Research Article

Received: 10 July 2014 Revised: 25 February 2015 Accepted article published: 13 March 2015 Published online in Wiley Online Library: 13 April 2015

(wileyonlinelibrary.com) DOI 10.1002/ps.4004

Effects of CO_2 dissolution on phase distribution and degradation of dimethyl disulfide in soils under grape production

Jeremy L Conkle,[a,b*] Jose Alfonso Cabrera,[a,c,d] John E Thomas,[e] Dong Wang[c] and Jay Gan[a]

Abstract

BACKGROUND: Dimethyl disulfide (DMDS) is a fumigant recently registered in parts of the United States. The fumigant has high pesticidal activity, but does not disperse in soils as well as other fumigants. This study assessed the use of CO_2 as a propellant to improve soil dispersion and diffusion by evaluating the partitioning and degradation of DMDS after carbonation in four vineyard soils collected in California.

RESULTS: The soil with the highest organic carbon content (Clarksburg) had the highest soil–water partition coefficient (K_d) ($P < 0.001$), which increased after carbonation. However, DMDS sorption decreased in the Mecca and Fowler soils. Henry's law constant (K_h), which measures a compound's potential for partitioning between air and water, doubled from 0.04 to 0.10 with the addition of CO_2, indicating less DMDS solubility. Carbonation did not negatively affect DMDS's half-lives in the different soils.

CONCLUSION: While trials are needed for validation of field-scale impacts, carbonation had mixed effects on soil partitioning and no discernable impact on degradation, but greatly decreased DMDS water solubility. This indicates that carbonation could improve some facets of DMDS diffusion and dispersion, depending on soil properties (carbon content and moisture), without greatly affecting its other behaviors.

Keywords: methyl bromide alternatives; adsorption; Henry's law constant; half-life; carbonation

1 INTRODUCTION

For several decades, methyl bromide (MeBr) was the most commonly used preplant soil fumigant in California grape production for controlling soilborne pests and pathogens, particularly plant-parasitic nematodes. However, owing to its ozone depletion potential, MeBr has been largely phased out under the 1987 Montreal Protocol.[1] Until recently, replanting grapes in California received an MeBr critical use exemption (CUE), but new regulations now exclude grape production.[2] While numerous potential MeBr replacements have been investigated for nematode control in grape replant situations, there exist uncertainties regarding their overall performance.[3,4] With the exception of MeBr, 1,3-dichloropropene (1,3-D) has the highest nematicide activity of commercial fumigants. However, it is highly regulated in California and not always available owing to township caps and buffer zone requirements. In addition, the currently registered rates of 1,3-D are less effective in heavy (clay loam) soils, common to grape-growing regions of California.[5] Given these regulations and limitations, alternative nematicide fumigants are urgently needed.

Dimethyl disulfide (DMDS), a volatile sulfur compound that has zero ozone depletion potential, is one of the more promising soil nematicide fumigants being studied.[6] Its nematicide control efficacy has been demonstrated under laboratory conditions as well as in microplots and fields with grape production.[7,8] The compound controls pests by blocking cytochrome oxidase activity, hindering mitochondrial respiration.[9] DMDS has been registered in over ten states in the United States as of January 2014, and it has been submitted for registration in California.[10,11]

DMDS has a lower vapor pressure (2.9 kPa at 20 °C) but higher octanol–water partition coefficient ($K_{ow} = 1.77$) than MeBr (190 kPa at 20 °C; $K_{ow} = 1.19$), making it relatively less volatile, more sorptive and therefore less capable of spreading through the soil profile to make contact with and eliminate pests such as nematodes.[12,13] Therefore, to increase DMDS field fumigation efficacy, it must be applied in higher amounts, allowed to fumigate

