Elemental Phosphorus–Sulfur Solutions for Direct Application to Soil. Plant Response and Nutrient Uptake

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Elemental phosphorus (yellow) and sulfur form a eutectic solution at 74 atom % P. This solution was shown to oxidize in soil providing both P and S for plant use. The oxidation of sulfur was much more rapid than normally occurs in soil, suggesting a chemical oxidation rather than biological. Some evidence was obtained that oxidation of S was accompanied by a delay in oxidation of P_4. A solution of P_4 dissolved in CS_2 was also found to provide P for plant needs, but not S. Sulfur applied as CS_2 was not recovered by plants during two cropping cycles totaling 150 days, nor was it found as SO_4–S in the soil at the conclusion of the test, suggesting that the CS_2 was volatilized. Phytotoxicity was evidenced when elemental phosphorus, alone or as the eutectic, was applied to soil. When P was applied in CS_2, P_4-induced toxicity was readily discernible. Yellow phosphorus and phosphoric acid appeared to have similar effect on uptake of Zn, Fe, or Mn, except as the sulfur content of the carrier influenced micronutrient uptake.

At the time these experiments were planned there was an international shortage of sulfur, which encouraged approaches to soil fertilization utilizing elemental phosphorus derived from electrolytic or reductive sources, as opposed to high sulfur consuming wet process phosphoric acid. It is interesting to note that one of the most striking effects of the recent attention by man to ecological problems, in this case air and water pollution, has been a completely altered worldwide sulfur availability. The oil industry and the ore smelters have made positive contributions to sulfur recovery and availability, so that at present, instead of a sulfur shortage, there is a sulfur glut.

Whatever the future economics may be in regard to phosphorus availability, the scientific and particularly agronomic aspects of fertilization with elemental phosphorus have had relatively little previous attention and suggest many avenues for investigation.

Elemental phosphorus (yellow) and sulfur form a eutectic mixture (at 74 atom % P) having a crystallization temperature of 9.8°C. Since both phosphorus and sulfur are essential plant nutrients, it is of interest to know if this eutectic mixture has agronomic properties that would prove advantageous in crop production.

Yellow phosphorus will also dissolve in CS_2 (1000 parts P in 100 parts CS_2 at 10°C). Published reports (MacIntire *et al.*, 1950) indicate extreme phytotoxicity when a solution of yellow phosphorus in carbon disulfide was applied to the soil. Results in this laboratory (Warnock, 1970) and elsewhere (Bohn *et al.*, 1970) have shown only slight phytotoxicity of yellow phosphorus alone. Because CS_2 is phytotoxic, it was also of interest to reevaluate the use of P_4 dissolved in CS_2 as a fertilizer, making allowance for the phytotoxicity of CS_2.

MATERIALS AND METHODS

A eutectic mixture of yellow phosphorus (P_4) and sulfur (S_8) was prepared by melting a weighed quantity of phosphorus under water and then adding the equivalent quantity of flowers of sulfur and shaking in a closed container to effect solution. The eutectic mixture remained flowable (supercooled) to about 4°C when chilled and melted at 10°C when warmed. Sufficient P_4 was also dissolved in CS_2 to give an equivalent P/S ratio, so that treatments could be applied to soil and provide the same levels of P and S for plant nutrition.

The soil used was a Sutherlin silt loam from Mendocino County, Calif. (Gowans, 1958). This soil was slightly acid (pH 6.0) with 3 ppm $NaHCO_3$-soluble P and 170 ppm exchangeable K. Previous experience had indicated the soil to be low in available S; hence a plant response to S was expected. Two fertilization regimes were applied. In the first, 136 ppm of N and 100 ppm of K were applied using urea and potassium nitrate. In the second, ammonium sulfate was substituted for urea so that 114 ppm of S was also applied.

Phosphorus was applied at 50 ppm in the soil from the P_4–S_8 eutectic, P_4 in CS_2, P_4 pellets, and H_3PO_4. The eutectic and CS_2 provided 17 ppm of S in the soil and an equal amount of S was added to soil where H_3PO_4 was applied to the soil fertilized with ammonium sulfate. Check treatments received no phosphorus.

Treatments were applied to the soil and 3 weeks allowed for the CS_2 to dissipate before tomato (*Lycopersicon esculentum*) seedlings were transplanted into the treated soil. Tomato plants had been germinated in a sand–soil potting mix. Plants were grown in the greenhouse for 55 days on treated soil and then harvested, rinsed in deionized water, and dried at 80°C. Dry weight was determined, and then tissue was ground in a stainless steel Wiley mill, wet ashed in nitric–perchloric acid, and phosphorus determined by the ammonium molybdate method (Johnson and Ulrich, 1959). Sulfur was determined on the digest by barium sulfate method (Blancher *et al.*, 1965) and Zn, Fe, and Mn by atomic absorption using a Perkin-Elmer 290 instrument and methods outlined in the manufacturer's handbook.

