

**METHYL BROMIDE MEASUREMENTS ON 10 AND 11 JUNE 2000,
CONDUCTED DURING FUMIGATION AND DE-GASSING OF STACKED
PALLETS OF COCOA BEANS IN TWO WAREHOUSES IN AMSTERDAM**

On behalf of Mr W. Veldman, VROM Inspectorate *regio Zuid-West*

CC

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1. INTRODUCTION

Fumigation with methyl bromide is used to control and prevent insect infestations. During fumigation, the objects to be fumigated are subjected to a prescribed methyl bromide concentration that differs according to the product group. De-gassing then takes place by means of ventilation, forced or otherwise. During both fumigation and de-gassing, a safety zone of 100 m is established around the object being fumigated. This distance is not based on measured gas concentrations, but has been calculated.

Some fumigation companies have indicated that this distance could be reduced, for example when treating product groups for which a low dosage of methyl bromide is effective. The distance within which harmful concentrations of methyl bromide could occur is expected to decline with a reduction of the dosage.

No measurement data are available which can confirm or disprove the assertions of the fumigation companies. The Environmental Inspectorate therefore would like to have a general idea about which concentrations are measurable outside the fumigated objects, both during fumigation and de-gassing, and has therefore requested the RIVM-IEM to conduct a series of indicative measurements with different types of fumigations.

The following report concerns a fumigation procedure conducted on stacked pallets of cocoa beans in a warehouse on 10 and 11 June 2000.

2. AIM

To ascertain methyl bromide concentrations, both during fumigation and while de-gassing the object, within the safety zone surrounding the fumigation object.

3. IMPLEMENTATION

3.1 FUMIGATION

On 10 June 2000, stacked pallets of cocoa beans were fumigated in two warehouses of the Fa. Schutte in Amsterdam. To this end, the stacked pallets with bales of cocoa beans were covered with a "tent" of plastic film, which reached to the floor with some overlap. To ensure an airtight seal with the floor, water-filled tubes were placed on top of the plastic film. These stacked pallets of goods covered with an airtight "tent" are called *klampen* in Dutch. These tents were then fumigated by making a hole in the film through which a hose was inserted; the opening around the hose was sealed and then methyl bromide gas was injected into the tent using a vaporizer (see Figure 1).

Twenty-four hours after the desired gas concentration (methyl bromide) was reached inside the tents, the plastic film was cut open near the floor so the remaining methyl bromide could disperse into the volume of air in the warehouse. The roof vents of the warehouse were also opened. The fumigation supervisor expected that the methyl bromide gas would leave the warehouse via the upward draft caused by open roof vents. Finally, the remaining film on top of the stacked pallets was removed. After the warehouse was declared gas-free, the plastic film was collected and disposed of. This disposal takes place without using respiratory protection.

Table 1 lists the times at which the various activities took place.

Table 1: Activities of the fumigation company

Date	Time	Activities
10/6/00	13:30 h	Begin fumigation in warehouse section 6
11/6/00	13:30 h	Cut open tents + ventilate warehouse
11/6/00	18:30 h	Concentration < 0.25 ppm reached (according to PID meter)

Figure 1: Fumigation of stacked pallets of cocoa beans



3.2 MEASUREMENTS

The measurements had to be carried out at varying distances from the fumigation objects. The fumigation objects were the tent-covered stacks (*klampen*); because they are theoretically sealed airtight, no harmful concentrations of methyl bromide should occur in the warehouse. Nevertheless, the safety zone generally begins at the building(front) in which the tent-covered stacks are located.

To provide a control for this study, measurement equipment was also placed within the warehouse (warehouse 7A).

Figure 3 shows the measurement and sampling locations, while Table 2 lists which type of measurement/sampling took place at which location.

