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Methyl bromide emissions from agricultural field fumigations in California

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Abstract. Methyl bromide is the most abundant brominated hydrocarbon gas in the atmosphere and is significant as a source of stratospheric bromine radicals that destroy ozone. However, estimated sources and sinks of methyl bromide exhibit a deficit in sources of ~70 Gg/yr (one Gg = 10^9 g), and the proportion of natural and anthropogenic sources is not known well. Known sources include agricultural fumigation (preplant and postplant), structural fumigation, biomass burning, gasoline additives, and oceans. The oceans, however, also act as a net sink for methyl bromide; that is, globally, consumption is greater than production. Early estimates of emissions of methyl bromide from fumigated agricultural fields from models were 30–60% of the amount applied. To test this estimate, we studied emissions from six field fumigations using chambers to measure the flux of methyl bromide, soil bromide analyses to measure degradation, and soil gas down to 90 cm or more to monitor methyl bromide with time in the soil profile. We found between 24–74% of applied methyl bromide was emitted. The average emission found in these experiments was 49 ± 19% based on chamber measurements and 52 ± 20% based on the soil bromide measurements. Factors affecting emissions included the polyethylene film covering the soil, the injection method, the injection depth, and the chemical and physical properties of the soil. The main factors controlling the emissions in our studies are discussed.

1. Introduction

Methyl bromide is the most abundant organic bromine-containing gas in the atmosphere [*Schauffler et al.*, 1993]. Methyl bromide is destroyed by hydroxyl radicals in the troposphere, but some can be transported into the stratosphere where it is photooxidized releasing bromine atoms, which attack ozone catalytically [*Wofsy et al.*, 1975]. Unlike chlorofluorocarbons, methyl bromide has both natural and man-made sources, and it is difficult to assess the fraction of atmospheric methyl bromide produced from man-made sources, and whether it significantly affects the global environment. Recent research is redefining our understanding of the sources and sinks of methyl bromide.

Estimated budgets of atmospheric methyl bromide have been deduced by *Yvon-Lewis and Butler* [1997] and *Butler and Rodriquez* [1996] who drew upon many recent studies. With an atmospheric methyl bromide burden of about 145 Gg and an atmospheric residence time of 0.7 years, the total of annual sinks must be about 207 Gg, assuming steady state, and total annual sources must equal the sinks. Known sources are at most 137 Gg/yr. Estimates of methyl bromide released by combustion of leaded gasoline [*Baker et al.*, 1998] are lower than listed by Yvon-Lewis and Butler so that known sources are

perhaps only 125 Gg/yr, implying unknown sources of over 80 Gg/yr.

The oceans were thought to be a net source of methyl bromide to the atmosphere [*Lovelock*, 1975; *Singh et al.*, 1983; *Singh and Kanakidou*, 1993; *Khalil et al.*, 1993] until *Lobert et al.* [1995] investigated emissions of methyl bromide from the oceans in the east Pacific Ocean from 44°N–45°S, covering open and coastal waters. They analyzed samples by gas chromatography/mass spectrometry enabling positive identification and precluding coelution problems. Their results showed up to 100% supersaturation in coastal waters and up to 50% undersaturation in the open ocean. Others suggested that the cold polar oceans could pose a significant net source of methyl bromide [*Anbar et al.*, 1996; *Pilinis et al.*, 1996]. Therefore another expedition took place in the Southern Ocean from 75°N–55°S where again it was found that the ocean was undersaturated [*Lobert et al.*, 1997]. Presently, oceans are considered a significant net sink of methyl bromide; that is, consumption is greater than production [*Yvon-Lewis and Butler*, 1997]. When *Shorter et al.* [1995] deduced a potentially large soil surface sink of 42 ± 32 Gg/yr for methyl bromide, the budget of methyl bromide became even more unbalanced. *Jeffers and Wolfe* [1997] showed that several types of green plants degrade methyl bromide at ppm levels, and further experiments are needed to assess the impact of this sink on the global methyl bromide budget. Some plants may also produce and release methyl bromide [*Saini et al.*, 1995; *Gan et al.*, 1998].

Methyl bromide is also produced by combustion of leaded gasoline and emitted by fumigation practices. The *World Meteorological Organization (WMO)* [1995] stated a mean of 15

Gg/yr methyl bromide emitted from the combustion of leaded gasoline from 1991–1992, but also cited another study that showed a range of 0.5–1.5 Gg/yr. Recently, Baker et al. [1998] reported a value of 3 to 4 Gg/yr. Methyl bromide produced from biomass burning is estimated to be 19 Gg/yr [Andreae et al., 1996] and 14–24 Gg/yr [Blake et al., 1996] based on the ratio of methyl bromide to carbon monoxide in smoke plumes.

Preplant fumigation accounted for 80% of total industrial methyl bromide production in 1992, and usage in preplant fumigation increased from 30.4 to 57.4 Gg/yr from 1984–1992 [WMO, 1995]. The Northern Hemisphere accounts for 95% of the usage for preplant fumigation based on 1990 estimates. In the United States, California and Florida are the primary users, and strawberries, tomatoes, peppers, and flowers are the main crops on which preplant fumigation is used [Watson, 1992].

There are many advantages in using methyl bromide for field fumigations. Because of methyl bromide's high vapor pressure and low boiling point, transport is rapid, and depth of penetration is extensive. A polyethylene film is typically used to cover the soil just after fumigation for several days to minimize emissions and maximize retention in the soil. A few days after fumigation, farmers prepare the field for planting making the waiting period between fumigation and planting very short. Because it is a broad spectrum fumigant, methyl bromide eliminates the major pests that occur in the soil, and thus a variety of chemicals is not needed. However, methyl bromide is very toxic to humans, and bromide from the decomposition of methyl bromide can be concentrated in plant tissue which is toxic to some types of plants [Brown and Rolston, 1980; Maw and Kempton, 1973, and references therein].

A mixture of chloropicrin and methyl bromide is often used instead of pure methyl bromide. This mixture has been used in the strawberry industry in California since the 1960s [Mulder, 1979, and references therein] and it works in a synergistic way. For example, this mixture reduces methyl bromide's dependency on soil conditions and is more effective against verticillium than the use of each compound separately [Mulder, 1979, and references therein]. Chloropicrin also serves as a warning agent for methyl bromide; it is a lachrymatory agent (causes tears to form in humans).

