A-2.2.2 Study on Evaluation of Methyl Bromide Emission to the Atmosphere in Soil Fumigation in Japan

Contact person Yasuo Ishii
Section Director
Section of Pesticide Environmental Assessment, Division of Pesticide,
Department of Farm Chemicals
National Institute of Agro-Environmental Sciences
Ministry of Agriculture, Forestry and Fisheries
Kan-nondai 3-1-1, Tsukuba, Ibaragi, 305 Japan
Tel:+81-298-38-8330 Fax:+81-298-38-8199
E-mail:ishiiy@niaes.affrc.go.jp

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1. Introduction

Of late, there is a growing concern over CH_3Br role in depletion of stratospheric ozone, especially because the potential for ozone destruction per Br atom may be 30-60 times that for a Cl atom. CH_3Br is not entirely anthropogenic in origin as many sources of CH_3Br exist. However, there is substantial uncertainty in quantitatively defining these sources. About 70 % of industrially produced CH_3Br (68 Gg yr^{-1}) is used as an agricultural fumigant against soil parasites of plants due to its wide spectrum of action. During fumigation, a part of CH_3Br is degraded in the soil but some amount is emitted into the atmosphere. Currently, 28 Gg yr^{-1} (range: 14.4 to 40.7) CH_3Br is believed to be emitted during fumigation, constituting a significant proportion of the total global emissions of 122 Ggyr^{-1} (range: 48 - 228). Based on mainly indirect measurements in controlled environments, several authors reported that amount of emissions varied with soil type, humidity, pH, organic matter content and method of application. Direct measurements on emissions from fumigated fields are limited however.

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 single chemical or non-chemical alternative has yet emerged as its substitute. 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. However, as their impact on the environment and human health is not well understood, they are considered risky and unsuitable as long-term replacements. It is difficult to adequately satisfy demand for CH_3Br as a soil fumigant, as only some critical use exemptions and emergency use are permitted now.

Restrictions on CH_3Br usage 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. Improved field management practices such as the use of gas-tight films, shallow injection in combination with irrigation, deep injection (ca. 60cm depth), and application of ammonium thiosulfate or a soil bacterium, etc. have been shown to limit CH_3Br emission in several countries. The machinery injection methods can reduce the amount of CH_3Br application and its emission during exposure period. However, such injection techniques are not entirely suitable in Japanese conditions, as fields are generally too small to employ those methods. Besides agricultural fields and residential areas coexist, 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.

2. Research Objective

The aim of this work is to examine factors determining CH_3Br emission from soil fumigation under field conditions, assess if current estimates of agricultural contribution are realistic, and estimate the extent of possible reduction in global CH_3Br concentration in the atmosphere by the phase-out of CH_3Br as a soil fumigant. We tried to test various methods for reducing dosage and emission while maintaining its effectiveness.

3. Experimental Methods

A field experiment was conducted on Hydric Hapludand soils at the National Institute of Agro-Environmental Sciences, Tsukuba, Japan. "Cold gas method" of fumigation was followed by releasing CH_3Br (32.8 g m^{-2}) from cans onto the soil surface (15m^2) under a 0.05-mm thick polyethylene or polyvinylchloride film, which was removed after 7 d. An automated gas chromatography system equipped with flame ionization detectors (GC-FID) and four 7.5L chambers (diam. 24.5 cm) was used to determine emission flux. The chambers were placed directly on the film or soil surface. Losses due to adsorption on surface of chambers were ca. 2.2%. Concentrations of CH_3Br in the air below the film and at soil depths of 30, 60, 90, 120 and 150 cm were measured.

4. Results and Discussion

The dynamics of CH_3Br flux and cumulative emission from the field are shown in Fig. 1. Emission flux was very high at the beginning (due to high CH_3Br concentrations below the film) and decreased with time for approximately 7 d after fumigation. However, It varied by as much as 13 times on a clear day during the first 7 d. The rate of CH_3Br emission was strongly dependent on solar radiation, temperature and CH_3Br concentration below the film. Maximum emission occurred when solar radiation was intense and temperatures below the film were high. Emission was minimum during early morning when temperature was low. A momentary increase in emission rate was observed soon after removing the film, because of a sudden release of CH_3Br retained under the film and in the soil. Emission rate decreased exponentially with time. Covering the soil with film substantially reduced the amount of CH_3Br emitted, and the rate of emission was negligible after 14 d.