3.2.1 Photovac 10SPlus

Instrument: Photovac 10SPlus portable gas chromatograph, equipped with a CPSil5 column, temperature 40°C, flow 12 ml/min

The Photovac 10SPlus portable gas chromatograph was placed at location A in warehouse 7A. During fumigation and de-gassing, this instrument took in an air sample every 10 minutes which was analyzed by means of gas chromatography. The analysis results are shown in Appendix 1. Measurements with the Photovac were conducted only in the warehouse.

3.2.2 Active charcoal tubes

Materials: SKC petroleum charcoal tubes, part A & part B

During the fumigation phase, samples were taken using active charcoal tubes (petroleum charcoal) with a constant flow pump at location A. The sampling was stopped briefly before cutting open the tents, and new active charcoal tubes were installed at location A. In addition, active charcoal tubes were installed at locations B, C, and D. During the de-gassing, samples were taken with these new sets of charcoal tubes approximately every four hours.

3.2.3 Adsorption badges.

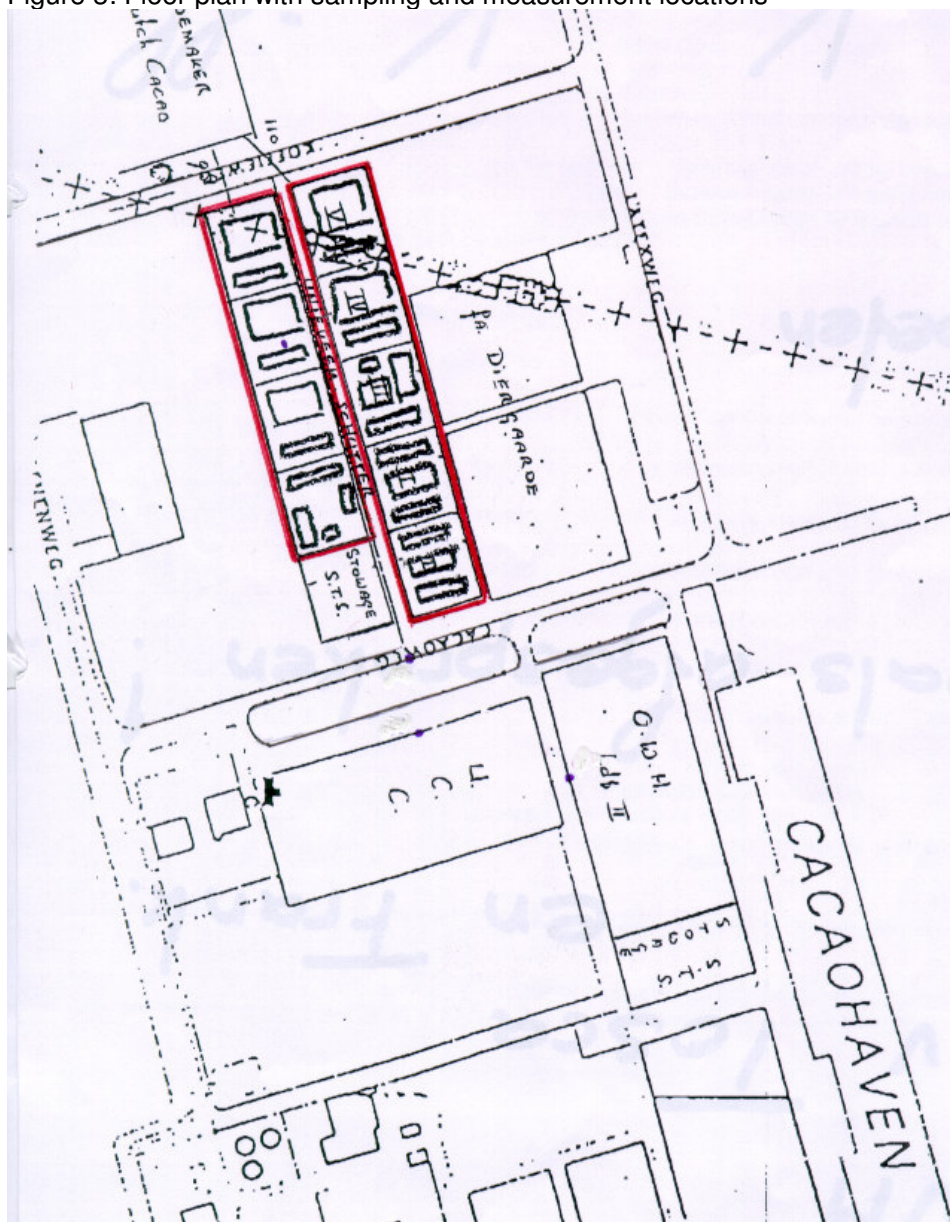
Materials: 3M 3500 organic vapour monitor (see Figure 2).

