

## THE EFFECTS OF STRAW AND SULFATE AMENDMENTS AND TEMPERATURE ON SULFIDE PRODUCTION IN TWO FLOODED SOILS<sup>1</sup>

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### ABSTRACT

A physiological plant disorder in California rice, associated with soluble sulfides, hydrosulfides, and insoluble metallic sulfide production in the soil, causes severe injury to plants. Under flooded cultural conditions, roots become blackened, leaves develop a gray-green color, wither, and die, and panicles usually produce sterile florets.

We studied the effects of straw, sulfate amendments, and temperature on acid-volatile and water-soluble sulfides in two acid soils (San Joaquin sandy loam and Willows clay). Straw amendments significantly increased the acid-volatile and water-soluble sulfides in both soils. The amounts of acid volatile sulfide produced were further enhanced by the addition of sulfate and by higher temperature. Although low temperature significantly reduced the production of acid-volatile sulfide, it enhanced the accumulation of water-soluble sulfides. High concentrations of water-soluble sulfides found in Willows clay in the presence of straw and sulfate may be responsible for the observed poor growth of rice under field and glasshouse conditions. Sulfide can be adsorbed by kaolinite, and the amounts of sulfide adsorbed increased with increasing concentrations of sulfide in solution. Sulfide retention was controlled by the availability of surface adsorption sites, because the sulfide adsorption increased with increasing gram volume ratio. Low temperature adversely affected the adsorption of sulfide by kaolinite.

### INTRODUCTION

A physiological plant disorder associated with the occurrence of soluble sulfides, hydrosulfides, and insoluble metal sulfides in the rhizosphere of flooded rice occurs in California and many parts of the world, as reviewed by Hollis (1967). Hydrogen sulfide in the soil solution may be directly toxic to rice by affecting physiological processes, by destroying the oxidative power of rice roots, and by impairing nutrient uptake. The concentration of water-soluble sulfide ( $H_2S + HS$ ) in most flooded soil solutions is generally low. However, in certain flooded rice soils, usually acid in reaction and too low in sufficient active iron to precipitate the sulfide ion as insol-

uble iron sulfide, but containing high levels of organic matter, hydrogen sulfide can accumulate significantly and cause sulfide toxicity.

Sulfide toxicity in California rice is manifest about the time of late tillering, becoming increasingly severe until leaves and emerging panicles show an abnormal gray-green color; later wilting and drying occur, and panicles show a high level of floret sterility.

Sulfide formation occurs most rapidly in soils with a low redox potential and low pH values. These, together with high levels of oxidizable carbon, are considered important factors in regulating in situ concentrations of hydrogen sulfide in flooded rice fields (Ogata and Bower 1965; Allam et al. 1972). Depending on the redox potential and sulfate contents of soils, the amounts of sulfide produced may range from a few parts per million to about 2000 ppm (Harter and McLean 1965; Connell and Patrick 1969). Solu-

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ble sulfides can be changed substantially by altering the water temperature. Vamos (1964) shows that temperature plays a contributing role in affecting the equilibrium concentrations of sulfide in solution. Low temperatures increase the solubility of oxygen in aqueous solution and may subsequently enhance the oxidation of iron sulfide. The acidity generated during oxidation may also release sulfide into solution. Moreover, low temperatures could suppress the ability of clay minerals to absorb sulfides. The ability of clay minerals, such as bentonite, to adsorb sulfide has previously been demonstrated by Allam et al. (1972). Determination of the effect of temperature on sulfide production, together with soil sulfate and organic matter levels, is of particular importance for rice production on soils where sulfide production is a potential problem.

The purpose of this investigation was to determine the effects of straw and sulfate additions and temperature on water-soluble and acid-volatile sulfide production in two representative rice soils. We also examined the effects of temperature and sulfide concentration on sulfide absorption by kaolinite.