Once injected into the soil, methyl bromide undergoes transformations and transport. Reversible sink processes include physical and chemical adsorption, and irreversible processes include chemical decomposition within the soil matrix [Brown and Rolston, 1980], hydrolysis, reaction with soil organic matter, and degradation by soil bacteria [Miller et al., 1997; Oremland et al., 1994; Rasche et al., 1990; Connell Hancock et al., 1998; Hines et al., 1998]. Finally, emission into the atmosphere is a transport loss process. Soil conditions such as pH, moisture content, carbon and nitrogen content, bulk density, porosity, and application method and film type are important for transport and conversion in the soil. Methylation of carboxyl-, nitrogen-, and sulfur-containing groups in organic matter is considered the primary pathway of chemical degradation [Gan et al., 1994; Arvieu, 1983; Maw and Kempton, 1973, and references therein]. Alkaline conditions enhance degradation through hydrolysis [Maw and Kempton, 1973].

In 1995 the Environmental Protection Agency imposed a freeze on methyl bromide production at 1991 levels with a complete ban in 2001. Yet at that time it was not clear how much methyl bromide escaped during preplant fumigations. It had been estimated that 50% (30–60%) of applied methyl

bromide was emitted into the atmosphere [Singh and Kanakidou, 1993; Albritton and Watson, 1992]. However, field studies have shown a range of 21–87% emission from preplant fumigation [Gan et al., 1997; Yates et al., 1997, 1996a, b; Yagi et al., 1993, 1995]. Accordingly, measurements on emissions were needed to quantify the effectiveness of a ban. The questions to be answered were how much methyl bromide was actually emitted from fumigation practices, and could fumigation practices be refined so as to limit emissions? Therefore emissions from field fumigations under ordinary practices were investigated. We studied six such field fumigations referred to as MeBr I through MeBr VI.

To make reliable estimates on emissions, one must account for the pathways of methyl bromide transport and conversion in the soil. The following mass balance approach was followed:

amount applied = amount emitted

$$+ \text{ amount converted to Br}^- + \text{ amount in soil gas} \quad (1)$$

The amount applied was measured during each experiment. The amount emitted was determined using chambers placed on top of the polyethylene film and soil surface, the amount converted was determined using soil cores (by difference from cores before and after the fumigation) for bromide analysis up to 110 cm depth, and the amount of methyl bromide in the soil gas was obtained using soil sampler probes to 90 cm depth. Field measurements showed that negligible amounts of methyl bromide gas remained in the soil several days after fumigant application. Also, although soil bromide amounts at each depth can vary with horizontal position in a field [Yates et al., 1996a], the amount converted to bromide in (1) is determined by measuring at various depths and then integrating vertically to obtain a total column amount. This vertical integral is much more constant with position than are amounts at individual depths; in particular, the standard error of the mean vertical column amount should be approximately the standard deviation at one depth divided by the square root of the number of depths sampled (six to eight depths were sampled in this study). An example is given below in the discussion of experiment MeBr III.

2. Experimental Methods

Only a brief discussion of experimental methods will be given; the reader is referred to Yagi et al. [1993, 1995] and Williams [1997] for further details of experimental methods. Two types of specially equipped tractors were used to inject the methyl bromide/chloropicrin mixture through shanks that penetrated the soil. In MeBr I a tractor was used with 10 shanks which penetrated to a depth of 25 to 30 cm. For the remaining projects a new tractor-mounted device was used, the Noble Plow, which had only four shanks with a V-shaped extension at the base injecting the mixture at a depth of ~35 cm versus the 10 shank method in MeBr I. Deeper injection was expected to minimize rapid emissions due to longer and less direct escape paths to the surface as compared to MeBr I. Also, the Noble Plow with its V-shaped extensions was to allow for greater uniformity of application. Simultaneously, the application device laid a continuous sheet of polyethylene film over the just-fumigated soil. While laying a sheet, a device applied glue to the edge of the previous sheet and pressed the parallel overlapping edge of the next sheet to seal the seam. The transverse edge of the plastic sheet at the end of each tractor

Table 1. Summary of Fumigation Method, Application, Date, and Location for Each of the Six Field Fumigation Experiments

Project	Location (Irvine, California)	Date Field Fumigated	CH_3Br/ CCl_3NO_2, %/%	CH_3Br Applied, g/m^2	Method	Film Type	Days Covered With Film	Number of Chambers Used
MeBr I	Alton/Sand Canyon	Sept. 10, 1992	75/25	25.6	10 shanks	LDPE	4	4
MeBr II	Jeffrey/Irvine Center	Oct. 8, 1993	75/25	24.3	Noble	HDPE	5	5
MeBr III	Jeffrey/Irvine Center	Sept. 23, 1994	75/25	23.3	Noble	HDPE	5	8
MeBr IV	Alton/Sand Canyon	Aug. 14, 1995	67/23	20.8	Noble	HDPE	5	8
MeBr V	Jeffrey/Sand Canyon	Aug. 25, 1995	75/25	25.7	Noble	HDPE	5	8
MeBr VI	Highway 5/Highway 405	Sept. 18, 1995	75/25	31.0	Noble	HDPE	5	8

LDPE, low-density polyethylene; HDPE, high-density polyethylene.

pass was sealed by overfilling with large amounts of soil. The usage of these films was intended to minimize methyl bromide emissions and to increase the effectiveness of smaller dosages of methyl bromide [*Hamaker et al.*, 1983]. The width of the plastic film was ~245 cm, and the glued section was ~23 cm wide.

Flux chambers made from polyvinyl chloride pipes with removable lids were used to measure the fluxes from the surface before and after film removal (ID, 30 cm; OD, 32 cm; volume, 13 L). The tops were covered with aluminum foil to minimize temperature changes inside the chamber. The chambers were sealed to the plastic tarpaulin using a silicone rubber adhesive sealant, RTV 108 (General Electric). Tests proved that volatile emissions from the sealant did not interfere with the chromatography. Also, laboratory tests showed only a loss of 5.6%/h with 40 ppm methyl bromide injected into the chamber sealed to the plastic film. Two smaller chambers were used to measure the flux through the glue strip of overlapping polyethylene sheets. Samples of chamber air were analyzed by flame ionization gas chromatography (Hewlett Packard 5890 Series II) using a 105-m, 0.53 mm (ID) Vocol column (Supelco).

After the first 4 to 5 days of each experiment, the chamber area was marked on the film, the chambers were removed, the film was lifted, and the chambers were replaced in the soil several cm deep. After each experiment, we measured the thickness of the film underneath each chamber. Buildup of methyl bromide inside the chambers was monitored by sampling after 10 and 20 min. Ten-minute flux measurements were found to be sufficient. A standard containing 49.96 ± 0.50 ppm methyl bromide in nitrogen prepared by Scott Specialty Gases was used for calibration. Replicate analyses of field samples taken from the flux chambers agreed to within 2%.