Figure 2: 3M 3500 Organic Vapour Monitor (adsorption badges)



During the fumigation phase, adsorption badges were exposed to the air at locations A, B, C and D. Before the tents were cut open, the badges at all locations were replaced by new badges, which were then exposed to the outside air during the de-gassing phase for approximately 4 hours.

Figure 3: Floor plan with sampling and measurement locations



The fumigated sections of the warehouses are outlined in red.

Table 2: type of measurement/sampling at each location

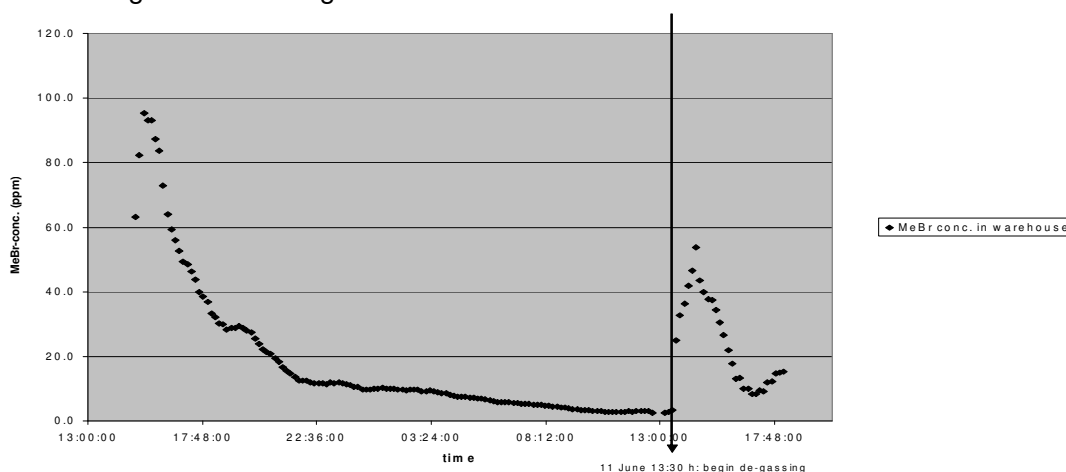
Location	Phase	Photovac measurement	Activated charcoal tube sampling	Adsorption badge exposure
A	Fumigation	yes	yes	yes
	De-gassing	yes	yes	yes
B	Fumigation	no	no	yes
	De-gassing	no	yes	yes
C	Fumigation	no	no	yes
	De-gassing	no	yes	yes
D	Fumigation	no	no	yes
	De-gassing	no	yes	yes

4. RESULTS

4.1 PHOTOVAC MEASUREMENTS

In Figure 4, the results of the Photovac 10SPlus are shown on a graph, converted to hourly average values for both the fumigation phase and the de-gassing phase.

Figure 4: Concentration of methyl bromide in warehouse with tent-covered stacks of cocoa beans during and after fumigation



4.2 ACTIVE CHARCOAL TUBES AND ADSORPTION BADGES

Table 3 shows the results of the sampling with active charcoal tubes and adsorption badges.

