Effect of Waterlogging and Organic Matter on the Loss of Applied Sulfur¹

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ABSTRACT

Gypsum and elemental S (56 kg/ha) were applied to lysimeters before the first fall rains. Waterlogging and barley straw (Hordeum vulgare L.) (11,200 kg/ha) were additional variables imposed in all possible combinations. Nitrogen was applied uniformly to all tanks, and cereal and grass were grown during two seasons. In the first year after application of gypsum, 45 and 41 kg/ha S were recovered in the leachate from freely drained soil with and without straw, respectively. The free draining tanks treated with elemental S gave values of 10 and 7 kg/ha S recovered in the leachate for the straw and no straw treatments. Waterlogging decreased leaching loss of sulfur by an average of 40%. Oats (Avena sativa L.) planted when waterlogging was discontinued took up more S in the absence of straw and also more S was leached than on the freely drained treatment. However, no significant increase in uptake occurred in the succeeding grass crop as a result of the sulfur conserved by the waterlogging. It is concluded that where waterlogging occurs during the winter months in annual-type range soils, SO4-S leached from either applied or natural sources of sulfur is likely to be decreased, but also that sulfur conservation by this means is unlikely to aid the production of grasslands in California.

Additional Key Words for Indexing: anaerobic conditions, reduction of sulfate to sulfide, reduction of nitrate.

IN THE MORE HUMID regions of northern California many soils, even in upland areas of annual rangeland, become saturated with water during the winter months when heaviest rains occur. In spring as rains diminish and temperatures increase, the soils become aerobic. Many of these same soils are deficient in sulfur, and when properly applied this element results in substantial increases in forage production. Jones and Ruckman (1966) and Jones, Martin, and Williams (1968) compared the efficiency of elemental S and gypsum S under various conditions, but waterlogging was not considered in their studies. Starkey (1966) stated that marked changes are brought about by microorganisms in intermittently waterlogged soils containing substantial organic matter. Sulfate is reduced and iron sulfide is formed during the anaerobic metabolism of sulfate-reducing bacteria in the presence of adequate organic substances. When the soils are drained and become aerobic, the sulfides are oxidized back to sulfate by *Thiobacilli* and other microorganisms.

It was the purpose of this study to measure the effects of soil waterlogging with and without additions of organic matter on the leaching and plant uptake of sulfur applied as gypsum and elemental sulfur. As a secondary objective, leaching and uptake of nitrate nitrogen was also observed, though this element was not a treatment variable.

PROCEDURE

The 36 lysimeters used in this study are described in a previous paper (Jones et al., 1968). The tanks were filled with a Josephine loam and soaked with deionized water to promote settling before adding more soil to bring the soil level to within 2.5 cm of the top. Josephine is a noncalcic brown soil intergrading to solonetz with a clay mineral composition of 30%kaolinite, 50% vermiculite, and 3% montmorillonite (Begg, 1968). The cation exchange capacity was 12.0 meq/100 g, the pH was 6.0, and base saturation was 66%. Various cations were present as follows: Ca 5.9, Mg 1.2, Na 0.1, and K 0.7 meq/100 g soil.

The three sulfur treatments were none, finely divided gypsum, and finely divided elemental sulfur. The sulfur sources were applied at the rate of 1.13 g S/tank or 56 kg S/ha. The organic matter levels were none, and 227 g ground barley straw (*Hordeum vulgare* L.) (0.675% N, 0.16% S) per tank

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Table 1—Mean monthly temperature near experimental sitefor 1966-67 season, and monthly rainfall for the2 years of the experiment

	Te	mperature		_				
	-	Soil		Rainfall				
	Air	15-cm depth		1966-67	1967-68			
		-•c			-c			
July	20.5	29.9		0	0			
August	22, 9	31.0		6	0			
September	20, 1	26.5		3	0			
October	16, 8	22, 6		0	50			
November	10.7	15.2		240	82			
December	7.2	11, 1		192	134			
January	8.7	9.6		256	253			
February	11, 1	11.9		10	118			
March	7.8	12, 3		193	123			
Aprll	6.6	12.7		118	10			
May	16.6	21.0		9	19			
June	20, 1	24.9		36	0			
			Total	1,063	789			

or 11,200 kg/ha incorportated into the top 2.5 cm of soil. The soil moisture regimes established in the lysimeters during the 1966–67 winter season were free drainage and water table at the soil surface (waterlogged). After March 1, 1967 all tanks were allowed to drain freely. The 12 treatments were initiated October 21, 1966 in a factorial randomized block design with three replications. On the same date 2.27 g/tank (112 kg/ha) each of N as urea and P as concentrated superphosphate were applied to all tanks. On March 1, 1967 the N treatment was repeated. Air and soil temperatures for the 1966–67 season and rainfall for both years of the experiment are given in Table 1.