* *Correspondence to: Jeremy L Conkle, Coastal Health and Water Quality Lab, Department of Physical and Environmental Sciences, Texas A&M University Corpus Christi, Corpus Christi, TX 78412, USA. E-mail: jeremy.conkle@tamucc.edu*

a *Department of Environmental Sciences, University of California, Riverside, CA, USA*

b *Department of Physical and Environmental Sciences, Texas A&M University Corpus Christi, Corpus Christi, TX, USA*

c *Water Management Research Unit, Agricultural Research Service, US Department of Agriculture, Parlier, CA, USA*

d *Bayer CropScience, Fresno, CA, USA*

e *Soil and Water Science Department, University of Florida, Gainesville, FL, USA*

Table 1. Soil properties of four California grape production soils used in this study

Soil	Location in California	Soil classification	pH	TOC (mg OC g^{-1} soil)	Moisture (%)
Paso Robles	Central coast	San Ysidro loam	7.3	0.030	8.2
Clarksburg	North central	Sacramento clay	6.2	0.278	17.5
Mecca	South central	Delhi loamy sand	7.9	0.037	9.6
Fowler	Central	Carsitas gravelly sand	7.4	0.028	2.8

for longer periods or injected at a higher frequency. These options are either not allowed by the regulations (rates are currently capped at 455 lbs $acre^{-1}$) or are not cost effective. Fortunately, chemists recently discovered that supercritical CO_2 could enhance the extraction of DMDS from various matrices, suggesting that carbonation of fumigants, particularly DMDS, with CO_2 might increase their volatility and lead to improved soil dispersion.[14,15] This method was first tested with 1,3-D, where it increased soil dispersion.[16] The increase in soil dispersion is believed to be the result of temporary dipole moment interactions between CO_2 and the fumigant.[16] The objective of this study was to evaluate the effects of carbonation on DMDS phase distribution and degradation, which drive nematode control efficacy in typical California grape-growing soils.

2 MATERIALS AND METHODS

2.1 Chemicals

Dimethyl disulfide (DMDS; ≥98%) was purchased from Sigma-Aldrich (St Louis, MO) and ethyl acetate (EA; 99.9%) from Fisher Scientific (Pittsburgh, PA). The CO_2 (99.95%) used to carbonate DMDS and the 5000 ppm CO_2 standard gas used to calibrate the GC-TCD (thermal conductivity detector) were purchased through Airgas (Radnor, PA).

2.2 Soils

Four soils, collected from fields under commercial grape production in California, were used to test the effects of carbonation on DMDS phase distribution and degradation. The soil properties and classifications are shown in Table 1. The soils were analyzed by the Division of Agricultural and Natural Resources Laboratory, University of California Davis, for pH (saturated paste)[17] and total organic carbon (TOC; loss on ignition),[18] while the moisture contents were determined in our lab at the University of California Riverside by drying soils at 100 °C until their weights were constant (~24 h).

2.3 DMDS carbonation

The carbonated spiking solution was created in a 10 mL serum bottle capped with a PTFE-lined butyl rubber septum (Fisher Scientific) and crimped with an aluminum seal. The vial contained 2 mL of DMDS that was bubbled with carbon dioxide (99.95%) through a 20 gauge needle into pure DMDS at room temperature. A second, 26 gauge needle was inserted into the septum with the tip residing about 2 cm above the DMDS to flush the air of the bottle and ensure that CO_2 dissolved in DMDS. The bubbling occurred for 3 min before each needle was removed.

To test the concentration of dissolved CO_2, 2 µL of the carbonated DMDS was injected into a Shimadzu gas chromatograph (GC) 8A fitted with a thermal conductivity detector (TCD) operated at 100 °C and an Alltech Haysep Q (8 ft; 80/100 mesh) stainless steel column (O.D. 0.125 in) at 36 °C. The instrument was calibrated with a seven-point standard curve from 100 to 1200 ppm of CO_2. Carbon dioxide concentrations were measured in both the carbonated and non-carbonated DMDS spiking solutions. When samples were spiked prior to incubation, dissolved CO_2 concentrations in DMDS were checked every 30 samples, and if the level was off by >10% the spiking solution was recapped and recarbonated following the approach described above. The average CO_2 concentration dissolved in DMDS across the experiment was 46.5 ± 2.2 mg mL^{-1}. Carbon dioxide was not detected in the non-carbonated DMDS.