After removing roots of the first crop, the soil was reworked, fertilized with 136 ppm of N and 100 ppm of K, but no P nor S, and then replanted to tomatoes. This second crop was grown for 49 days and then harvested as before.

Following the second crop, soil samples were taken from two replicates in each treatment. Sulfate-S was extracted with ammonium acetate–acetic acid (Bardsley and Lancaster, 1965) and then determined colorimetrically by the barium chloranilate method (Bertolacini and Barney, 1957). Soil pH was determined in water (Peech, 1965) and available P was determined by extraction with $NaHCO_3$ solution (Olsen *et al.*, 1954).

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RESULTS AND DISCUSSION

First Crop. All three elemental phosphorus sources resulted in marked growth increase over the checks, but were not equal to the corresponding phosphoric acid treatment (Table I). Tomato plants fertilized with elemental phosphorus developed a chlorosis that has been shown to be characteristic of elemental P toxicity (Warnock, 1970). Both the eutectic and P_4 dissolved in CS_2 behaved much like P_4 pellets in terms of plant response. Neither preparation appeared to be appreciably more phytotoxic than yellow phosphorus in the first crop.

Phosphorus concentration in the tissue was lower where the plants were fertilized with the eutectic or CS_2 solutions (data not reported) and phosphorus uptake was considerably less (Table I). Phosphorus from P_4 was significantly less available when it was added to soil either as the eutectic or dissolved in CS_2. The mechanism by which P availability was reduced is not clear. Intimate placement of P and S in the eutectic undoubtedly contributed to the reduced uptake of P from elemental phosphorus.

When plants were grown without benefit of $SO_4^=$ fertilization, phosphoric acid produced more growth and higher P uptake than did P_4. Phosphoric acid also resulted in more growth than did P_4 in the presence of $SO_4^=$, but P uptake was equal. P uptake was reduced as much as 30% where tomatoes were fertilized with $SO_4^=$. Sulfur fertilization also reduced soil pH (Table II) and increased Mn in the plants (Table III). In acid soil, such as used here, "fixation" of P is often increased as pH is reduced (Kurtz, 1953), but in this test $NaHCO_3$-soluble P in the soil after two crops showed no response to $SO_4^=$ treatment (Table II).

Because this soil was known to be low in available sulfur, it was anticipated that plants fertilized with $SO_4^=$ would be larger than those on the no-$SO_4^=$ regime. However, only plants fertilized with P_4 or H_3PO_4 in the presence of $SO_4^=$ were larger than their corresponding treatments on the no-$SO_4^=$ regime. It appeared that toxicity or limited P availability restricted growth enough to prevent response to S when plants were fertilized with the eutectic or P_4 in CS_2 solution.

Sulfur taken up by the first crop was severely limited in the absence of $SO_4^=$ fertilization. Plants fertilized with phosphoric acid or yellow phosphorus but no sulfur accumulated less than 9 mg of S. Carbon disulfide apparently dissipated without leaving sulfur available to the plants, as it produced no increase in S uptake.

The eutectic increased S content of the plants more than two-fold. In the $+SO_4^=$ regime, significant increases in S uptake existed between treatments in the order checks $<$ P_4 in CS_2 $<$ P_4–S_8 eutectic $<$ P_4 $<$ H_3PO_4 + S. The eutectic solution and P_4 dissolved in CS_2 were phytotoxic, which presumably accounts for the reduced S uptake on these treatments.

Some estimate of the rate of S oxidation is possible from the S content of plants on the no-$SO_4^=$ treatment. Each pot received 29 mg of S in the eutectic treatment. Plants on these pots contained 12 mg of S/plant more than those on other phosphorus treatments. Thus, the average recovery by the first crop was slightly over 40% of the S supplied in the P_4–S_8 eutectic. This uptake occurred within 76 days from the time the sulfur was applied to the soil as elemental sulfur, and was more rapid than would be expected. For example, Jones *et al.* (1968) reported that fine elemental sulfur became available mostly in the second year following application to three California soils in open lysimeters.

Second Crop. The Sutherlin soil fixes phosphorus rather strongly, and carryover of P to the second crop was limited.