About 32% of applied CH_3Br escaped into the atmosphere by 11 d in trial 1, as against nearly 44% by 15 d in trial 2. Such a wide variation in emission was mainly due to the variation in CH_3Br loss on the first day because about 4.4 and 16% of applied CH_3Br was lost in trials 1 and 2 respectively. The variation in loss on the first day of fumigation may be related to differences in temperature below the film which, in turn, are dependent on intensity of solar radiation. In trial 2, solar radiation exceeded 2.6 MJ m^{-2} hr^{-1} while temperature reached 56 °C on the first day as against 1.5 MJ m^{-2} hr^{-1} and 39 °C respectively in trial 1. Because of a higher emission loss, soil CH_3Br concentration in trial 2 was, on an average, less than half of that in trial 1.

During fumigation, a part of CH_3Br undergoes degradation by interaction with soil organic matter and hydrolysis, which results in production of bromide ion, Br^-. Br^- production was maximum near the soil surface, where temperature and organic matter content were generally high. Estimations based on Br^- concentrations and water content at various soil depths showed that about 294 and 221 g were degraded in the soil profile in fumigated areas in trials 1 and 2 respectively. These values represent 59.7 and 44.9% of the applied amount.

Reassessment of other field experiments leads us to propose that global emission estimates of CH_3Br soil fumigant can be reduced substantially from the current estimate of 57.5 (range: 30 to 85) to 40.6 % (range: 28 to 53). By considering the atmospheric life span of CH_3Br as 0.8 y (range: 0.6 to 1.4), its phase-out as a soil fumigant may thus have only a limited positive effect in reducing the mean global atmospheric concentration. Although our results fall within the wide range of previous emission estimates, we believe that they are of considerable significance. To our knowledge, this is the first evidence to indicate the high importance of solar radiation in emission flux.

Such restrictions have led to an intensive search for improved technologies in CH_3Br fumigation to reduce dosage and emission from fumigated plots into the atmosphere, while maintaining its effectiveness for disease and weed control. CH_3Br emission reduction with field management practices, such as the use of gas-tight films, shallow injection (ca. 25 cm depth) in combination with irrigation, deep injection (ca. 60 cm depth), and application of ammonium thiosulfate or a soil bacterium, etc. have been tested. These methods can reduce the amount of CH_3Br application and its emission during exposure period, and are appropriated injection methods.

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 PE and PVC films in combination with a non-woven high density polyethylene fiber sheet (Tyvek, DuPont). Tyvek, when used a cover sheet, is considered to shield solar radiation by diffuse reflection.

The shielding technique was evaluated in a field experiment from 2 to 12 September in 1996 (Trial 3) and from 10 March to 2 April in 1997 (Trial 4) on Hydric Hapludand soils at the National Institute of Agro-Environmental Sciences, Tsukuba, Japan. 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 CH_3Br flux and cumulative emission from the field with and without Tyvek sheet are shown in Fig. 2. 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 than in hot season, 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, and the problem of waste processing is small. Therefore, this technique holds promise for commercial use.

In previous studies, we found that using a gas-tight film (Orgalloy film, elf atochem) in surface application considerably reduced emission loss to 7.6% of the applied amount during 7 days of application (1.4% through the film and 6.2% from surrounding soil surface of the treated area) in Fig. 3. However, emission was high soon after removing the film, amounting to 33% emission over the entire period. The total emission is thus largely similar to that after using conventional films such as polyethylene. The standard dose of CH_3Br application in Japan varies from 15 to 30 g m^{-2}, which is near threshold level, and it is difficult to reduce the dosage dramatically by using a gas-tight film alone. We presumed that emission could be reduced significantly if CH_3Br degradation is enhanced by a photocatalyst, although this approach has not yet been well investigated.

TiO_2 photocatalyst was suspended in the solvent, spread ca. 3 g/m^2 on Tyvek sheet, and then heat-sealed with a barrier film. After placing the sheet in the center of a separable chamber (effective irradiation diameter: 10cm, the upper and lower chamber volumes ca. 400 ml and ca. 280 ml, respectively), distilled water (1ml) and CH_3Br (2.5ml) were introduced into the lower chamber. Irradiation was performed with a 500-W Xe arc lamp approximated to AM 1.5 G at room temperature.

