Using Irrigation and Organic Amendment to Reduce Fumigant Emissions

Project No.: **09-AIR5-Gao**

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Objectives:

The goal of this project is to develop effective, economical and environmentally sound methods to minimize fumigation emissions for Prunus and other perennial crop production systems that require pre-plant soil fumigation. The specific objective is to determine the effectiveness of irrigation and composted dairy manure incorporation into surface soil on emission reductions from soil fumigation.

Interpretive Summary:

Environmental regulations require significant emission reduction of soil fumigants to protect air quality in California. Methods that are effective, economically feasible and environmentally sound are the most desirable. Soil moisture is possibly an important factor that can be managed to achieve lower emissions. The objective of this study was to determine the effects of soil water content from air-dried soil to about field capacity in three different textured soils (Delhi sand, Hanford sandy loam, and Madera loam) on the emission and distribution in soil of 1,3-dichloropropene (1,3-D) and chloropicrin (CP) in soil column experiments. After injecting equal amounts of *cis*-1,3-D, *trans*-1,3-D, and CP, emission and gaseous fumigant distribution in the columns were monitored over time. With similar patterns, the emissions of the three compounds followed the order of *cis*-1,3-D > *trans*-1,3-D > CP. Increasing soil water content significantly reduced the emission peak flux, delayed its occurrence time, and reduced total emission losses in sandy loam and loam soils. Furthermore, higher gaseous fumigant concentrations were found in high soil water content treatments reflecting the ability of soil moisture to reduce fumigant diffusion to the soil surface. The effect on the emission reduction in the coarse textured soils was less than in the finer textured soils, which may be related to its high air-filled porosity. The results indicate that increasing soil water content to

proper levels can be an easily operated, effective, and low-cost strategy to control fumigant emissions while still achieving good efficacy.

Introduction:

Soil fumigation is a common practice used to control soil-borne pests or replant diseases so that healthy Prunus trees (including almond) and grapevines can be established, especially in replant situations. With methyl bromide production limited due its contribution to the depletion of the stratosphere ozone, growers have adopted alternative fumigants such as Telone (1,3-dichloropropene or 1,3-D) and chloropicrin (CP) (CDPR, 2005; Trout, 2006). The California Department of Pesticide Registration considers all soil fumigants to be volatile organic compounds (VOC) that can react with nitrogen oxides under sunlight to form harmful ground-level ozone (smog). To reduce VOC emissions, regulations on soil fumigant use in California are in place to control fumigant emissions. Additional restrictions for risk reduction are being developed by federal and the state regulatory agencies (CDPR, 2009; USEPA, 2009). These regulations have had and will continue to have great impact on the availability of alternative fumigants to growers.

Emission reduction can be achieved through physical and/or chemical (reactive) barriers (e.g., tarping, irrigation, and soil amendments using chemicals or organic materials). Emission loss also depends on fumigation methods (e.g. injection depth, shank designs and chemigation), fumigant properties and soil/environmental conditions. Our previous research identified that water seals can reduce 1,3-D and CP emissions even more effectively than the standard high density polyethylene (HDPE) plastic tarp and reduce fumigation costs (Gao and Trout, 2007; Gao et al., 2008b). We also found that 1,3-D and CP emission reduction can be achieved without reducing fumigant concentrations in soil when irrigation is applied prior to fumigation (pre-irrigation) by creating a moist soil profile (Gao et al., 2008a). It is important to note that excess amounts of water in soil can inhibit fumigant transport in the soil that may lead to poor efficacy (Thomas et al., 2003; McKenry and Thomason, 1974). The range of optimum soil water content that reduces emissions while not reducing fumigant concentration or transport to affect efficacy may vary greatly in different soil types. Using water is a low-cost strategy in comparison with plastic tarps, and is thus applicable to a wide range of commodity groups especially for those with low-profit margins.

Objectives:

The goal of this project is to develop effective, economical and environmentally sound methods to minimize fumigation emissions for Prunus and other perennial crop production systems that require pre-plant fumigation. This project focused on irrigation methods and organic amendment to control emissions. Investigation on the role of organic (manure) incorporation/amendment in reducing fumigant emissions were investigated during the previous year of the project and reported in the 2008-2009 project report to the Almond Board of California and presented at the 2009 Almond Industry Conference (Gao et a., 2009). The specific objective of the 2009−2010 project was to determine the effects of soil water content on emission reduction from soil fumigation and the distribution of fumigants in soils to foresee the potential fumigation exposure on pests. To cover a large range of soils, three different soil types were selected for the study.

Materials and Methods:

Soils and Treatment. Soil column experiments were conducted to determine the effect of soil water content in three different textured soils on 1,3-D and CP emissions, fumigant distribution in the soil gas-phase and the fate of fumigants in the soil. Closed-bottomed stainless steel columns were used in this research with a 25-cm height and 15.5-cm i.d. Details about these columns are described in Qin et al. (2009).

The three soils with different textures were: Delhi sand (mixed, thermic Typic Xeropsamments); Hanford sandy loam (coarse-loamy, mixed, superactive, nonacid, thermic Typic Xerorthents); and Madera loam (fine, smectite, thermic Abruptic Durixeralfs). The Delhi sand was collected from a field near the city of Atwater, Merced County, CA. The Delhi series soils are districted in the eastern side of the San Joaquin Valley, Central Valley, and intermountain valleys in the western part of southern California. The series is used for growing grapes, peaches, truck crops, and alfalfa. The principal native plants are buckwheat and a few shrubs and trees. Typical vegetation is annual grasses and forbs (NRCS, 2004). The Hanford sandy loam was collected from the USDA-ARS San Joaquin Valley Agricultural Sciences Center, Parlier, Fresno County, CA. Hanford series soils are widely distributed in the San Joaquin Valley and in the valleys of central and southern California and typically are used for growing a wide range of fruits, vegetables and general farm crops (NRCS, 2004). The Madera loam was obtained from Bright’s Nursery in Le Grand, Merced County, CA. The Madera soil series is used mainly for irrigated cropland and is distributed in the eastern side of the Sacramento and the San Joaquin Valley (NRCS, 2004). **Table 1** shows the properties of the soils collected.

