Bull. Environ. Contam. Toxicol. (1998) 61:695-701

Environmental Contamination and Toxicology

Methyl Bromide and Bromide Ion in Soil After Experimental Greenhouse Fumigation

A. Dimitriou,[1] H. Tsoukali[2]

[1] Laboratory of Forensic Medicine and Toxicology, Faculty of Medicine, Aristotle University of Thessaloniki, 54 006 Thessaloniki, Greece
[2] Department of the Environment, University of Aegean–Greece, Karantoni 17, 81 100, Mitilini, Greece

Received: 10 August 1998/Accepted: 30 October 1998

Methyl bromide is currently used intensively in agriculture as an insecticide, a fungicide, a nematicide and a herbicide for the treatment of the soil. In the soil methyl bromide is degraded to bromide ion. Possible reactions are the methylation of the compounds in the organic material which contain oxygen-, sulphur- and nitrogen-groups, and hydrolysis where bromide ion and methanol are produced (wegman 1981; WHO 1995). Bromide ion is taken up by plants and is accumulated according to the physical and chemical properties of the soil, the climate conditions, the plant species and the type of plant issue (WHO 1995). It enters the human body through the foodchain with consequences to health.

This project aims at estimating the concentration of methyl bromide and bromide ion residues in soil after soil treatment in greenhouses with methyl bromide. The chemical, mechanical and physical soil properties (e.g. the organic material, the acidity (pH), the specific gravity and the porosity) were estimated. Meteorological parameters inside the greenhouse were also measured in addition to the soil humidity and temperature.

MATERIALS AND METHODS

The application of methyl bromide was carried out in an experimental greenhouse

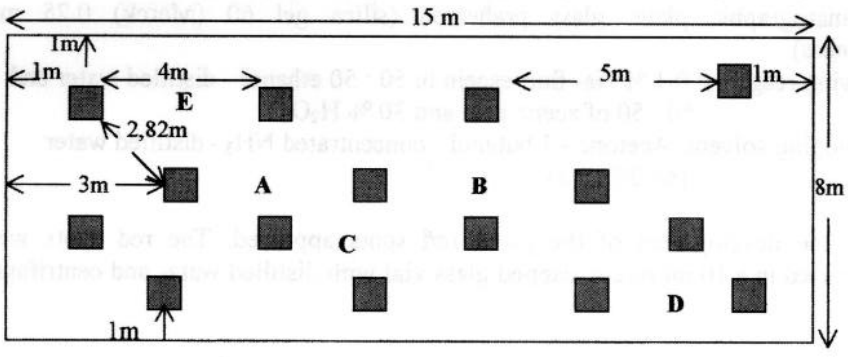

Figure 1. The application of methyl bromide in the greenhouse soil

Correspondence to: A. Dimitriou

of a 458.5 m^3 volume and soil area of 120 m^2. As the recommended dosage is 85 g/m^2, 15 evaporating cans of 680 g methyl bromide were used and placed underneath a plastic foil of high density.

As is shown in figure 1, evaporating cans were placed at a distance of a 4 m longitude and at 2.82 m diagonally in four series. In all series, apart from the second, four cans were placed. The first and the last can of the first and third series were placed at a distance of 1 m from the edges of the greenhouse.
Cans were opened by making a hole with a hammer and nail through the plastic. The hole in the plastic was immediately covered with adhesive tape. During soil fumigation the greenhouse openings were closed. The plastic foil was removed 4 days after fumigation.

Soil sampling began the day after the removal of the plastic foil, that is on the 5^{th} day after fumigation, and was completed within 21 days later. A soil sampler of 1.50 m length with a cylinder of a 15 cm diameter and a 23 cm height was used. The soil sampling was done in a 25 cm depth from five sites whose location is also shown in figure 1. Soil samples of approximately 100 g, were placed in plastic containers of high density and were analyzed within the same day.

For the determination of methyl bromide, 4 g soil were placed in a glass vial of 20 ml and were eluted in 10 ml of carbon disulfide (CS_2) solution. The analysis was done by gas chromatography. Instruments and conditions were as follows:
Gas chromatograph: SRI model 8610
Detector: Flame Ionization (FID)
Column: Capillary (0.53 mm X 25 m), OV-1, with 60-80 mesh
Oven Temperature: 45° C
Carrier gas: Nitrogen (N_2) at flow rate of 15 ml/min
The detection limit was 1 ng of methyl bromide and the recovery from fortified samples was 90 %.

For the determination of bromide ion a 50 g of soil sample was dried for eight hours in a furnace at 130 °C. The analysis was performed according to Gordts (1979) by thin layer chromatography under the following conditions:
Chromatographic plate: glass preheated (silica gel 60 (Merck) 0.25 mm thickness).
Spraying reagents: 0.1 % Na- fluorescein in 50 : 50 ethanol - distilled water and 50 : 50 of acetic acid and 30 % H_2O_2
Developing solvent: Acetone - 1 butanol - concentrated NH_3 - distilled water (65:20: 10:5).

