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IN northern Idaho, gypsum is used as a fertilizer on acid soils in the cutover areas, primarily as a source of sulfur. The need for sulfur-containing materials on legumes in these areas has been recognized since 1922 *(9)*. Since then the value of sulfur fertilizers for legumes has been corroborated by investigators in Washington, Oregon and Idaho *(6, 10, 11, 13)*.

There are no reports in the literature regarding the relative efficiencies of sulfur sources in supplying this nutrient to crop plants, nor are there reports on the residual supplying power of these materials. In this report, green manures or plant residues are classed as sulfur sources. Plowing under green manure crops has been a recommended practice for many years. Green manure not only adds organic matter to soil, thereby improving the physical characteristics, but also returns to the soil many plant nutrients, including nitrogen *(1, 15)*, phosphorus *(4)*, calcium *(8)*, potassium *(2)*, and magnesium.

Incorporating the radioisotope, sulfur-35, in various fertilizers affords an accurate method for determining plant uptake of sulfur from such materials as gypsum, ammonium sulfate, ferrous sulfate, elemental sulfur and green manure. Furthermore, the half-life of sulfur-35 is 88 days which permits a study of year-to-year carry-over of available sulfate from the application of these sulfur fertilizers.

This report describes the techniques developed and the results obtained during a study concerning (1) sulfur uptake from various sources, (2) the response of legume crops to sulfur fertilizer treatments, and (3) the residual effects of some of the sulfur fertilizer treatments. Northern Idaho soils were used in these experiments.

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Materials and Methods

The sulfur sources were tagged with radiosulfur in the laboratory. Gypsum and ammonium sulfate were dissolved in water and radioactive sulfur in the form of sulfur-35 in H_2SO_4 was added. The salts were recrystallized and ground for homogeneity *(7)*. Commercial ferrous sulfate, approximate formula $Fe_2(SO_4)_3.9H_2O$, was digested for several days in weak acid solution containing the tracer. Excess acid solution was washed out of the salt on a Buchner filter and the product dried and ground. Tagged elemental sulfur was prepared by dissolving sulfur in carbon disulfide and adding tagged elemental sulfur. After complete mixing, the solution was evaporated to dryness in vacuum and the product ground. Tagged green manure was prepared by growing peas in sand-culture flats. These were supplied nutrient solution containing radioactive sulfate. The plants were harvested, air-dried and ground.

The above materials were each blended with inactive counterpart so that each approximated the same specific activity, 2.5×10^4 counts per minute per mgm. sulfur.

Specific activity determinations were run on the products by precipitating sulfate as $BaSO_4$-BaS^*O_4 from gypsum, ammonium sulfate and ferrous sulfate. Elemental sulfur and green manure were analyzed for sulfate using a Parr oxygen bomb, and the $BaSO_4$-BaS^*O_4 precipitated *(12)*. The precipitates were filtered off on No. 42 Whatman filter discs using stainless steel filter devices under suction. The precipitates were air dried and the sulfur-35 activity counted in a preflush flow counter using Q-gas. The precipitates were then ignited and weighed.

All five tagged sources were used in a greenhouse study on Palouse silt loam and on Mission silt loam soils. The treatments were based on a rate of 30 pounds of sulfur per acre and mixed in weighed batches of soil. These soil preparations were then divided up into No. 10 food cans. The treatments were replicated six times. Beans were the indicator crop and four plants were grown in each can. The bean plants were harvested, air dried, weighed and ground for total sulfur and radiosulfur analyses. The soils were then cropped a second time to beans in order to determine differences in sulfur availability from the five fertilizer sources.

In the field, tagged gypsum and elemental sulfur were applied in May, 1954 to Palouse silt loam at Moscow. Alfalfa, spring wheat and peas were the indicator crops. Residual effects of the sulfur sources were studied on these plots for three years. Treatments were at the rate of 30 pounds of sulfur per acre, and were replicated six times. At the Sandpoint Branch Station three sources, gypsum, ammonium sulfate and elemental sulfur, were applied to spring wheat in the same experimental design. Plant yields were determined in all field studies as well as total sulfur and radiosulfur analyses. Winter kill and erosion prevented determinations for residual effects the following year at the Sandpoint site.