CH_3Br concentration at the beginning of the test was about 6000 ppm and it decreased to a few ppm within 48 hours after irradiation. Degradation products of CH_3Br were identified as CO_2 and HBr. 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. 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 days). 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, as against over 1,000 ppm with a gas-tight film. Our experiments also showed that CH_3Br emission was reduced to less than 1% of the applied amount by using the sheet containing TiO_2, as against about 57% and 33% with polyethylene (0.05 mm thickness in traditional method) and gas-tight film respectively. 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.

The multi-layer sheet can be used easily and repeatedly without any major modifications in current practice of soil surface application. Further, the problem in disposing this sheet is minimal. We, therefore, believe that the technique is useful for reducing CH_3Br emissions substantially and that multi-layer sheet containing TiO_2 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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Reference

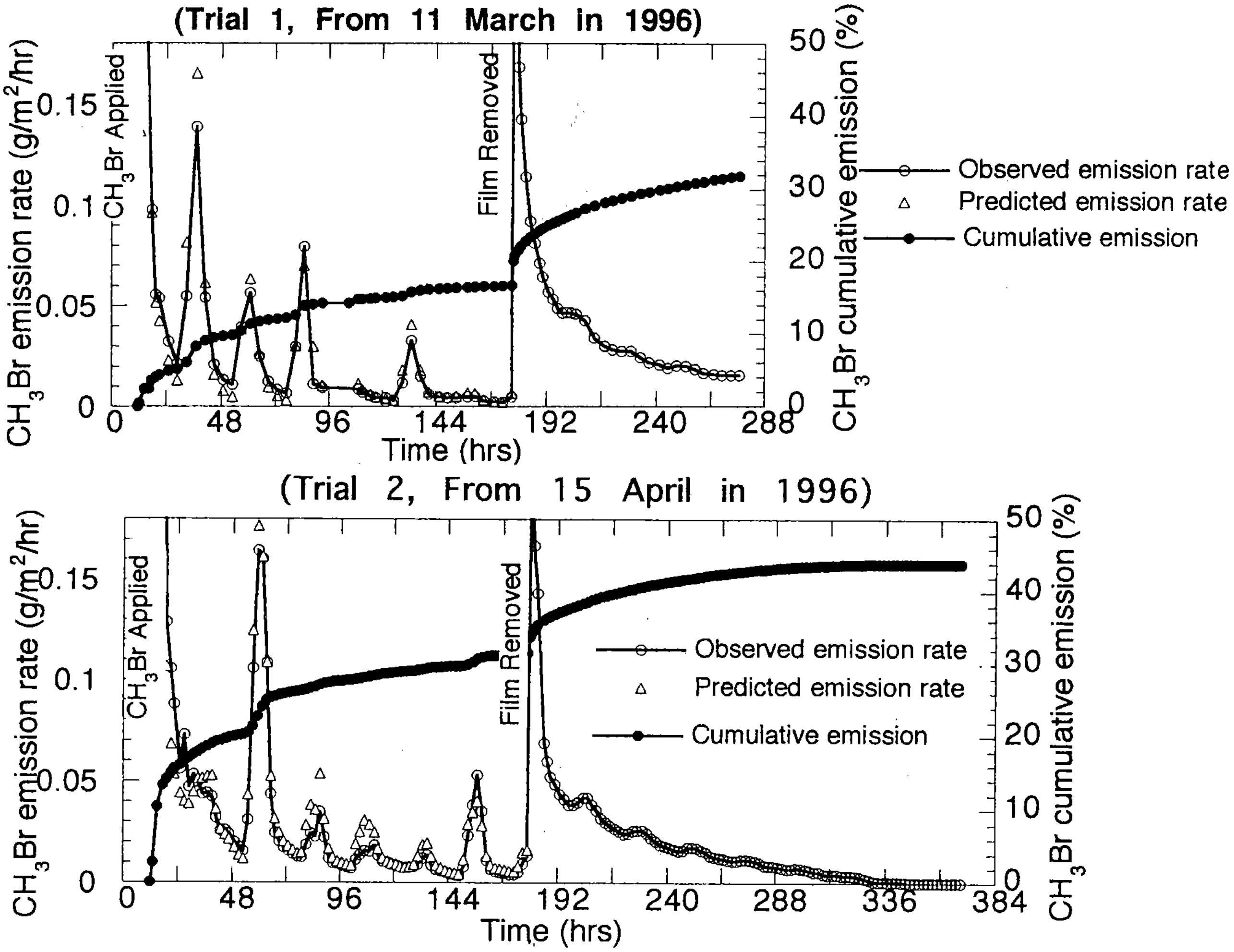

Fig. 1 CH_3Br emission rates ($g/m^2/hr$) and cumulative emission to the atmosphere as fraction of the applied amounts. Data points are means of three measurements. Soil was covered with a film for 7 d and then removed. Open triangles denote that predicted emission rates.