After the development of the plate, red spots appeared. The red spots were transferred in a 10 ml screw capped glass vial with distilled water and centrifuged

in 3000 rpm for 3 min. Finally the supernatant liquid was placed in 1 x 1 ml cuvettes and measured in a spectrophotometer at 521 nm (Gordts 1979).
The detection limit was 10 μg/g bromide ion per soil.

RESULTS AND DISCUSSION

Under the prescribed gas chromatography conditions methyl bromide was eluted in 4,3 min.

Table 1. Mean concentration of methyl bromide in soil of each sampling site of the greenhouse surface in a depth of 25 cm (μg /g)

Day	Site A	Site B	Site C	Site D	Site E
5	30.0	32.0	32.0	30.0	30.0
6	17.5	17.0	18.0	18.0	16.0
7	13.0	14.0	13.0	14.0	15.0
9	12.0	13.0	11.0	10.0	11.6
12	8.2	8.0	6.0	7.0	9.0
16	5.2	4.5	4.8	4.5	4.7
18	*	*	*	*	*
19	*	*	*	*	*
21	*	*	*	*	*

* no detectable

In Table 1, the methyl bromide concentration is presented in each sampling site. The values are the mean concentrations of three measurements in each site.

As is shown from the results, methyl bromide in spite of its volatility remained in the ground up to 16 days after fumigation. It has been reported that methyl bromide could be detected up to 3 weeks after fumigation in different soil types, the highest content being found in upper layers (0-40 cm) (WHO 1995).

The maximum and minimum concentration of methyl bromide for all the sampling sites was detected on the fifth and sixteenth day after fumigation respectively. On the sixth day, concentration was reduced approximately to 43 % in all sites. The reduction of the methyl bromide concentration, continued at a rate of about 20 % (from the 6^{th} to 7^{th} day and from the 7^{th} to 9^{th} day) and 30 % (9^{th} to 12^{th} day and from the 12^{th} to 16^{th} day) after fumigation. As was witnessed the concentrations of methyl bromide in each sampling site were of no significant difference.

The procedure mentioned above was applied for the qualitative and quantitative concentration of bromide ion. Soil samples from sampling sites were also analyzed before the application of methyl bromide. No bromide ion was detected. It is stated that the natural concentration of bromide in soil, is less than 10 μg/g, depending on the type of soil and geographical situation (Hoffman et al 1974). It is also reported that the measured bromide concentration in greenhouse soil before the application of methyl bromide was approximately 5 μg/g (Fallico et al 1991).

Table 2. Mean concentration of bromide ion in soil from each sampling site of the greenhouse surface, at a 25 cm depth (μg/g).

Day	Site A	Site B	Site C	Site D	Site E
5	52	52	52	52	52
6	65	65	65	65	65
7	70	70	69	70	69
9	82	78	84	80	98
12	119	119	110	100	100
16	122	122	123	120	118
18	127	127	127	128	125
19	135	133	140	139	132
21	140	139	142	142	140

In Table 2, the bromide ion concentration is presented in each sampling site. The values are the mean concentrations of three sample measurements in each site. As is shown, bromide ion concentration between several sampling sites did not differ significantly. The minimum and the maximum concentrations for all sampling sites were 52 μg/g and 142 μg/g, on the 9th and 21st day after fumigation respectively.

It is reported that two months after greenhouse soil treatment with methyl bromide, bromide levels of over 30 μg/g were measured (Fallico et al 1991). In an other report, a year after fumigation with 70-80 g methyl bromide / m^3 (the recommended dosage is 85 g/m^3), bromide values of 0.2 -11.5 mg/Kg were measured in soil in 30 cm depth (WHO 1995).

The sampling was completed within 21 days after the application of methyl bromide. The rate of bromide ion concentration increased, ranged between 25,6 % and 4 %. The actual increase is of 21.5, 6.58, 17.8, 36.58, 8.93, 4.09, 7.08 and 3.67 % in periods from the 5^{th} to the 6^{th}, 6^{th} to 7^{th}, 7^{th} to 9^{th}, 9^{th} to 12^{th}, 12^{th} to 16^{th}