The soils were collected from the field surface (~0−30 cm), air-dried, sieved through a 4-mm sieve, and homogenized thoroughly before being used. A different bulk density was used for the different textured soils based on field observations in surface soils (**Table 1**). Duplicate columns were established for each treatment. After the soils were packed uniformly into the columns, different amounts of water were added to the soil surface to achieve targeted soil water contents throughout the column. For the Madera loam, the target treatments were to achieve final water contents of 30, 45, 60, 75, 90 and 100% (w/w) of field capacity, represented as treatments W30, W45, W60, W75, W90 and W100, respectively. The FC level was chosen as the upper level because substantial amount of air-filled porosity should be present at this moisture condition. The Hanford sandy loam was treated at W30, W60, and W100 according to its FC (**Table 1**). For the Delhi sand soil, because of its low FC, we chose 60% FC as the lowest soil water content for the test and two additional water treatments (100% and 200% FC). For the lowest water contents (i.e., W30 for the Hanford sandy loam and the Madera loam or the W60 for the Delhi sand), water was added to the soil first and homogenized in plastic bags for 24 h before being packed into the columns. For the other treatments, water was added to the soil surface and the columns were sealed with aluminum film and allowed to equilibrate for about two months to achieve a uniform soil moisture condition throughout the column.

Emission sampling. Prior to fumigant injection, a flow-through gas sampling chamber replaced the aluminum foil on the top of the soil columns and was sealed to the column with sealant-coated aluminum tape. A mixture of 150 µL fumigant solution containing 67 mg (≈ 35 kg ha^{-1}) each of *cis*-1,3-D, *trans*-1,3-D, and CP (≈ 104 lbs/A total fumigant) was injected into the column center through a custom-made long needle syringe. A constant air flow rate of 110±10 ml min^{-1} was maintained through the sampling chamber by applying a vacuum to the discharge port, and monitored with a flow meter. Fumigant emissions from the soil surface in the column were sampled by collecting air samples with ORBO 613, XAD 4 80/40mg (Supelco, Bellefonte, PA) tubes connected to the outlet of the flow-through chamber. During the daytime, emission samples were taken at an increasing interval over time (1- 4 h). During the night hours or weekends, a chain of ORBO tubes connected in series was used for trapping all fumigants to avoid breakthrough. The ORBO sampling tubes were stored at -80 °C until they were extracted. The extraction and analysis procedures can be found in Qin et al. (2009). The detection limit (three times the standard deviation of the background noise level) for *cis*-1,3-D, *trans*-1,3-D and CP was 0.01, 0.01, and 0.001 mg L^{-1}, respectively.

Soil gas sampling. Soil gas fumigant concentrations for monitoring fumigant concentration changes over time in the columns were sampled during the experiment. Three gas sampling ports were installed at 0, 10, and 20 cm below the soil surface on the column. A Teflon tube was connected to the inside of each sampling port and extended to the center of the column. The gas samples were withdrawn from depths 0, 10, and 20 cm below the soil surface using a gas-tight syringe. Sampling was carried out at 3, 6, and 12 h, and 1, 2, 3, 5, 7, 9, and 11 d (12 d for the column study for Madera loam soil) after fumigant injection. Details about the gas sampling, sample processing and analysis can be found in Qin et al (2009).

Residual fumigants and others. At the end of the experiment, soil samples were taken at 0-5, 5-10, 10-15, 15-23 cm depth intervals to determine soil residual fumigants and soil water content. The soil extraction followed Guo et al. (2003). The analytical procedures were the same as fumigant emission samples, except a different solvent was used.

To evaluate the fate of fumigants in the soil at the end of the experiment, fumigant degradation was calculated by subtracting emission loss, fumigant in the soil gas-phase, and the residual fumigant in soil solid/liquid phases from the total amount of fumigant applied.

Results and Discussions:

Emission flux. The effect of increasing soil water content on emission flux from the column studies is illustrated in **Figure 1** for the Madera loam. Following a similar pattern, the flux increased following fumigant injection, reached a peak and then decreased over time for all treatments. In general, the emission flux of *cis*-1,3-D was relatively higher than that of *trans*-1,3-D and CP. Increasing soil water content reduced the peak emission flux and delayed their occurrence time (Fig. 1). A linear equation with a negative slope can be used to describe the correlation between the peak flux of each compound and soil water content: $Y = -0.33X + 80.97$ for *cis*-1,3-D ($R^2 = 0.98$); $Y = -0.21X + 51.24$ for *trans*-1,3-D ($R^2 = 0.98$); and $Y = -0.13X + 38.41$ for CP ($R^2 = 0.88$), where Y is the peak flux in $\mu g\ m^{-2}\ s^{-1}$ and X is soil water content ($g\ kg^{-1}$), n=12. A similar observation was made in a sandy loam soil when a range of soil water contents were tested on fumigant emissions at a higher fumigant application rate (Qin et al., 2009). The reduction in the peak flux can help reduce the potential exposure risks to workers and by-standers.