The waterlogged treatment was established by attaching tygon tubing as a drain for the selected lysimeters. The tubing was pulled up to form a loop at the same level as the soil surface. Moisture entering these lysimeters collected and did not drain away until the water level in the lysimeters had reached the soil surface.

The tanks lay fallow and were kept weedfree until March 1, 1967 when 180 kg/ha 'Sierra' oats (*Avena sativa*) were seeded. The oat yield was determined May 19, 1967 by clipping at ground level, oven drying, and weighing. Soft chess (*Bromus mollis*) was seeded September 27, 1967 at 112 kg/ ha and harvested April 15, 1968. The N treatment was reapplied September 27, 1967.

Leachate was collected in 19-liter carboys and measured as required. A proportional aliquot sample was retained and composited to represent each of the three collecting periods designated in Tables 2 to 5. Total S in plant tissue, SO_4 -S and NO_3 -N in the leachates, and SO_4 -S in the rainfall were deter-

 Table 2—Rainfall, lysimeter leachate, and runoff during three collection periods of the 1966-67 season

	Drainage treatments										
Collection		Freely drained		Waterlogged							
periods	Rainfall	Leachate	Leachate	Runoff	Total	SE					
	mm		mm								
11/1-12/31, 1966	432	367	147	122	269	9					
1/1-2/28, 1967	266	210	210	61*	271	11					
3/1-5/12, 1967	320	206	206		206	8					

* Trapped in the waterlogged tanks at the time they were drained, 2/28/67.

mined by the methods outlined by Johnson and Ulrich (1959). The method described by Steinbergs et al. (1962) was used to determine total sulfur in the soil sampled from the full depth of the tanks at the end of the experiment.

RESULTS

1966-67 Season

First Collection Period—In the fall of 1966 the first rain (18 mm) that germinated annual grassland species fell on November 6. The first leachates from the free drainage lysimeters were collected on November 16. By November 22, 227 mm of rain had fallen, but complete saturation of the waterlogged treatments did not occur until November 28 (Table 2). During the first leachate collecting period (November 1 to December 31, 1966) concentration of SO₄-S in leachates was about 1 ppm in the no S and elemental S treatments, regardless of drainage or organic matter treatments (Table 3). Dressings of gypsum increased SO₄-S concentrations in the leachates, and the increases were significantly higher where soil was waterlogged.

The higher SO_4 -S levels in the leachates from waterlogged lysimeters receiving gypsum may be the result of less leachate moving from the lysimeter (Table 2). This same explanation may apply to the decreased amount of total S leached from the gypsum treatments under the waterlogged condition. Of the 432 mm of rain which fell during the first collection interval, 367 mm moved through the lysimeters with free drainage, while only 147 mm was

Table 3-Effect of organic matter and drainag	e on the S leached and taken up	o from three S treatments in the	season of application
	(1966–67)		

Organic		Ch	eck			Gyr	sum S		Elemental S				
matter	No	one	Straw		No	one	St	Straw		lone	Straw		
Soil drainage	Free	Water- logged	Free	Water- logged	Free	Water- logged	Free	Water- logged	Free	Water- logged	Free	Water - logged	SE
						ppm SO ₄	S in leachate						
Collection dates								-					
11/1-12/31	0.4 a•	0.9 abc	0.6 ab	1.5 abc	3.3 cd	5,0 de	3.1 bed	6.5 e	0.7 ab	1.0 abc	0.5 a	1.3 abc	1.5
1/1- 2/28	0.5 a	0.6 a	1.3 ab	1.0 ab	9.2 d	4.3 bc	11, 8 d	5.1 c	0.8 ab	1.4 ab	1.6 abc	1.5 ab	2.1
3/1- 5/12	0.6 a	0.2 a	1.0 abc	0.6 ab	4.7 g	1, 8 cd	4.0 fg	3.2 ef	1.4 bc	0.4 a	2,6 de	0.6 ab	0.5
						ppm SO ₄	-S in overflow	w					
11/1-12/31	-	0. 2	0.3	0.1	-	3.3	-	3.5	-	0.4	0.2	0.3	
						mg S lea	ached per tan	k					
11/1-12/31	34 a	16 a	43 a	32	248 d	152 be	235 d	197 cd	50 ab	18 a	37 a	38 a	62
1/1- 2/28	23 a	17 a	56 a	41 a	401 c	198 b	518 d	212 b	35 a	63 a	70 a	66 a	58
Trapped 'till 2/28		5		3		21		36		7		9	
3/1- 5/12	25 abc	7 a	41 bed	25 abc	199 f	55 cd	16 8 f	123-e	60 d	16 ab	102 e	19 ab	17
Total S leached	82 ab	45 a	140 ab	101 ab	848 f	426 d	921 f	568 e	145 bc	104 ab	209 с	132 abc	144
Total S in overflow	-	7	1	3	-	24	2	66	-	15	-	7	
S uptake by oats	100 ab	71 a	132 be	100 ab	154 cde	207 fgh	152 bed	138 bc	217 fg	238 h	194 defg	158 cde	32
Grand total	182 ab	123 a	273 bed	204 abc	1,002 h	657 f	1,075 h	772 g	362 de	357 de	403 e	297 cd	164
Increase over check % of applied S accounted for					820 72 a	534 47 b	802 71 a	568 50 b	180 16 cd	234 21 c	130 11 d	93 8 d	

