RIVM report 609021041/2007

The dispersal of fumigants around ocean shipping containers

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This study was conducted on behalf of the VROM Inspectorate as part of the project M/609021 'Support for enforcement VROM Inspectorate'.

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Abstract

The dispersal of fumigants around ocean shipping containers

The National Institute for Public Health and the Environment advises establishing a restricted area around containers treated with detergents. No one should be allowed to enter this area without breath protection equipment. A restricted area of 50 metres around the containers should be established for large amounts of detergents, such as up to 5 kg methyl bromide or vikane. When smaller amounts (up to 1 kg for methyl bromide) are applied or occur, an area of 20 metres will be sufficient. Within these distances, concentrations may occur that are harmful to human health. This advice has been given to the Dutch Inspectorate of Housing, Spatial Planning and the Environment in response to the request made by the Inspectorate to simplify the existing rules on distances that vary depending on the substance and the use.

High concentrations of detergents exist in containers for export to foreign countries. The recommended distances should be applied for the use of methyl bromide, phosphine and vikane. Containers under the present rules are only treated with these detergents when the receiving country requires such a treatment. In the Netherlands the use of these substances is only applicable under strict regulations. The restricted areas should be established at the start of the treatment because of possible leakage from the containers. Before shipment of the containers they are cleared of the detergents by opening the doors and letting the detergents evaporate. This process causes concentrations around the containers that are harmful to human health.

Import containers may also contain detergents. In practice, other detergents than the three used for export containers are found in import containers in the Dutch harbours. Since the concentrations in import containers are substantially lower, a distance of 20 metres will be sufficient to protect people from hazardous concentrations due to leakage or evaporation.

Another recommendation is to prohibit (starting) the release of the detergents under calm weather conditions. High concentrations may then occur for some time and at longer distances.

Key words: methyl bromide, phosphine, vikane, pest control, containers

Rapport in het kort

De verspreiding van gassingsmiddelen rond containers

Het RIVM adviseert de VROM-Inspectie om een zone rondom ‘gegaste’ havencontainers te creëren waar alleen mensen met adembeschermingsapparatuur mogen komen. Voor grote hoeveelheden ontsmettingsmiddelen (tot 5 kg voor de stoffen methylbromide en sulfurylfluoride) geldt een afstand van 50 meter tot de container. Bij kleinere hoeveelheden (tot 1 kg) volstaat 20 meter. Binnen deze zones zijn de concentraties van vrijkomende gassen schadelijk voor de volksgezondheid. Aanleiding voor dit advies was de wens de regelgeving over ontgassing te vereenvoudigen en zo de handhaving te verbeteren.

De hoge concentraties komen meestal voor bij exportcontainers. Die moeten soms voor vertrek met bestrijdingsmiddelen worden behandeld om de inhoud of het pakkingsmateriaal te ontsmetten (gassen). De maatregel geldt vanaf het moment waarop het gassen aanvangt. De ontstane gassen worden vervolgens verwijderd voordat de containers de haven verlaten (ontgassen).

De genoemde afstanden zijn gebaseerd op de concentraties die in Nederland bij het gassen en ontgassen vrijkomen. Als internationale voorschriften het gebruik van methylbromide, fosfine en sulfurylfluoride voorschrijven, gelden in Nederland wettelijke gebruiksvoorschriften.

In importcontainers, die soms nog resten ontsmettingsmiddelen bevatten, zijn de concentraties lager en volstaat een afstand van ten minste 20 meter, aldus het advies. Deze kleinere hoeveelheden zijn nog hoog genoeg om de gezondheid schade toe te brengen, zodat enige afstand tot de containers is geboden. Kort na aanvang van de ontgassing kunnen namelijk relatief hoge concentraties voorkomen. Bovendien kunnen gassen lekken uit de nog gesloten containers, waardoor in de nabijheid hoge concentraties circuleren.

Een andere aanbeveling is de ontgassing bij windstil weer te verbieden. Dit voorkomt dat de gassen in hoge concentraties op het terrein blijven hangen.

Dit onderzoek is uitgevoerd in opdracht van de VROM-Inspectie.