All soils demonstrated that the increase of soil moisture decreased the emission peak flux, which can be seen in **Table 2** for selected treatments. The comparison of fluxes for different soils with the same soil water content based on their FC (i.e., 30, 60, and 100% FC) are illustrated in **Figure 2** for *trans*-1,3-D. Little reduction in peak flux was observed in the sandy soil as the soil water content increased from 60% to 200% FC. Dramatic peak flux reduction can be seen in the finer textured soils. The peak fluxes of W100 were 12-15% of that of W30 (85-88% reduction) and occurred about 5-10 hours later for the different compounds in the Hanford sandy loam. For the Madera loam, the peak fluxes of W100 were 15-23% of that of W30 (77-85% reduction) and occurred 10-15 hours later. These data indicate that increasing soil water content up to FC level resulted in greater emission reduction in finer textured soils than coarse textured soil.

Cumulative emission loss. Cumulative emission loss from summing the products of flux and time increased over time until a plateau was reached. **Figure 3** shows the emission losses of chloropicrin as an example. The total emission losses by the end of the experiment from all the treatments for the three soils are given in **Table 2**. Generally speaking, the Delhi sand showed no reduction in cumulative loss for the 1,3-D isomers although a small reduction in CP losses were observed when soil water content was increased to 200% FC (24% reduction). For the other two soils, reductions in total emission losses were relatively small (1-18%) when soil water increased from 30% to 60% FC; but much larger reductions (24-49%) were observed when water increased to 100% FC.

The cumulative emission data from the column study can be used only to show the relative fumigant emission information from the soil water treatments. The total emission losses from this column study were much higher than expected under field conditions. This was due to the closed-bottom column effects as the fumigants can only escape through upward transport (i.e., emission). In a field, however, gases can move in three dimensions in the soil profile. For this reason, it is expected that the absolute emission loss would be lower for a given soil water treatment under field conditions.

Gaseous fumigant distribution in soil columns. Similar distribution patterns of fumigant concentrations in the soil gas-phase were observed for all three compounds; thus, **Figure 4** only shows the *cis*-1,3-D data. The highest concentration was determined at the first sampling time (3 h) near the injection depth (10 cm) in all water treatments. The lowest values were observed in the driest Delhi sand soil and the highest were in the wettest Madera loam soil. Upon injection into the soil, fumigants diffused quickly and achieved uniform distribution or higher concentrations in the lower depths (caused by surface emission loss). The fumigant concentrations in the soil gas-phase generally decreased over time in all treatments due to emission loss and degradation.

The soil column study showed that the measured fumigant gas concentrations in the soils with high water content (FC levels) were consistently higher than those in the drier soils. This was due to more retention and slower emission rates in the moist soils. Other studies also reported that higher water content gave higher fumigant concentrations and lower emissions in soils (Ajwa and Trout, 2004; Thomas et al., 2004). However, the benefits of increasing soil water content to a certain level would diminish because excess amounts of water can significantly reduce diffusion rate that would result in non-uniform distribution of fumigants and affect fumigation efficacy. The laboratory findings need to be confirmed via field tests with efficacy investigations.

Residual fumigant and the fate of fumigants. The residual fumigants extracted from soil samples at the end of the experiments are given in **Table 3**. The residual fumigant concentrations were generally low; the highest levels only 1.9%, 4.1%, and 0.2% of applied *cis*-1,3-D*, trans*-1,3-D and CP, respectively. For sandy loam and loam soils, treatment W100 had significantly higher residual fumigant amounts than the drier soils. Among the three residual fumigant compounds, *trans*-1,3-D was retained the most while CP was retained the least. Others also reported higher residuals of 1,3-D and CP in soils with near field capacity water content as compared to the dry soils (Thomas et al., 2003, 2004). In general, fumigants in the soil gas-phase at the end of experiment were much less than the residual fumigants in soil solid/liquid phases.

Because fumigants in the soil gas-phase and residual fumigants were minor portions of the whole, the calculated amount of fumigant degraded in the various water treatments (**Table 3**) is largely determined by the emission losses. Highest degradation was found in treatment W100 of loam soil which contributed degration of up to 39.8%, 47.9%, and 78.7% of applied *cis*-1,3-D, *trans*-1,3-D, and CP, respectively. As high soil water content can retain fumigants in soils for a longer period of time, more fumigants were subject to degradation via chemical or biological mechanisms. In addition, some studies reported that high soil water content accelerated fumigant degradation through hydrolysis (Guo et al., 2004; Gan et al., 1996), although the effects were not found significant in other studies (e.g., Dungan et al., 2001). A faster dissipation of CP was observed as compared to 1,3-D isomers.

Effect of soil texture and water content on emissions. Soil water content determined at the end of the experiment showed that a relatively uniform soil water content profile was achieved in each column treatment (**Figure 5**). Because of the low FC for the Delhi sand soil, the air-filled porosity at the highest water treatment (W200) was not much different from the W60 treatment and only slightly lower than the driest sandy loam and the loam soils (W30) (**Figure 6**). Compared to W30, the air-filled porosity was reduced 11-12% in treatment W60 and 26-28% in treatment W100 for the sandy loam and loam soils (**Figure 6**). Fumigant diffusion and emissions are largely affected by the air-filled porosity because fumigant diffusion rates in the gas phase are much higher than in the liquid phase.