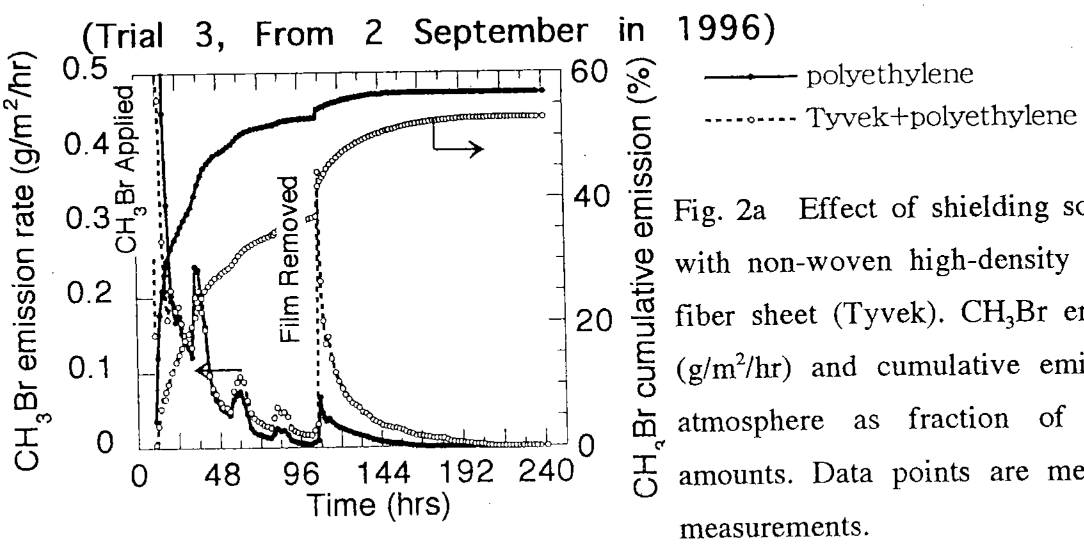

Fig. 2a Effect of shielding solar radiation with non-woven high-density polyethylene fiber sheet (Tyvek). CH_3Br emission rates ($g/m^2/hr$) and cumulative emission to the atmosphere as fraction of the applied amounts. Data points are means of three measurements.