Measuring radiosulfur—Sulfur-35 is a relatively soft beta emitter (E_{max} 0.17 mev.) so that self absorption, window and air absorption, and counting geometry are important factors in measurement. At low levels of sample activity, absorption of the soft beta particles by these factors can be limiting to the point of reducing the sample counts to near background rates. Plant tissue contains only 0.2 to 0.3 percent sulfur so that even doubling the weight of the charge undergoing combustion does not necessarily increase appreciably the rate of count of sulfur-35 activity. Thus it was important to adopt a procedure that provided optimum conditions for counting.

A preliminary experiment was set up to compare end window counting *(5)* and gas flow counting of $BaSO_4$-BaS^*O_4 precipitates. The end window tube used was the customary TGC-2 model (less than 2 mgm./cm.[2]) in a lead shield. The flow counter was an RCL preflush model using Q-gas. Solutions carrying increasing incre-

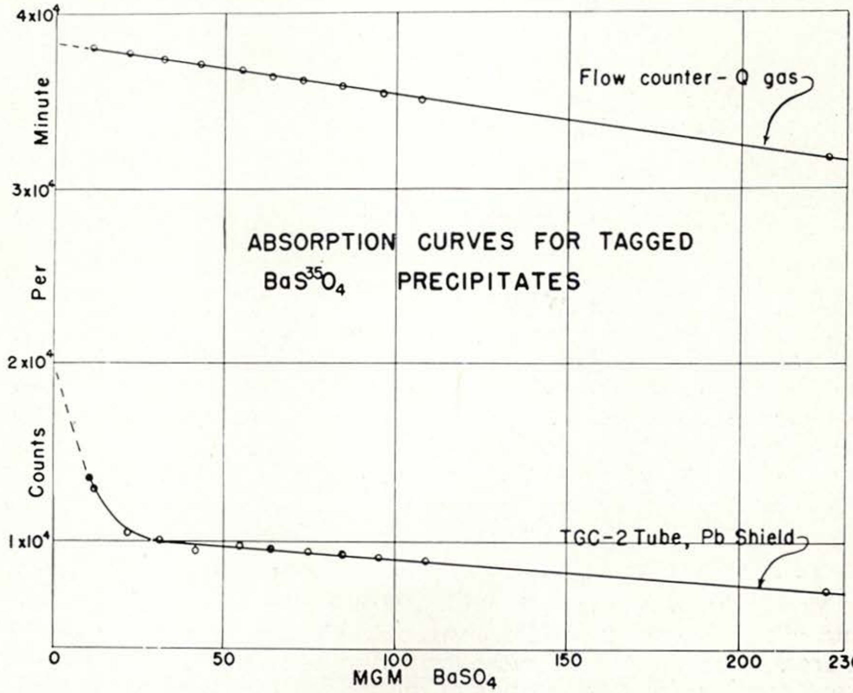

Figure 1.—Absorption curves for BaS^*O_4 precipitates counted by an end window G-M tube in a lead shield, and by a gas flow counter.

ments of Na_2SO_4 for a range of zero to 230 mgm. of $BaSO_4$ were prepared. A constant level of sulfur-35 in sulfate form was added to each sample. There were thirteen variables of $BaSO_4$ each with nine replications. The $BaSO_4$ was precipitated, allowed to digest several days, then filtered off on No. 42 Whatman filter paper discs in 1-inch diameter stainless steel filters under suction. The precipitates were air dried, and activities determined by both counting procedures. The results, mgm. $BaSO_4$-BaS^*O_4 versus counts per minute, were plotted for comparison and these data are presented in Figure 1.

Results and Discussion

Graphically displayed in Figure 1 are the results of counting $BaSO_4$-BaS^*O_4 precipitates of increasing weight when the sulfur-35 was constant. The activity of the precipitates was corrected for background and time only. Background count in the lead shield was 30 counts per minute and in the gas flow counter 60 counts per minute. Absorption, geometry and coincidence corrections were not applied to these data since the purpose was to compare the respective count rates from the two methods of counting, rather than to determine the absolute activity present.

The activity of the first sample, weighing about 11 mgm., was approximately 1.3×10^4 counts per minute using the end window tube, and 3.8×10^4 using the gas flow counter. The half thickness of the $BaSO_4$ precipitate was between 30 and 40 mgm. as shown by the leveling off in the sharp downward rate of the lower curve in the figure. Here the curve stabilized as the samples became thicker and only a certain top section of the thick samples was being counted by the end window tube. The radiations from below this top section were self-absorbed within the samples. The pattern in the upper curve was different. In the gas flow counter, particles comprising the samples were surrounded with the ionizable Q-gas so that many more events were recorded. The degree of self-absorption here would depend on the size of crystals.