2.4 Phase distribution experiments

Batch equilibrium experiments were used to determine the effects of carbonation on the DMDS air–water partition coefficient (or Henry's law constant K_h) and soil–water partition coefficient K_d. In order to determine these partition coefficients, vials with 10 mL of water and vials with 10 g of oven-dried (100 °C for 24 h) soil were prepared. These vials were spiked with either 10.6 mg of carbonated or non-carbonated DMDS (1000 mg DMDS kg^{-1} soil), capped with PTFE-lined butyl rubber septa and sealed with aluminum crimps. All vials were shaken horizontally for 2 min before being incubated at 24 °C for 24 h. After incubation, 1 mL of headspace was withdrawn from each vial with a 10 mL airtight syringe and slowly introduced into a 2 mL GC vial containing 1 mL of ethyl acetate and immediately crimped. The vials were stored at −20 °C until analysis within 5 days. At least four replicates were measured for each treatment.[19]

Henry's law constant (K_h; dimensionless), the sorption coefficient (K_d; L kg^{-1}), the organic carbon partition coefficient (K_{oc}) and the Freundlich coefficient (K_f) were determined as described by Ajwa *et al.*[12] The measured concentration of DMDS in the headspace of each vial in relation to the spiked concentration was used to calculate concentrations of DMDS partitioned in the soil, water or to the vials (and stopper). The K_h values were determined in vials containing 10 mL of water by mass balance using the DMDS value measured in the headspace (C_a; mg L^{-1}) and determined in the water (C_w; mg L^{-1}). The K_d values were determined by dividing the DMDS partitioned in the soil (C_s; mg kg^{-1}) by that in the water (C_w). The K_d was then divided by the soil organic carbon content (mg g^{-1} soil) to determine the K_{oc}. An additional experiment was performed to assess the dependence of K_d on DMDS concentration. Vials were incubated as described above with both carbonated and non-carbonated DMDS, but with spiking amounts of 25, 50 and 100 mg of DMDS only using the Mecca soil. These data were then fitted to the Freundlich equation to derive K_f and assess the non-linearity of the sorption isotherm across a concentration gradient.

2.5 Degradation experiments

Degradation of DMDS was studied over a 28 day period. Typically, after fumigant application, fields are covered with a tarp for 12–21

Table 2. Soil adsorption K_d and K_{oc} values of carbonated and non-carbonated DMDS in four California grape production soils

	K_d (L kg^{-1})		K_{oc}	
Soil	Non-carbonated	Carbonated	Non-carbonated	Carbonated
Paso Robles	1.01 ± 0.00	1.01 ± 0.03	33.76 ± 0.10	33.71 ± 1.15
Clarksburg	1.04 ± 0.00	1.16 ± 0.00	3.75 ± 0.01	4.16 ± 0.01
Mecca	1.04 ± 0.00	0.97 ± 0.02	27.99 ± 0.06	26.26 ± 0.45
Fowler	1.03 ± 0.00	0.97 ± 0.02	36.89 ± 0.09	34.71 ± 0.67

days. Our objective was to assess degradation over a period of time that was slightly longer than typical field fumigations to assess potential efficacy declines due to degradation and carbonation.

Samples of soil (10 g dry weight equivalent) in 20 mL headspace vials were crimp sealed. The soil samples were spiked with carbonated or non-carbonated DMDS at the maximum field application rate of 60 mg kg^{-1} soil (510 kg ha^{-1}). Immediately after spiking, each vial was sealed and shaken horizontally for 2 min. The soil samples were incubated at 10, 24 or 35 °C, and four replicates were collected from each treatment on days 0, 7, 21 and 28. Samples were stored at −80 °C but moved to −20 °C for 1 h prior to extraction. Upon removal from the freezer, vials were promptly decapped, and 10 mL of ethyl acetate and the desiccant anhydrous sodium sulfate were added to each vial. Sample vials were recapped and shaken for 2 h on a horizontal shaker. After settling, a 1.0 mL aliquot of the supernatant was withdrawn and transferred into a GC vial for analysis

The half-life of DMDS was determined by fitting the remaining concentration at different sampling intervals to the first-order decay model: $C_T = C_0\ e^{-kT}$, where C_T and C_0 are the fumigant amounts in soil at time T and 0 respectively, k is the first-order rate constant (day^{-1}) and T is the time, in days, after treatment.