Trefwoorden: gassing, ontgassing, importcontainers, exportcontainers, methylbromide, sulfurylfluoride, fosfine, afstandseis, gebruiksvoorschriften

Contents

Summary

On behalf of the VROM Inspectorate, the RIVM conducted a study into the concentrations of fumigants that occur near containers undergoing degassing. Degassing means that containers which have been treated with gaseous pesticides are opened so that these gases can 'blow away'. The study focused on determining the distance at which the concentrations of these gases were still above the norm that is used to protect the population against hazardous effects. Research was conducted on export containers and import containers.

In the research involving *export containers,* two sets of three empty containers were fumigated with methyl bromide, phosphine and sulfuryl fluoride using the normal method for export containers. After at least 24 hours, the degassing procedure began by opening the doors. The concentrations of the fumigants were measured downwind. The majority of the fumigants appeared to be released soon after opening the containers, leading to high concentrations downwind that lasted for several minutes.

The measurement results were supplemented with model calculations to determine the distance at which the concentrations exceeded a norm. Concentrations around the limit value can occur up to 20 metres away from the container (phosphine). At a 50 metre distance, the concentrations were no more than 20% of the norm.

With *import containers*, the quantities in the containers were lower, but there were also more uncertainties, such as uncertainties about the specific gases that were used.

From these data, the RIVM has derived separation distances from containers that are undergoing degassing; within these distances, people should not be allowed without personal protection equipment (respiratory protection). The RIVM recommends basing the separation distance on the quantity and type of substance used in the containers. The specific recommendations are:

- 20 metres if the quantity of substances in the containers to be degassed is no more than 1 kg of methyl bromide or sulfuryl fluoride or 10 g of phosphine;
- 50 metres if the quantity of decontamination substances in the containers to be degassed is no more than 5 kg of methyl bromide or sulfuryl fluoride, or up to 60 g of phosphine;
- For larger quantities, degassing can take place only in consultation with the VROM Inspectorate.

These separation distances are in force until the containers are free of the hazardous substances used for fumigation (are declared to be 'gas free').

These conclusions apply during weather with good possibilities for dispersal. The RIVM recommends that degassing be forbidden during other types of weather, for example when wind speeds are lower than 0.5 metre per second (wind speed 0 on the Beaufort scale in the current weather report).

Abbreviations

ATSDR	Agency for Toxic Substances and Disease Registry, see http://www.atsdr.cdc.gov/
CTB	Board for the Authorisation of Pesticides
ECT	Europe Container Terminals
GC-MS	Gas chromatograph - Mass spectrometer
MAC value	Maximum acceptable concentration of a substance at the workplace. The MAC value is defined as the maximum concentration of a gas, fume or aerosol of a substance in the air at the workplace that is generally not harmful to the health of the employees or their offspring if inhaled during the period of employment.
MeBr	Methyl bromide
MPR	Maximum Permissible Risk
NIOSH	National Institute for Occupational Health and Safety
OLM	Online monitoring apparatus
PH_3	Phosphine
PHAST	Process Hazard Analysis Software Tool
RIVM	National Institute for Public Health and the Environment
SO_2F_2	Sulfuryl fluoride (Vikane)
VI	VROM Inspectorate
VROM	The Ministry of Housing, Spatial Planning and the Environment

1. Introduction

1.1 Importance of the research

In some cases, *containers with export goods* must be treated against spoilage or contamination of goods, pallets and/or wood packaging material. Some countries require treatment with pesticides such as methyl bromide or phosphine. If containers in the Netherlands must be fumigated, then stringent regulations apply to protect employees and the population against exposure to excessive concentrations of these hazardous substances. For example, there are demands on the required distance between the containers to be fumigated and houses or other buildings occupied by people. These separation distance requirements are based largely on model calculations. Dispersion models have a high level of uncertainty if used for calculating dispersion across a short distance from a source and around obstacles.

For fumigated *import containers*, there are no separation distance requirements in force for the degassing procedure. Import containers that have been fumigated or are suspected of being fumigated are degassed – preferably at a safe location and using a safe method. In practice, import containers are fumigated with a wide range of substances and sometimes with mixtures of substances.