Soil samples were typically collected at three sites from depths of 3, 10, 20, 30, 60, and 90 cm to determine the physical and chemical properties of the soil. Soil pH was measured using an Orion Triode pH electrode, model 91-57BN and Orion 290 A readout. The bromide content in the soil was measured using a bromide-ion electrode and a double junction reference electrode manufactured by Orion Research, Boston. The bromide electrode was calibrated using NaBr solutions (0.1, 1, 10, and 20 parts per million) prepared in 0.4 M NaNO$_3$. Soil samples from each of three sites about 4 m apart were physically combined before analysis as in the work of *Yagi et al.* [1995]. Duplicates of each standard, blank, and soil depth were measured. For example, in experiment MeBr II, replicates of standards were within 1.5%, blanks were within 1%, and samples (0–90 cm) were within 4%. Soil bromide amounts were measured before and after the field fumigation. Soil carbon and nitrogen amounts were determined with a Carlo Erba NA

1500 Series 2 Carbon/Nitrogen analyzer. The bulk density and moisture content were determined by the mass of the dry soil, mass of water, and the core volume.

Soil-gas concentrations of methyl bromide were taken using soil-sampler tubes reaching 10, 20, 30, 60, and 90 cm. Gastight glass syringes (5 and 10 mL) were used to withdraw samples from the tubes; samples from the syringes were injected immediately into glass serum bottles (117 mL volume) that were prefilled to atmospheric pressure with clean background air. Storage tests on the serum bottles showed a loss of 7% at 14.9 ppm methyl bromide and 4% for 267 ppm methyl bromide over a period of 4 days. The soil-gas samples were transported to UC Irvine and analyzed by flame ionization gas chromatography with direct injection onto a 6-foot long, 1/8 inch OD, 10% OV-101 column (Hewlett-Packard) held at approximately 75°C. Secondary standards were prepared by injection of pure methyl bromide into evacuated stainless steel canisters and diluted with room air. These standard concentrations were determined using the primary (Scott) standard. Standards were injected periodically between sample injections within the concentration range of the samples. Repeated injections of methyl bromide standards at 18.2, 126.4, 974.3, and 4940 ppm typically showed repeatability of 2%. The detection limit was ~1 ppm. In experiment MeBr II we used two sets of soil-sampling tubes including a new one with smaller internal volumes (<1 mL); side-by-side deployment showed good agreement with results obtained through the earlier tubes [see *Yagi et al.*, 1995]. Air temperatures just above soil surface and below the plastic tarp materials were measured during each sampling period and may be requested from the authors.

3. Results and Discussion

3.1. Experiments MeBr I and II

A summary of the specifications and location of each fumigation experiment appears in Table 1. MeBr I and MeBr II experiments have been discussed in previous publications [*Yagi et al.*, 1993, 1995]. Briefly, the emission of methyl bromide based on flux measurements for MeBr I was 74 ± 5%. The data from one chamber were removed in determining this estimate due to a hole in the underlying film that was discovered after the experiment. When data from all four chambers are included, the emission estimate is 87 ± 36%, as was reported by *Yagi et al.* [1993]. We believe the three-chamber estimate because the hole in the film under the chamber clearly permitted anomalously high emissions during the first 4 days of the experiment and also because of the independent estimate of emissions from (1) based on residual bromide found in the field. The amount of methyl bromide converted to soil bromide
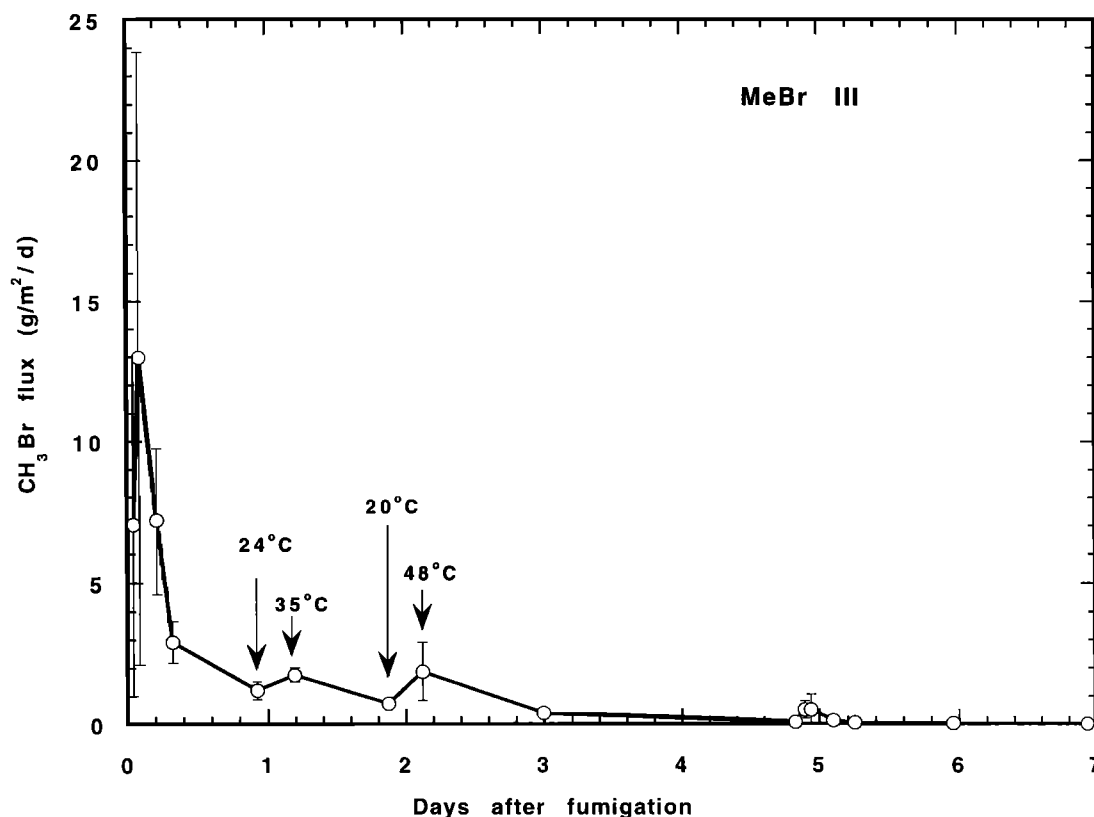
Figure 1. Average measured methyl bromide flux for each of the 16 sampling periods during MeBr III. Temperatures measured under the film are shown at four sampling times. Fluxes from seven chambers were averaged (see text). Error bars represent plus or minus one standard deviation around the average flux.

due to decomposition was 5.8 ± 0.5 g/m^2 CH$_3$Br or $23 \pm 2\%$ of the amount applied. The overall uncertainty in the amount converted to bromide was mainly due to differences in soil bulk density. The chambers with the thickest film beneath them exhibited the smallest fluxes [*Yagi et al.*, 1993]. In MeBr I we used 12 sampling periods: two on the day on which fumigation occurred, one each on days 2 and 3, five on day 5 (beginning immediately after removal of plastic tarp), two on day 6, and one on day 7.