2.6 Chemical analysis

Concentrations of DMDS were measured on an Agilent 6890 N GC with a 5973 mass spectrometer using selected ion monitoring (GC/MS-SIM). The GC was fitted with an Agilent DB-5 MS column (60 m × 0.25 mm × 0.25 µm). Two ions were used to quantify DMDS (94 *m/z*, parent and 74 *m/z*, qualifier). The injector temperature was 50 °C, while the detector was set at 250 °C. The column temperature ramp was as follows: initial temperature 50 °C, held for 0.5 min, increased to 100 °C at 25 °C min^{-1}, held for 3 min, before decreasing to 50 °C at 99 °C min^{-1} and holding for 2 min. The total run time was 8.01 min, and the DMDS retention time was 5.60 min. The concentrations expected during analysis based on experimental design fell comfortably within the 1 – 100 ppm range; therefore, these values were used as the upper and lower limits for instrument calibration with a standard curve. During method development DMDS retention times, peak shape (height and width) and linearity were highly consistent across the 1 – 100 ppm range. With this consistency and confirmation during method development, it was determined that a three-point standard curve was sufficient for the DMDS calibration curve.

2.7 Statistical analysis

All samples were prepared with four or more replicates. Significant differences between sorption (K_d and K_{oc}) treatments (within and across carbonated and non-carbonated) were tested with an ANOVA followed by a *post hoc* Tukey test. All statistical analysis was performed in R (v.3.0.2; The R Foundation, Vienna, Austria).

3 RESULTS AND DISCUSSION

3.1 Phase distribution

The sorption of DMDS to soil with or without carbonation was evaluated in four grape production soils from California. Three (Paso Robles, Mecca and Fowler) of the four soils had similar pH, total organic carbon (TOC) and moisture contents, while the Clarksburg soil had ∼8× higher TOC along with a lower pH and higher soil moisture content (Table 1). The K_d values of carbonated and non-carbonated DMDS for each soil are shown in Table 2. The Clarksburg soil had significantly higher K_d values ($P < 0.001$) than the other three soils in the absence of CO_2, while the Paso Robles soil had a significantly lower K_d value than those for the other three soils ($P < 0.001$). While there is a significant K_d difference between the four soils under non-carbonated conditions, it is small, and therefore it is difficult from these microcosm experiments to determine whether an effect would be observed in the field.

The K_f value (1.08) estimated from the sorption isotherm in the Mecca soil was similar to its K_d values. Their similarity is the result of the Freundlich non-linearity constant (n) being close to unity (0.98). As n is not 1, there may be a slight increase in soil adsorption (and K_d values) with increasing concentrations until saturation is reached.

The K_d values of other soil fumigants such as MeBr (0.04 – 0.10 L kg^{-1}), methyl isothiocyanate (0.045 L kg^{-1}), 1,3-D (0.40 – 0.60 L kg^{-1}) and chloropicrin (0.03 – 0.14 L kg^{-1}) in loamy soils are 1 – 2 orders of magnitude lower than those found for DMDS in this study.[12,20–22] This difference in sorption potential may partially be explained by the higher vapor pressures of the other fumigants (3.1 – 190 kPa at 20 °C), as compared with 2.9 kPa for DMDS.[12] The higher sorption potential of DMDS could be advantageous over other fumigants as it may lead to longer compound retention in the soil that could increase efficacy when effectively dispersed in the soil.

