ESTIMATION OF SOME TECHNIQUES OF REDUCING METHYL BROMIDE EMISSION FROM SOIL FUMIGATION UNDER THE JAPANESE HORTICULTURAL CONDITIONS

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Introduction

Methyl bromide (CH_3Br) is a major fumigant used in the worldwide to control soil-borne diseases in many crops such as cucumbers, gingers, tomatoes, melons, green peppers, etc. About 75 % of industrially produced CH_3Br is used for this purpose. Following the Montreal Protocol, in which CH_3Br was included as one of the stratospheric ozone depleting substances, 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[1-3]. For now, 1,3-dichloropropene and chloropicrin are seen as the best alternatives to CH_3Br for preplant fumigation, and their sales are increasing steadily. They are considered risky and unsuitable as long-term replacements. It is already difficult to adequately satisfy demand for CH_3Br as a soil fumigant, as only some critical use exemptions and emergency use are permitted now.

Such restrictions have led to an intensive search for improved technologies to reduce both dosage and emission from fumigated plots into the atmosphere, while maintaining its effectiveness for disease and weed control. Various kinds of improved field management practices in combination with machinery injections have been shown to limit CH_3Br emission in several countries. However, such machinery injection techniques are not entirely suitable in Japanese conditions. In Japan, field sizes are generally small to apply machinery injection methods, and farmers themselves usually apply CH_3Br without depending on special applicators. Soil surface applications such as cold or hot gas methods are currently in vogue. Further, the standard dose of CH_3Br in Japan varies from 15 to 30 g m^{-2}, which is near threshold level, and it is difficult to reduce the dosage dramatically.

The purpose of this study is to develop and evaluate some new soil fumigation techniques suitable for Japanese horticultural conditions, including the shielding solar radiation with non-woven high-density polyethylene fiber sheet (Tyvek, DuPont), the use of a Very Impermeable Film (VIF, Orgalloy film, elf atochem) for CH_3Br, and the new multilayer sheet which consisted of an impermeable layer, a titanium dioxide (TiO_2) photocatalyst layer, and a support layer, from the upper to lower layer.

Methods and Materials

Direct measurements of CH_3Br emission flux under field conditions were carried out on Hydric Hapludand soils at the National Institute of Agro-Environmental Sciences, Tsukuba, Japan. "Cold gas method" was used for fumigation by releasing CH_3Br (32.8 g m^{-2}) from cans onto the soil surface (15 m^2) under a film, which was removed after 7 d. 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, sheets or soil surface. Concentrations of CH_3Br in the air below the film and at soil depths of 30, 60, 90, 120, 150 cm were measured. Two detectors were used for measuring gas concentrations: the Brüel & Kjær 1301 FT-IR-photoacoustic spectrometer for CH_3Br, CO_2, and water vapor, and the gas chromatograph for CH_3Br.
The shielding solar radiation and the use of VIF techniques were evaluated in field experiments from 2 to 12 September in 1996 (Trial 1) and from 10 March to 2 April in 1997 (Trial 2). Further, reducing CH_3Br emissions with a sheet containing TiO_2 photoctalyst was evaluated from 5 to 30 May (Trial 3), from 26 August to 20 September (Trial 4), 16 November to 5 December in 1998 (Trial 5), and 4 to 20 August in 1999 (Trial 6).
The impermeable layer to CH_3Br was selected by measuring the transmittance of the ultraviolet light (400 nm or less). TiO_2 photocatalyst (ST-01, Ishihara Sangyo Kaisha, Ltd.) was spread ca. 3 g/m^2 on the non-woven high-density polyethylene fiber sheet (Tyvek), then heat-sealed with a barrier film. This sheet was set up in the center of the separable chamber (10 cm in the effective irradiation diameter, the upper and lower chamber volume ca. 400 ml and ca. 280 ml, respectively) and then distilled water (1 ml) and CH_3Br gas (2.5 ml) were introduced to the lower chamber. Irradiations were performed with a 500-W Xe arc lamp (Wacom) approximated to the AM1.5 G at room temperature.