There appears to be a linear relationship between the air-filled porosity and emission loss of 1,3-D isomers and CP integrating data from all the columns: $Y = 1.69X + 9.66$ for *cis*-1,3-D ($R^2 = 0.68$); $Y = 2.12X - 13.44$ for *trans*-1,3-D ($R^2 = 0.78$); and $Y = 0.81X - 0.98$ ($R^2 = 0.25$) for CP, where Y is the total emission loss (% of applied) and X is air-filled porosity (%), n=23. These data may suggest that reducing the air-filled space to a proper level may be the key to ensure emission reduction in different types of soils. The correlation between the CP emission loss and air porosity was less profound than 1,3-D isomers.

Conclusion:

This study indicated that high soil water content (up to FC) can significantly reduce peak emission flux and cumulative emission loss for sandy loam and loam soils. Much higher soil water content is likely needed to reduce emissions in sandy soils. Higher gaseous fumigant concentrations were also found in soils with high soil water content, indicating a potential benefit for increased fumigant exposure to soil-borne pests. Therefore, it is possible to improve efficacy as long as the maximum uniform distribution of fumigant diffusion in the soil can be achieved. A proper air-filled porosity may be used as an indicator to determine proper soil water content for ensuring emission reduction while not reducing fumigant diffusion in soils. In field applications, it has been rare to fumigate soils with water content as high as FC levels. Therefore, the laboratory findings need to be tested further under field conditions to conclude how high soil water content can be used in soil fumigation to achieve maximum emission reduction and efficacy results.

Research Effort Recent Publications:

Qin, R., S. Gao, D. Wang, B.D. Hanson, T.J. Trout, and H. Ajwa. 2009. Relative effect of soil moisture on emissions and distribution of 1,3-dichloropropene and chloropicrin in soil columns. Atmos. Environ. 43:2449–2455.

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Table 1. Selected properties of soils used in this research

Soil properties	Delhi sand[†]	Hanford sandy loam	Madera loam
Bulk density, g cm^{-3}	1. 5	1.4	1.3
Sand, g kg^{-1}	950	548	404
Silt, g kg^{-1}	50	396	344
Clay, g kg^{-1}	0	56	252
Water content at 33 kPa suction, g kg^{-1}	29	170	230
Organic matter content, g kg^{-1}	NA	7.4	11.2
Cation exchange capacity, $cmol_c$ kg^{-1}	NA	6.8	20

[†] NA, not available

Table 2. Peak emission flux and total emission loss of fumigants affected by soil water content[†]

Soil	Treatment	Peak emission flux (μg m^{-2} s^{-1})			Total emission loss (% of applied)		
		cis-1,3-D	*trans*-1,3-D	CP	*cis*-1,3-D	*trans*-1,3-D	CP
Delhi sand	S-W60	43.3 (n/a)	27.8 (n/a)	30 (n/a)	76.0 (n/a)	71.7 (n/a)	30.4 (n/a)
	S-W100	41.8 (0.6)	27.3 (0.2)	28.3 (1.0)	79.7 (1.3)	73.5 (1.8)	24.0 (1.4)
	S-W200	40.2 (5.1)	25.5 (1.7)	26.9 (3.0)	79.1 (1.2)	72.9 (1.3)	23.0 (0.3)
Hanford sandy loam	SL-W30	64.8 (3.1)	36.4 (3.7)	54.1 (2.9)	78.9 (7.9)	76.6 (6.9)	38.0 (5.6)
	SL-W60	21.5 (1.5)	13.5 (0.1)	16.8 (1.2)	78.3 (0.2)	72.5 (0.4)	31.1 (1.0)
	SL-W100	9.1 (4.0)	5.5 (2.7)	6.7 (4.0)	59.8 (13.7)	50.6 (13.6)	22.0 (10.3)
Madera loam	L-W30	62.2 (3.4)	40.1 (1.0)	29.8 (2.8)	82.2 (2.0)	77.9 (0.0)	41.5 (0.4)
	L-W60	35.2 (0.6)	22.9 (0.9)	23.4 (1.0)	77.6 (0.7)	70.0 (0.7)	34.6 (0.9)
	L-W100	9.1 (1.9)	6.1 (1.4)	6.9 (2.1)	58.6 (6.4)	49.3 (6.5)	21.2 (4.5)

[†] Values in the table were averages of the duplicates with the standard deviation in parenthesis.

Table 3. Effect of soil water content on the fate of *cis*-1,3-D, *trans*-1,3-D and CP in soil columns at the end of the experiment†.

Soil	Treatment	Residual fumigant (mg kg^{-1})			Degradation (% of applied) §		
		cis-1,3-D	*trans*-1,3-D	CP	*cis*-1,3-D	*trans*-1,3-D	CP
Delhi sand	S-W60	0.10 (0.01)	0.17 (0.01)	0	23.0 (0.1)	26.6 (0.1)	69.6 (0)
	S-W100	0.19 (0.03)	0.39 (0.03)	0.02 (0.01)	18.4 (1.7)	22.3 (2.1)	75.7 (1.5)
	S-W200	0.09 (0)	0.22 (0.01)	0	20.5 (1.2)	30.7 (1.2)	74.8 (0.3)
Hanford sandy loam	SL-W30	0.09 (0.06)	0.22 (0.12)	0	20.3 (7.6)	21.2 (8.1)	62.0 (5.6)
	SL-W60	0.03 (0.03)	0.13 (0.07)	0	21.2 (0.2)	25.8 (0.3)	68.9 (1.0)
	SL-W100	0.13 (0.04)	0.29 (0.03)	0	38.1 (13.3)	45.4 (13.3)	78.0 (10.3)
Madera loam	L-W30	0.02 (0.02)	0.12 (0.27)	0.01 (0.01)	17.6 (2.1)	21.2 (0.6)	58.4 (0.4)
	L-W60	0.03 (0.03)	0.14 (0.06)	0.01 (0.01)	22.1 (0.9)	28.7 (0.8)	65.3 (0.9)
	L-W100	0.19 (0.12)	0.31 (0.34)	0.02 (0.03)	39.8 (5.4)	47.9 (4.2)	78.7 (4.6)

† Values in the table were the percentage of the applied fumigant amount with the standard deviation in parenthesis; § Degradation calculated by difference between the amount applied and the measured residual fumigant, the total emissions, and the soil gas at the end of experiment.

