PLANT NUTRIENT UTILIZATION

Effect of Uptake of Radiocalcium

HYDE S. JACOBS and J. V. JORDAN
University of Idaho, Moscow, Idaho

Ploughing under green manure crops and other plant residues is a recommended practice, as these materials not only add organic matter to the soil and improve its physical properties but also return to the soil many plant nutrients, including nitrogen, phosphorus, potassium, and calcium. In northern Idaho and certain other sections of the United States, gypsum is used as a soil amendment on acid soils primarily as a source of sulfur, notwithstanding the fact that lime is the universal amendment for acid soils. The objective of this investigation was to compare the availability of calcium to barley when the calcium was supplied as gypsum, calcium carbonate, and green manure. Alaska peas were used as the green manure crop.

The availability of calcium in green manure has not been reported in the literature, although several investigators have compared its availability in lime and in gypsum. Fried and Peech (*8*) found that lime was superior to gypsum in increasing plant growth and that more calcium was absorbed by alfalfa and perennial rye grass from lime than from gypsum. Some investigators have used radioactive calcium salts to make comparisons of availability. Ririe and Toth (*18*) used radioactive calcium in the carbonate, sulfate, and phosphate forms. They determined that calcium was most available to alfalfa as the carbonate and least available as the sulfate. Blume and Hall (*3*) also used radioactive calcium in the carbonate, sulfate, and phosphate forms and concluded that calcium was most available to tobacco as the phosphate and least available as the sulfate.

Dunn (*7*) attributed a difference in calcium uptake from lime and gypsum to soil acidity. On soils which were slightly acid, both lime and gypsum increased the uptake of calcium significantly, but on a more acid soil only the lime treatments caused increases in calcium uptake, whereas the gypsum treatments caused decreased uptake and poor plant growth.

Fried and Peech (*8*) suggested that injury to plants on acid soils may be due to aluminum, iron, or manganese. They noted that gypsum greatly increased the concentration of these elements in available forms in the soil, whereas lime reduced their availability. Lignon and Pierre (*13*) showed that barley, the plant used in this study, was harmed by 1 p.p.m. of soluble aluminum. Others (*15–19*) have found that differences in availability may be due to the kind of plant used in measuring calcium uptake.

Materials and Methods

The sources of calcium used were gypsum, lime, and green manure, each tagged with calcium-45. The tagged green manure was obtained by growing seven flats of Alaska peas in sand culture, using a nutrient solution (*12*) containing calcium-45 as tagged calcium chloride in amounts varying from 50 to 450 microcuries per flat. After harvest, the plant material was air-dried, ground, and blended to give a product having a corrected specific activity of 7560 counts per minute per milligram of calcium.

Labeled gypsum and calcium carbonate were prepared from tagged calcium chloride in the laboratory. The corrected specific activities of these preparations were 31,216 and 40,617 counts per minute per milligram of calcium, respectively.

Gypsum and calcium carbonate labeled with calcium-45 were prepared using tagged calcium chloride. Briefly, gypsum was prepared by dissolving appropriate amounts of labeled and ordinary C.P. calcium chloride in water and precipitating the sulfate by adding, first, a large excess of sulfuric acid, and later, 95% ethyl alcohol. Following digestion on the steam table for 3 hours, the sulfate was filtered off, washed free of chlorides, and dried in vacuum for 1 hour at 80° C. Yields of 99% or better are possible and the rate of activity recovered is high. Drying procedure and time, and whether or not plaster of Paris predominates in the product, appear to be critical factors affecting the yield.

Labeled calcium carbonate is prepared by dissolving appropriate amounts of analyzed calcium chloride, labeled and ordinary, in acid solution. Tagged calcium carbonate is precipitated by addition of excess sodium carbonate. Following digestion at 65° C. and standing overnight, the carbonate is filtered off and dried at 70° C. Yield of tagged calcium carbonate was high, at 99.40%.

The soil used in this study was Helmer silt loam having a pH of 6.0. Exchangeable calcium, magnesium, and sodium were 1.78, 1.83, and 2.02 meq. per 100 grams, respectively. Field capacity was 45% water.