The lower volatility and higher sorption of DMDS relative to MeBr and other fumigants imply that DMDS may not efficiently disperse in soil, which is essential for the eradication of soilborne pathogens, especially for crops such as grapevines that have deep root zones. Previous research indicates that CO_2 could be used as a propellant to improve DMDS dispersion in soils.[14,15] To evaluate the potential effect of CO_2 on soil – water distribution, we measured K_d of carbonated DMDS. The average K_d for DMDS with CO_2 (1.03 ± 0.08 L kg^{-1}) was nearly identical to that found for DMDS without CO_2 (1.03 ± 0.01 L kg^{-1}). When individual soils were compared, some differences were observed. These differences, while significant, were relatively minor, and therefore from this microcosm study it is difficult accurately to predict broader effects at the field scale. For example, the K_d values for carbonated DMDS were significantly lower than those for non-carbonated treatments in Mecca and Fowler soils ($P < 0.001$) (Table 2). Carbonation decreased DMDS soil partitioning in these two soils, suggesting

Table 3. Half-life values of carbonated and non-carbonated dimethyl disulfide in four California grape production soils. Blanks represent treatments where quantifiable degradation was not observed

Temperature (°C)	k	$t_{1/2}$ (day^{-1})	r^2	k	$t_{1/2}$ (day^{-1})	r^2
	Paso Robles			Paso Robles (CO_2)		
10	–	–	–	–	–	–
24	–	–	–	–	–	–
35	0.0082 ± 0.0035	85	0.28	0.0092 ± 0.0018	75	0.65
	Clarksburg			Clarksburg (CO_2)		
10	–	–	–	–	–	–
24	–	–	–	–	–	–
35	0.0052 ± 0.0012	134	0.58	0.0058 ± 0.0011	119	0.67
	Mecca			Mecca (CO_2)		
10	–	–	–	–	–	–
24	0.0048 ± 0.0022	143	0.25	–	–	–
35	0.0192 ± 0.0037	36	0.67	0.0150 ± 0.0068	46	0.27
	Fowler			Fowler (CO_2)		
10	–	–	–	–	–	–
24	–	–	–	0.0262 ± 0.0070	26	0.50
35	0.0163 ± 0.0032	43	0.67	–	–	–

that CO_2 might improve soil dispersion. However, the opposite was observed in the Clarksburg soil, where carbonation was found to increase K_d significantly ($P < 0.001$). This difference may be attributed to the substantially higher organic matter content in the Clarksburg soil; however, the underlying mechanism for the enhanced sorption was not investigated in this study.

A similar trend was found with regard to the effects of CO_2 on sorption relative to soil carbon (K_{oc}) (Table 2). The Clarksburg soil had significantly higher ($P < 0.001$) sorption after carbonation, while both Mecca and Fowler soils exhibited significantly lower ($P < 0.001$) sorption in the presence of CO_2. After normalization to soil OC content, it is evident that K_{oc} values for Clarksburg soil were substantially smaller than the other soils. This finding suggested that sorption of DMDS was only partially dependent on soil OC content.

From the batch phase distribution experiments, the dimensionless Henry's law constant (K_h) was estimated to be 0.04 ± 0.005 for DMDS at room temperature. However, after carbonation, K_h increased to 0.10 ± 0.011. This value was calculated by dividing the headspace concentration by the dissolved concentration. Therefore, increasing K_h values indicate less DMDS dissolving in solution. This increase in K_h due to carbonation decreases DMDS aqueous partitioning and should result in improved dispersion and diffusion after subsurface injection, particularly in moist soils, ultimately leading to greater pest control efficacy. Future studies under field conditions are needed to validate the effect of carbonation on DMDS soil distribution under varying application scenarios.