#### MATERIALS AND METHODS

Two soils, Willows clay and San Joaquin sandy loam, were used for the sulfide investigation. Willows clay is a fine, montmorillonitic, thermic Typic Pelloxerent, and San Joaquin sandy loam is a fine, kaolinite, thermic Abruptic Durixeralf soil. Soils collected from fields were air-dried and crushed to pass through a 2-mm sieve. Some physical and chemical characteristics of the soils are shown in Table 1. The methods of analysis included: organic C by the method of Walkley and Black (1934), and percentage of clay by the method of Jackson (1956). Soil pH was determined in a 1:2 soil-water suspension. Twenty-five grams of soils was added with 50 ml distilled water in an Erlenmeyer flask. The equivalent of 0, 75, and 150 kg per ha

of sulfur as potassium sulfate and 0, 0.3, and 0.6% of ground rice straw on an air-dried soil basis were also added to the soil suspension. The Erlenmeyer flask was then tightly sealed and incubated anaerobically at 16, 20, and 24°C for 4 mo. At the end of the reaction time, the pH and Eh of the soil solution were determined separately, using a combination of glass and platinum electrodes. The water-soluble sulfides were determined by pipetting 10 ml of the clear supernatant liquid from the flask to 10 ml 0.4 N KOH + 1 N KNO<sub>3</sub> solution and then analyzed for sulfide concentration, using a sulfide electrode. During the determination, an N<sub>2</sub> gas atmosphere was maintained in a special chamber to prevent oxidation of sulfide by molecular oxygen from the atmosphere. The acid-volatile sulfide was determined by adding 10 ml of 6 N HCl solution and thoroughly mixing it in a reaction flask. Nitrogen gas was introduced into the acidified soil suspension and bubbled through a collecting tube containing 50 ml 1 N KOH. The sulfide concentration in the 1 N KOH solution was subsequently determined with a sulfide electrode.

The adsorption of sulfide by kaolinite was determined by weighing 0.1 to 1.0 g of washed kaolinite (Baker Lot No. 122743) into 30 ml of solutions containing 2 to 30 ppm S in Erlenmeyer flasks. The suspension was shaken at 10, 16, and 25°C for 6 h. The concentration of sulfide ranged from 2 to 30 ppm S. Nitrogen gas was introduced into each flask, and the flasks were tightly sealed. The preliminary investigation indicated that no significant loss of sulfide due to sulfide oxidation had occurred in 6. At the end of 6 h reaction time, the suspension was filtered through a Whatman no. 42 paper under vacuum. Ten milliliters of the filtrate was withdrawn for sulfide determination. The amount of sulfide adsorbed was the difference between the initial and final sulfide concentrations.

#### RESULTS AND DISCUSSION

Figure 1 shows the content of acid-volatile sulfide in the Willows clay and San Joaquin sandy loam soils as a function of redox potential (Eh) in millivolts at the end of the 4-mo incubation period. Soil Eh significantly affected the concentration of sulfides produced in these two soils. Both soils without straw amendments had positive Eh values and contained low concentrations of acid-volatile sulfide, even though a high

TABLE 1  
*Some properties of San Joaquin sandy loam and Willows clay soils*

Soil type	pH, 1:2	Clay, %	Organic matter, %	CEC, meq/ 100 g
San Joaquin sandy loam	4.9	5.5	4.8	10.8
Willows clay	5.5	33.0	5.6	42.6

rate of sulfur, equivalent to 150 kg/ha of sulfate-sulfur was applied prior to the incubation. With amendments of straw at rates equivalent to 0.3 and 0.6% on an air-dry soil basis, the soil Eh dropped and appreciable amounts of acid-volatile sulfide were formed. The amounts of sulfide produced further increased with additions of sulfate and higher temperatures (Table 2). At the same temperature and straw amendment rates, Willows clay produced more acid-volatile sulfide than that of San Joaquin sandy loam, especially at the higher temperature value (24°C).