The soil was fertilized so that after the labeled calcium sources were applied, 100 pounds of nitrogen, 200 pounds of phosphorus pentoxide, 50 pounds of potassium oxide, and 110 pounds of sulfate per acre would have been added to the soil. The soil was incubated at field capacity for 6 weeks; then the radioactive calcium sources were applied. Soil containers were gallon cans painted inside with an asphalt emulsion. To each container were added 2540 grams of air-dry soil and the calcium fertilizers mixed uniformly through the soil. There were two rates of application, corresponding to the calcium in 200 and in 100 pounds of gypsum per acre. The treatments were replicated four times.

Hannchen barley was grown to measure the uptake of calcium. There were four plants per pot and the pots were randomized in the greenhouse. The growing period was from December 24, 1952, until June 1, 1953, when the plants were harvested. Lights were used from December 30 until harvest and regulated to give a 16-hour photoperiod each day. The plants received distilled water as needed. There was no leaching, although conditions for good drainage were provided. After the plants had been growing a month, minor elements and 25 pounds of nitrogen per acre were applied to each pot. The plants were grown until all but a few of the smaller tillers had matured. The heads and the straw were harvested and analyzed separately for total calcium, radiocalcium, nitrogen, and phosphorus.

Prior to analyses, the air-dry plant

samples were ground in a Wiley mill to pass a 20-mesh screen. Calcium was determined by the oxalate method of Shapter (*17*). The calcium oxalate was filtered off, so the precipitate was in a convenient form for measuring radiocalcium and total calcium. Radioactivity measurements were made using an N.I.C.C. windowless flow counter (Model D 46A, Nuclear Instrument and Chemical Corp., Chicago 10, Ill.). The radiocalcium was measured in counts per minute, then corrections were made for time, self-absorption, and coincidence losses. Following this determination, the precipitate was dissolved in 0.5*N* sulfuric acid and the amount of calcium determined by titrating the oxalate with 0.03*N* potassium permanganate.

The Shapter method (*17*) was also used in the determination of soil calcium. Soluble calcium was determined on samples of the saturated soil extract (*20*). Extractable calcium was determined in an ammonium acetate extract of the soil taken according to the modified method of Hosking (*10*). Exchangeable calcium was determined by subtracting the soluble soil calcium from the extractable soil calcium.

Phosphorus was determined by the method of Koenig and Johnson (*11*). Nitrogen was determined using a modified Kjeldahl method (*2*).

Soluble aluminum, iron, and manganese were determined in the saturated soil extract by the method of Peech and English (*16*).

Yield of Barley

Plant yields from the 100- and 200-pound rates cannot be compared, since minor physical injury in three of the replications (one pot from each treatment all at the 200-pound rate) distorts the mean values for rates. Hence, the values in Table I are actually means of eight replications—that is, rates are disregarded.

Data in Table I indicate that more total plant material was produced on the gypsum and green manure treatments than on the lime treatment. The average weights of plants grown on the gypsum and green manure treatments were 10.87 and 10.82 grams per pot, respectively. These weights were significantly higher at the 5% level than the 10.07-gram mean weight from the lime treatment. Barley grown on the gypsum treatment produced the most heads, while that grown on the green manure treatment produced the most straw.

Uptake of Soil and Fertilizer Calcium by Barley

Table II shows that there were no significant differences in total calcium uptake by the plants due to treatment. Although the data are not tabulated, neither was there any significant difference due to rate. Uptake of soil and fertilizer calcium by plants grown on the gypsum, lime, and green manure treatments averaged 26.66, 26.57, and 27.82 mg. per pot, respectively. The average total calcium taken up by the barley heads on the green manure treatment was 4.79 mg. per pot, which was significantly higher at the 5% level than the 4.20 and 3.88 mg. taken up from the gypsum and lime treatments, respectively. No significant difference in uptake of soil and fertilizer calcium occurred in the straw due to treatments. These average total calcium uptake values were 22.46, 22.69, and 23.03 mg. per pot for the gypsum, calcium carbonate, and green manure treatments, respectively.