3.2 Persistence of DMDS in soil

Many commercial grape field soils are fumigated and often covered with a plastic tarp or film for 12–21 days to control target pests. The 28 day laboratory degradation incubation experiment therefore lasted longer than field tarped fumigation treatments. Degradation of DMDS (carbonated or non-carbonated) was measured at three temperatures (10, 24 and 35 °C) in the four soils. Essentially, no detectable DMDS degradation was found in 15 of the 24 total treatments, and poor model fit (r^2 from 0.25 to 0.50) was observed for three of the nine half-life values that could be calculated (Table 3). The poor model fit was likely due to the very slow compound degradation, as initial and final concentrations did not drastically change. In addition, five of the nine estimated half-life values were twice as long as the maximum incubation period, while three exceeded 4 times the 28 day incubation duration, making these values rough estimates of DMDS persistence. No degradation of DMDS was observed in the 10 °C treatments; at 24 °C, only the Fowler soil with CO_2 and the Mecca soil without CO_2 had quantifiable half-lives (26 and 143 days respectively) (Table 3). Degradation of DMDS was observed in all of the 35 °C treatments, except for the Fowler soil with CO_2. The lack of observed degradation over the 28 day incubation prevented a thorough statistical evaluation of the CO_2 effects. However, from the available data there appeared to be no discernable differences between carbonated and non-carbonated treatments.

The half-life values of DMDS (26–143 days) in this study are much longer than those reported by Chellemi *et al.*,[19] who observed DMDS half-lives of 1–6 days in a Dothan sandy loam. However, Ajwa *et al.*[12] suggested that the half-life of DMDS in soil could be 2–3 times that of methyl isothiocyanate (1–13 days), which would be within the range of some half-life values observed in this study.[12] The stability of DMDS may explain its long nematode control efficacy (150 or 180 days) observed in a recent grape fumigation field study.[8] Nevertheless, based on calculated half-life values, very little degradation would occur during typical field fumigation periods (12–21 days). Therefore, DMDS efficacy should not decline owing to degradation during fumigation events, and its longer half-life and subsequent longer soil retention are advantages over other fumigants.

4 CONCLUSION

DMDS is a newly registered fumigant for controlling soilborne pathogens in several states. However, gaps exist in our basic

understanding of its behavior in soils. The results of this study demonstrate that, in addition to its relatively low volatility, DMDS has a higher sorption potential and longer environmental persistence than many current-use fumigants. Under field conditions, these factors may allow the soil to retain DMDS for longer periods of time, resulting in extended pesticide efficacy. However, its lower volatility may also result in localized control, which can inhibit the dispersion and diffusion of DMDS in soil. Thomas *et al.*[16] found that CO_2 addition greatly improved the dispersion of Telone C35 (a mixture of chloropicrin and 1,3-dichloropropene). Our study showed that, while carbonation had a significant but small effect on sorption to soil and a negligible effect on the degradation of DMDS, it greatly increased DMDS's Henry's law constant. The increased K_h should result in improved dispersion and distribution in subsurface treatments, especially in wet soils. Using the results of these laboratory studies, field studies must now seek to quantify the larger-scale effects of carbonating DMDS and its efficacy in relation to other current-use soil fumigants.

ACKNOWLEDGEMENT

Part of this study was funded with a grant award (2011-51102-31185) provided by the USDA National Institute of Food and Agriculture through its Methyl Bromide Alternatives Transition Program.

