Bull. Environ. Contam. Toxicol. (1985) 34:824–831

Bulletin of Environmental Contamination and Toxicology

Dissipation of 1,2-dibromo-3-chloropropane (DBCP), *cis*-1,3-dichloropropene (1,3-DCP), and Dichloropropenes from Soil to Atmosphere

William N. Albrecht[1] and Karen Chenchin[2]

[1]Pesticide Hazard Assessment Project, University of Hawaii, Honolulu, HI 96822 and [2]Maui Pineapple Company, Kahului, Maui, HI 96732

Subsoil fumigation is the customary procedure for achieving control against most species of nematodes that may infest root portions of crops. Specifically, Hawaiian pineapple culture has relied upon DBCP, 1,3-DCP (TELONE II), ethylene dibromide (EDB), and a mixture of dichloropropanes and dichloropropenes (D-D) to prevent infestations of the root-knot nematode. Preplant fumigation at prescribed rates effectively depletes populations of nematodes until a time when root systems are established enough to withstand the pest.

Fumigants are by necessity, volatile materials. They quickly disperse from the liquid to the vapor phase. In this manner, large, three-dimensional areas of subsoil can be fumigated from applications along a rather narrow path. The fumigant disperses throughout its effective radius in the soil matrix; its movement influenced by soil type, moisture content, temperature, and organic content of the soil. Ultimately, the material is either bound or degraded in the soil, translocated via soil water, or vented to the atmosphere. Little published information is available on the atmospheric dispersal, atmospheric chemistry, and ultimate dry or wet disposition of fumigants from the atmosphere into the ecosystem (Munnecke and Van Gundy 1979).

Occupational exposures to workers who perform the fumigation are determined by the rate and depth of application, their proximity to the fumigation machinery, and the length of time spent in the field. Background levels of fumigant can be measured in the air above the field for some time after the initial application. Until equilibrium is established, fumigant will move from soil to atmosphere at a rate proportional to the aforementioned factors which determine its behavior. In an effort to measure airborne background levels, and to determine the relative rate and duration of the upward flux, an air sampling experiment was performed.

MATERIALS AND METHODS.

Maui Pineapple Company Field 274 was chosen for the experiment. With a machine specially designed for simultaneous fumigant application and pineapple crown planting, DBCP was applied at 12 inches (0.30 m) depth at a rate of 4 gallons per acre (31.2 liters per hectare). 1,3-DCP was applied at a rate of 35 gal/a (293 l/ha) at a depth of 18" (0.45 m). Telone II is a Dow Chemical Company registered trademark for a (Z) or *cis*- and (E) or *trans*- mixture of 1,3-dichloropropene. Usual commercial formulations contain 92% active agent with 3 to 5% 1,2-dichloropropane. Telone II has a vapor pressure of 21 mm Hg @ 20°C a boiling point of 104°C, and is soluble in water at 20°C to 1000 ppm (Martin and Worthington 1974). DBCP (17.1 lbs/gal; 2 kg/l) has been used as a soil fumigant since 1955. In 1979, most of its agricultural uses were cancelled by EPA. It is still used on Maui in limited amounts, and will be phased out when existing stocks are depleted. It has a vapor pressure of 0.8 mm Hg @ 20°C, boils at 196°C, and is soluble in water at approximately 0.1 %.

Each row of pineapple is covered at the time of planting with a 25 micron thick, black polyethylene film which acts as a vapor barrier. Over a section of one newly fumigated row was placed a commercial, white, cylindrical, plastic wastebasket (10 gal/ 38 l capacity). A thermometer and sampling port were inserted through the side of the container. The edges of the container were covered with soil, and air samples were taken inside of it at the same time that air samples were taken at ground level and at 42" (1.05 m) above the ground. The intent of the container was to negate or to minimize the effects of wind or rain on the collection of the air samples, and to provide a means of obtaining 'concentrated' samples when and if ambient levels fell below the limits of detection. Two air samples were taken at 42" and one each inside the container and at ground level for 10 days after fumigation, and then at 20, 22, 27, and 30 days after fumigation.

Soil moisture, air temperature, temperature inside the container, and soil temperature at 18" depth were measured on each day of sampling. In addition, daily weather data, including relative humidity, wind speed and direction, rainfall, and barometric pressure were recorded.