Table I. Dry Weight of Tissue and Uptake of Phosphorus and Sulfur by Two Crops of Tomatoes in Relation to Fertilization

	First crop			Second crop		
Treatment	Dry wt, g	P uptake, mg	S uptake, mg	Dry wt, g	P uptake, mg	S uptake, mg
No-$SO_4^=$ fertilization						
P_4–S_8 eutectic	7.26	11.7	21.0	4.33	5.7	3.1
P_4 in CS_2	8.00	12.7	8.9	2.18	4.7	1.0
P_4	7.38	15.6	9.0	2.47	5.0	1.2
H_3PO_4	8.67	17.8	8.5	2.19	5.5	1.1
Check	0.27	0.3	1.5	0.24	0.2	0.5
Soil fertilized with $SO_4^=$						
P_4–S_8 eutectic	7.00	9.5	44.2	4.08	4.9	18.9
P_4 in CS_2	6.88	9.2	36.1	2.81	4.1	10.0
P_4	9.20	15.5	63.9	5.01	6.0	17.4
H_3PO_4 + S	10.35	14.8	77.3	4.81	5.4	25.2
Check	0.53	0.5	3.9	0.29	0.3	1.0
LSD, @ 0.05 =	1.04	2.3	9.9	1.17	1.4	4.8

Table II. Soil pH and $NaHCO_3$-Soluble P in Relation to Treatments Applied

Treatment applied	Soil pH[a] no-$SO_4^=$	Soil pH[a] plus-$SO_4^=$	$NaHCO_3$-Soluble P,[a] ppm no-$SO_4^=$	$NaHCO_3$-Soluble P,[a] ppm plus-$SO_4^=$
P_4–S_8	5.5	5.2	5.8	7.5
P_4 in CS_2	5.3	5.2	5.7	5.1
P_4	5.4	5.2	6.4	7.1
H_3PO_4	5.4	5.4	6.8	6.9
Check	5.1	5.0	3.7	3.9

[a] Average two samples.

Table III. Micronutrient Uptake of Two Crops of Tomato Plants in Relation to Fertilization

	mg/plant					
	First crop			Second crop		
Treatment	Zn	Fe	Mn	Zn	Fe	Mn
No-$SO_4^=$ fertilization						
P_4–S_8 eutectic	0.55	0.98	1.43	0.46	0.42	1.24
P_4 in CS_2	0.53	0.95	1.22	0.25	0.18	0.45
P_4	0.39	0.88	0.62	0.23	0.16	0.45
H_3PO_4	0.43	0.79	0.71	0.19	0.22	0.30
Check	0.05	0.12	0.09	0.04	0.02	0.12
Soil fertilized with $SO_4^=$						
P_4–S_8 eutectic	0.56	0.70	1.59	0.49	0.44	2.12
P_4 in CS_2	0.56	0.80	1.62	0.38	0.34	1.62
P_4	0.60	1.02	1.53	0.54	0.37	2.45
H_3PO_4 + S	0.64	0.89	1.64	0.48	0.34	2.06
Check	0.07	0.11	0.20	0.04	0.03	0.21
LSD @ 0.05 =	0.10	0.26	0.22	0.11	0.15	0.44

Plant growth was undoubtedly restricted by the low availability of residual P. In addition, symptoms of S deficiency developed on plants on the no-$SO_4^=$ fertilization regime. Plants fertilized only with H_3PO_4, P_4, or P_4 in CS_2 became yellow early in the second crop. Thereafter they grew slowly and at harvest tissue was observed to be unusually brittle and easily broken. At the conclusions of the test, plants fertilized with the P_4–S_8 but no-$SO_4^=$ were still green and growing well. These plants appeared to be somewhat lighter in color, however, than plants fertilized with sulfate, suggesting incipient S deficiency.

Table IV. Sulfate–S in Soil Following the Second Crop and Sulfur Removed by the Plants in Relation to S Applied

Treatment applied	No-$SO_4^=$ S added	No-$SO_4^=$ S recovered In soil	No-$SO_4^=$ S recovered In crop	No-$SO_4^=$ Total	Plus-$SO_4^=$ S added	Plus-$SO_4^=$ S recovered In soil	Plus-$SO_4^=$ S recovered In crop	Plus-$SO_4^=$ Total
	S-mg/pot							
P_4–S_8	29	12.8	24.1	36.9	224	206	63.1	264
P_4 in CS_2	29	14.3	9.9	24.2	224	188	46.1	234
P_4	0	27.1	10.2	37.3	195	134	81.3	215
H_3PO_4 (+S)	0	18.6	9.6	28.2	224	130	102.5	232
Check	0	37.8	2.0	39.8	195	382	4.9	387

In the absence of S fertilization, second crop tomatoes produced about 2 to 2.5 g of dry tissue per pot. When $SO_4^=$ was supplied, growth was doubled. Sulfur from the eutectic resulted in growth almost equal to that from yellow phosphorus or phosphoric acid in the plus-$SO_4^=$ block.

