Supporting Information

Emissions of 1,3-dichlorpropene and chloropicrin after soil fumigation under field conditions

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(Total 2 pages, 3 Figures, 0 Tables)

Aerodynamic Method

The aerodynamic method *(1-3)* requires information on atmospheric wind speed, temperature and concentration gradients which provide a measurement of the pesticide flux from the soil surface. To use this method, one assumes a spatially uniform source and a large upwind fetch distance. The necessary upwind fetch distances are generally from 50–100 times the height of the sampling instruments. The fumigant concentration in the air was sampled at 0.1, 0.4, 0.8, 1.6, 2.4 and 3.6 m above the soil surface so that the concentration profile as a function of height could be determined. A linear regression equation was fitted to semi-log plots for the wind speed and concentration measurements to obtain values for the gradient, which reduces effects of measurement variability.

The aerodynamic method was originally developed for neutral atmospheric conditions. The method can be extended to stable and unstable atmospheric conditions by incorporating empirical adjustment factors. The aero-dynamic equation for the surface flux, $f_z(0, t)$, is

$$f_z(0,\ t) = k^2 \frac{\left[\bar{C}_1(t) - \bar{C}_2(t)\right]\left[\bar{u}_2(t) - \bar{u}_1(t)\right]}{\phi_m(t)\ \phi_c(t)\ ln(z_2/z_1)} \qquad \text{(S1)}$$

$$f_z(0,\ t) = \frac{-k^2 z^2}{\phi_m(t)\ \phi_c(t)}\left(\frac{\partial \bar{C}(t)}{\partial z}\right)\left(\frac{\partial \bar{u}(t)}{\partial z}\right)$$

where $f_z(0, t)$ is the interval-averaged vertical flux density at the soil surface [μg/m^{2}s], k is von Karmon's constant (~0.4), t is the interval-averaged wind speed [m/s], z is height above the soil surface [m] and $\bar{u}$, $\bar{C}$ are the interval-averaged wind speed [m/s] and concentration [μg/m^3] above the soil surface, and ϕ is a stability correction where the subscripts m and c indicate momentum and fumigant.

The gradient-based stability corrections for a particular time interval, t, can be estimated using *(4)*

$$\phi_m = (1-16R_i)^{-0.33} \quad \phi_c = 0.885\ (1-22R_i)^{-0.4} \quad R_i < 0 \qquad \text{(S2)}$$

$$\phi_m = (1+16R_i)^{0.33} \quad \phi_c = 0.885\ (1+34R_i)^{0.4} \quad R_i > 0$$

where R_i is the Richardson's number (e.g., g/T $(\partial T/\partial z)$ $[\partial u/\partial z]^{-2}$), g is the gravitational acceleration (i.e., 9.8 m/s^2), and T is the absolute temperature. In addition to Equation (S2), several other stability corrections have been proposed *(3-5)*. Further information on the use of the aerodynamic method to measure fumigant emissions can be found in the literature (*6-10*).

Schematic of Field Site

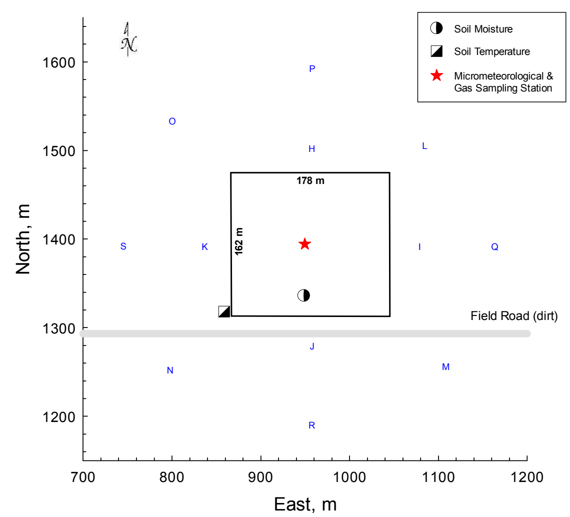

Figure S1. Schematic of the experimental layout. The gray line indicates a field road. The symbols indicate the position of the sampling equipment. The letters are the locations of the off-site samples.

Soil Water Content

Figure 2 shows the initial and ending soil water content (cm^3 cm^{-3}). The initial water content varied from 0.1 – 0.34 cm^3 cm^{-3} at the start of the experiment and redistributed to a range from 0.05 – 0.40 cm^3 cm^{-3} by the end of the experiment.