The concentration of water-soluble sulfides ( $H_2S + HS^-$ ) in soil solution as a function of Eh is shown in Fig. 2. In a manner similar to the acid-volatile sulfide, the concentration of water-soluble sulfides was low at a positive Eh, but increased significantly as Eh values declined, as affected by the straw amendments. Low Eh and

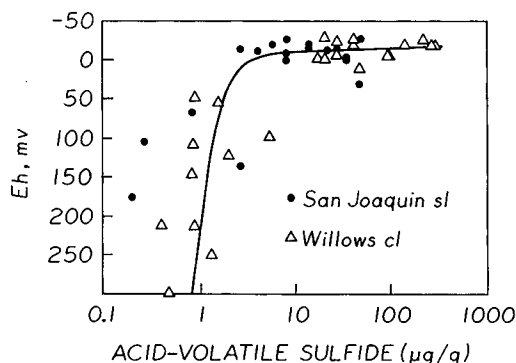


FIG. 1. The effect of Eh on the production of acid-volatile sulfides in Willows and San Joaquin soils.

temperature and high sulfate contents favored more accumulation of water-soluble sulfides in the soil solution. At the same temperature and rate of straw amendment, the concentration of water-soluble sulfides was higher in the Willows clay soil than in the San Joaquin sandy loam soil.

The redox potential, labile organic matter content, and pH are important soil characteristics affecting the production of acid-volatile and water-soluble sulfides in submerged soils and in sediments (Allam et al. 1972; Goldhaber and Kaplan 1975; Ogata and Bower 1965). The water overlaying the soils and sediments restricts the free movement of air into the soils and sediments. They become deficient in dissolved oxygen as a consequence of anaerobic organic matter decomposition, and the Eh values dropped

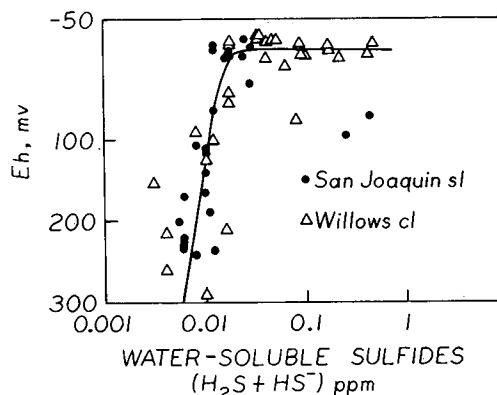


FIG. 2. The effect of Eh on the concentration of water-soluble sulfides in soil solution of Willows and San Joaquin soils.

TABLE 2

Effects of temperature and sulfate on acid-volatile and water-soluble sulfide formation in San Joaquin sandy loam and Willow clay with 0.6% straw added

Soil type	Sulfate-S added kg/ha	Temperature, °C							
		16		20		24		Mean	
		A, ppm	B, µg/g	A, ppm	B, µg/g	A, ppm	B, µg/g	A, ppm	B, <sup>a</sup> µg/g
San Joaquin sandy loam	0	0.024	8	0.018	4	0.008	27	0.02	13.0
	75	0.032	8	0.018	8	0.006	21	0.02	12.3
	150	0.052	48	0.028	13	0.028	47	0.04	36.0
Mean		0.036	21.3	0.021	8.3	0.014	31.7		
Willows clay	0	0.04	27	0.03	40	0.08	132	0.05	66.8
	75	0.21	20	0.03	20	0.08	212	0.09	84.0
	150	0.44	27	0.48	ND	0.17	292	0.36	159.5
Mean		0.23	24.6	0.18	30.0	0.09	212.0		

<sup>a</sup> A = water-soluble sulfide; B = acid-volatile sulfide. ND = not determined.

to between  $-120$  to  $-160$  mV. The intensity of soil reduction depends to a great extent on the availability of organic carbon and on its rate of turnover. The reduction of the sulfate to sulfide also requires relatively fresh organic matter, predominantly of partially degraded cellular components. Without straw amendments, the San Joaquin sandy loam and Willows clay maintained relatively oxidative conditions, and similarly only small quantities of water-soluble and acid-volatile sulfides were formed. With the incorporation of straw in the soils prior to soil incubation, the increased availability of organic carbon stimulates sulfate reduction and consequently increases the production of acid-volatile sulfide in the soils. It is not known, however, why Willows clay produces more acid-volatile sulfide than San Joaquin sandy loam at the same rate of straw amendment. Whether Willows clay contains a higher initial population of sulfate-reducing bacteria, which favors more rapid reduction of sulfate, or whether the formation of acid-stable pyrite ( $\text{FeS}_2$ ) is more easily achieved in San Joaquin soil remains to be investigated. The formation of pyrite under stimulated paddy conditions is thermodynamically feasible (Pitts et al. 1972) and may be a means of resolving this question.