In addition to escape flux and soil-bromide amounts, soil gas concentrations were measured from under the film to 90 cm depth. Results for MeBr I were shown by *Yagi et al.* [1993]. Soil-gas data from MeBr II confirmed the most important conclusion for our purposes, that the soil concentrations of CH$_3$Br were less than 1 ppm after 7 days, representing a negligible fraction of the amount applied. Using mass balance, equation (1), a total of $97 \pm 23\%$ of the methyl bromide applied was accounted for. The soil concentration, bromide, and flux data may differ from field to field because the transport and transformation of methyl bromide in soil depends upon the type of soil conditions and characteristics present at the time of fumigation. Therefore a second fumigation project was planned to better discern the soil conditions which affect emissions.

Experiment MeBr II took place at another location in Irvine (see Table 1). The same chamber apparatus was used for this experiment except that five chambers were used instead of four. The emission over the entire sampling period was $36 \pm 6\%$ of the total applied. The increase in Br$^-$ content of the soil after fumigation was measured to be 16.9 ± 2.3 g/m^2 as methyl

bromide, or $70 \pm 9\%$ of that applied. The measured soil-bromide increase, $70 \pm 9\%$, implies that $30 \pm 9\%$ of the applied CH$_3$Br was emitted, which agrees fairly well with that calculated from the chamber measurements, 36%. Thus a mass balance of $106 \pm 11\%$ was obtained. In MeBr II we used 14 sampling periods distributed over the 8 days following fumigation as follows, listed as samplings per day: 3, 1, 1, 1, 0, 5, 2, 1.

The soils in MeBr II were less dense at all layers, and the surface of the soil had greater moisture content than the previous year, that is, during MeBr I. In MeBr II, soil concentrations were less than those of MeBr I. These data are not shown here; they are available upon request to the authors. The concentrations became more uniform within a day for MeBr II and within about 2 days for MeBr I at all depths. This may be due to the modified injection method (that insures more uniformity), less disturbance of the soil (fewer shanks protruding into the soil and therefore less escape paths to cause more initial variations), and a higher moisture content in the surface layer which may have acted as a seal to slow the diffusion to the surface and possibly increased partitioning into the liquid phase. The reduced emissions in MeBr II in comparison to MeBr I may be partially due to the high-density film used, injection method and greater injection depth, and greater uptake into the soil due to soil properties.

3.2. MeBr III

Eight chambers were used to measure flux in MeBr III, and the average flux as a function of time after injection is shown in Figure 1. Vertical error bars in Figure 1 are standard deviations around the mean. In MeBr III we used 16 sampling

periods distributed over the 8 days after fumigation as follows: 4, 2, 2, 1, 0, 5, 1, 1. Data from each of these 16 periods appear in Figure 1. The temporal profile follows a pattern similar to that of the previous projects. Two chambers gave relatively larger fluxes than the other chambers. Upon examination, the plastic film located underneath chamber D was found to be stretched excessively, and the other was found to have a pin-sized hole in it (chamber E). Chamber D gave fluxes approximately 3 to 7 times that of the other chambers, and chamber E gave fluxes about 2 to 7 times larger within the first 4 hours after fumigation. After the experiment, a hole was found in the film under chamber E. These problems occurred because the field surface was much more uneven, with deeper rows which made the film tighter across the soil surface in places. It is important for effective fumigation and for experiments like ours that the field be prepared well so as to avoid large, localized stresses on the plastic film that can lead to rips and holes. Integrating over the entire time period of the experiment yielded a cumulative emission of 26 ± 8% (mean and standard deviation) of the 23.3 g/m^2 applied. Ignoring data from chamber E and using data from only seven chambers yielded an emission estimate of 24 ± 5%; we believe that this estimate is preferred.

The effect of temperature on the flux was also investigated in this experiment. Figure 1 shows the average fluxes observed at each of the 16 sampling periods during MeBr III; error bars are one standard deviation around the mean value. While the emissions from the field generally decreased after the first few hours from fumigation until the end of day 4 (when the plastic tarp was lifted), we observed some increases of emissions with time inside the pattern of monotonic decrease. Four sample points are shown with temperature taken under the film at the time of sampling. The flux increased with temperature between sampling periods five and six and then again between periods seven and eight, while corresponding temperatures increased from 20° to 35°C and from 20° to 48°C, respectively. Because under-tarp temperatures do vary with time of day, sampling times should be adjusted so that estimate of emissions can be as accurate as possible. Daytime average surface temperatures (°C) for these 8 days were 30, 26, 22, 25, N/A, 28, 26, 17 (early morning only); (no surface temperature data were taken on day 4). Corresponding average temperatures under the plastic tarp were 40, 30, 34, and 30 on days 1–4.

The conversion of methyl bromide to bromide ion from 0–90 cm was 48% of the total applied. Adding to the 24% emitted yields a total of only 72%. Therefore mass balance was not achieved; that is, 28% was missing. During the experiment a 4 inch diameter opening in the plastic film was observed in one of the sampling lanes about 4 days after the experiment started, and the hole may have been open earlier. Possibly more methyl bromide conversion took place in the soil beneath the tarp away from our study site, and some emissions were not accounted for. To investigate, we took additional soil samples at two sites approximately 30 and 50 feet away from the first set of samples for bromide analyses. The amount converted at 30 and 50 feet away (different tractor lanes) was 51 and 74%, respectively. Therefore more bromide conversion took place with increasing distance from the perturbed area with the hole in the film. This implies that less CH$_3$Br escaped from field areas far from the hole than from the area near the hole in the plastic tarp.