* Values within a row followed by the same letters are not significantly different at the 5% level. Sulfate sulfur values were determined in the laboratory to the nearest 0.02 ppm.

Table 4—Effect of waterlogging and organic matter on nitrogen in leachate and oats during the 1966-67 season. Urea was applied at the rate of 2.27 g N/tank on October 21, 1966 and again on

March	1,	1967	
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		Organic matter								
	No	one	11,200) kg/ha						
Interval	Freely drained	Water- logged	Freely drained	Water- logged	SE					
		g N leac	hed/tank							
11/1-12/31 1/1- 2/28 3/1- 5/12	1.95 d 1.59 c 0.86 a	0,70 b 0,04 a 1,80 c	1.27 c 0.97 b 0.76 a	0,21 a 0,04 a 1.08 b	0.26 0.10 0.34					
		ppm NO ₃ -N	In leachate							
11/1-12/31 1/1- 2/28 3/1- 5/12	26 c 37 c 20 ab	14 ab 0, 2 a 43 c	18 b 23 b 19 a	8a 0.1a 27b	7 2 4					
		ppm NO ₃	-N in oats							
	245	1,769	277	296	569					

collected from the high water table treatments. Concentration of S was 0.5 ppm in the 122 mm of rainfall which was collected as runoff from the waterlogged lysimeters receiving either no S or elemental S. Runoff from high water table lysimeters treated with gypsum contained about 3.0 ppm of SO₄-S. There was no significant difference in the amount of S leached from the check or the elemental S treatments regardless of waterlogging or organic matter application.

Second Collection Period—During the period January 1 to February 28, most of the rain fell during the last 10 days of January, and there was little or no runoff. Concentrations of SO_4 -S in the check and elemental S treatments were all around 1 ppm and were not significantly changed by waterlogging or addition of organic matter (Table 3). Where gypsum was used in conjunction with free drainage the SO_4 -S level in the leachates was about 10 ppm. Waterlogging decreased the value to about 5 ppm, and the addition of organic matter did not significantly change the concentration.

The amount of S leached where elemental S was applied was not different from the no S treatments. Where gypsum was applied less S was leached from the waterlogged than from the freely drained lysimeters.

Third Collection Period—During the period of March 1 to May 12, concentration of SO_4 -S in the leachate from the lysimeters treated with gypsum and elemental S was reduced by prior waterlogging (Table 3). Applications of barley straw significantly increased SO_4 -S concentration in the leachate from the gypsum-waterlogged treatment and the elemental S-freely drained treatment. The amount of S leached from the lysimeters during the third interval was decreased by the waterlogging treatment. The addition of organic matter in conjunction with the waterlogging did not appear to have a consistent effect upon the total S leached during the spring period.

1966-67 Season Totals—Where no S was applied, total S leached over the entire season was not significantly changed by waterlogging or organic matter (Table 3). In the case of gypsum, waterlogging decreased the total amount of S leached, but where elemental S was applied the decrease due to waterlogging was not statistically significant. The tendency for leaching of sulfur to increase

upon the addition of organic matter was probably a reflection of the sulfur present in the barley straw which amounted to 363 mg S/tank. S added by the rain amounted to 30 mg/tank.

Uptake of S by the oats where gypsum or elemental S were applied was increased by the prior waterlogging but was not significantly influenced by straw. Oats are usually planted in the fall in this region, but were planted in the spring here to avoid the direct effects of waterlogging and to emphasize the indirect effects through the sulfur cycle.