The concentrations of water-soluble sulfides in the Willows clay were significantly higher than those in the San Joaquin soil. Although low pH is a prominent factor controlling the production of hydrogen sulfide in paddy soils (Allam et al. 1972), it is not considered to be a significant factor in the production of sulfides found in this experiment, for the Willows clay produces more sulfides, in spite of its higher pH values, than San Joaquin soil does.

Because the concentrations of Fe extractable by ammonium acetate (pH 4.8) in incubated San Joaquin soil are considerably higher than those for the Willows clay (Mikkelsen and Kuo, unpublished data), it is possible that more ferrous iron is immediately available in San Joaquin soil for suppressing the water-soluble sulfides that form insoluble iron sulfide precipitates, pyrite precipitates, or both.

Water-soluble sulfides are highly toxic to rice plants through inactivation of terminal oxidase in rice roots. The concentration critical to normal growth of rice plants was reported to be 0.07 to 0.1 ppm S (Allam and Hollis 1972). The high concentrations of water-soluble sulfides found in the solutions of the Willows clay in the presence

of fresh straw and sulfate could be responsible for the poor growth of rice plants observed under glasshouse and field conditions.

The rate of sulfate reduction in an anaerobic environment is temperature-dependent (Cho and Ponnampetuma 1971). High temperature favors more rapid reduction of sulfate. Likewise, less acid-volatile sulfide, in the form of iron sulfide, is produced in the soils incubated at low temperature ( $10^\circ\text{C}$  for example), as observed in this experiment (Table 2). The concentration of water-soluble sulfides, however, appears to increase at a lower temperature, in spite of the fact that a lower temperature may retard the formation of acid-volatile sulfide. The increased dissolved oxygen in aqueous solution at low temperature will allow oxidation of iron sulfide or pyrite, if present in muds, to occur and will eventually produce sulfuric acid to enhance the soil acidification and accumulation of water-soluble sulfides (Vamos 1964). However, in closed system where free air movement is restricted, the increase of water-soluble sulfides would not be possibly due to iron sulfide or pyrite oxidation and to soil acidification. It is possible that low temperature may either retard the formation of iron sulfide or decrease the ability of soil particles to adsorb sulfide. The ability of clay minerals to adsorb sulfide as a mechanism to control sulfide concentration in solution has previously been demonstrated by Allam et al. (1972).

The adsorption of sulfide by kaolinite is shown in Fig. 3. The sulfide adsorption by kaolinite

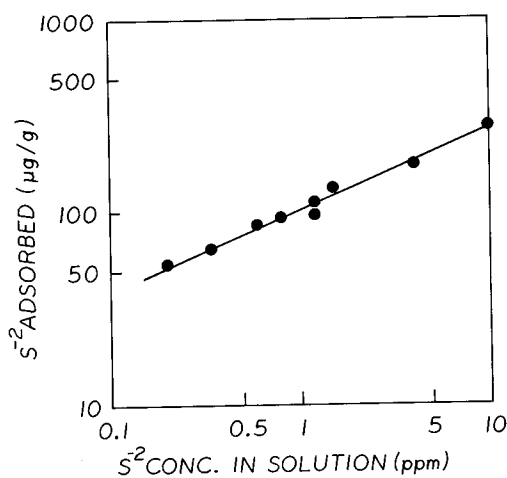


FIG. 3. The sulfide adsorption by kaolinite as a function of sulfide concentration in solution plotted on a logarithmic scale.

increased with increasing sulfide concentrations in solution and can be described by the classical Freundlich adsorption isotherm in the range of sulfide concentrations investigated. An increase of the gram volume by increasing the weight of kaolinite added in the suspension from 0.1 to 1.0 g per 30 ml of 3 ppm  $S^{2-}$  initial sulfide concentration, enhanced the amounts of sulfide adsorption by kaolinite (Fig. 4). This suggests that sulfide adsorption by kaolinite is regulated by the availability of surface adsorption sites, rather than by the precipitation in the aqueous solution. An increase in the weight of kaolinite in the suspension provides more surface area available for surface adsorption and reinforces the