Generally, 1 gram of plant tissue is used for determining sulfur by the oxygen or peroxide Parr bomb procedure. This produces 15 to 30 mgm. of $BaSO_4$. This weight of precipitate was not sufficient to exceed the half-thickness and the samples were subject to counting errors arising from radiation scattering. Therefore, the extrapolation of the lower curve as shown in Figure 1 is for descriptive purposes only. At such low weights of precipitate the curve probably rises steeply from the near-zero to some point higher than is shown for the first point of the curve, i.e., 11 mgm. $BaSO_4$. At these low weights of precipitate data were not reproducible, possibly due in part to filter paper impregnation which altered the nature of the $BaSO_4$ sample.

Examination of the top curve shows that the low weight samples were not subject to these errors when counted in an ionizing gas atmosphere in the flow counter *(3)*.

The geometry of the samples counted under the end window tube was not constant, as the precipitates varied in thickness. The line would fall more rapidly if the geometry had been constant. Geometry in the gas flow counter was constant.

Resolving time of the gas flow counter was specified as 150 microseconds, and for the end window tube 6 microseconds. Thus coincidence corrections on the flow counter determinations would be very much greater due to the relatively longer resolving time. This is possibly the only disadvantage of using the flow counter but even this can be largely discounted by using lower levels of activity, and this is generally the case in radiotracer studies.

Table 1.—Plant yield and sulfur uptake by beans grown in the greenhouse on two soils fertilized with five tagged sulfur sources.

Treatments	Soils							
	Palouse				Mission			
	cpm/mgm $BaSO_4$		Dry Weight		cpm/mgm $BaSO_4$		Dry Weight	
	1st crop	2nd crop	1st crop	2nd crop	1st crop	2nd crop	1st crop	2nd crop
			grams	grams			grams	grams
Checks	....	....	7.34	8.21	....	....	3.50	3.72
$CaSO_4 2H_2O$	4126	6255	6.69	9.54	3950	5532	3.11	3.45
$Fe_2(SO_4)_3 9H_2O$	2725	8431	7.82	8.56	2461	6528	3.12	3.61
$(NH_4)_2SO_4$	3[illegible]03	4278	5.15	6.21	2521	3350	2.95	3.11
Peas— green manure	1132	9212	8.63	10.40	1770	7522	3.40	3.98
Sulfur	59	1928	6.80	6.95	103	1526	3.05	3.12

Data in Table 1 illustrate the relative ability of sulfur source materials to furnish sulfate to a growing crop. Gypsum, ammonium sulfate and ferrous sulfate, in that order, supplied the most sulfate to beans growing on both Palouse and Mission soils in the first cropping. Green manure followed next, with elemental sulfur a poor last. However, in the next crop, about 3 months later, the availability of sulfate from all of these materials had changed. For example, on both the soil types, the green manure and ferrous sulfate were the better suppliers of sulfur, in that order. The availability of elemental sulfur had also increased markedly. Bean plant yields generally improved at the second harvesting but this may be due to secondary effects rather than directly attributable to the sulfur in the fertilizing materials. This statement applies particularly to the green manure treatments on both soils which produced significantly higher yields at the second cropping.

Table 2.—Residual effect of two source materials of supplying sulfur to alfalfa (Palouse silt loam)

Treatment	Year	Percentage of total sulfur in alfalfa absorbed from fertilizer at three cuttings June 11	July 28	Sept. 16	L.S.D. 0.01
		%	%	%	%
Gypsum	1954	22.9	10.2	5.4	4.2
Sulfur		2.1	1.2	2.3	1.0
Gypsum	1955	32.1	25.6	18.5	6.1
Sulfur		12.6	8.3	5.0	3.2
Gypsum	1956	7.2	6.8	5.5	2.7
Sulfur		2.1	2.9	2.1	1.5

In Table 2 the data show how applications of gypsum and sulfur in 1954 were still being absorbed by alfalfa in 1955 and1956. The percentage values are relative to the total plant sulfur present and are not to be interpreted as percentage utilization of the 30-pound rate of sulfur applied to the soil in 1954. Thus in 1954 at the first cutting, 22.9 percent of the sulfur in the plant had been absorbed from the gypsum, but only 2.1 percent had been absorbed from the elemental sulfur. In 1955 the absorption of sulfur from these two sources increased very significantly. In 1956, the second residual year, absorption of fertilizer sulfur decreased significantly. By 1957, the sulfur-35 decay had progressed so far that accurate determinations above background count were not possible.