Soil properties were compared to verify if more conversion may have taken place due to differences in soil with each
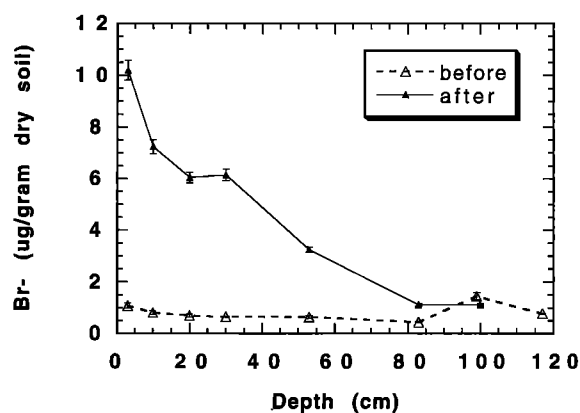

Figure 2. Bromide amounts measured versus depth in the soil of experiment MeBr IV before and after fumigation. Three soil cores from each indicated depth were combined before measurement. Error bars represent one standard deviation of bromide measurement of each combined sample. Vertical integrals of soil bromide amounts were calculated from these data and from corresponding data for other experiments.

location (see *Williams* [1997] for data). No properties consistently single out the differences found between all three sites. For example, in 10, 20, and 30 cm depths, percent nitrogen was lowest, and percent total C at 3 and 90 cm depths was greater for the sampling site relative to the other two sites 30 and 50 feet away. Greater carbon and nitrogen content in the soil yields greater conversion in the soil. These results help support but cannot verify that our sampling site was indeed disturbed due to rapid loss through the hole in the polyethylene film. We consider 74 ± 8% conversion of CH$_3$Br to be the most reliable estimate because the area sampled was farthest away from where the hole was located. Fortunately, in MeBr III we explored spatial variability of soil bromide amounts. We compared soil bromide amounts by extracting extra soil cores before and after the fumigation. As always, we physically combined soil cores for each depth from three subsites within 4 m of each other and did this at two different sites; initial bromide column amounts differed by only 2.5%, and final column amounts differed by 13%. Amounts at individual depths differed more than did the column-integrated amounts, as has been seen by other investigators [*Yates et al.*, 1996a]. In this way, a mass balance of 98 ± 9% was then obtained.

3.3. MeBr IV–VI

Experiments MeBr IV, MeBr V, and MeBr VI were mounted to obtain data from fields with differing soil characteristics. Because the experiments could be done only with participating farmers in the area, we were limited in the choice of soil characteristics. The results for MeBr IV–VI will be only summarized here because the basic observations did not differ significantly from MeBr I–III. Nonetheless, we show in Figure 2 the soil bromide before and after fumigation for MeBr IV (same site as MeBr I) to illustrate that the assumption in MeBr I, that the initial bromide content was constant versus depth, was appropriate. The average emission was 63 ± 12% of the total methyl bromide applied. From the bromide analysis, 6.5 ± 0.4 g/m^2 or 31 ± 2% methyl bromide was converted, giving a mass balance of 94 ± 12%. In MeBr IV we used 17 sampling periods distributed over the 8 days following fumigation as follows: 5, 2, 2, 1, 1, 0, 5, 1.

Table 2. Summary of the Mass Balances for MeBr I–VI

	Percent Converted	Percent Emitted	Total
MeBr I (1992) and MeBr IV (1995) Both at Site 1			
MeBr I	23 ± 2*	74 ± 5*	97 ± 5
MeBr IV	31 ± 2	63 ± 12	94 ± 12
MeBr II (1993), MeBr III (1994), and MeBr V (1995) All at Site 2			
MeBr II	70 ± 9	36 ± 6	106 ± 11
MeBr III	74 ± 8	24 ± 5	98 ± 9
MeBr V	41 ± 13	45 ± 8	86 ± 15
MeBr VI (1995) Site 3			
MeBr VI	47 ± 9	50 ± 9	97 ± 13
Average emissions			
Using Br⁻ measurements		52 ± 20	
Using chamber measurements		49 ± 19	

The calculation of CH_3Br converted involved the amount of bromide ($\mu g/g$ dry soil), water absorption, and bulk density. Most of the error in percent conversion was due to differences in bulk density. $N = 3$ samples for 3, 10, 20, and 30 cm and $N = 2$ for 60 and 90 cm (except for MeBr VI, where $N = 5$ for 60 cm and $N = 3$ for 90 cm). Statistical error for the percent emitted depended on the number of chambers used in each experiment ($N = 3$ for MeBr I, $N = 5$ for MeBr II, $N = 7$ for MeBr III, and $N = 8$ for MeBr IV, V, and VI).

*The results for MeBr I are the least certain (see text).

For MeBr V an average emission of 45 ± 8% was obtained from the eight chambers. The amount of methyl bromide converted was 8.2 ± 2.5 g/m² or 32 ± 10%. The preliminary mass balance was 77 ± 10%. To obtain a more accurate mass balance, more soil cores were collected ~30 feet from the previous samples. The methyl bromide amount converted to bromide in these cores was 50 ± 9% (12.8 ± 2.2 g/m² CH_3Br). From the average of both sites, 41 ± 13% methyl bromide was converted. The mass balance then becomes 86 ± 15%. Significant differences were not found when comparing soil properties at both locations (see *Williams* [1997] for data). In MeBr V we used 17 sampling periods distributed over the 8 days following fumigation as follows: 5, 2, 2, 1, 1, 0, 5, 1.

In experiment MeBr VI we also used eight chambers but one of them, chamber E, gave unusually high emissions, and a pin-sized hole was found in the polyethylene film underneath this chamber. Accordingly, data from chamber E were removed, and an average emission of 50 ± 9% for MeBr VI was observed based on seven chambers. The corresponding data for all eight chambers including chamber E were 54 ± 15%. Soil bromide analysis showed 47 ± 9% or 14.6 ± 4.2 g/m² of methyl bromide was converted in the soil. A total mass balance of 97 ± 13% was obtained. In MeBr VI we used 13 sampling periods distributed over the 8 days following fumigation as follows: 5, 2, 2, 1, 1, 0, 1, 1.

Table 2 shows a summary of the results of all six experiments. Averaging over all six field fumigations, the fraction emitted was 49 ± 19% according to the chamber fluxes and 52 ± 20% according to the residual bromide amounts. There are few other such data with which to compare. *Majewski et al.* [1995] performed two field studies, one with an uncovered field and one with a high-barrier plastic film tarp. In the former case, 89% of the applied methyl bromide escaped, while only 32% escaped from the tarped field. *Yates et al.* [1996a, b] studied a well-instrumented fumigated field that had been covered by standard plastic tarp material; they estimated methyl bromide losses using several methods (appearance of soil bromide and micrometeorological techniques). All of their data indicated losses of about 62 ± 10% of the amount applied, similar to a result from *Wang et al.* [1997b], who found losses of

64% when using conventional polyethylene tarps. Several other previous experiments are discussed below.