Consequently, little factual data are available about the concentrations of substances that occur surrounding containers in practice; therefore it can not be determined whether the separation distance requirements currently used in practice are adequate.

1.2 Assigned task and research aims

The VROM Inspectorate strives to acquire more understanding of the concentrations that can actually occur surrounding containers during the degassing of both export and import containers. With this understanding, the VROM Inspectorate can determine whether the current guidelines for separation distance offer sufficient protection for public health. The VROM Inspectorate requested the RIVM to establish a measurement programme that provides insight into the concentrations occurring at varying distances during the degassing of export and import containers.

1.3 Research questions

The RIVM has formulated the following research questions:

– with respect to export containers:

1. What concentrations of fumigants occur, especially downwind, of export containers that are being degassed?
2. Are there observable differences in the dispersion of different fumigants?
3. How do the concentrations relate to the available and applicable norms for the general public?

4. At which distances do the concentrations fall below these norms, given the weather conditions during the measurements?
5. Are the results that were collected under the practical conditions during the research usable for making an estimate of the situation during other weather conditions and for a representative part of the time?

– with respect to import containers:

6. What concentrations of fumigants occur in the situation in practice on the terrain of European Container Terminals (ECT) in the vicinity of import containers that are being degassed?
7. How do these concentrations relate to the available and applicable norms for the exposure of the public?
8. At which distances are the concentrations below these norms, given the weather conditions during the measurements?
9. Are the results that were collected under the corresponding practical conditions usable for making an estimate of the situation during other weather conditions and for a representative part of the time?
10. Are the results of the various sampling and analysis techniques for methyl bromide sufficiently comparable with each other?

– with respect to containers undergoing degassing:

11. What separation distance requirements can be established so that the norms for the exposure of the public are satisfied?

1.4 Outline of the report

This report concerns practical experiments about the dispersal of fumigants around containers undergoing degassing. In chapter 2, currently known data are collected, such as the results from previous studies, the regulations concerning fumigation and the applicable norms for fumigants. Chapter 3 contains a description of the available measurement methods for the various fumigants. The experimental design is described in chapter 4, the results in chapter 5 and an interpretation of these results in chapter 6. The final chapter presents the conclusions.

2. Existing data

2.1 Research on fumigation

In the past, the RIVM has conducted various studies concerning fumigated containers.

In 2000, research was conducted into the concentrations of methyl bromide surrounding a fumigated container and into the leak tightness of containers (Knol, 2000a and 2000b). In this study into the concentrations of methyl bromide surrounding a container undergoing degassing, two containers were degassed (dosage 45 gm^{-3}). The progression in the methyl bromide concentrations in the containers was determined by periodically measuring the concentrations in the closed container during a 24-hour period. In addition, the concentration of methyl bromide was measured at distances of 10 m and 50 m from the container. In one container, 5% of the fumigated quantity was observed after 24 hours, in the other container this was still 100%. During degassing, the methyl bromide concentrations for one of the containers at 10 m exceeded the MAC value, and at 50 m were below the MAC value.

In the study of the leak tightness of containers (Knol, 2000b), two randomly chosen containers were fumigated with methyl bromide, where a dosage of 45 g m^{-3} was used. The concentrations in the containers were measured during a 24-hour period.
Results of this study were as follows:
- the methyl bromide gas introduced into the container became completely mixed only several hours after fumigation began;
- in one container the concentrations decreased to 62% of the original concentration, and in the other container to 4%;
- the containers, which superficially appeared to be identical, therefore had differing air change rates.

Other research has shown that goods inside fumigated containers can absorb the fumigants and can continue to emit these substances for a long time (Knol, 2005a and 2005b).

2.2 Public health norms for fumigants

In terms of exposure and effects, the situation concerning containers undergoing degassing involves the exposure of the public for periods ranging from several minutes to several hours, in addition to the fact that workers can also be exposed. Table 1 includes the available norms for the fumigants investigated. This table includes the directly available norms in addition to other norms such as intervention values (concerning exposure during calamities. Source: VROM Inspectorate, 2006), MAC values (to protect workers during their entire working lives) or chronic or sub-chronic norms).