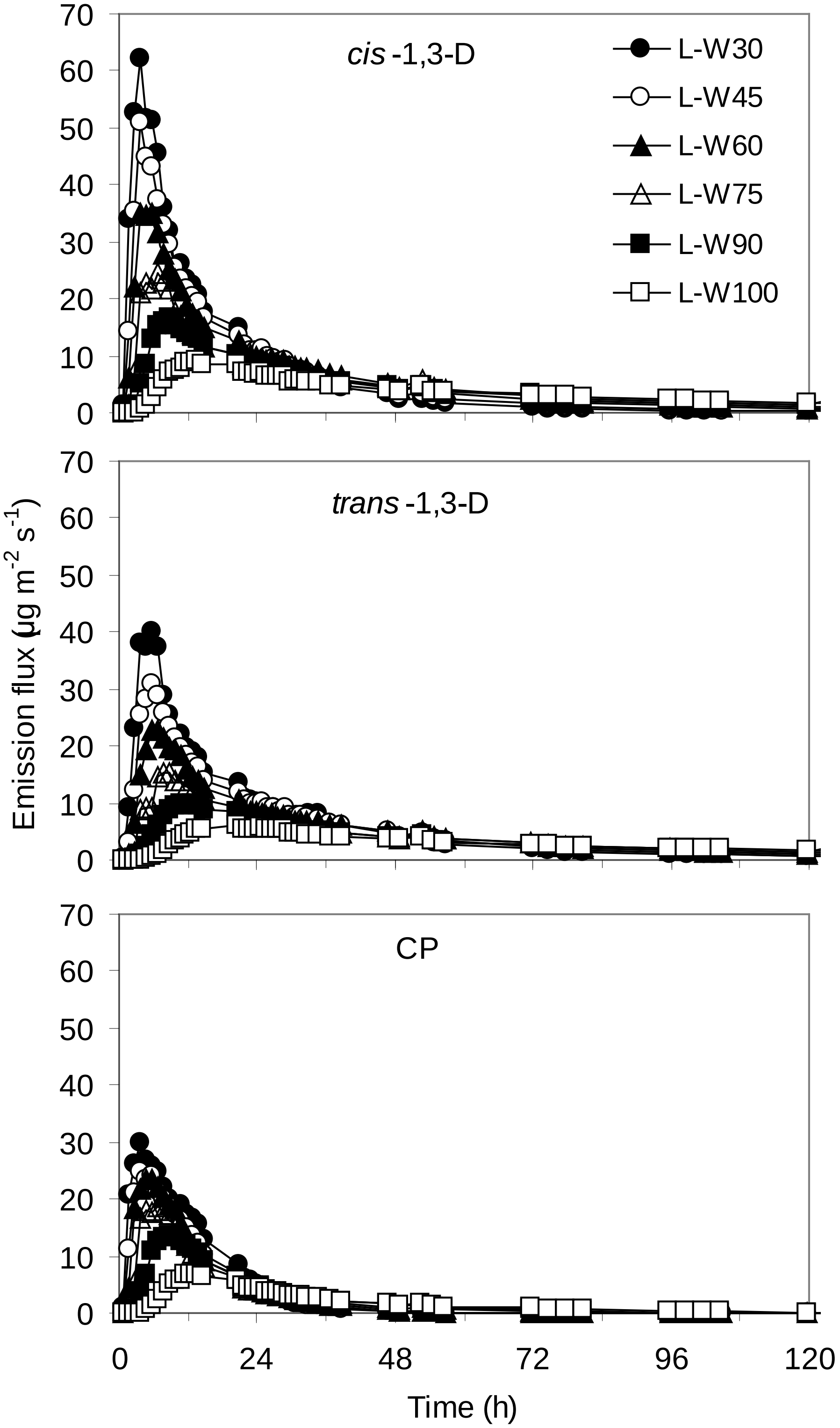

Figure 1. Emission flux of *cis*-1,3-D, *trans*-1,3-D, and CP from different soil water contents in the Madera loam (L) soil. W30-W100 represents soil water content at 30% -100% field capacity levels.