The three cuttings taken each year show a decreased absorption as the growing season progressed. However, the validity of this needs to be tested at more locations. Thomas *et al. (14)* working with wheat and barley found a high initial absorption of radiosulfur by the leaves, followed by a decreasing concentration as the radiosulfur was distributed throughout the plant during the growing season.

Table 3.—Recovery of sulfur by alfalfa, wheat and peas from gypsum and elemental sulfur (Palouse silt loam)

Treatment	Crop	Sulfur recovered by year 1954	1955	1956	Total recovery
		lb/A	lb/A	lb/A	lb/A
Gypsum	alfalfa	6.45	8.77	6.51	21.73
Sulfur		2.91	4.28	2.12	9.31
Gypsum	wheat plant	5.80			
Sulfur		0.55			
Gypsum	peas		6.20		12.00
Sulfur			5.12		5.67

In Table 3 the data indicate how much fertilizer sulfur was recovered in three years cropping by alfalfa. More than twice as much sulfur was recovered from the gypsum application than was recovered from the elemental sulfur. In 1955 a pea crop followed a 1954 crop of wheat and more sulfur was recovered from the gypsum than from the elemental sulfur by a factor exceeding 2. In the first residual year, 1955, the availability of the elemental sulfur had increased significantly.

The data in Table 4 are presented differently than the data from the Moscow experiments. At the Sandpoint site, wheat samples were collected for sulfur uptake measurements but yields were not determined, so recovery values could not be calculated. Results show that in the Mission soil, as in the Palouse soil, more sulfur was absorbed from ammonium sulfate and gypsum than from elemental sulfur. Specific activity values of the plant parts indicate that wheat grown on Palouse soil absorbed more fertilizer sulfur than wheat grown on Mission soil. It is reasonable to interpolate this relationship and state that more fertilizer sulfur was recovered by wheat grown on Palouse soil. Field observations showed that wheat growing on the Palouse soil outgrew and outyielded that grown on Mission soil. Beans grown in the greenhouse experiments as shown in Table 1 support this statement.

Table 4.—Total sulfur in two soils, and in wheat plant parts; and specific activity of plant parts on the various treatments.

Treatments	Total sulfur in soils*		Total sulfur in plant parts				Specific activity (cpm/mgm S) in plant parts			
	Palouse	Mission	Palouse grain	(1954) straw	Mission grain	(1956) straw	Palouse grain	Palouse straw	Mission grain	Mission straw
	%	%	%	%	%	%				
Checks	0.035	0.020	0.18	0.16	0.09	0.05	....	......	......	......
$(NH_4)_2SO_4$	....	0.024	0.24	0.20	0.16	0.13	....	......	172	125
$CaSO_4.2H_2O$	0.038	0.025	0.23	0.20	0.16	0.13	1160	642	174	123
Elemental S	0.039	0.024	0.21	0.19	0.16	0.12	192	121	135	118
LDS (0.01)	....	....	0.04	0.04	0.05	0.04	112	99	21	7

* At harvest

In Table 4, are analyses for total sulfur in the two soils, both treated and untreated. The 30 pounds per acre rate of sulfur applied in the various sources did not increase significantly the percent sulfur in the two soils. However, there was significantly more sulfur in the Palouse soil than in the Mission soil.

Effect on yields—Previous tests have shown the favorable effects of applications of fertilizers containing sulfur to alfalfa from the standpoint of increased yields and quality of hay produced.

Table 5 gives the average annual yields of alfalfa in a fertility test extending over a period of seven years and the yields of winter wheat following the plowing under of the alfalfa. The indicated fertilizer treatments were given to the plots while they were in alfalfa and no fertilizers were added prior to the seeding of wheat. The increases in the wheat yields obtained resulted from treatments applied while the land was in alfalfa. It is interesting to note that the highest wheat yields were obtained on those plots

Table 5.—Effects of fertilizer additions on the yields of alfalfa and the winter wheat crop following seven years of alfalfa*

Fertilizer—rate given in pounds per acre per year	Alfalfa		Winter wheat	
	Ave. yield	Increase over checks	Yields	Increase over checks
	tons per acre	tons per acre	bushels per acre	bushels per acre
1. Check—no fertilizer applied to alfalfa	2.55	......	44.7	....
2. Treble superphosphate, 40 pounds	2.97	0.42	41.1	-3.7
3. Gypsum, 100 pounds	4.08	1.53	58.8	+14.1
4. Gypsum, 100 pounds; treble superphosphate, 40 pounds	4.44	1.89	61.0	+16.3
5. Gypsum, 100 pounds; sulphate of potash, 50 pounds	4.67	2.12	58.1	+13.4
6. Gypsum, 100 pounds; treble superphosphate, 40 pounds; sulphate of potash, 50 pounds	4.09	1.54	61.3	+16.6
7. Sulfur, 18 pounds	3.83	1.28	68.5	+23.8
8. Sodium nitrate, 125 pounds	2.61	0.06	51.9	+7.0
9. Ammonium sulfate, 100 pounds	4.11	1.56	68.0	+23.3