The total amount of S accounted for from the gypsum applied with free drainage was 71 and 72% with and without straw and with waterlogging 50 and 47% with and without straw. The total amount of S accounted for from the elemental S was much less, ranging from 8 to 21%.

The N leached from the tanks was not affected significantly by S treatments, and so those data are not presented here. Waterlogging greatly decreased the amount of N leached during the winter months but increased it during the spring after free drainage was reimposed (Table 4). Application of straw decreased the amount of N leached under both drainage conditions. Nitrate N concentrations and total N leached followed similar trends. The fact that straw decreased the level of N while having little effect on the level of S during the first season might be explained by the N/S ratio of 4.2. A N/S ratio of from 10 to 17 would be more in balance with microbial needs, and thus the straw was relatively low in N compared with S.

1967-68 Season (Residual Effects)

The concentration of SO_4 -S in the leachate where no sulfur was applied was not significantly affected during any sampling period in the year after waterlogging and organic matter treatment (Table 5). Where gypsum had been applied, waterlogging in the previous year without organic matter gave higher concentrations of SO_4 -S in the leachate during the winter than where soils were freely drained and where organic matter was applied with waterlogging. In the spring there was no difference due to waterlogging or application of organic matter. After the first sampling period, the concentration of SO_4 -S in the leachate where elemental S had been applied was higher than in the check or where gypsum had been applied, but there was no difference due to the application of organic matter or the waterlogging treatments.

The total amount of S leached from the soil during the second year followed the same pattern as the SO₄-S concentrations, since there was no difference in the volume of leachate from the various tanks during this year. Where gypsum had been applied, the highest values occurred with the waterlogged and no organic matter treatment. Where elemental S had been applied, all values were greater than in the gypsum or check treatments, but there was no difference due to waterlogging or organic matter treatment. About 100 mg S/tank was added in the rainfall during the season.

The uptake of S by the soft chess grass was increased by the elemental S application but not by gypsum. Waterlogging and organic matter did not significantly affect S uptake, except where no S was applied there was significantly more S uptake where waterlogging and organic matter were imposed together than where neither were used. The amount of residual S recovered from the elemental S application was significantly higher than from gypsum except for the waterlogged-no straw treatment.

The concentration and total amount of nitrate nitrogen was not significantly affected during the second year, and the data are not presented.

DISCUSSION

The most striking result during the first season was the decrease in concentration of SO₄-S and the diminished loss of S in the leachate from the gypsum treatment brought about by waterlogging during the rainy winter months. When reducing conditions are imposed, Fe is reduced and rendered more soluble, and this is followed in a few days (at a lower redox potential) by S reduction which reacts with Fe, forming compounds less available to plants (Harter and McLean, 1965; Patrick and Mahapatra, 1968). The presence of abundant iron in Josephine soil is indicated by the red color of the soil and by evidence from plant tissue analysis (authors' unpublished data). It is postulated that sulfate was reduced to sulfide which precipitated as iron sulfide. Whereas, Harter and McLean recorded the production of 2,000 ppm sulfide under waterlogged conditions without the release of H₂S from the soil, SO₄-S available for reduction here ranged only up to 25 ppm computed for the surface 15 cm of soil where gypsum was applied. Furthermore, we observed no plant injury, although excess H₂S is highly toxic because it inhibits respiratory enzymes (Mitsui, 1956; Harter and McLean, 1965). So it is unlikely that much sulfur was lost by volatilization of H₂S.

Nitrate has been shown to take priority over sulfate during the reduction process (Cornell and Patrick, 1969), and as long as nitrates are present sulfate reduction may be delayed. However, in our experiment nitrate levels in waterlogged treatments fell to very low levels (0.2 ppm or less) by the end of December 1966, and so it is unlikely that nitrate inhibited sulfate reduction after that. The presence of added organic matter only slightly increased leaching loss of gypsum-derived sulfate. More rapid and intensive reducing conditions have been observed to result from adding available energy in the form of organic matter (Ogata and Bower, 1965). Since the organic matter applied here was incorporated only in the surface 2.5 cm, to simulate the position of surface litter on the range, it probably did not have as much effect as a more thorough incorporation would have.

The leaching of elemental S was not significantly affected by waterlogging during the winter months. However, apparently less S was oxidized under waterlogging than in the freely drained tanks, because the concentration of SO_4 -S in the leachate and the total S leached was less in spring from tanks waterlogged than from tanks freely drained during winter. No doubt some oxidation of sulfur occurred during the period between the first rain (November 6) and the time the soils reached saturation 3 weeks later. The amounts must have been very small, however, since none of the elemental S treatments produced significant increases in concentration of SO_4 -S in the leachate over the check.