Results and Discussion

In previous study, direct measurements under field conditions showed that the rate of CH_3Br emission flux was strongly dependent on solar radiation, temperature and CH_3Br concentration below the film. The results indicated that fumigation on cloudy days or around sunset is a simple but effective method in minimizing CH_3Br emission into the atmosphere. Further shielding of solar radiation can be more effective. To reduce emission flux into the atmosphere further by restraining the increase in temperature during application, we improved the method of application by using conventional polyethylene (PE) and polyvinyl chloride (PVC) films in combination with a non-woven high density polyethylene fiber sheet (Tyvek). Tyvek, when used a cover sheet, is considered to shield solar radiation by diffuse reflection.
Temperature below the film without Tyvek sheet varied widely in a day reflecting changes in intensity of solar radiation. Temperature was, however, nearly equal to ambient temperature when Tyvek sheet was used. The results suggest that the use of Tyvek sheet considerably reduced emission losses by 35 to 40% during application, and by 14 to 23% on the whole as compared with control (without Tyvek). This technique was more effective in cool (Trial 2) than in hot season (Trial 1), further, had larger values of C x T product (Concentration x Time). The Tyvek sheet can easily be obtained as agricultural materials and used repeatedly. The problem of waste processing is smaller, because VIFs containing chlorine such as polyvinylidene chloride (PVDC) are especially difficult to be destroyed by fire. Moreover, VIFs are generally more expensive than conventional films such as PE and PVC.
EVOH (60 μm: LDPE/ethylene-vinyl alcohol copolymer/LDPE) and fluorinated polymer films (50 μm) are excellent with respect to a barrier film and UV-transmittance, however, EVOH was selected because of facility in heat-sealing. CH_3Br concentration at the beginning of examination was about 6000 ppm, 48 hours after the irradiation, it decreased to several ppm (Fig. 1). Some degradation products of CH_3Br were identified as carbon dioxide and hydrogen bromide. The decrease in CH_3Br decomposition ability was observed during repeated use up to 5 times, because of detachment of TiO_2 particles. It was possible to prevent these detachment by mixing with 10 % PTFE fine particles.

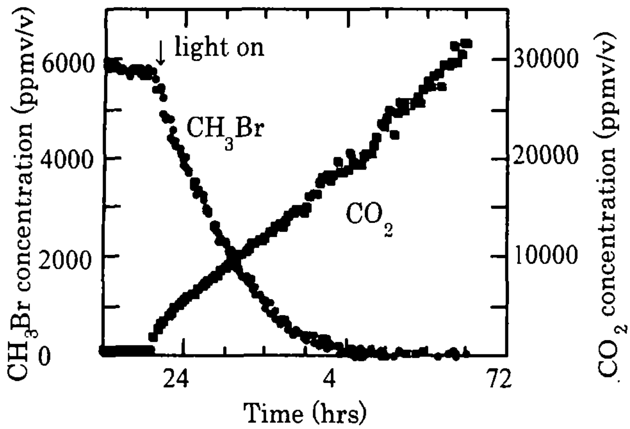

Fig. 1. CH_3Br conversion into CO_2 by photooxidation

CH_3Br concentration at the beginning of the experiment was over 15,000 ppm in the field experiment. Although decomposition and removal rates of CH_3Br are slow and dependent on solar radiation, CH_3Br concentration below the sheet declined rapidly during the period of covering in the field (7 or 9 d). Although the solar radiation and ambient temperature varied widely in each experiment, just before the removal of the sheet, CH_3Br concentration between the sheet and soil surface decreased to a few ppm with the multi-layer sheet in all experiments, as against over 1,000 ppm with a gas-tight film. As HBr generated was neutralized immediately by the soil in field conditions, most CH_3Br recovered in the field at the end of the experiment was near the soil surface and the sheet. Our experiments also showed that CH_3Br emission was reduced to less than some % of the applied amount by using the sheet containing TiO_2. Moreover, CH_3Br concentrations below the multi-layer sheet and gas-tight film were largely similar until the middle of fumigation period. This indicates that under field conditions, the use of multi-layer sheet may not greatly reduce the efficacy of CH_3Br fumigation.

These new techniques of CH_3Br soil fumigation can be applied easily without any major modifications in current practice of soil surface application. We, therefore, believe that these techniques are useful for reducing CH_3Br emissions substantially and holds promise for commercial use. Simultaneously, however, we must study ways to improve methods of application of various chemical alternatives to CH_3Br.

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