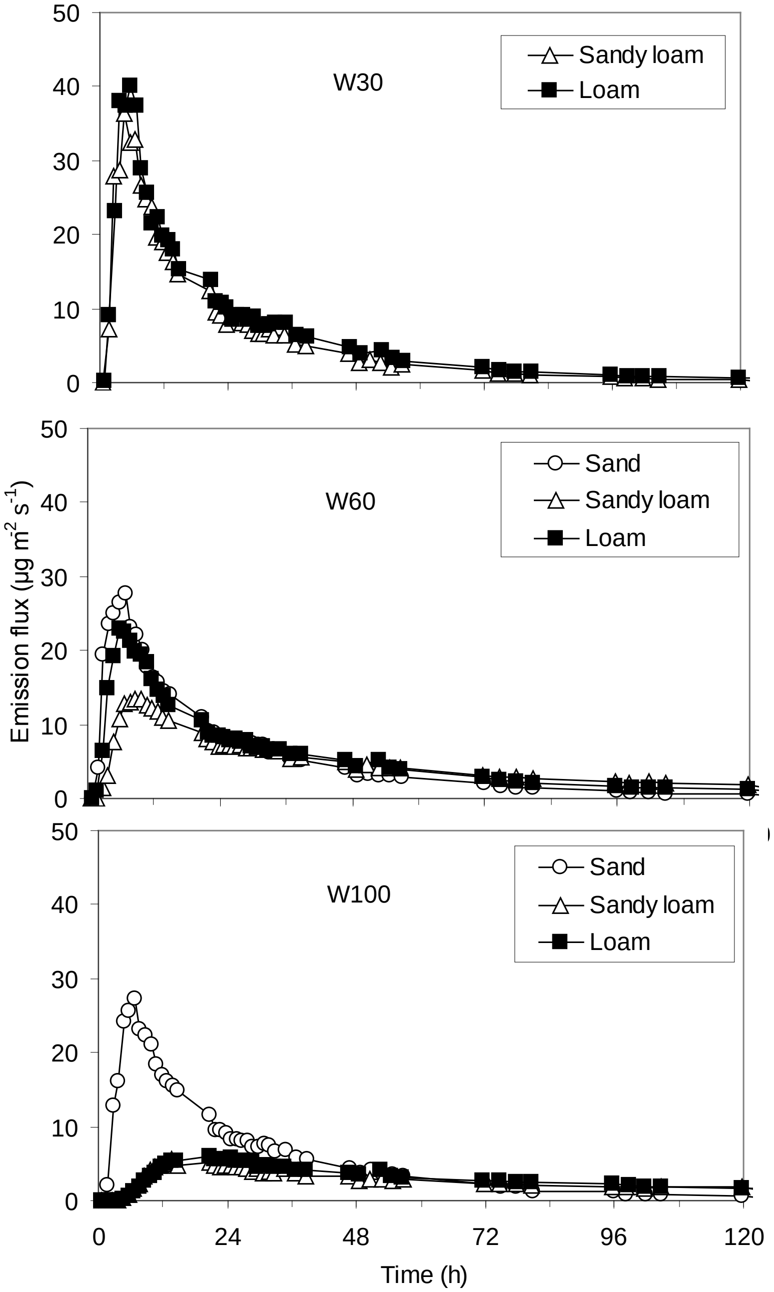

Figure 2. Emission flux of *trans*-1,3-D in three different textured soils (S, Delhi sand; L, Hanford sandy loam; L, Madera loam) under three soil water content levels (i.e., W30, W60, W100 for 30%, 60% and 100% field capacity, respectively).