* Fertilizers applied to alfalfa for seven years. No fertilizer added to winter wheat following.

which had previously produced high alfalfa yields; that is, on the plots to which sulfur was applied in one form or another while they were in alfalfa. The increased wheat yields can therefore be accounted for by the more vigorous growth of the alfalfa plants on the plots where the existing sulfur deficiencies were corrected.

The value of sulfur-containing compounds added to the alfalfa plots in these experiments can be stated on the basis of increased income resulting from this practice. When the yields of alfalfa for the 7-year period and the yields of wheat for 1 year are evaluated at the rate of $10.00 per ton for the hay and $1.70 per bushel for the wheat, it is found that the returns above the fertilizer costs for the various treatments containing sulfur ranged from $11.12 to $18.32 per year. For the 8-year period these increases amounted to $106.06 to $151.02 per acre.

Additional data indicate how the use of sulfur materials materially improved the yield of winter wheat over a five year period. This experiment was conducted on Field 7 at the Experiment Station in Moscow. Average annual yields under different treatments were as follows: gypsum, 29.8 bushels per acre; sulfur, 29.1; lime, 28.5; and check, 22.9.

Effect on nutrient content of forage—Tests at Moscow on Palouse silt loam and at Sandpoint on Mission silt loam showed that fertilization of alfalfa and peas by sulfur materials significantly increased the protein content of those crops. The phosphorus content of alfalfa also increased at the Sandpoint site. A few examples are shown in Table 6.

Table 6.—Influence of fertilization with sulfur materials on nutrient content of alfalfa and Alaska peas.

Location	Soil	Crop	Treatment	Protein	Phosphorus
				%	%
Moscow	Palouse silt loam	alfalfa, 1 cutting	checks	14.13	0.283
			S materials*	16.31	0.235
Moscow	Palouse silt loam	peas	check	25.54	....
			gypsum*	27.35	....
Sandpoint	Mission silt loam	alfalfa, 3 cuttings	checks	15.96	0.192
			S materials*	16.99	0.203

* Averages for all rates.

Summary

1. Techniques were developed for determining specific activities of plant samples. Absorption curves have been prepared showing the efficiency of Geiger tube counting and gas flow counting of $BaSO_4$-BaS^*O_4 precipitates.

2. A green manure crop of peas furnished amounts of sulfur to a growing crop of beans that were comparable to amounts furnished by inorganic sulfur sources.

3. Radiosulfur has a half-life which permits residual absorption studies over a period of years, or successive cropping.

4. Gypsum, commercial ferrous sulfate, ammonium sulfate, green manure peas and elemental sulfur were tagged with radiosulfur for a greenhouse experiment on Palouse silt loam and Mission silt loam. These treated soils were cropped with beans to determine the uptake of sulfur from the fertilizer materials. The residual effect of these materials was studied with a second crop. The first crop of beans contained more radiosulfur from green manure and ferrous sulfate. Elemental sulfur furnished more sulfur for the second crop but was, in both cases, the least effective treatment.

5. In field experiments at Moscow, the residual effects of applying gypsum and elemental sulfur were studied for two years on alfalfa, and on wheat followed by peas.

6. Sulfur fertilizing materials increased the protein content of alfalfa at Moscow and Sandpoint, and of peas at Moscow. The phosphorus content of alfalfa at Moscow was depressed by sulfur fertilization, but was increased at the Sandpoint site.

7. There were economic yield increases of alfalfa through using sulfur fertilizers over a 7-year period. Economic gains in the yield of winter wheat followed this period of treatment.

8. When tagged gypsum and sulfur were applied at the rate of 30 pounds sulfur per acre in 1954, alfalfa recovered 21.73 pounds of sulfur from the single gypsum application over a 3-year period and only 9.31 pounds from the elemental sulfur application. Wheat followed by peas, over a 2-year period, utilized 12.10 pounds of sulfur from the single gypsum application and 5.67 pounds from elemental sulfur.

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