	51.4	NA	NA	NA	
<u>10-2.5-25-0</u>																					
A	NA	0.20	1.47	910	0.44	0.08	0.52	100	120	140	12	4.3	1.2	0.72	0.55	0.66	NA	NA	NA	NA	
B	NA	0.19	1.46	820	0.42	0.07	0.45	140	150	123	10	3.4	1.3	0.57	0.45	0.58	6.6	NA	NA	NA	
C	NA	0.20	1.56	1030	0.39	0.07	0.33	100	110	133	11	3.8	2.4	0.37	0.61	0.59	NA	NA	NA	NA	
D	NA	0.23	1.36	1010	0.38	0.07	0.58	150	150	114	12	4.2	1.0	0.52	0.76	0.65	5.6	NA	NA	NA	
F	NA	0.20	1.45	930	0.38	0.08	0.41	1340	1000	213	13	4.3	0	0.64	0.40	0.18	NA	NA	NA	NA	
G	NA	0.18	1.09	930	0.39	0.08	0.59	1230	1100	191	13	3.2	1.3	1.18	0.13	0.45	62.9	NA	NA	NA	
H	NA	0.22	1.29	930	0.40	0.08	0.60	1290	1050	170	14	3.3	2.1	1.02	0.21	0.71	20.8	NA	NA	NA	
I	NA	0.20	1.43	890	0.37	0.08	0.43	1590	1200	185	20	3.8	1.3	1.28	0.17	0.62	NA	NA	NA	NA	

Table II. Continued.

Treatment	N	P	K	S	Ca	Mg	Na	Al	Fe	Mn	Zn	Cu	Ni	Cr	Mo	Co	F	Zr	Hf	Pb
	-	-	-	-%-	-	-	-	-	-	-	-	-	-	-	-ppm-	-	-	-	-	-
<u>0-2.5-100-15</u>																				
A	NA	0.24	1.73	1140	0.41	0.08	0.45	100	140	177	13	3.4	0.9	0.69	0.34	0.95	6.8	NA	NA	NA
B	NA	0.23	1.43	1180	0.39	0.07	0.60	70	100	153	19	4.0	1.5	0.77	0.35	0.87	NA	NA	NA	NA
C	NA	0.30	1.86	1140	0.42	0.08	0.44	160	170	180	11	4.5	1.7	0.69	0.66	1.01	5.8	NA	NA	NA
D	NA	0.23	1.66	1090	0.35	0.07	0.39	140	140	152	9	3.5	1.2	1.00	0.41	0.67	NA	NA	NA	NA
F	NA	0.20	1.12	1070	0.39	0.09	0.63	2040	1600	241	12	3.5	1.3	1.20	0.15	0.46	44.3	NA	NA	NA
G	NA	0.23	1.27	1020	0.37	0.08	0.54	1400	1150	194	12	3.6	1.0	0.70	0.23	0.98	NA	NA	NA	NA
H	NA	0.25	1.93	1070	0.41	0.10	0.20	1030	800	192	12	4.0	2.4	0.83	0.16	1.10	NA	NA	NA	NA
I	NA	0.27	1.67	1290	0.40	0.10	0.46	1510	1300	230	14	5.0	2.1	1.04	0.15	0.69	24.4	NA	NA	NA
<u>10-2.5-100-15</u>																				
A	NA	0.21	1.38	1110	0.49	0.08	0.59	230	240	178	13	3.5	1.5	0.65	0.42	0.78	6.9	NA	NA	NA
B	NA	0.21	1.48	1140	0.56	0.06	0.45	80	130	152	12	3.2	1.0	0.62	0.83	0.78	NA	NA	NA	NA
C	NA	0.23	1.73	1290	0.52	0.08	0.39	120	130	140	12	4.3	1.3	0.74	0.78	0.72	3.7	NA	NA	NA
D	NA	0.24	1.73	1090	0.47	0.08	0.32	130	130	122	14	3.6	2.5	0.54	>1.0	0.72	NA	NA	NA	NA
F	NA	0.20	0.97	960	0.43	0.09	0.69	1640	1400	207	14	3.4	1.3	1.28	0.14	0.66	NA	NA	NA	NA
G	NA	0.22	1.60	1090	0.43	0.09	0.37	1280	1150	192	17	4.3	1.8	0.91	0.55	1.37	44.5	NA	NA	NA
H	NA	0.25	1.44	1470	0.45	0.10	0.64	1310	1150	213	17	4.0	1.5	1.32	0.24	0.85	41.9	NA	NA	NA
I	NA	0.26	1.36	1050	0.36	0.09	0.43	1340	1050	166	15	2.7	0.9	0.70	0.16	0.49	NA	NA	NA	NA
<u>50-25-100-15</u>																				
A	NA	0.25	2.22	1900	0.56	0.10	0.31	310	270	160	18	4.8	2.4	0.65	0.82	0.91	6.1	NA	NA	NA
B	NA	0.20	1.62	1250	0.49	0.08	NA	60	80	115	19	3.9	2.1	0.55	0.52	0.59	5.5	NA	NA	NA
C	NA	0.20	1.45	1470	0.50	0.08	0.44	230	210	105	27	4.4	2.4	0.76	0.56	0.78	NA	NA	NA	NA
D	NA	0.23	1.64	1540	0.53	0.08	NA	130	110	126	41	4.4	2.2	0.49	0.73	0.74	NA	NA	NA	NA
F	NA	0.21	1.29	1340	0.44	0.08	0.62	1630	1250	180	28	3.4	2.9	0.64 ³	0.33	0.55	36.8	NA	NA	NA
G	NA	0.19	1.12	1290	0.52	0.08	0.69	1320	1100	167	34	3.4	1.8	0.62	0.21	0.72	12.7	NA	NA	NA
H	NA	0.22	1.30	1320	0.53	0.10	0.69	1500	1250	192	27	3.5	1.4	0.67	0.09	0.57	NA	NA	NA	NA
I	NA	0.26 ³	1.38 ³	1310 ³	0.49 ³	0.10 ³	0.60 ³	1550 ³	1240 ³	168 ³	30 ³	3.7 ³	1.6 ³	0.58 ³	0.21 ³	0.57 ³	NA	NA	NA	NA