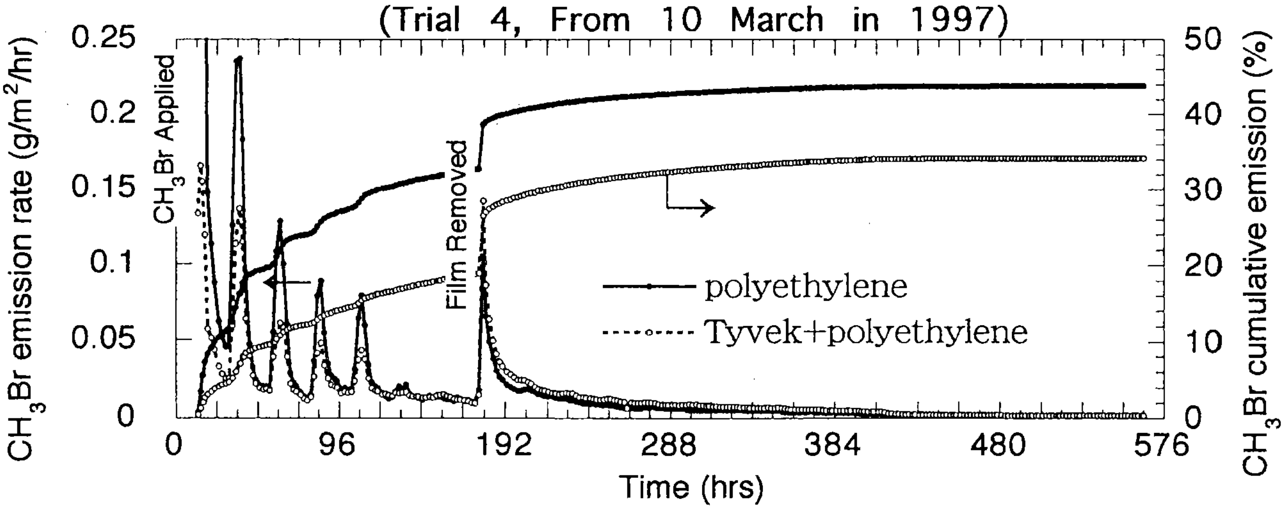

Fig. 2b Effect of shielding solar radiation with non-woven high-density polyethylene fiber sheet (Tyvek).