Toxicity from P_4 in CS_2 solution persisted into the second crop, as evidenced by reduced growth, particularly on the plus-$SO_4^=$ treatment. CS_2 failed to provide adequate S, although plants on this treatment did develop deficiency symptoms about 5 to 10 days slower than those receiving no sulfur. It appears that most of the CS_2 volatilized from the soil without oxidation to sulfate. Such a conclusion is consistent with data on CS_2 movement reported by Hannesson (1945).

Response to phosphorus sources in the second crop may be compared in the plus-$SO_4^=$ regime, where S was adequate. Growth of plants fertilized with the eutectic was equal to that of plants on P_4 and H_3PO_4, and superior to growth of plants fertilized with P_4 in CS_2 solution.

Phosphorus recovery by the second crop did not differ significantly between P sources, except for reduced P uptake from P_4 in CS_2. The latter was undoubtedly a result of persistent toxicity.

Sulfur recovery varied greatly between treatments. Plants receiving no sulfur accumulated only about 1 mg of S per plant. CS_2 did not increase S content of plants in the second crop. Plants on the eutectic treatment were able to take up about 3 mg of S per plant. Where $SO_4^=$ had been applied, S recoveries were 10 to 25 mg/plant.

Micronutrient Uptake. Phosphorus fertilization is known to influence plant uptake of micronutrients, especially Zn, Fe, and Mn. The concentration of these elements in the tissue was determined and the uptake per plant calculated to determine whether or not the P sources used in this test influenced the accumulation of these nutrients differently (Table III).

Check plants made very poor growth and consequently accumulated little of the micronutrients. Where P fertilization was more adequate, $SO_4^=$ increased uptake of Zn. This was true for both crops. Also, in both crops there was a tendency for lower zinc concentration in tissue where P_4 and H_3PO_4 were the P sources (data not shown). This appeared to be tissue dilution, as P sources did not differ significantly in the amount of Zn taken up per plant.

Iron content of tissue did not differ significantly in the first crop. In the second crop there was less Fe taken up by S-deficient plants. Iron concentration in tissue of plants fertilized with P_4 in CS_2 was higher than other treatments, presumably because of reduced growth due to toxicity of this treatment.

Sulfur fertilization increased Mn in plants in both crops, but especially in the second crop. Sulfur deficient plants contained only 20 to 25% as much Mn as those with adequate S. In the second crop, plants on the eutectic treatment, where S was at incipient deficiency, had Mn contents midway between that of plants S-deficient and those adequately supplied with S. There was a tendency in both crops for plants fertilized for P_4 or H_3PO_4 to have lower concentration of Mn in the tissue than plants on other P sources. This appears to be tissue dilution, as the source of P had no significant effect on Mn uptake.

Manganese levels were generally high and check plants in the second crop accumulated in excess of 500 ppm of Mn in the tissue. Manganese availability in soil varies greatly with pH (Christensen *et al.*, 1950) and differences noted here may be attributed to the effect of $SO_4^=$ on pH (Table II).

Sulfur Remaining in Soil. It was of interest to verify the level of available sulfur in soil after removal of the second crop.

Pots of soil from the no-$SO_4^=$ treatments contained less than 30 mg of S after two crops (Table IV), except for the check, where P deficiency had limited S removal. Soil fertilized with 29 mg of S from the eutectic contained only 12.8 mg of S at the end of the cropping sequence, confirming the observation that plants on these pots had depleted the available S supply and were at incipient S deficiency when harvested. Sulfur added as CS_2 was not recovered by the crop nor found as extractable sulfate in the soil, indicating it had been lost from the system.

Extractable S in the plus-$SO_4^=$ treatments was in excess of 130 mg of S per pot. There were three distinct levels of available S in the soil, apparently the end result of S applied less S removed. Plants fertilized with H_3PO_4 or P_4 had removed 103 and 81 mg of S per pot, respectively. More S was determined to be available in the check soil than could be accounted for as S added less that removed in two crops. Whether this is due to sampling error or to S not accounted for in this crude S balance is not known.