Uptake of Fertilizer Calcium by Barley

Data in Table III indicate that the gypsum and green manure treatments furnished an average of 0.66 and 0.67 mg. of calcium per pot, respectively, to the barley crop. These amounts were significantly higher than the 0.51 mg. supplied by the lime. This difference was significant at the 1% level. To the heads alone the gypsum and green manure treatments supplied an average of 0.28 and 0.29 mg., respectively, of calcium per pot. These amounts were significantly greater at the 1% level than the 0.22 mg. of calcium supplied by the calcium carbonate.

There was also a significant difference in fertilizer-calcium uptake due to rate of application. The higher rate of application furnished an average of 0.78 mg. of calcium per pot compared with the 0.44 mg. supplied at the lower rate. This difference was significant at the 1% level. The heads recovered calcium from the applied sources in almost the same proportion in which it was applied. The lower rate furnished an average of 0.18 mg. of calcium per pot and the upper rate 0.34 mg. per pot, which is a proportion of 1 to 1.9. The calcium in the two rates was applied in the proportion of 1 to 2. Like the heads, the straw absorbed significantly more fertilizer calcium at the upper rate than at the lower rate. The 0.44 mg. of calcium per pot absorbed by plants on the upper rate was significantly higher at the 1% level than the 0.26 mg. absorbed by plants on the lower rate of treatment.

On the basis of plant uptake, the calcium from the green manure treatment was fully as available as the calcium from the gypsum, and both sources furnished more available calcium than the calcium carbonate. The relative calcium availability from green manure has not been reported previously; however, the results of this study showing calcium from gypsum to be more available than calcium from calcium carbonate conflict with other published reports (*3, 9, 18*).

Several authors (*1, 5, 6*) have observed that high hydrogen ion concentration interfered with calcium absorption, although this was discounted by others (*4, 14*). In this experiment excessively high hydrogen ion concentration was avoided and acidity apparently did not interfere with calcium uptake. This is borne out by the values for calcium uptake in Table III.

The average pH of the gypsum, calcium carbonate, and green manure treatments was 6.04, 6.12, and 5.63, respectively. These figures were obtained by averaging the hydrogen ion concentration and converting this value to pH. The hydrogen ion concentration of the green manure treatments was significantly higher at the 1% level than the calcium carbonate or gypsum treatments although the latter treatments did not differ significantly from each other. The only significant difference in hydrogen ion concentration due to rate of

Table I. Effect of Calcium Source on Barley Yield from Both Rates of Treatment

Plant Part (Air-Dry)	Treatment per Pot			L.S.D.[a]	
	Gypsum	Lime	Green manure	(0.01)	(0.05)
Whole plant[b]	10.87	10.07	10.82	...	0.66
Heads	5.38	4.76	4.91	...	0.50
Straw	5.49	5.31	5.91	0.55	0.39

[a] Least difference between means required for significance at 1 and 5% levels.
[b] Excluding roots.

Table II. Uptake of Soil and Fertilizer Calcium by Barley from Both Rates of Treatment

Plant Part	Treatment per Pot, Mg.			L.S.D. (0.05)
	Gypsum	Lime	Green manure	
Whole plant[a]	26.66	26.57	27.82	2.99
Heads	4.20	3.88	4.79	0.60
Straw	22.46	22.69	23.03	2.64

[a] Excluding roots.

application occurred in the green manure treatment. The upper rate had received twice as much organic matter as the lower rate and consequently was more acid. The average pH values, calculated as above, were 5.53 and 5.78 for the upper and lower rates, respectively. Even though these differences were significant at the 1% level, the difference amounted to only 0.25 pH unit.

Microchemical tests for aluminum, iron, and manganese in the saturated soil extracts were negative. There was less than 1 p.p.m. of aluminum in the extract of the original soil. Absence of the effects of soluble aluminum, iron, and manganese may be one reason for the difference between calcium availability reported herein and that reported by other investigators.