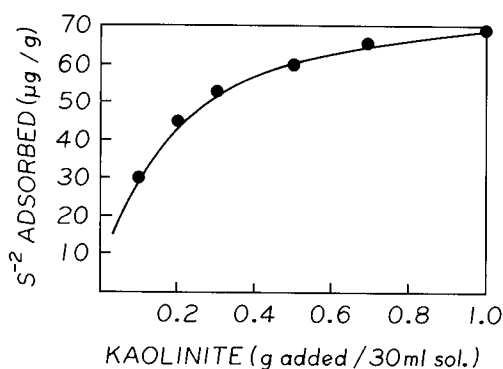


FIG. 4. The effect of gram volume on sulfide adsorption by kaolinite.

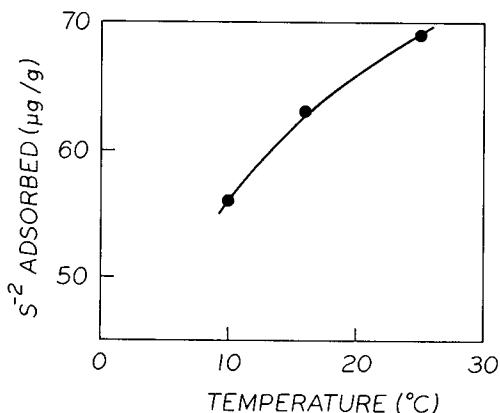


FIG. 5. The effect of temperature on sulfide adsorption by kaolinite.

surface sorption concept. Sulfide adsorption by kaolinite was further enhanced at a higher temperature (Fig. 5). The sulfide adsorption by kaolinite increased from 55 g/g to 69 g/g when the temperature was raised from 10 to 25°C. This temperature effect on sulfide adsorption could partially explain the higher concentrations of water-soluble sulfides in Willows clay and San Joaquin sandy loam soils at low temperature. The reduction of the sulfide-adsorbing capability of the soils at low temperature will undoubtedly increase the soluble sulfides concentration in solution.

#### REFERENCES

- Allam, A. I., G. Pitt, and J. P. Hollis. 1972. Sulfide determination in submerged soils with an ion-selective electrode. *Soil Sci.* 114:456-467.
- Allam, A. I., and J. P. Hollis. 1972. Sulfide inhibition of oxidases in rice roots. *Phytopathology* 62:634-639.
- Cho, D. Y., and F. N. Ponnampereuma. 1971. Influence of soil temperature on the chemical kinetics of flooded soils and the growth of rice. *Soil Sci.* 112: 184-194.
- Connell, W. E., and W. H. Patrick, Jr. 1969. Reduction of sulfate to sulfide in waterlogged soil. *Soil Sci. Soc. Am. Proc.* 33:711-715.
- Goldhaber, M. B., and I. R. Kaplan. 1975. Controls and consequences of sulfate reduction rates in recent marine sediments. *Soil Sci.* 119:42-55.
- Harter, R. D., and E. O. McLean. 1965. The effect of moisture level and incubation time on chemical equilibria of a Toledo clay loam soil. *Agron. J.* 57: 583-588.
- Hollis, J. P. 1967. Toxicant diseases of rice. Bull. 614. Louisiana State University.
- Jackson, M. L. 1956. *Soil chemical analysis—Advanced course*. Published by the author, Univ. of Wisconsin, Madison, Wis.
- Ogata, G., and C. A. Bower. 1965. Significance of biological sulfate reduction in soil salinity. *Soil Sci. Soc. Am. Proc.* 29:23-25.
- Pitts, G., A. I. Allam, and J. P. Hollis. 1972. Aqueous iron-sulfur systems in rice field soils of Louisiana. *Plant Soil* 36:251-260.
- Vamos, R. 1964. The release of hydrogen sulphide from mud. *J. Soil Sci.* 15:103-108.
- Walkley, A., and C. A. Black. 1934. An examination of the Deggaraff method for determining soil organic matter and proposed modification of the chromic acid titration method. *Soil Sci.* 37:29-38.