For methyl bromide, there is an available norm which stipulates the maximum exposure of the public for short periods. This concerns an hourly average concentration of 10 mg m^{-3}. This value is based on acute effects for the public, and is therefore very useful in this study as a reference value.

For chloropicrine, 1, 2-dichloroethane and sulfuryl fluoride, no norms are available concerning the exposure of the public during periods ranging from several hours to minutes for normal working conditions. The only norms available are intervention values for calamities and working safety norms (MAC values).

For phosphine, the best available norm is that for 24-hour exposure.

Table 1 Summary of public health norms

Substance	Concentration		Norms to protect public health
	ppm	mg m^{-3}	
Methyl bromide	2.5	10	Maximum hourly average for the public (see Appendix 2)
	25	100	Information guideline[1] (intervention value 1 hour)
	50	200	Alarm limit value[1] (intervention value, 1 hour)
	250	1000	Life-threatening limit value[1] (intervention value, 1 hour)
			Other, less useable norms:
	0.075	0.3	subchronic exposure (Knol, 2005b)
	0.02	0.1	chronic exposure (MTR[3])
	0.25	1	MAC value[4] (with skin indication)
Chloropicrine	0.03	0.2	Information guideline[1] (intervention value 1 hour)
	0.3	2	Alarm limit value[1] (intervention value, 1 hour)
	1.5	10	Life-threatening limit value[1] (intervention value, 1 hour)
			Other, less useable norms:
	0.1	0.7	MAC value
1,2-dichloroethane	40	200	Information guideline (intervention value 1 hour)
	120	500	Information guideline (intervention value 1 hour)
	480	2000	Life-threatening limit value (intervention value, 1 hour)
			Other, less useable norms:
	0.01	0.05	Chronic limit value (Baars et al., 2001)
	1.5	7	MAC value
	3	14	MAC value, 15 minute average
Sulfuryl fluoride	3	12	Short-term limit value for bystanders (EU, 2006)
			Other, less useable norms:
	5	20	MAC value[2]
Phosphine	0.01	0.02	Limit value for 24-hour exposure (RIVM, 2000)
	0.01	0.017	Limit value for 2-week exposure (RIVM, 2000)
	1	2	Alarm limit value[1] (intervention value, 1 hour)
	7	10	Life-threatening limit value[1] (intervention value, 1 hour)
			Other, less useable norms:
	0.0002	0.00025	Chronic limit value (RIVM, 2000)
	0.1	0.14	MAC value
	0.2	0.28	MAC value, 15 minute average

[1] The intervention values are values that are used in case of calamities; therefore they do not apply as accepted exposure concentrations during regular activities (VROM Inspectorate, 2006).
[2] The Health Council of the Netherlands has proposed lowering the MAC value to 2.4 ppm (10 mg m^{-3}) (Gezondheidsraad, 2004).
[3] Maximum Permissible Risk (VROM, 1999).
[4] Maximum acceptable concentration of a substance at the workplace.

2.3 Existing legislation and regulations

In the statutory usage regulations for methyl bromide (CTB, 2006), there are three separation distance requirements with respect to the space within which no people are allowed during the entire period of fumigation and degassing. The standard requirement is 100 m. There are two exceptions to this rule:

- When fumigating containers, all activities in the open air on company terrain between 10m and 100 m of the fumigation location are permitted as long as the concentration of methyl bromide remains below the statutory limit value of 0.25 ppm (1 mg m^{-3}).
- If less than 25 kg of methyl bromide is used for fumigation, the separation distance requirement of 100 m is reduced to 50 m at locations where such a fumigation does not take place more frequently than six times per year.

For fumigation with phosphine, there is also a separation distance requirement of 100 m (CTB, 2006). This distance may be reduced to 50 m if less than 1 kg of phosphine is used at locations where such fumigation does not take place more than six times per year.

For fumigation with sulfuryl fluoride, this substance is currently not approved (CTB, 2006). A request for approval is being considered. The applicant has proposed a distance separation requirement of 10 m for all fumigations with this substance; this is indicated as a safe distance by the applicant.