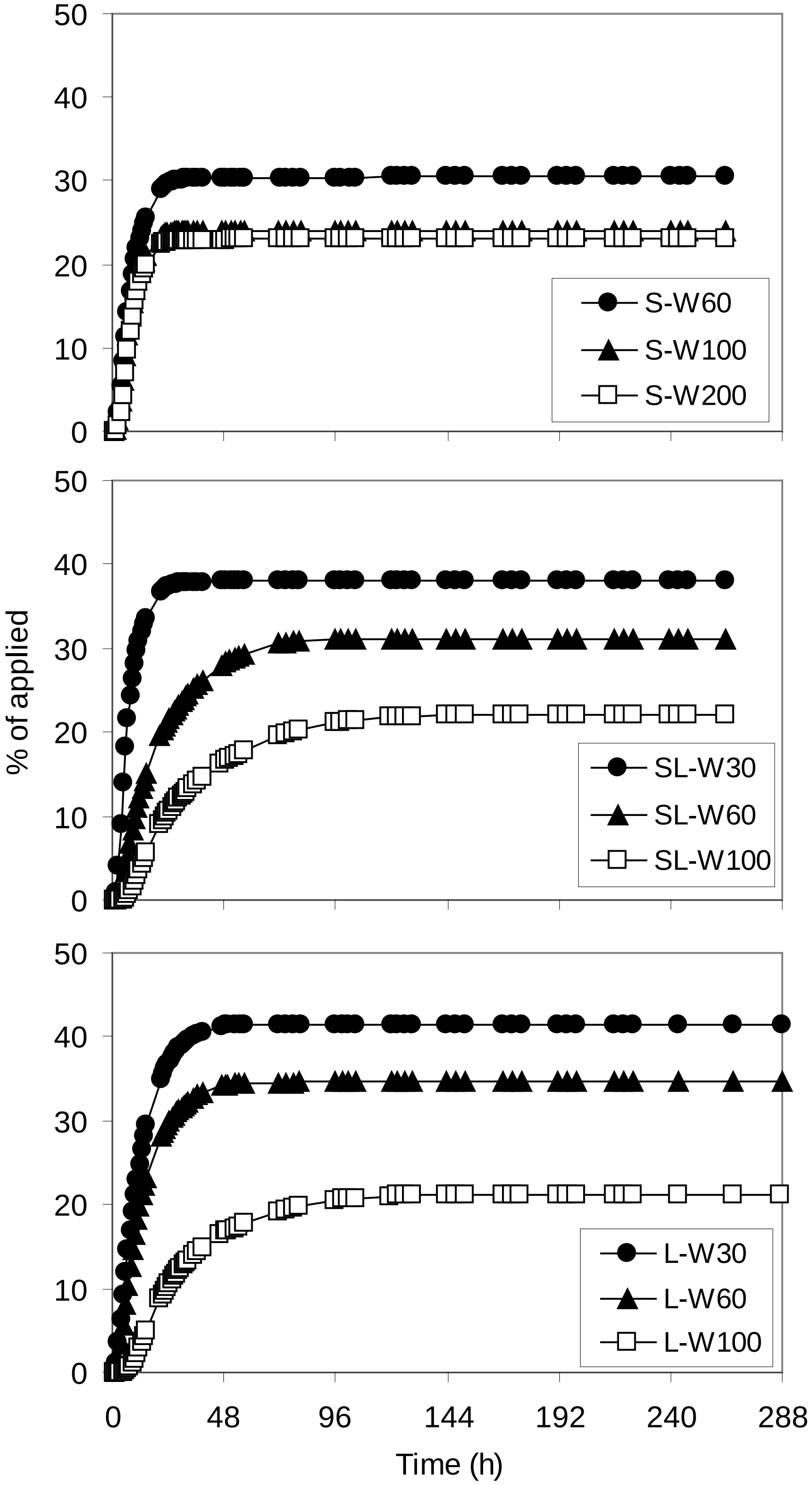

Figure 3. Cumulative emissions of fumigant chloropicrin in three different textured soils: S, Delhi sand (top); SL, Hanford sandy loam (middle); L, Madera loam (bottom). W30, W60, W100, and W200 represent 30%, 60%, 100%, and 200% field capacity, respectively.

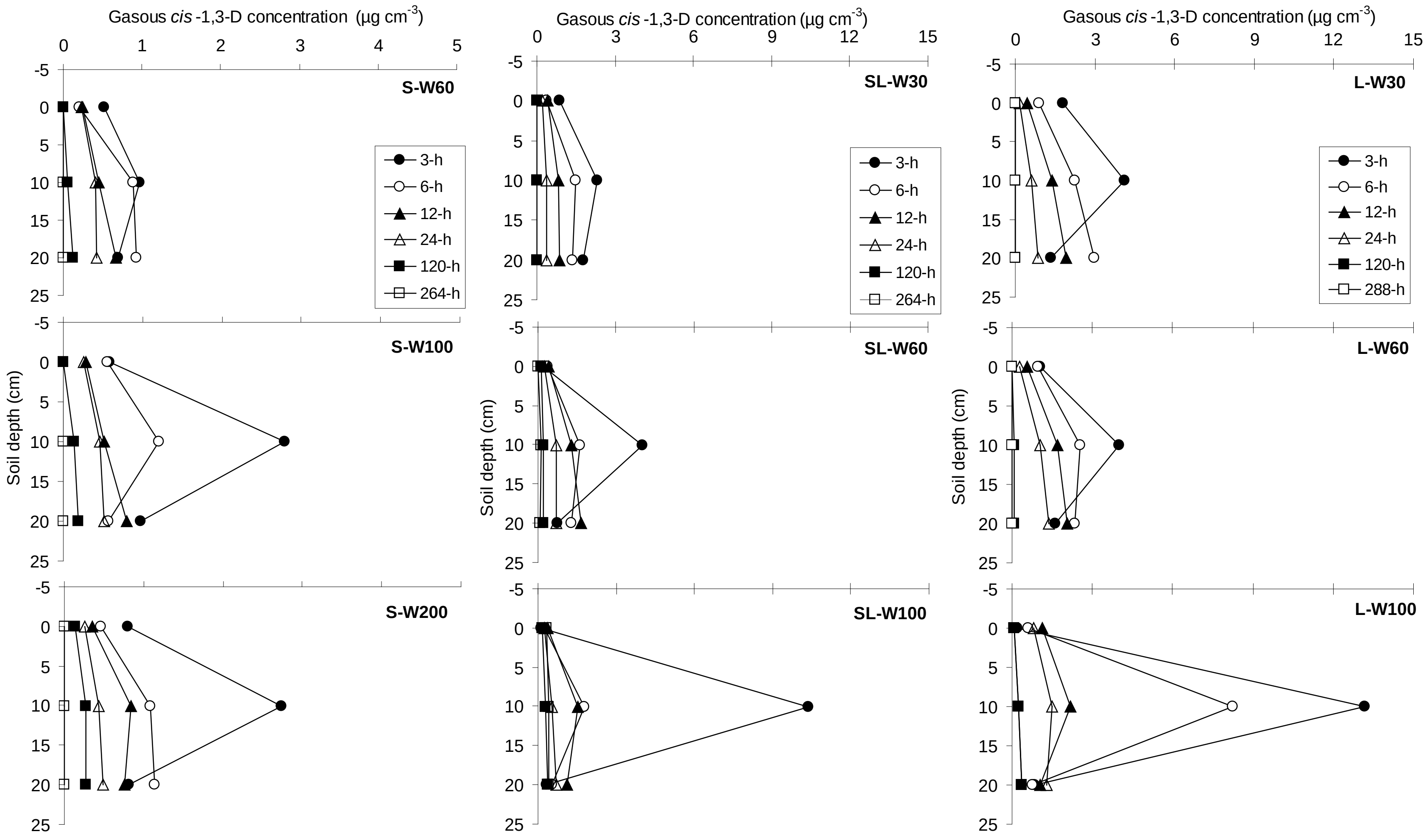

Figure 4. Change in soil gaseous fumigant (*cis*-1,3-D) concentrations from Delhi sand soil (S), Hanford sandy loam (SL), and Madera loam (L). W30, W60, W100, and W200 represent 30%, 60%, 100%, and 200% field capacity, respectively.

