THE EFFECT OF AMMONIUM THIOSULFATE ON REDUCING FUMIGANT CONCENTRATION UNDER TARP

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Introduction: Soil fumigants are intensively used to control soilborne pathogens and weeds to achieve high yield in high value crops. The fumigants, 1,3-dichloropropene (1,3-D) and chloropicrin (CP), are increasingly being used as alternatives to methyl bromide (MeBr), however, their emissions following application may contribute to air pollution. Therefore, development of techniques that minimize emissions of 1,3-D and CP will be beneficial for protecting workers, bystanders, and the environment as well as for maintaining viable use of these important pest control tools. Surface barriers, especially plastic films with low permeability such as virtually impermeable film (VIF) are effective to reduce fumigant emissions by retaining fumigants under the tarp. The accumulation of fumigants under the tarp, however, can be released into the air when the plastic film is removed or planting holes are cut. Chemical remediation (e.g., thiosulfate application to degrade fumigants) has been found effective to enhance fumigant degradation and reduce emissions from soils (e.g., Wang et al., 2000). We hypothesize that chemical remediation can also be effective for reducing fumigant concentrations under high barrier tarps after fumigation and before planting. The objective of this study was to determine the effectiveness of drip-application of ammonium thiosulfate (ATS) to reduce 1,3-D and CP concentrations under barrier films in soil columns.

Materials and Methods: A Hanford sandy loam soil (coarse-loamy, mixed, superactive, nonacid, thermic Typic Xerorthents) was used for this study. Surface soils were collected and air-dried to a water content of about 5% (w/w) and sieved through a 4 mm screen. Soil was packed to a total depth of 22 cm at a uniform bulk density of 1.4 g cm^{-3} into close-bottomed stainless steel columns (25 cm height x 15.5 cm i.d.). The columns were sealed with a glass cover at the top simulating a high barrier for fumigants. The experiment was conducted at laboratory room temperature (22 ± 3°C). One hundred µL *cis*-1,3-D (122 mg) and 40 µL CP (66 mg) (similar mixture to Telone C35), which equals to 21 mg/kg_{soil} 1,3-D and 11 mg/kg_{soil} CP respectively, were injected into the column center at the 10 cm soil depth. Results showed that after 6 h, a uniform fumigant distribution was achieved in the soil columns. After 22 hours, six treatments in duplicate were applied to the columns: 1) control (CK); 2) drip 100 ml water only (Water); 3) drip 100 ml ATS solution contained the amount of ATS to fumigant at

1:1 molar ratio (Water+ATS1:1), which is equivalent to 38 mg/kg $_{soil}$ ATS; 4) drip 100 ml ATS solution at 2:1 ATS:fumigant ratio (Water+ATS2:1); 5) drip 100 ml ATS solution at 4:1 ATS:fumigant ratio (Water+ATS4:1); and 6) drip 200 ATS solution at 2:1 ATS:fumigant ratio (Water2+ATS2:1). The water or solution were dripped at a flow rate of 1.5 mL/min via a drip tubing (1.6 mm i.d.), which was installed in the center of the column at 3 cm depth below the soil surface. Fumigant concentrations of gas samples were determined above the soil and below the seal as well as at 10 and 20 cm depths below the soil surface. Monitoring was conducted for 12 days. At the end of the experiment, soil samples were taken, extracted and analyzed for residual fumigants.

Results: The concentration of 1,3-D and CP in the soil-gas phase was greatly affected by ATS applications. The more ATS was applied, the lower concentration of fumigant (correspondingly the fast degradation) was observed especially at early time points (Fig. 1). Under the ATS treatments, the degradation of 1,3-D showed first order degradation kinetics with the highest degradation rate in the treatment of Water+ATS4:1 and lowest in the control (Table 1), however, the degradation rate slowed down substantially as time prolonged. As a result, 1,3-D remained in the soil-gas phase and was detected even at the end of experiment. The differences in 1,3-D degradation rates between the treatments also decreased with time. The finding indicates that the effect of ATS on fumigant degradation was promising in the initial period. With time, ATS also degrades as it is unstable in the soil. The concentration of CP in soil-gas phase decreased at a much faster rate than 1,3-D and was not detectable after 4 days, possibly due to its faster degradation rate than 1,3-D as well as the lower amount injection into soil than 1,3-D. Similar to 1,3-D, CP followed first order degradation kinetics. The 1,3-D and CP concentrations decreased slightly faster in water application only in comparison to the control and in Water2+ATS2:1 in comparison to Water+ATS2:1. This indicates that the effect of water applied to soil on fumigant degradation was minor. At the end of the experiments, extracted 1,3-D from soil samples was low for all the treatments but the total mass of 1,3-D and CP in the soil clearly showed the effect of ATS, i.e., much lower in ATS treatments compared to the control and water application only (Table 2).

Conclusion: Our results suggested that drip application of ATS to surface soil can be an effective method to reduce fumigant concentrations under high barrier plastic films. The degradation effects of ATS on 1,3-D and CP occurs in a relatively short period of time after ATS application. To enhance fumigant degradation by chemical remediation, either a large amount of ATS or multiple applications may be needed. Field tests are necessary to confirm these findings and to determine the effective quantity and application frequencies of ATS after fumigation in order to achieve maximum efficacy and minimum environmental risk.

Reference:

Wang, Q., Gan, J., Papiernik, S. K., and Yates, S. R. 2000. Transformation and detoxification of halogenated fumigants by ammonium thiosulfate. Environ. Sci. Technol. 34: 3717-3721.

