EMISSION LOSSES OF CHLOROPICRIN AND 1,3-DICHLOROPROPENE FROM SOIL FUMIGATION

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Methyl Bromide (CH_3Br) is a major fumigant used in Japan to control soil-borne diseases in crops such as cucumbers, gingers, tomatoes, melons, green peppers, etc. The use of CH_3Br as a soil fumigant is to be phased out by 2005, but no new chemical or non-chemical alternative has yet emerged as its substitute. For now, 1,3-dichloropropene, chloropicrin, dazomet, *etc*. are seen as the best alternatives to CH_3Br. It is already difficult to satisfy demand for CH_3Br as a soil fumigant adequately, whereas there are not remarkable changes in the amount of 1,3-dichloropropene, chloropicrin and dazomet that have been used in major CH_3Br use areas. Under the Protocol, from 1 January 2001 a 50% cut in production and consumption of CH_3Br, based on 1991 levels, was done in Japan. Therefore, it is predicted that the consumption of these chemical alternatives will increase more.

Our monitoring results of fumigants in the atmosphere during several months in horticultural areas showed that even under the current situation, fumigants such as 1,3-dichloropropene, chloropicrin, methyl isothiocyanate (MITC) and CH_3Br of high concentration (over several hundred $\mu g/m^3$) were detected frequently, but these high concentrations were temporary, and most air samples contained several $\mu g/m^3$ of fumigants. Restrictions on CH_3Br usage required an intensive search for improved technologies to reduce both dosage and emission of alternative chemicals from fumigated plots into the atmosphere, while maintaining its effectiveness for disease and weed control and providing adequate safety for people who live and work in areas where soil fumigations occur to multiple fields. The purpose of this study was to quantify the volatilization dynamics and emission loss rates of 1,3-dichloropropene and chloroicrin under Japanese horticultural conditions. The experiment was conducted in the field to allow various environmental conditions.

Emission losses of chlorpicrin and 1,3-dichloropropene were evaluated in field experiments from 26 Sep. to 16 Oct. in 2001 on Hydric Hapludand soils at the National Institute for Agro-Environmental Sciences, Tsukuba, Japan. "Manual injection method" was used for applying Dorochlor (80% chlorpicrin, 82.0 g/m^2) and D-D (92 % 1,3-dichloropropene, 38.2 g/m^2) into soil depth of ca. 17cm. Treated areas were 30 m^2 (5 m x 6 m), which were immediately covered with conventional polyethylene films (0.05mm thickness), then removed after 13 days (9 Oct.). An automated gas chromatography system, equipped with flame ionization detectors (GC-FID) and four 7.5 L chambers (diam. 24.5 cm) was used

to determine emission flux. The chambers were placed directly on the film or soil surface. In addition, air samples for these chemicals were collected using 4 STS-25 air samplers (Perkin Elmer) and multi-bed absorbent tubes packed with graphite carbon black (100 m^2/g, 60/80 mesh, 190 mg) and carbon molecular sieve (1200 m^2/g, 60/80 mesh, 100 mg). These air samples were analyzed by ATD-GC-MS (automatic thermal desorption system-gas chromatography-mass spectrometry). Concentrations of chloropicrin, cis- and trans-1,3-dichloropopene in the air below the film and at soil depths of 30, 60, 90, 120, 150 cm were measured.

The maximum emission flux reached, respectively, about 353 mg/m^2/hr and 160 mg/m^2/hr for chloropicrin and 1,3-dichloropropene with polyethylene films (Figure 1). This maximum was reached at next day after injection and the emission rate decreased slowly. The emission flux follows a diurnal pattern with large fluxes near solar noon when the temperature was high and low emission was near midnight with low temperatures. The emission rates were dependent on solar radiation, temperature and chemicals' concentration below the film. For these chemicals, however, the drastic diurnal flux patterns as CH_3Br were not observed. Our experiments also showed that emission losses reached, respectively, about 24.6 % and 16.6 % of the applied amounts for chloropicrin and 1,3-dichloropropene. These results will significantly reduce their potential environmental risk and may promote the long-term use as a chemical alternative to CH_3Br without suffering from loss to additional chemicals.

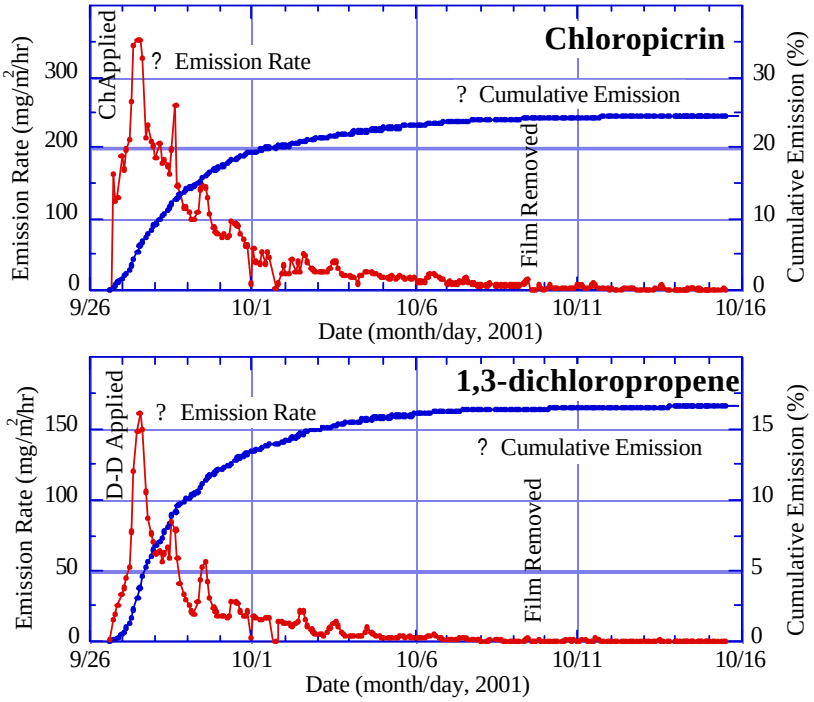

Figure 1. Chloropicrin and 1,3-dichloropropene emissions to the atmosphere. Data points are means of each two measurements. Soil was covered with a polyethylene film (0.05 mm thickness) for 13 days and removed.
1,3-dichloropropene = **cis**-1,3-dichloropropene + **trans**-1,3-dichloropropene