What factors control the emission of methyl bromide from fumigated soils? Increasing injection depth decreases emissions [*Yates et al.*, 1997; *Wang et al.*, 1997a]. Plastic films that are thicker and/or inherently less permeable can also reduce emissions [*Yagi et al.*, 1993; *Wang et al.*, 1997b], and the use of highly impermeable films can virtually eliminate losses [*Yates et al.*, 1998]. Figure 3 shows that methyl bromide emissions in our experiments increased with decreasing average film thickness. MeBr I is the only project that used low-density polyethylene film (Table 1), and it gave higher percent emission compared to the high-density polyethylene film. A second point in Figure 3, that from MeBr III, is very uncertain because two of the eight flux chambers displayed extremely high fluxes in that
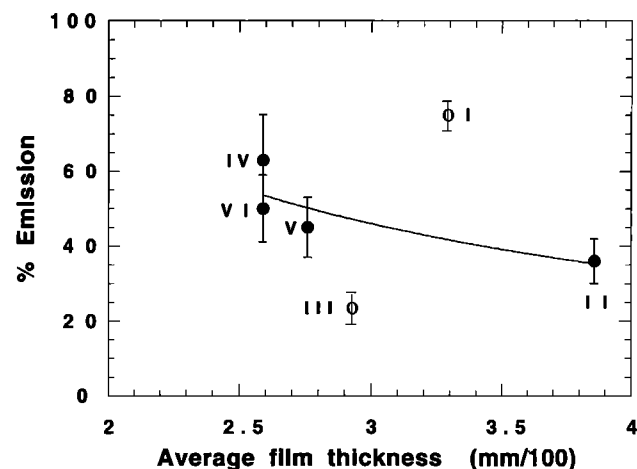

Figure 3. Measured cumulative emissions (as percent of amount applied) versus average polyethylene film thickness for each project. Experiment MeBr I used low-density polyethylene film. In MeBr III some spatial nonuniformities were observed (see text). Experiments II, IV, V, and VI showed that emissions decrease as film thickness increases; a parabola has been fit to those data.
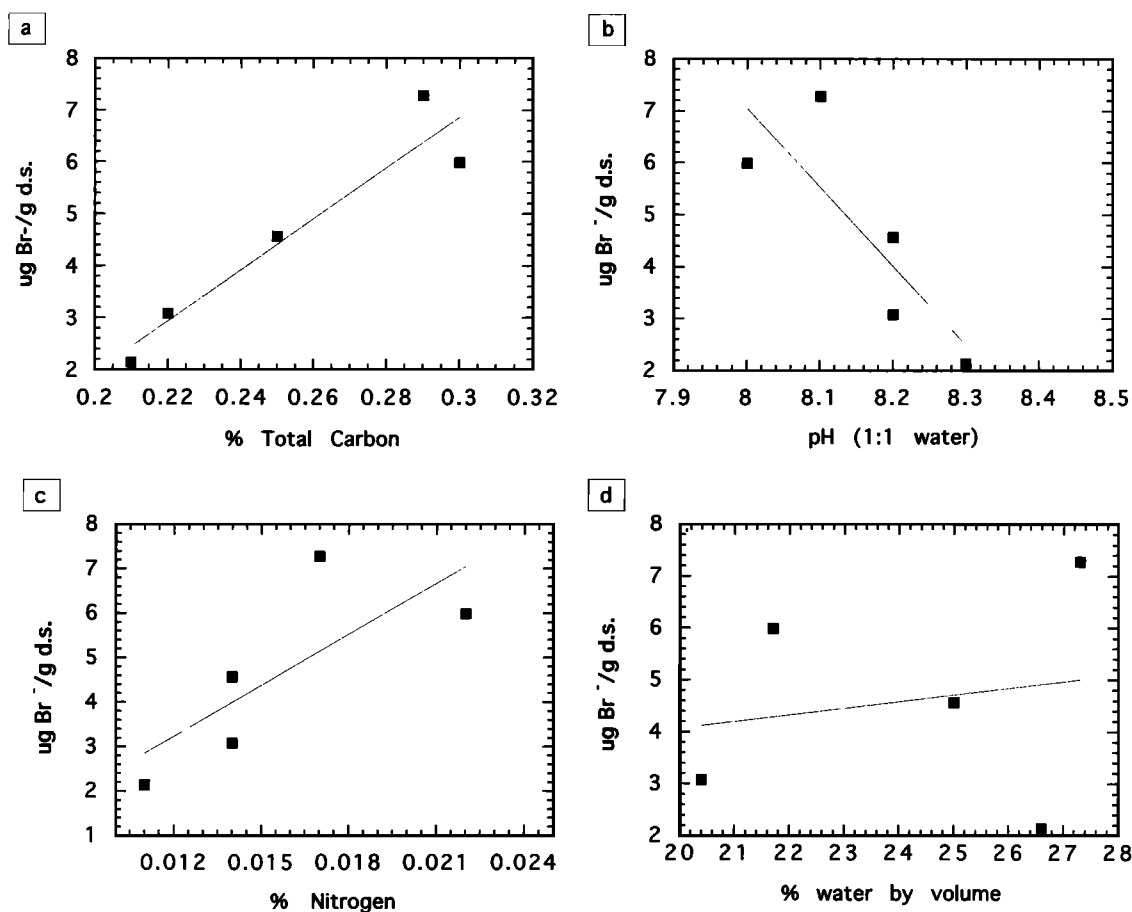
Figure 4. Soil samples at 60 cm for MeBr VI were taken at five subsites at the conclusion of the experiment. Correlations between measured bromide content (μg Br$^-$/g dry soil) and (a) percent total carbon, (b) pH, (c) percent total nitrogen, and (d) percent water content are shown. The linear correlation coefficients (R value of the line) are 0.949 (Figure 4a), 0.828 (Figure 4b), 0.760 (Figure 4c), and 0.185 (Figure 4d).

experiment and the amount of bromide remaining in the soil after the fumigation varied with distance from the experimental site. The remaining data from experiments MeBr II, IV, V, and VI show a similar pattern to that reported by *Yagi et al.* [1993, Figure 2]; emissions increase rapidly with decreasing film thickness. The average film thicknesses of MeBr IV and VI were the same. It is likely that the higher emissions seen in MeBr IV compared to MeBr VI were due to lower pH and higher percent H_2O on the field of MeBr IV (see below). This result, combined with the striking evidence from *Yates et al.* [1998] of near-zero emissions from fumigated fields covered with newly developed (nearly) impermeable films, shows that agricultural emissions of CH_3Br fumigant can be minimized with proper usage of high-quality films.