Table 3: Results of sampling with active charcoal tubes and exposure of adsorption badges

Situation	Location	Distance to fumigation object (m)	Concentration Methyl bromide (mg/m ³)	
			Active charcoal tube	Badge
Fumigation	A	0	1.00	0.2
	B	20		< D.L.
	C	50		< D.L.
	D	100		< D.L.
De-gassing	A	0	27	10
	B	20	0.5	0.02
	C	50	0.08	< D.L.
	D	100	0.04	< D.L.

< D.L. = below the detection limit

5. DISCUSSION

5.1 DURING FUMIGATION

The results of the measurements with the Photovac 10SPlus showed that the plastic tents were not airtight: immediately after the methyl bromide was injected, the gas concentration in the warehouse increased rapidly. After this, the concentration fell to approximately 2 ppm during the period that the plastic tents were filled with gas.

The leakage was also shown from the fact that measurable average concentrations of methyl bromide were detected by the active charcoal tubes and absorption badges during the fumigation period in the warehouse.

Outside the warehouse, none of the three measurement points with adsorption badges showed methyl bromide in concentrations above the limit of detection.

5.2 DURING DE-GASSING

After the plastic tents were cut open, the methyl bromide concentration in the air in the warehouse, which had stabilized during the fumigation period, rose to a peak concentration of approximately 50 ppm ($\approx 200 \text{ mg/m}^3$).

During the first four to five hours after the end of fumigation, the samples taken with active charcoal tubes and adsorption badges both showed methyl bromide concentrations well above the MAC value for this substance ($= 1 \text{ mg/m}^3$).

During the first four hours of the de-gassing period, measurable concentrations of methyl bromide were detected in the air outside the warehouse at all three measurement points B, C and D, but were below the MAC value for this substance. These measurements were conducted with active charcoal tubes.

The samples taken with adsorption badges showed methyl bromide in the air only at the 20 m distance (measurement point B); at locations C and D, no measurable concentrations of methyl bromide in the air could be detected with the adsorption badges.

5.3 GENERAL ASPECTS

The results obtained from samples taken with the adsorption badges and the active charcoal tubes that were taken at the same location during the same time period show significant differences, where the concentrations of methyl bromide in the air shown by the badges are lower or much lower than those obtained with the active charcoal tubes. It is possible that methyl bromide is adsorbed less onto active carbon during passive sampling than during active sampling; passive sampling could therefore lead to an underestimation of the methyl bromide concentration in the air.

6. CONCLUSIONS

The method used in this study to seal the fumigation tents did not result in a gas-tight enclosure of the fumigation objects.

During the fumigation period, the methyl bromide concentration in the warehouse outside the fumigation tents was above the MAC value for methyl bromide. The MAC value is used as a statutory limit value for methyl bromide; outside the safety zone, this value must never be exceeded.

During the fumigation period, no methyl bromide was shown in measurable concentrations at a 20 m distance, 50 m distance and 100 m distance from the warehouses, measured using adsorption badges.

During the de-gassing of the warehouse, methyl bromide was shown to be present in measurable concentration in the air outside the warehouse. These concentrations were lower than the MAC value for methyl bromide.

Based on the present study, the safety zone of 100 m, which is in force from the beginning of fumigation until the warehouse is declared to be gas-free after de-gassing, does not have to be expanded. However, reducing the safety zone also appears to be unjustified in view of the fact that measurable concentrations of methyl bromide were shown in the air during the de-gassing period at 100 m from the fumigation object.

7. RECOMMENDATIONS

Active charcoal tubes appeared to give a better result than passive sampling on adsorption badges. We recommend that both sampling methods for methyl bromide again be compared with each other during a follow-up study on fumigation.

After the fumigation object is declared gas-free, the plastic film is removed from the stacked bales of cocoa beans. Because methyl bromide gas is heavier than air, there is a significant risk that methyl bromide has collected under the plastic film and that this gas will be released when the film is removed. We recommend that a study be conducted about the extent to which workers are exposed to methyl bromide during this phase of fumigation, when respiratory protection aids are not used.