In May 1967 soil pH averaged 6.0 in the surface 15 cm, and there were no significant differences among treatments. It is considered probable that S oxidation had not produced any marked decrease in soil pH during the previous autumn and winter. The same soil incubated in the laboratory with fine S applied has given no measurable change in pH in a 4-week period with amounts of S applied up to 200 ppm. Neither has amounts of S up to 50 ppm produced any pH change in 10 weeks of incubation. Thus, there probably was no impairment of the activities of sulfate-reducing bacteria due to pH as it was maintained in a range favorable to them.

Substantial amounts of applied sulfur were unaccounted for at the end of the experiment and presumably remained in the soil. Analysis of the soil for total sulfur did not help to substantiate treatment differences, however, because of the relatively large amount of S present (mean of 10.48 g/tank vs. 1.13 g/tank applied), and the variability among replicates. Thirty percent of the gypsum S and 57% of the elemental S (means for four treatments) were un-

Table 5—Second	lseason	residual	effect	of	organic	matter	and	drainage	on the	e S	leached	and	taken	up	from	three	S	treatments
							(196	67-68)						-				

Ormania		C	heck			Gyp	sum S		Elemental S				
matter	No	ne	Sti	raw	No	None		raw	None		Straw		
Soil drainage	Free	Water- logged	Water- Wa ogged Free log		Free	Water- logged	Water- Free logged		Free	Water- Free logged		Water- logged	SE
				·······	ppm SO4-S in	leachate							
Collection dates 12/8- 1/8 1/9- 2/21 2/22-3/20	0,9 ab* 0,6 a 0,1 a	1.2 a-d 1.1 a 0.2 a	0.7 a 0.9 a 0.1 a	l,5a-e 1.1a 0.1a	1.4 a-e 1.9 a 0.2 a	3.3 g 4.0 b 0.4 a	1,8 c-f 1,2 a 0,2 a	1.0 a-c 1.7 a 0.1 a	1.9d-f 5.1b 1.0b	2.2 ef 5.1 b 1.1 b	2.5 fg 4.7 b 1.1 b	1.7 b-f 5.3 b 1.2 b	.5 .8 .2
					mg S leached	per tank							
12/8- 1/8 1/9- 2/21 2/22-3/20	15а 34а 1а	19 ab 61 a 2 a	11 a 45 a 1 a	23 ab 57 a 1 a	23 ab 103 a 2 a	52 c 218 b 3 a	28 ab 69 a 2 a	13 a 91 a 1 a	31 b 274 b 8 b	28 ab 267 b 11 b	36 be 239 b 9 b	26 b 274 b 10 b	11 43 2
Total leached	50 a	82 a	57 a	81 a	128 a	273 b	99 a	105 a	313 Ъ	306 ъ	284 Ъ	310 Ъ	78
S uptake by soft chess	97 a	127 ab	151 abc	162 bed	142 ab	173 bed	168 bcd	159 bcd	257 e	202 cde	238 e	212 de	35
Grand total	147 a	209 ь	208 ъ	243 c	270 d	446 e	267 d	264 cd	570 g	508 f	522 f	522 f	112
Increase over check % of applied S accounted for					123 11 c	237 21 b	59 5 c	21 2 c	423 37 a	299 26 b	314 28 ab	279 25 b	

* Values within a row followed by the same letters are not significantly different at the 5% level.

accounted for, and 37% of the sulfur applied under freely drained conditions and 50% under waterlogged conditions (means for four treatments) were unaccounted for and most likely retained by the soil. In previous lysimeter work on a coarse-textured, well-drained range soil, Vista sandy loam, a mean of 21% of the sulfur applied in three rates of gypsum was retained by the soil after a single wet season (McKell and Williams, 1960). However, after 3 drier-thannormal years 65% of the gypsum sulfur and 89% of elemental sulfur initially applied remained unaccounted for in another study on the same soil (Williams et al., 1964). Volatilization of H_2S was ruled out because of the well-drained character of the soil, and adsorption and microbial immobilization were considered probable mechanisms for soil retention.

The organic residue typically left after grazing, which is very much less on annual-type range than the amount of straw applied here, is likely to have little effect on the sulfur economy of either waterlogged or well-drained range soils in California.

Where waterlogging of California annual-type grassland occurs during the winter months, the amount of SO_4 -S leached from either natural or applied sources is likely to be decreased. However, at the same time the adverse effect of waterlogging on range plant growth probably outweighs any possible sulfur-conserving advantage from waterlogging.

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