While the thickness of the plastic tarp material explains much about the variations between experiments, soil properties may also influence emissions. In experiment MeBr VI we noticed large differences in texture and clay content in the soil samples. Accordingly, we gathered and analyzed additional soil cores from 60 cm depth to permit correlation plots to be made using bromide contents and various soil properties. Figures 4a–4c display fairly linear relationships between the μg Br$^-$/g dry soil and percent total C, pH, and percent nitrogen (R > 0.75). Surprisingly, pH was negatively correlated with the amount of Br$^-$ in soil, opposite to observations by *Gentile et al.* [1989] in natural fresh water. Percent H_2O showed no corre-

lation with methyl bromide conversion in soil (Figure 4d). However, when pH, percent total carbon, and percent nitrogen were plotted against μg Br$^-$/g dry soil/percent H_2O, significant correlations resulted (Figures 5a–5c). Therefore water alone did not have an effect, but a combination of the properties with water content was important. This illustrates the complexity of the system for methyl bromide degradation; soil properties must be considered as a system rather than individually to understand and manipulate the degree of methyl bromide degradation in soil.

Figure 6 shows carbon and nitrogen amounts, bulk densities, moisture levels, and pH values for all six experiments. In MeBr I and IV (the same field), percent total nitrogen was greater in MeBr I for 3, 20, 30, and 90 cm, while pH was practically identical at all depths, except MeBr IV was greater at 3 cm, and moisture content and bulk density were greater in MeBr I than IV at 30 cm which was the approximate injection depth. However, only depths 3 and 30 cm were analyzed for MeBr I for moisture content. Also, daytime temperatures were greater for IV throughout the experiment. However, the film used in MeBr I was of low-density polyethylene, and MeBr IV had high-density polyethylene film. Also, the tractor equipment in MeBr I used an attachment having 10 shanks that penetrated the soil to approximately 25 to 30 cm depth. In MeBr IV the attachment was of a new design, the Noble Plow, to help reduce emissions (see Experimental Methods section).
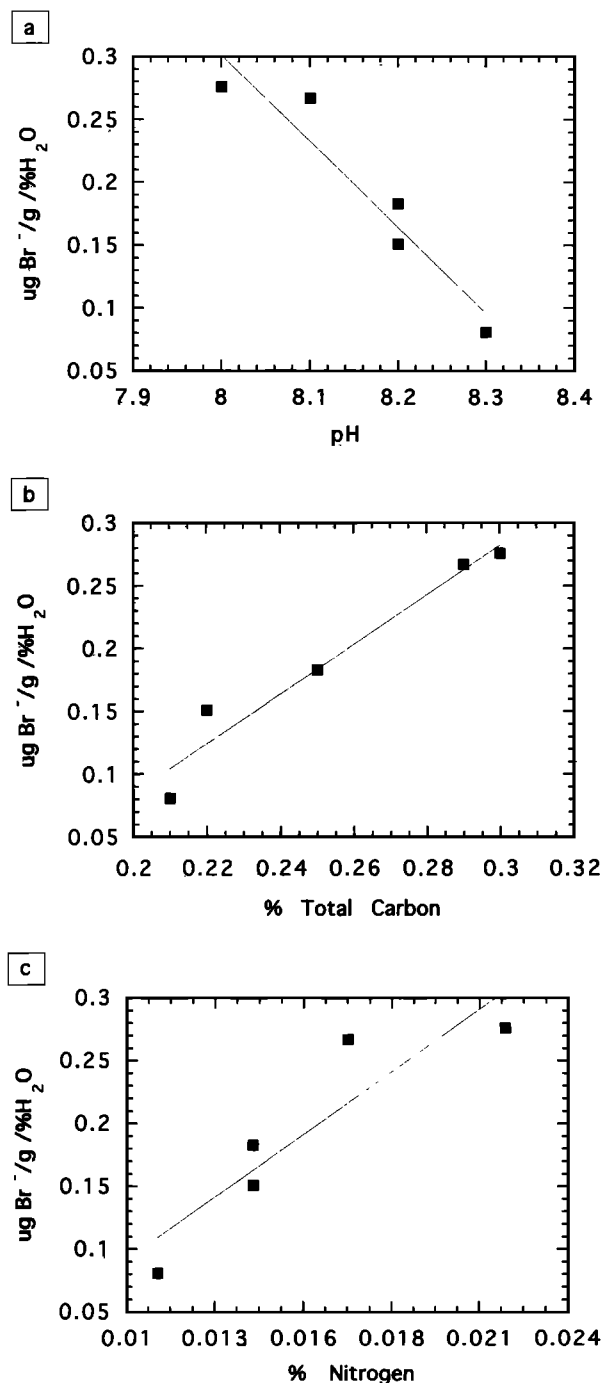
Figure 5. Soil samples at 60 cm for MeBr VI were taken at five subsites at the conclusion of the experiment. Correlations between measured bromide content (μg Br$^-$/g dry soil)/ percent water and (a) pH, (b) percent total carbon, and (c) percent total nitrogen are shown. The linear correlation coefficients (R value of the line) are 0.951 (Figure 5a), 0.975 (Figure 5b), and 0.906 (Figure 5c).

Previous studies led us to expect greater conversion of methyl bromide to bromide in soils with high organic carbon, nitrogen, and pH [*Gentile et al.*, 1989; *Gan et al.*, 1994]. In these six experiments we found no single soil variable to be dominant in controlling methyl bromide emissions. Figure 5 does show interesting correlations between postfumigation soil bromide

contents (normalized to moisture amounts), when plotted against pH, carbon amounts, and nitrogen amounts after MeBr VI.

4. Conclusions

The average methyl bromide emission found in six field fumigation experiments near Irvine, California, was 49 ± 19% based on flux chamber measurements and 52 ± 20% based on the soil bromide measurements. Nearly all methyl bromide injected into the soil was accounted for because mass balances were achieved in these experiments within 6% except for MeBr V. This mass balance provides supportive evidence of our methods. In these experiments, amounts of gaseous methyl bromide remaining in the soil after 7 days were negligible. These measured gaseous losses to the atmosphere are in the same range as those found from other fields in southern California that had been covered with similar quality polyethylene tarping material, that is, about 60 ± 10% [*Yates et al.*, 1996a, b; *Wang et al.*, 1997b].

The quality of the plastic tarping used to cover the fumigated field was found to exert strong control on gaseous emissions. The fumigated field covered by low-density tarp material (MeBr I) showed the highest methyl bromide losses, and fields with relatively thin high-density polyethylene films (MeBr II–VI) showed higher losses than those with thicker films. See also *Yates et al.* [1998]. Punctures or tears in tarping material were occasionally found to occur in the field, causing greater losses of gas. In our experiments these punctures and tears occurred where the plastic tarp material was stretched over surface soils that had not been properly leveled and smoothed. Thus, in locations around the world where low-quality plastic films (or none) are used to cover fumigated fields or where fields are not prepared ideally before they are covered with films, emissions should be higher than we report here.