Air samples were collected on SKC Lot 107 100/50 charcoal tubes. Battery operated Dupont Model P4000 pumps pulled air through the tubes at a rate of 95 cc/min. The samples were desorbed the same or next day with 2 ml benzene (desorption efficiency 65%) and analyzed by gas chromatography using a Hewlett-Packard Model 5840 equipped with 63Ni electron capture detector. The GC column was 1.8 m X 4 mm i.d. glass packed with Supelco GP 4% SE-30 and 6% SP-2401 on 100/120 mesh Supelcoport and operated at 120°C. Values were corrected for desorption efficency and reported as micrograms of material per tube. The *cis*-isomer of the Telone II mixture was measured, as was the remainder of the mixture (mixed isomers) which is reported as dichloropropenes. The limits of detection per injection for the fumigants were: DBCP, 5 picograms (pg); *cis*-DCP, 25 pg; dichloropropenes, 100 pg.

RESULTS AND DISCUSSION.

Measurements of fumigants are quantitative at ground level and at 42". Concentrations as measured inside the container are only useful as an indication of fumigant behavior irrespective of wind and rain. Figure 1 shows the change in concentration of the fumigants over time as measured at ground level. Figures 2 and 3 likewise show the concentration changes over time as measured inside the container and at a height of 42" above ground. Figure 4 is a composite plot of *cis*-1,3-DCP and dichloropropenes for ground level versus container concentrations.

Soil temperature at 18" remained fairly constant over the duration of the experiment in the range of 78-79°F (25.6-26.1°C). Soil moisture at 12" was variable in the range of 20.8-35.7% (n=15; x=28.8; sd=4.36). At 18", the moisture content was slightly higher than at 12", over the range of 25.5-38.8% (n=15; x=30.4; sd=4.55). Air temperature during the experiment was at its daily maximum at noon (range: 80-86°F; 26.7-30.0°C). Inside the container, temperatures varied from 80-90°F (26.7-32.2°C), but in general were at or around 85°F (29.4°C). Trade winds from the northeast were prominent in the range of 5-15 miles per hour (2.3-6.9 m/sec). Relative humidity ranged from 46 to

FUMIGANT CONCENTRATIONS AT GROUND LEVEL

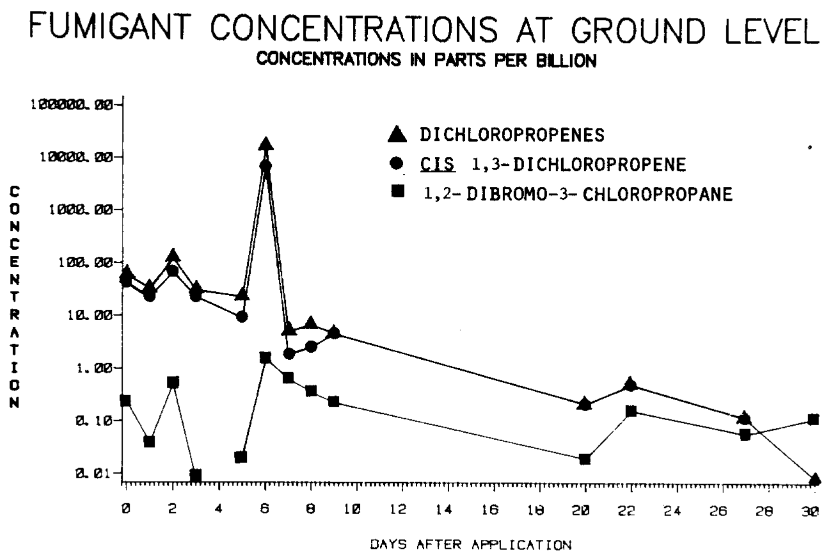

FIGURE 1

FUMIGANT CONCENTRATIONS IN WASTEBASKET

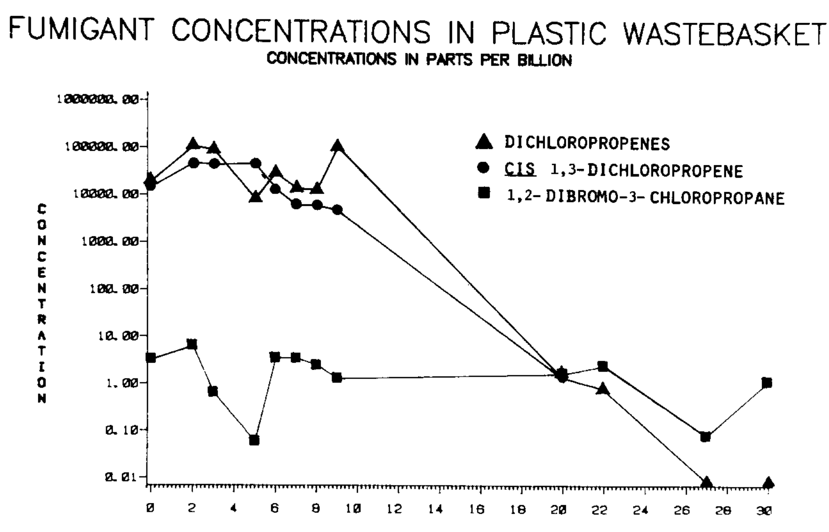

FIGURE 2

70%. Light rains (less than 7mm/24 hr) were recorded on tw occasions.