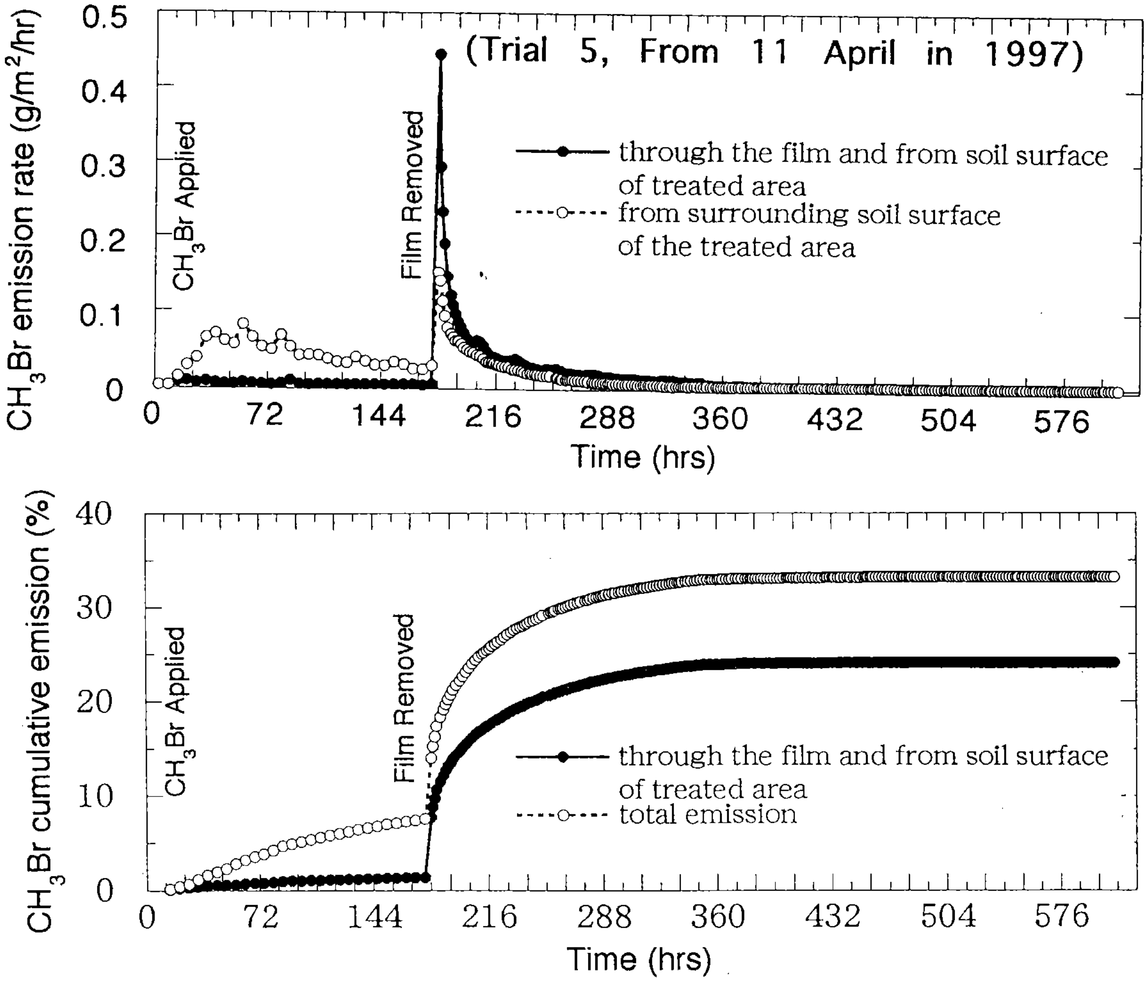

Fig. 3 Reducing emission of CH_3Br: effect of a barrier film

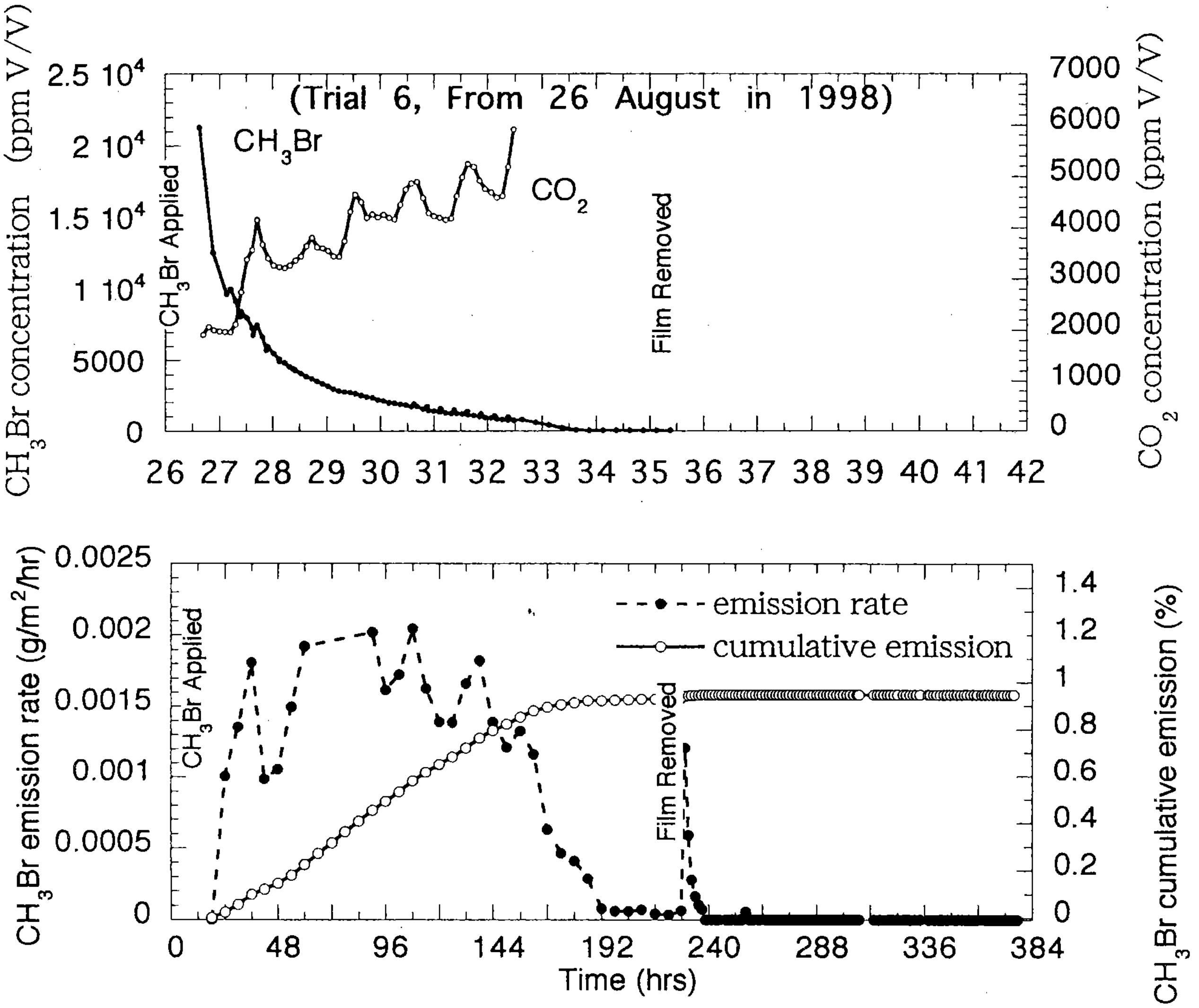

Fig.4 Reducing emission of CH_3Br: effect of a sheet containing TiO_2 photocatalyst