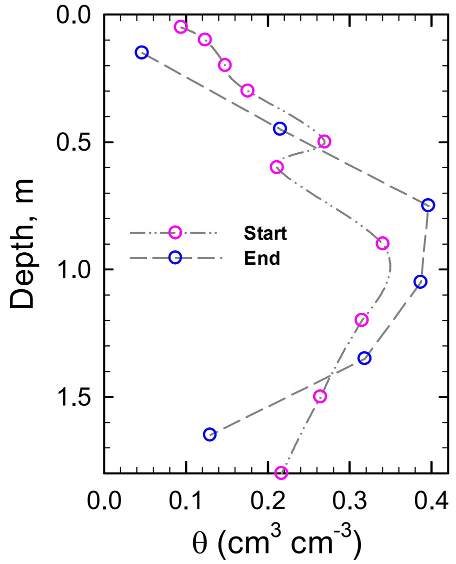

Figure S2. Soil water content during the experiment.

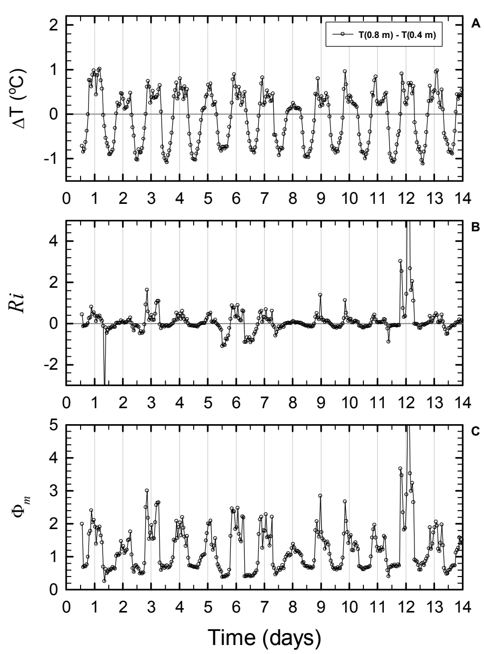

Figure S3. In A, the temperature difference. In B, the gradient Richardson's number. In C, the atmospheric stability parameter for momentum: $\Phi_m = (1 \pm 16\, R_i)^{\pm 1/3}$, where the plus sign is used when $R_i > 0$, otherwise the minus sign is used.

References

(1) Parmele, L.H.; Lemon, E.R.; Taylor, A.W. Micrometeorological measurement of pesticide vapor flux from bare soil and corn under field conditions. *Water, Air, Soil Pollut.,* **1972**, 1, 433-451.

(2) Denmead, O.T.; Simpson, J.R.; Freney, J.R. A direct field measurement of ammonia emission after injection of anhydrous ammonia. *Soil Sci. Soc. Am. J.,* **1977**, 41, 1001-1004.

(3) Brutsaert, W. Evaporation into the atmosphere. Reidel, Dordrecht, **1982**, 299 pp.

(4) Rosenberg, N.J.; Blad, B.L.; Verma, S.B. Microclimate, The biological environment. John Wiley & Sons, New York, 1983, 495 pp.

(5) Fleagle, R.G.; Businger, J.A. An introduction to atmospheric physics, 2nd Ed. International Geophysics Series, Vol 25. Academic Press, New York, **1980**, 432 pp.

(6) Yates, S.R., F.F. Ernst, J. Gan, F. Gao, and M.V. Yates. 1996. Methyl bromide emissions from a covered field. II. Volatilization. J. Environ. Qual. 25:192-202.

(7) Yates, S.R., Gan, J., Wang, D. and Ernst, F.F. Methyl bromide emissions from agricultural fields. Bare-soil, deep injection. Environ. Sci. Technol. 31:1136-1143. 1997.

(8) Yates, S.R., Knuteson, J. Ernst, F.F., Zheng, W. and Wang, Q. The Effect of Sequential Surface Irrigations on Field-scale Emissions of 1,3-dichloropropene. Environ. Sci. Technol. 42:8753-8758. 2008.

(9) Yates, S.R., Knuteson, J., Zheng, W., Wang, Q. Effect of Organic Material on Field-scale Emissions of 1,3-Dichloropropene. J. Environ. Qual..40: 1470-1479. doi:10.2134/jeq2010.0206. 2011

(10) Majewski, M.S.; Glotfelty, D.E.; Seiber, J.N. A comparison of the aerodynamic and the theoretical-profile-shape methods for measuring pesticide evaporation from soil. *Atm. Environ.,* **1989**, 23, 929-938.