Fumigant concentrations in ambient air at ground level showed a preliminary peak at two days after fumigation. DBCP then declined to zero measurable at three days. The behavior of DBCP was similar as measured inside the confines of the container. Although levels were still detectible, they too, fell continuously after the day 2 peak until day 5. Over the evening of day 5-6, 6mm of rainfall was recorded which coincided with a large spike of fumigant release as measured on day 6. This release was sustained over the next four days, and measurable levels of DBCP were found at ground level for the remainder of the experiment.

Inside the container, DBCP declined after day 2 until day 5. Levels fluctuated slightly over the 16 days, and vacillated at the same level for 24 days after day 6. As measured at 42", DBCP behavior was similar, with a gradual decline from day 6 to day 30, albeit at very low levels.

At ground level, *cis*-1,3-DCP and dichloropropenes were observed to maintain a steady concentration until day 6 when rainfall was recorded and values rose to 100 times the previously recorded concentration. No such increase was measured in the container. Container concentrations remained steady at least until day 9. Inside the container, the analytical distinction between *cis*-1,3-DCP and dichloropropenes was not evident as measured on day 20; all of the material measured being the *cis*- isomer. After day 22, concentrations fell to none detected.

Similarly, at ground level, day 9 was the last day that the distinction bewteen isomers was possible, while levels fell to none detected at day 30 for all 1,3-DCP's. At 42", levels were measurable for the duration of the experiment which may reflect fumigant migration from other areas of the same field or other fields.

Fumigant behavior as observed in the flux from soil to atmosphere encompasses a multitude of variables, many of which are difficult to control in a field experiment. The primary variability lies within the make-up of the soil being fumigated and its moisture and organic matter content, and the temperature of the soil. Secondarily, the physical and chemical