Oxidation of Sulfur in P_4–S_8 Eutectic. Recognizing that sulfur from the P_4–S_8 eutectic solution becomes available to plants, it was of interest to determine whether the rate of oxidation of S in the eutectic was different from that of P_4 and S_8 applied separately.

Twenty-gram portions of sand in open vials were treated with 10 mg of S_8 from the eutectic or from S_8 alone. P_4 at approximately 29 mg/vial was placed in a third treatment, while a fourth received 10 mg of sulfur mixed with the sand plus P_4 pellets placed as in the previous treatments. After incubation at room temperature for either 4, 12, or 36 days, three replicate vials from each treatment were extracted with ammonium acetate–acetic acid solution. SO_4–S in the extract was determined by the barium chloranilate method. Sulfur was found to oxidize rapidly (Table V).

The P_4–S_8 eutectic used to apply these treatments had been prepared 2 weeks prior to application and some concern

Table V. Oxidation of Sulfur to Sulfate in Relation to Treatment[a] and Time of Incubation

Treatment	mg SO_4–S/vial[b] 4 days	12 days	36 days
P_4–S_8 eutectic	4.39	4.02	3.22
P_4 + S_8 separate[c]	0	0	0.07
S_8[c]	0.03	0	0.47
P_4	0	0	0.16
Check	0	0	0.04
LSD @ 0.05 =	0.80	0.10	1.34

[a] 10 mg of S per vial. [b] Average three replicate vials each date. [c] Flowers of sulfur mixed with sand.

Table VI. Oxidation of Sulfur to $SO_4^=$ at 6 Days from Freshly Prepared P_4–S_8 Eutectic

	mg SO_4–S/vial 1	2	3	4	Avg
P_4–S_8 eutectic	6.75	8.63	8.63	8.48	8.12
P_4 + S_8[a] separate	0	0	0	0	0
LSD @ 0.05 = 1.27					

[a] Flowers of sulfur mixed with sand.

existed that the sulfur may have partially oxidized prior to addition to the sand. To check this possibility, fresh P_4–S_8 eutectic was prepared and applied to sand immediately in four replicate vials. A comparative treatment, also replicated four times, was established in which equal sulfur was added to the sand but not in direct contact with the P_4 pellet. After 6 days these vials were extracted as previously described. Results are presented in Table VI.

The results confirm the rapid oxidation of sulfur in the eutectic.

The rapid oxidation of S in the eutectic must be largely a chemical oxidation, in contrast to biological process known to be responsible for most sulfur oxidations in soils. Some autoxidation of sulfur is known to occur in soils (Burns, 1967), but this discovery with respect to the rapid oxidation of sulfur in the P_4–S_8 eutectic (up to 86% recovery as SO_4–S in 6 days) is original with this work (Kohn and Warnock, 1971).

There appeared to be some depression of SO_4–S with time, as noted by the series 4.39, 4.02, 3.22, for 4, 12, and 36 days incubation, respectively. The reason for this is not clear. Perhaps microbial growth was immobilizing the sulfate so that it was not extracted, but this was not verified. Nor is it clear why the fresh P_4–S_8 yielded more SO_4–S than the 2-week-old material. Some oxidation appeared to occur while the P_4–S_8 eutectic was stored under water in the laboratory. Because of this apparent oxidation during storage, it is possible some oxidized sulfur was lost into the water above the eutectic. If so, this would account for somewhat lower recovery of SO_4–S from the older eutectic.

A chemical interaction between sulfur and elemental phosphorus occurred, since biochemical (organism) oxidation of S is far too slow to provide the levels of sulfate found. Perhaps interaction between P_4 and S_8 in the eutectic gave rise to sulfides, which in turn were oxidized and hydrolyzed to sulfate. Another possible explanation may have been that P_4 acted as a fuse, initiating oxidation of sulfur.

Elemental P applied as the eutectic solution apparently persisted longer in the soil, as evidenced by oxides of P visible when treated soil was exposed to air. This indicated that rapid oxidation of S was accompanied by delayed oxidation of the P_4. The lower availability to plants of P from the eutectic when compared to P_4 pellets, as found in these studies, is consistent with the apparent delay in P oxidation, while S in the eutectic is being preferentially oxidized.

If sulfur is preferentially oxidized, at the expense of phosphorus, one might anticipate that phytotoxicity would be increased, because of greater persistence of P_4 in the soil. Such was not found in this study, perhaps because the 3-week delay between application of elemental phosphorus and transplanting of tomatoes allowed time for oxidation of the phosphorus. More complete evaluation of these points and the merits of elemental phosphorus for direct application to soil will have to await further studies.

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