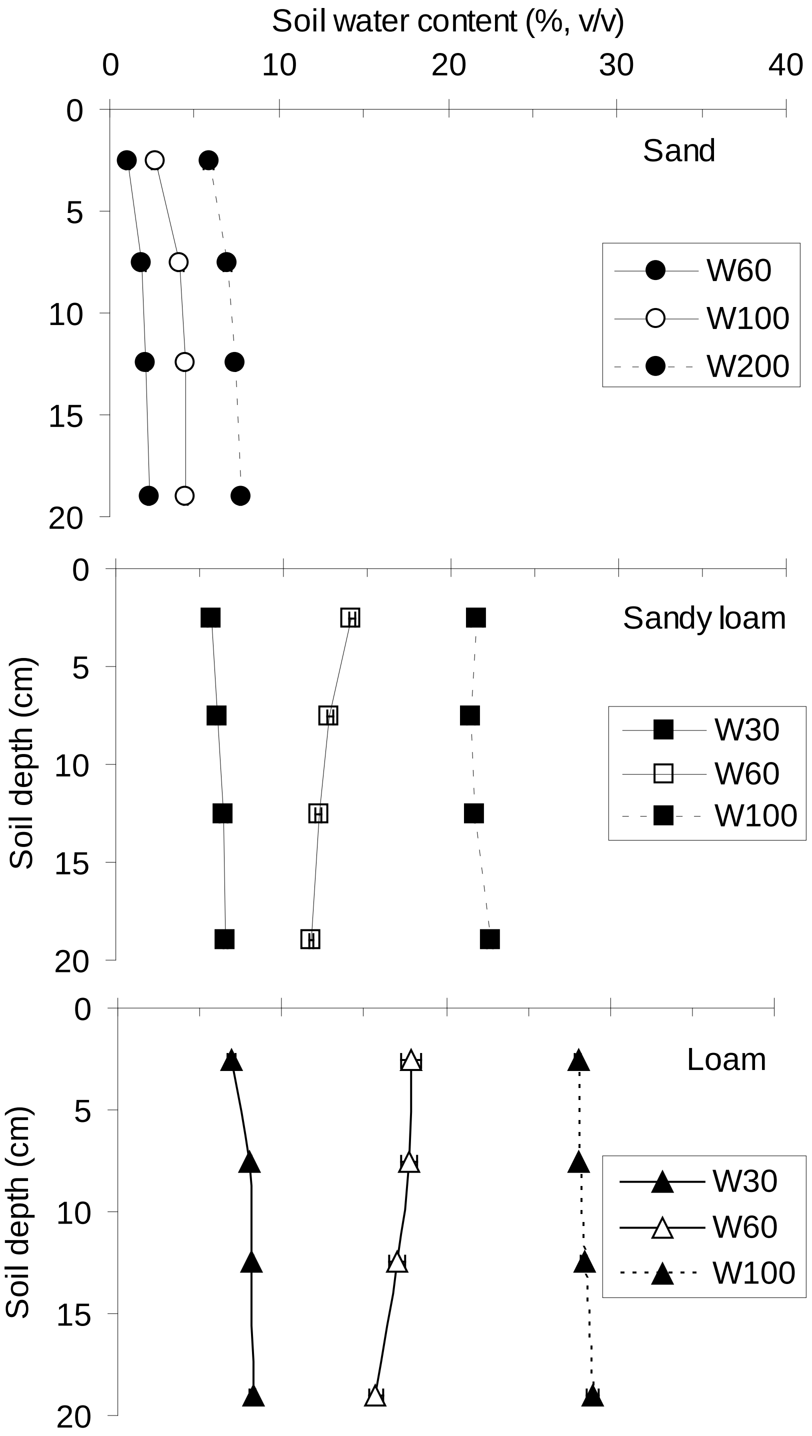

Figure 5. Soil water content (%, w/w) in three soils: Delhi sand (top); Hanford sandy loam (middle); Madera loam (bottom). W30, W60, W100, and W200 represent 30%, 60%, 100%, and 200% field capacity.

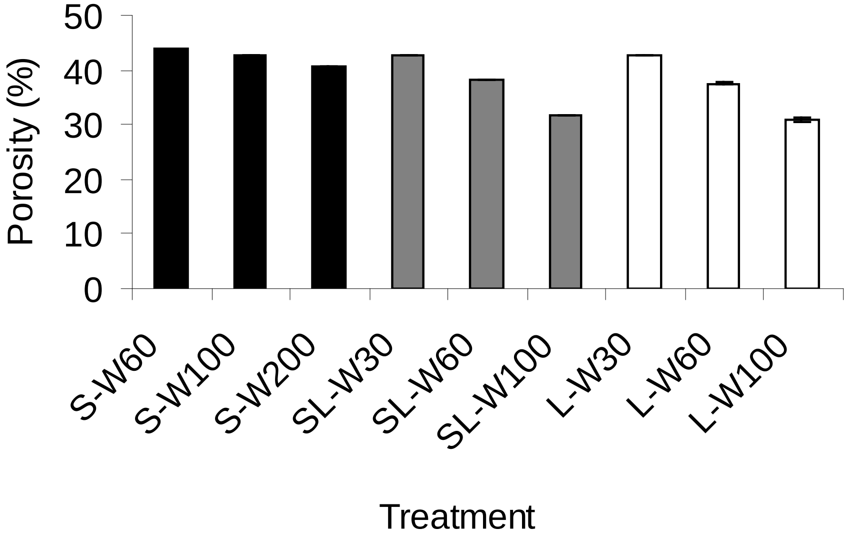

Figure 6. Air-filled porosity in soil column treatments. Delhi sand,S, Hanford sandy loam, SL, and Madera loam, L. W30, W60, W100, and W200 represent 30%, 60%, 100%, and 200% field capacity, respectively.