FUMIGANT CONCENTRATIONS AT 42 INCHES

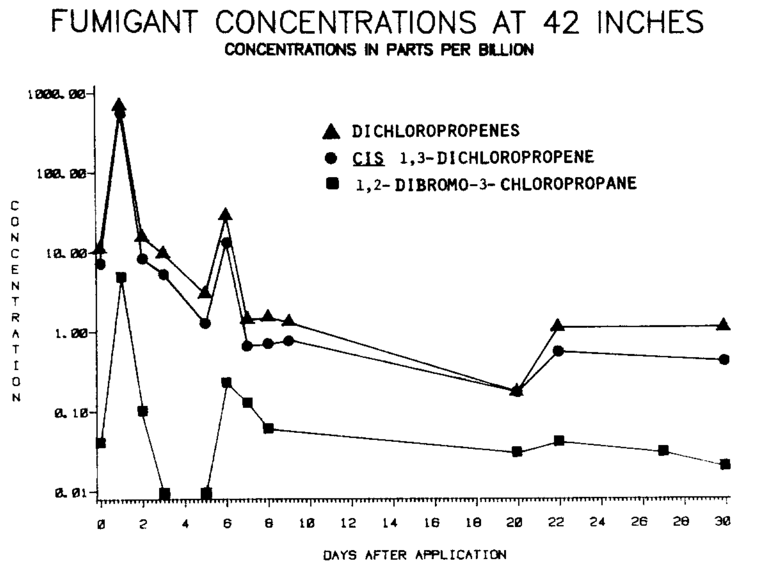

FIGURE 3

FUMIGANT BEHAVIOR - WASTEBASKET VS AMBIENT

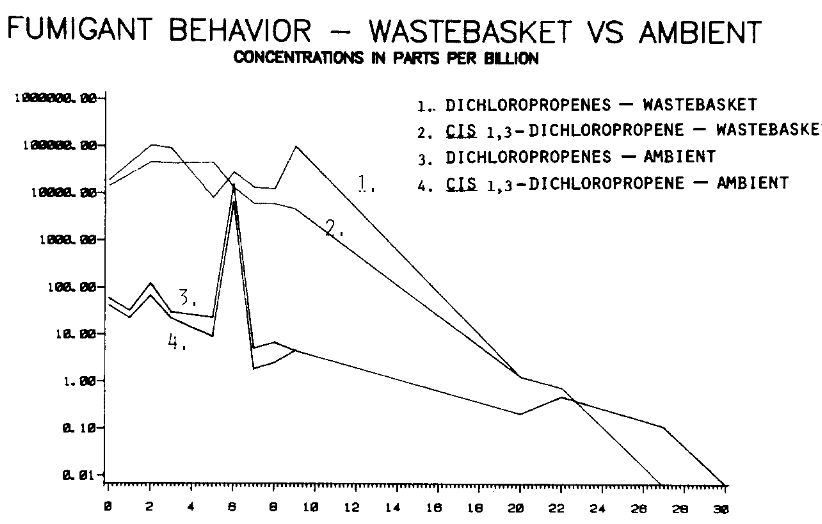

FIGURE 4

properties of the fumigants will determine their behavior within the soil matrix, while at the soil/air interface, weather conditions play the most important role. Fortunately, Hawaiian weather in mid-July does not vary a great deal.

It is of interest that *cis*-DCP and dichloropropenes were detected in the air at levels 10-100 times greater than DBCP. The application rate for 1,3-DCP is 10 times that for DBCP on a molar basis (DBCP; 4 gal/a; 17.1 lbs/gal; sp.g. 2.08; mw 236.4; 131.5 moles/a | 1,3-DCP; 35 gal/a; 92%; sp.g. 1.2; mw 112; 1329 moles/a). This was observed even though the application depth of 1,3-DCP is 1.5 times that of DBCP.

Faster movement of DCP toward atmospheric equilibrium can partially be explained by the forty-fold difference in vapor pressure between DCP and DBCP (21.0 vs. 0.58 @ 20°C) and a water /air distribution ratio of 20.2 vs 163.8 (Munnecke and Van Gundy 1979). DBCP's vapor pressure and water/air distribution ratio mean that movement in water films is more important than movement in the vapor phase. It is also many times more soluble in water than DCP and this also retards its movement toward the air/soil interface. One estimate of the total retention of a subsoil application of 1,3-DCP into a warm, moist, silty loam soil is 90-95% (Thomason and McKenry 1974).

The light rain recorded on day 5-6 is thought to have generated the secondary spike in fumigant release by a two-phase transfer of material, similar to the co-distillation of azeotropes. The first phase would be from soil to water on or near the surface of the soil, and then from soil to air by evaporation (volatilization). The rain effected both fumigants in a similar manner.

Saltzman and Kliger (1979) found that forty hours after DBCP application, the concentration in all soils measured had dropped by 53 to 100%. They attribute the losses entirely to volatilization, since in a parallel study, DBCP was totally recovered from samples stored in stoppered vessels over a forty hour period.

This loss from soil due to volatility is reflected in the none detected measurements of DBCP at 42" and at ground level. The ability to measure DBCP at low concentrations inside the container may be due to the 'stoppering effect' of slow dispersal out of the container.

The addition of water after a DBCP treatment was observed by the aforementioned authors in the same paper to displace DBCP from its binding sites on the soil and increase loss by 10% from sandy soils (42% in high clay soils). The long-term dispersal behavior of the fumigants may be conjectured as shown by air samples taken to determine the personal exposures of hand planters which enter fumigated pineapple fields up to 6 to 8 weeks after fumigation. All hand planters measured (n=15) had zero detectible exposures to DBCP (<100 ppt) over the duration of their 8 hr shift, but 8/15 did have measurable 1,3-DCP exposures (range 2.4-18.5 ppb) (Albrecht 1983). This would indicate that dichloropropenes can be mobilized by environmental conditions even after airborne levels have initially declined to zero.

Acknowledgments. The authors would like to acknowledge the valuable assistance of Mr. Jon Oshiro, Mrs. Ethel Abreu, and Mr. E.B. Siwak.

REFERENCES.

Albrecht WN, Coye MJ (1983) Health Hazard Evaluation HETA 81-236. National Institute for Occupational Safety and Health, Cincinnati, Ohio

Martin H, Worthington CR (eds) (1974) Pesticide Manual, 4th edn. British Crop Protection Council, London

Munnecke DE, Van Gundy SD (1979) Movement of fumigants in soil, dosage responses, and differential effects. Ann Rev Phytopathol 17:405-429

Saltzman S, Kliger L (1979) Volatilization of 1,2-dibromo-3-chloropropane (DBCP) from soils. J Environ Sci Health 14: 353-366

Thomason IJ, McKenry MV (1974) Movement and fate (of 1,3-dichloropropene and 1,2-dibromoethane) as affected by various conditions in several soils. Part I. Hallgardia 42: 393-420

Received June 4, 1984; Accepted July 10, 1984