In these experiments we did not attempt to estimate rates of hydrolysis and decomposition of methyl bromide nor did we quantify amounts adsorbed to soil particles. To obtain mechanistic understanding of methyl bromide degradation and to be able to predict losses from a given field, one must quantify the effectiveness of these processes. Note that *Oremland et al.* [1994] did not observe methanol production through the hydrolysis of methyl bromide in sediment experiments, implying that hydrolysis was not the important mechanism of degradation in their experiments.

Another loss process which needs quantification is the role of microorganisms in the degradation of methyl bromide [*Connell Hancock et al.*, 1998]. Controlling a field's conditions would be ideal to test how and to what degree soil chemical and physical properties and microorganisms affect emissions. Also, more laboratory experiments are needed to determine how soil properties interact to provide the best conditions for reducing methyl bromide emissions into the atmosphere. Because the factors controlling emissions are not completely clear and because soil properties differ with location, we cannot claim that the results reported here are representative of fumigations elsewhere. Indeed, these results further illustrate the complexity of the system being studied and of identifying the variables that combine to control emissions.

In general, methods of reducing emissions can be achieved by increasing the carbon and nitrogen contents and pH and manipulating the microbiology [*Connell Hancock et al.*, 1998], using gastight and thicker films and deeper injections [*Wang et al.*, 1997a, b; *Yates et al.*, 1998; *Yagi et al.*, 1995; *de Heer et al.*,
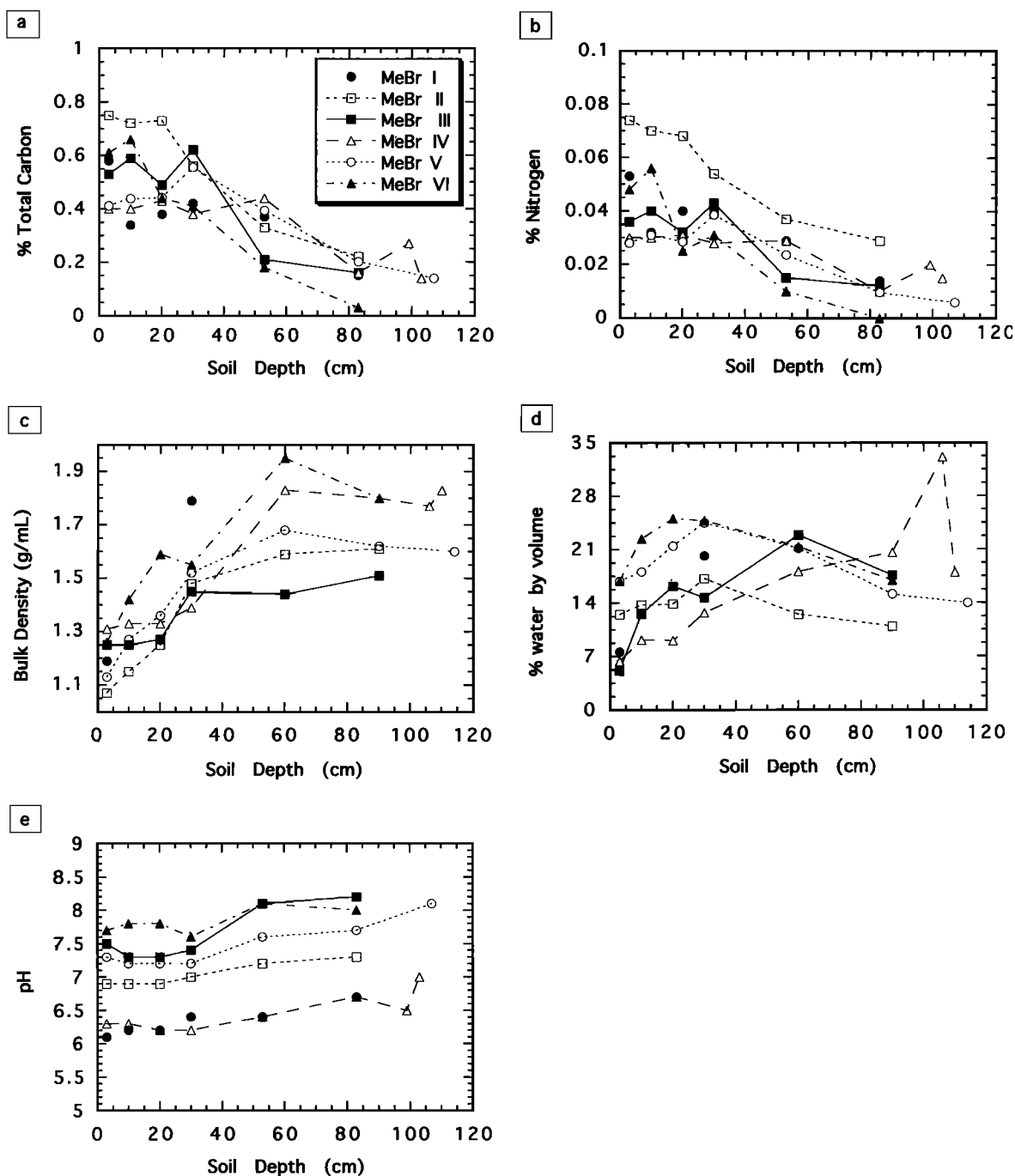
Figure 6. Measured initial amounts of (a) total percent carbon, (b) total percent nitrogen, (c) bulk density, (d) percent water, and (e) pH for all six projects versus depth in the soil. Data for the six field projects are displayed as follows: MeBr I (solid circle), MeBr II (open square with dashed line), MeBr III (solid square with solid line), MeBr IV (open triangle with dashed line), MeBr V (open circle with dashed line), and MeBr VI (solid triangle with dashed line), as illustrated in Figure 6a.

1983]. Some of these suggestions are made solely for decreasing emissions to the atmosphere. However, efficacy cannot be sacrificed if the industry continues to fumigate with methyl bromide. For example, increasing carbon content of the soil increases degradation but also decreases the concentration-time product necessary for the soil pathogens to be effectively killed. Therefore, when methods or experiments to reduce emissions are tested, parallel studies in efficacy are essential. Finally, the phaseout date for methyl bromide as a soil fumigant

was recently extended to 2005 by the U.S. Congress so that this chemical can be used against a new pest, the Asian long-horned beetle [*Morse*, 1998]. This continued usage of the chemical might encourage further research aimed at minimizing emissions.

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