Code: 0 waste - 2.5 lime - 100 P - 15 S.

¹Waste and lime applications = tons/acre; P and S applications = lbs/acre.²Replicates A-D; wet waste application area. Replicates F-I; dry waste application area.³Estimated.

APPENDIX III

Table III-a. Dry matter yield of ryegrass grown on waste treated Dayton sicl soil.

Waste T/A	Treatment			Dry matter yield (ton/acre)							
	Lime T/A	P lbs/A	S lbs/A	Replications*							
				A	B	C	D	F	G	H	I
0	2.5	25	15	5.1	3.7	2.9	3.3	3.1	2.1	2.3	3.2
5				3.6	3.3	2.1	2.5	2.7	2.7	2.8	2.5
10				3.3	3.7	2.9	4.0	2.9	3.4	3.6	2.7
25				2.9	3.4	2.9	3.3	3.5	2.8	2.7	2.7
50				4.0	3.7	4.8	3.5	3.1	2.6	3.8	3.2
0	2.5	25	0	3.2	2.5	3.1	2.8	2.9	2.3	3.1	2.8
10				2.4	3.8	2.7	4.8	2.8	3.1	2.6	3.6
0	0	25	15	3.2	3.1	4.3	3.1	2.8	2.7	2.2	2.5
25				4.0	3.7	2.3	4.6	3.6	2.6	2.8	2.8
0	2.5	100	15	3.3	3.8	4.3	2.6	2.3	1.7	3.2	3.3
10				3.1	3.1	2.7	2.8	3.1	3.1	2.5	2.4
50				2.9	2.9	2.2	2.9	2.3	2.7	2.7	2.5

*Replications A-D, waste applied wet; replications F-I, waste applied dry.

Table III-b. Clean seed yield on waste treated Dayton sicl soil.

Waste T/A	Treatment			Clean seed yield (lbs/acre)							
	Lime T/A	P lbs/A	S lbs/A	Replications*							
				A	B	C	D	F	G	H	I
0	2.5	25	15	1708	1075	1017	945	931	1468	590	1156
5				806	892	516	758	902	1055	1084	931
10				1046	1271	595	1473	868	1295	1223	945
25				753	897	859	1358	1463	854	834	930
50				1142	1271	1602	1243	1401	955	1444	1151
0	2.5	25	0	1065	801	921	792	931	758	1051	873
10				724	1070	873	1353	1065	1103	983	1209
0	0	25	15	950	983	1482	777	859	993	844	796
25				1338	897	940	1329	1521	792	1108	1314
0	2.5	100	15	844	988	523	892	792	633	547	1314
10				950	1147	811	935	1065	1358	681	888
50				1103	844	792	1012	811	1007	1195	1065

*Replications A-D, waste applied wet; replication F-I, waste applied dry.