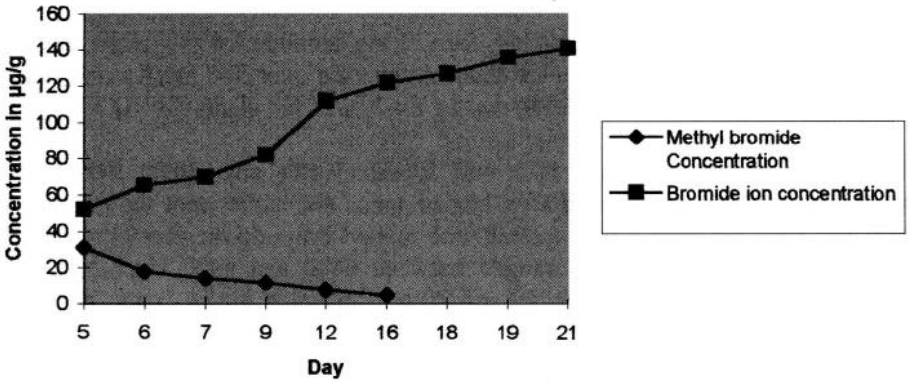

Figure 2. Mean concentration of methyl bromide and bromide ion in soil samples from each sampling site in the same day

day after fumigation. From the results, it is estimated that the rate of bromide ion increase per day ranged from 2.3 to 21 %. It is reported that the rate of methyl bromide degradation into bromide ion per day is 6-14 % at 20 °C (Wegman 1981).

Figure 2, reveals the mean concentration of methyl bromide and bromide ion in soil samples. The values are the mean concentration of the samples from each site in the same day.

The soil of the experimental greenhouse was clay of 45 % porosity and specific gravity equal to 2.25 g/ml. The organic material was 1.70 g % and the pH was 6.8. Relative humidity and temperature of the soil during sampling was measured by soil sensors connected to a computer. Relative humidity and temperature values ranged from 50 % to 20 % and 22 °C to 25 °C respectively. The maximum and the minimum values for both parameters were measured in the 5th and 21st day of fumigation respectively.

The use of methyl bromide in agriculture poses a problem related to the presence of bromide ion in plants with a consequence to public health through the food chain. According to FAO/WHO the level causing no toxicological effect is 9 mg bromide / Kg body weight per day, and the acceptable daily intake (ADI) is 1 mg/Kg body weight (WHO 1995).

Levels of bromide ions could be elevated in foods of plant origin grown in soils fumigated with methyl bromide. The amount of residues depends on the type of foodstuff (Star-rat and Bond 1990). It is reported that after soil fumigation with methyl bromide, bromide ion levels were 20-51 mg/Kg in tomatoes, 8-44 mg/Kg in string beans, 3-27 mg/Kg in peppers, 6 - 165 mg/Kg in cucumbers. Lettuce

grown on unfumigated soil contained less than 10 mg bromide ion /Kg while most lettuces grown on fumigated soil were found to contain over 500 mg/Kg and the concentration of bromide ion was 2000 mg/Kg for 2 % of the plants (WHO 1995).

Application of methyl bromide as a soil fumigant can also affect animals. Bromide intoxication was reported after horses, goats and cattle were fed oat hay that that had been cut from a field treated with methyl bromide the previous year. The bromide residues of the hay ranged between 6800 and 8400 mg/Kg. The estimated mean daily intake was 9, 49 and 70 g of bromide ion in goats, horses and cattle respectively. Signs of intoxication reported included lethargy, weakness and ataxia (Knight et al 1977).

Concentration of methyl bromide and bromide ion were also measured in irrigation, drainage and surface water around greenhouses, after soil fumigation with methyl bromide (Wegman 1981). Bromide ion was measured in Greece in 1998 in potable mineral water bottled by various companies, and as a result the authorities decided on an accepted level of 10 mg/l.
Methyl bromide has a significant place as a fumigant because of its efficiency. The general population may be exposed to residues of bromide in food because of soil treatment with methyl bromide.

Acknowledgements. This project was a part of Ph.D Thesis. I would like to thank professor Th. Lekkas rector of the University of Aegean and professor B. Nathanael who, apart from professor H. Tsoukali, were my supervisor scientific committee.

REFERENCES

Fallico R and Ferrante M (1991) Exposure to inorganic bromides from greenhouse crops where bromide was applied for soil fumigation. Zent. Hyg Umweltmed 191 : 555 –562

Gordts LA, Vendezande A, Van Cauwenberge P, Van Haver W (1979) Quantitative Thin-Layer Chromatographic Determination of Br residues in Crops after soil treatment by methyl bromide. Agr and Food Chem 27 : 132 – 134

Hoffman GM, Malkomes HP (1974) Bromides residues in vegetable crops after soil fumigation with methyl bromide. Agric Environ 1 : 321 - 328

Knight HD, Costner GC (1977) Bromide intoxication of horses, goats and cattle. J Vet Med Assoc 171 : 446-448

Starrat AN, Bond EJ (1990) Methylation of food commodities during fumigation with methyl bromide. In : Environmental Health Criteria Methyl Bromide World Health Organization, Geneva, p 117

Wegman RCC, Greve PA , De Heer H, Hamaker PH (1981) Methyl Bromide and

Bromide ion in drainage water after leaching of glasshouse soils. Water Air Soil Pollution, 16 : 3-11
WHO (1995), Environmental Health Criteria Methyl Bromide World Health Organization, Geneva