Ratio of Soil Calcium To Fertilizer Calcium

The ratios in Table IV indicate that a correlation existed between the ratio of soil calcium to fertilizer calcium on the soil exchange complex and the ratio of soil calcium to fertilizer calcium in the plant. Significantly more calcium was supplied by gypsum to the soil exchange complex than by either calcium carbonate or green manure. By harvest time the gypsum had supplied an average of 1 out of every 18 parts of exchangeable calcium, calcium carbonate 1 out of every 21 parts, and green manure one out of every 19 parts. The difference between the amounts of calcium supplied by gypsum and calcium carbonate was significant at the 1% level, and the difference between that supplied by the green manure and the calcium carbonate was significant at the 5% level.

Table IV also shows that the gypsum and green manure furnished 1 out of every 44 parts of calcium taken up by the plants from these treatments, whereas the calcium carbonate furnished only 1 out of every 58 parts. The differences were significant at the 1% level.

Significantly more fertilizer calcium was taken up from the gypsum and green manure treatments than from the calcium carbonate treatment. Thus it appears that those sources of calcium which replaced the soil calcium on the exchange complex to the greatest degree were the most available, for they supplied the most fertilizer calcium to the crop.

Table IV. Ratios of Soil Calcium to Fertilizer Calcium in Various Media[a]

Media	Treatment Gypsum	Lime	Green manure	L.S.D. (0.01)	(0.05)
Barley plant	43.70	57.55	43.98	9.76	...
Soil exchange complex	17.93	21.18	19.05	2.24	1.62

[a] Irrespective of rates of treatment.

The ratios in Table IV show the extent to which the various calcium sources replaced soil calcium on the exchange. The smaller the ratio, the greater the extent to which soil calcium was replaced.

If there were perfect correlation between the ratio of soil calcium to fertilizer calcium on the soil exchange complex and the ratio of soil calcium to fertilizer calcium in the barley plants, then the plants would contain soil and fertilizer calcium in a ratio equal to the ratio of soil calcium to fertilizer calcium on the exchange. This would be true assuming equilibrium existed. In this study, however, the fertilizer calcium was applied and the barley crop planted within a few days of each other, so it is unlikely that equilibrium conditions existed until after the plants were at least partly grown. Consequently, the calcium obtained by the plants from the exchangeable calcium supply before equilibrium was attained would be disproportionately higher in soil calcium than would be expected if judged by the ratio prevailing at the time of equilibrium. For ex-example, in the gypsum treatment the ratio of exchangeable soil calcium to fertilizer calcium was 18 and the ratio of soil calcium to fertilizer calcium in the barley plants from this treatment was 44. These values would probably be closer together if equilibrium had existed between exchangeable soil and fertilizer calcium at the time the barley was planted.

On the basis of the ratio of exchangeable soil calcium to fertilizer calcium it would appear that the most fertilizer calcium should have been taken up from the gypsum treatment, since the lowest value for the ratio occurred in this treatment. Instead, barley from the gypsum and green manure treatments took up essentially the same amounts of fertilizer calcium. Probably the high solubility of the calcium in the green manure accounted for its availability being equal to that of the calcium in gypsum.

Table III. Fertilizer Calcium Recovered by Barley Crop from Both Rates of Treatment

Plant Part	Treatment per Pot, Mg. Gypsum	Lime	Green manure	L.S.D. (0.01)
Whole plant[a]	0.66	0.51	0.67	0.09
Heads	0.28	0.22	0.29	0.05
Straw	0.38	0.29	0.38	0.08

[a] Excluding roots.

Summary and Conclusions

Gypsum, calcium carbonate, and a green manure crop of Alaska peas, all labeled with calcium-45, were used to determine the availability of the calcium from each source to a crop of Hannchen barley. Results indicated that the yield of total plant material was higher on the gypsum and green manure treatments than on the calcium carbonate treatment. However, the upper rate of calcium application appeared to depress total plant production.

Calcium from gypsum and calcium from the green manure were equally available to the barley and both sources furnished more calcium than calcium carbonate.

The ratio of soil calcium to fertilizer calcium on the soil exchange complex was apparently correlated with calcium availability to the barley crop.

More soluble calcium was furnished by the green manure crop of peas than by the mineral calcium sources, calcium carbonate and gypsum.