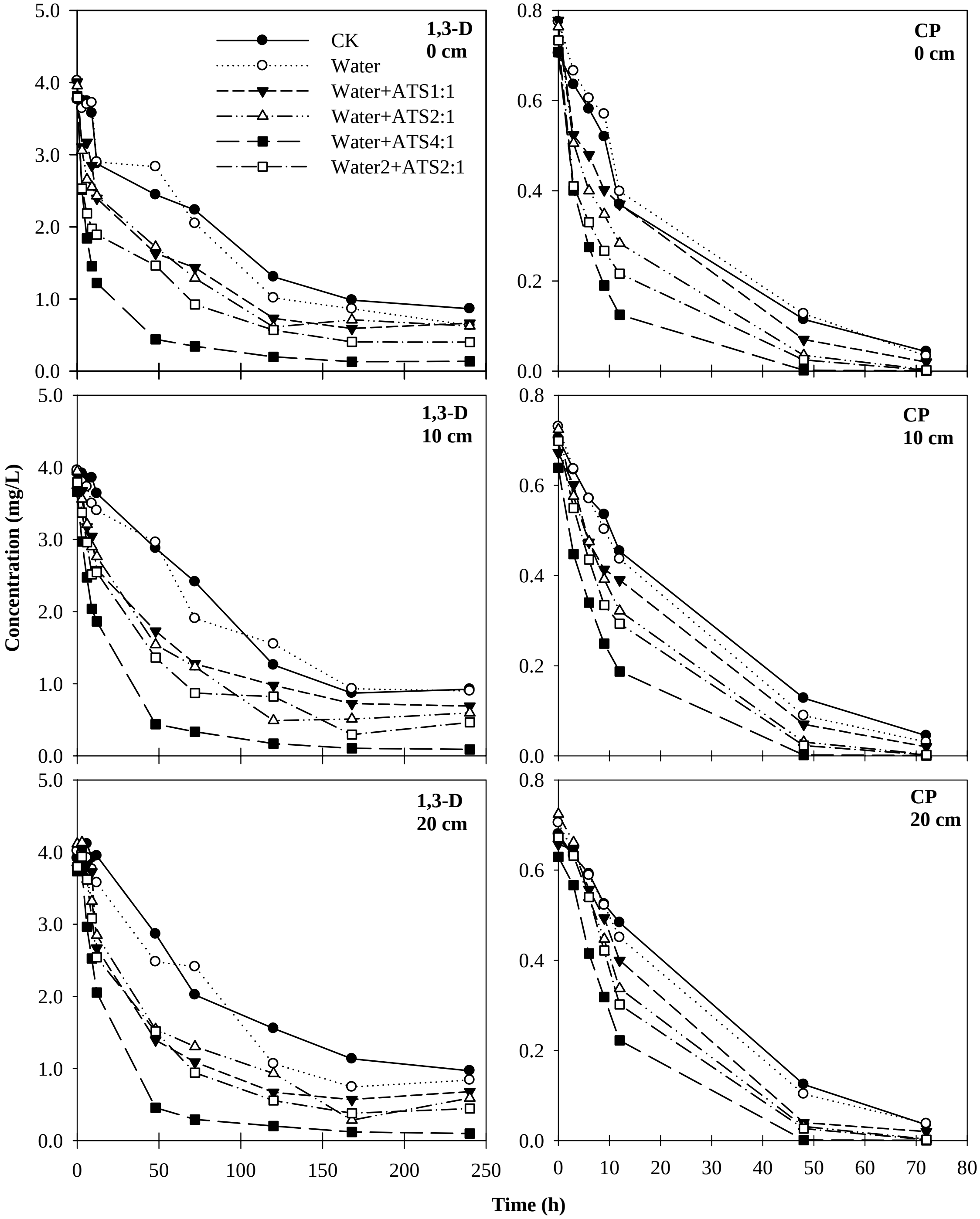

Fig. 1. The effect of ATS solution on the degradation of fumigant (cis-1,3-D and CP) as a function of time at 0 (above soil surface), 10 and 20 cm depth in soil columns.

Table 1. Best-fitting of first-order degradation rate constant k (h^{-1}) for cis-1,3-dichloropropene (1,3-D) and chloropicrin (CP) in the column study (numbers in parentheses are correlation coefficient r^2)

Treatment	1,3-D*	CP**
CK[1]	0.008 (0.996)	0.039 (0.998)
Water[1]	0.009 (0.992)	0.042 (0.998)
Water+ATS1:1[2]	0.018 (0.950)	0.050 (1.000)
Water+ATS2:1[3]	0.034 (0.992)	0.073 (0.993)
Water+ATS4:1[3]	0.066 (0.996)	0.102 (0.971)
Water2+ATS2:1[3]	0.041 (0.993)	0.078 (0.992)

* Correlation for 1,3-D based on the data during 1) 168-h, 2) 48-h, and 3) 12-h

** Correlation for CP based on the data during 72-h

Table 2. The fate of cis-1,3-dichloropropene (1,3-D) and chloropicrin (CP) in a soil column study

Treatment	Initial stage	The end of the experiment		
		Gas	Liquid + solid	Total
	-------------------------- cis-1,3-D (mg) --------------------------			
CK	122.50	2.09	9.46	11.55
Water	122.50	1.76	8.99	10.74
Water+ATS1:1	122.50	1.53	6.13	7.66
Water+ATS2:1	122.50	1.37	5.55	6.91
Water+ATS4:1	122.50	0.25	2.60	2.85
Water2+ATS2:1	122.50	0.95	4.78	5.73
	------------------------------ CP (mg) ------------------------------			
CK	66.28	0.00	0.06	0.06
Water	66.28	0.00	0.05	0.05
Water+ATS1:1	66.28	0.00	0.00	0.00
Water+ATS2:1	66.28	0.00	0.04	0.04
Water+ATS4:1	66.28	0.00	0.03	0.03
Water2+ATS2:1	66.28	0.00	0.03	0.03