REFERENCES

1 Johnson JA, Walse SS and Gerik JS, Status of alternatives for methyl bromide in the United States. *Outlooks Pest Manag* **23**(2):53–58 (2012).
2 *Critical Use Exemption Nominations from the Phaseout of Methyl Bromide.* [Online]. USEPA (2014). Available: http://www.epa.gov/ozone/mbr/2014_nomination.html [10 December 2013].
3 Cabrera JA, Wang D, Schneider SM and Hanson BD, Subsurface drip application of alternative fumigants to methyl bromide for controlling nematodes in replanted grapevines. *Pest Manag Sci* **68**(5):773–780 (2012).
4 Cabrera JA, Wang D, Schneider SM and Hanson BD, Effect of methyl bromide alternatives on plant parasitic nematodes and grape yield under vineyard replant conditions. *Am J Enol Vitic* **62**(1):42–48 (2011).
5 Hanson BD, Gao SD, Gerik J, Qin RJ, Cabrera JA, Jhala AJ *et al.*, Preplant 1,3-D treatments test well for perennial crop nurseries, but challenges remain. *Calif Agric* **67**(3):181–189 (2013).
6 Gillis M, DMDS 2003 field trials in California, in *Annu Int Res Conf – Methyl Bromide Alternatives and Emissions Reductions*. Methyl Bromide Alternatives Outreach, San Diego, CA (2003).
7 Cabrera JA, Wang D, Gerik JS and Gan J, Spot drip application of dimethyl disulfide as a post-plant treatment for the control of plant parasitic nematodes and soilborne pathogens in grape production. *Pest Manag Sci* **70**(7):1151–1157 (2014).
8 Cabrera JA, Gan J, Hanson BD and Wang D, Factors affecting the nematicidal activity of dimethyl disulfide, in *Annu Int Res Conf – Methyl Bromide Alternatives and Emissions Reductions*. Methyl Bromide Alternatives Outreach, Orlando, FL (2010).
9 Auger J and Charles P, Biogenic emission, biological origin, and mode of action of DMDS, a natural ubiquitous fumigant, in *Annu Int Res Conf – Methyl Bromide Alternatives and Emissions Reductions.* Methyl Bromide Alternatives Outreach, San Diego, CA (2003).
10 *Label Search: Paladin.* [Online]. Agrian. Available: http://www.agrian.com/home/label-lookup/overview [7 October 2014].
11 Segawa R, California regulatory update for fumigants, in *Annu Int Res Conf – Methyl Bromide Alternatives and Emissions Reductions*. Methyl Bromide Alternatives Outreach, Orlando, FL (2010).
12 Ajwa H, Ntow WJ, Qin R and Gao S, Properties of soil fumigants and their fate in the environment, in *Hayes' Handbook of Pesticide Toxicology*, ed. by Krieger R. Academic Press, San Diego, CA, Ch. 9, 15 pp. (2010).
13 Wauchope RD, Buttler TM, Hornsby AG, Augustijn-Beckers PW and Burt JP, The SCS/ARS/CES pesticide properties database for environmental decision-making. *Rev Environ Contam Toxicol* **123**:1–155 (1992).
14 Park JY, Lee MK, Uddin MS and Chun BS, Removal of off-flavors and isolation of fatty acids from boiled anchovies using supercritical carbon dioxide. *Biotechnol Bioprocess Eng* **13**(3):298–303 (2008).
15 Roh HS, Park JY, Park SY and Chun BS, Isolation of off-flavors and odors from tuna fish oil using supercritical carbon dioxide. *Biotechnol Bioprocess Eng* **11**(6):496–502 (2006).
16 Thomas JE, Ou LT, Allen LH, Jr, Vu JC and Dickson DW, Improved soil fumigation by Telone C35 using carbonation. *J Environ Sci Hlth B* **46**(8):655–661 (2011).
17 Laboratory USS, pH reading of saturated soil paste, in *Diagnosis and Improvement of Saline and Alkali Soils, USDA Agricultural Handbook 60*, ed. by Richards LA. Agriculture USDo, US Government Printing Office, Washington, DC, 102 pp. (1954).
18 Nelson DW and Sommers LE, Total carbon, organic carbon and organic matter, in *Methods of Soil Analysis, Part 3, Chemical Methods – SSSA Book Series No. 5*, ed. by Bigham JM. Soil Science Society of America and Agronomy Society of America, Madison, WI, pp. 1001–1006 (1996).
19 Chellemi DO, Ajwa HA, Sullivan DA, Alessandro R, Gilreath JP and Yates SR, Soil fate of agricultural fumigants in raised-bed, plasticulture systems in the southeastern United States. *J Environ Qual* **40**(4):1204–1214 (2011).
20 Kim JH, Papiernik SK, Farmer WJ, Gan J and Yates SR, Effect of formulation on the behavior of 1,3-dichloropropene in soil. *J Environ Qual* **32**(6):2223–2229 (2003).
21 Gan JY, Yates SR, Wang D and Spencer WF, Effect of soil factors on methyl bromide volatilization after soil application. *Environ Sci Technol* **30**(5):1629–1636 (1996).
22 Gerstl Z, Mingelgrin U and Yaron B, Behavior of Vapam and methylisothiocyanate in Soils. *Soil Sci Soc Am J* **41**(3):545 (1977).