Hydrogen ion concentrations and the exceedingly low soluble aluminum, iron, and manganese concentrations prevailing in this study did not appear to affect the calcium availability to the barley crop.

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SOIL EFFECTS ON HERBICIDES

Adsorption of 3(*p*-Chlorophenyl)-1,1-dimethylurea As a Function of Soil Constituents

H. R. SHERBURNE and V. H. FREED

Agricultural Experiment Station, Department of Agricultural Chemistry, Oregon State College, Corvallis, Ore.

In a study of the rate of adsorption of 3(p-chlorophenyl)-1,1-dimethylurea (CMU) on different soil types, a method was developed for determining the amount of CMU adsorbed on various materials. Twelve different soils were tested and the absorption was correlated with mechanical composition. The results indicate that there is very high adsorption of CMU on organic matter and a significant rate of adsorption on inorganic clay particles.

THE HERBICIDE 3(*p*-chlorophenyl)-1,1-dimethylurea (CMU) has been reported to be less effective on a heavy soil than on a light soil and more persistent on the heavy soil (*5*). As this material is being used widely as a soil sterilant, such considerations are of practical importance.

It was proposed that this difference in activity and persistence in different soil types might be due to physical adsorption of the CMU molecule on the soil particles.

Therefore, an experiment was conducted to observe the difference in the quantity of adsorption on various soils and to correlate this adsorption with certain soil properties.

Experimental Methods

The soils used in this study were selected because of their varying composition. Asbestos, cotton, dicalite, kaolin, activated carbon, sawdust, and straw were also used as adsorbates in an attempt to determine whether adsorption of CMU is due to a particular type of adsorbing surface.

After many procedures had been tried the following method was developed to measure the quantity of adsorption.

A 10-gram sample of air-dry soil (except for the muck soil, where 1 gram was used) was placed in a 50-ml. plastic centrifuge tube with 25 ml. of 200 p.p.m. CMU solution, and agitated periodically for 0.5 hour. Similarly, lesser amounts of the highly adsorptive materials were used in the determination. Preliminary results indicated that equilibrium had been attained in this period of time. The tube was then centrifuged on a size 2 International centrifuge at an acceleration of 656 times gravity. After the centrifuge period of 0.5 hour, the supernatant liquid was clear. A 10-ml. aliquot was removed from the supernatant liquid and diluted to 50 ml. in a volumetric flask. The CMU in a 2-ml. portion was determined according to the microquantitative acid hydrolysis procedure outlined by Lowen and Baker (*6*).

The amount of CMU that was not recovered was considered to be adsorbed. The pH was determined on a Beckman pH meter (*7*). The organic matter was determined according to the dichromate reduction method (*7*), and the moisture of each soil sample was determined gravimetrically, so that all calculations could be made on a dry weight basis (*7*). On each soil a mechanical analysis determination was conducted according to the procedure outlined by Bouyoucos (*2*), with the modifications suggested by Tyner (*9*) and Kilmer and Alexander (*4*). The correlation coefficient was calculated to obtain the relationship between the amount of CMU adsorbed and the soil properties that were determined (*8*).

Results and Discussion

The amount of CMU found to be adsorbed by the various soils and other substances and the properties of the soils as determined by the methods indicated are summarized in Table I. The figures presented represent an average of two determinations within a limit of precision of $\pm 1.34\gamma$. The adsorption study reported was carried out under one set of experimental conditions with no attempt to determine the adsorption isotherm. However, this is what would be encountered in a field application of a given rate of the chemical. While this does not permit exact quantitative comparison of the amount of chemical adsorbed, it provides a basis for estimating the relative readiness with which the soil adsorbs the material and the probable comparative tenacity with which the chemical is held. The amount of adsorption on the other substances is reported in Table II.

The correlation coefficients that were calculated are recorded in Table III.

From the data presented in Table II it is evident that CMU is readily adsorbed by organic substances such as Norite, sawdust, and straw, but not on cotton, which is also organic.

A correlation of pH, per cent silt, and per cent clay with the amount of CMU adsorbed is not significant. However, a correlation of all other properties that were determined with the amount of adsorption is highly significant. It is