3. Measurement methods

3.1 Different measurement methods used

In this study, different measurement methods were used for measuring the concentrations of the various fumigants. Table 2 summarizes the methods used.

Table 2 Summary of measurement methods used

Sampling method	Component	Analysis method
Badges	Methyl bromide	GC-MS
Tedlar bags	Methyl bromide, chloropicrine, 1,2-dichloroethane, phosphine, sulfuryl difluoride	GC-MS
Canisters	Methyl bromide, chloropicrine, 1,2-dichloroethane, phosphine, sulfuryl difluoride	GC-MS
Active charcoal tubes	Methyl bromide, 1,2-dichloroethane	GC-MS
Sensors	Methyl bromide	Sensors

In this chapter, the methods will be described. For methyl bromide, various measurement methods are available. An additional aim was to compare the various methods with each other.

3.2 Badges in combination with GC-MS analysis

With the aid of 3M3500 Organic Vapor Monitors ('badges'), passive sampling can be conducted. This technique provides an average concentration over time for volatile organic components. The main advantage of this measurement method is that the badges are easy to use: they are light, handy in use and do not require any power source for the sampling.

A badge is constructed of a bed of activated charcoal, which is covered with a semi-permeable membrane. The membrane ensures that the various gases contact the activated charcoal with a known rate of diffusion. The sampling duration can range from several hours to several weeks.

Figure 1 A badge for passive sampling

Processing and analysing the samples
Processing begins by adding 1.6 ml cold dichloromethane to the badge. The extraction takes 30 minutes, during which the badge is regularly agitated. A portion of the extract is then placed in a 2 ml vial (a flask with a rubber stop), and analysis is conducted using GC-MS.

Characteristics
The characteristics of this technique are the following: time averaged (hours to weeks) sampling, easy to use, suitable for ascertaining concentrations on the order of μg m^{-3} to mg m^{-3}.

3.3 Tedlar bags in combination with GC-MS analysis

A Tedlar bag is a bag with an 0.7 litre capacity made of inert material; with a manually operated pump, it can be used to collect air samples. The air sample can be analysed with GC-MS for various substances, including most volatile hydrocarbons.

Sampling takes place within several seconds; consequently, the ascertained values are instantaneous concentrations.

Figure 2 A Vac-U-tube with a Tedlar bag

Analysis
Of the air that is present in the Tedlar bag, 50 ml is pumped onto a cold trap, after which the samples are analysed by means of thermal desorption with GC-MS.

Characteristics
The characteristics of this technique are the following:
- instantaneous and easy sampling, suitable for ascertaining concentrations on the order of μg m^{-3} to mg m^{-3};
- no pre-treatment of samples is required;
- suitable for ascertaining concentrations for a wide range of substances if the concentrations do not vary strongly (for example in a closed space).

3.4 Canisters in combination with GC-MS analysis

Canisters are metal balls that can be depressurized; the metal on the inside is provided with a non-absorbent coating. By opening a valve on the canister, air is pulled in until the pressure is equalized. A restrictor on the intake tube was used for this experiment which was adjusted so that the sampling lasted about two hours. A nanometer shows whether there is still low pressure in the canister.
If the canister is placed on the ground, the sampling height is about 35 cm.

Figure 3 A canister

Analysis
The analysis is conducted in the same way as with a Tedlar bag

Characteristics
The characteristics of this technique are the following:
- time-averaged and easy sampling, suitable for ascertaining concentrations on the order of µg m^{-3} to mg m^{-3};
- no pre-treatment of the sample is required.

3.5 Active charcoal tubes in combination with GC-MS analysis

Figure 4 Active charcoal tube with pump

Sampling with active charcoal tubes was conducted according to the NIOSH method 2520 with SKC-226-38-02 Petroleum charcoal-set tubes. These tubes are especially suitable for methyl bromide. By using Side-kick pumps, air was pulled through the active charcoal tubes for two hours, initially at a flow rate of 1.000 ml min^{-1} and later at 50 ml min^{-1}. The relative humidity was higher than 50%, but it was not necessary to place a dryer in front of the samplers.

The characteristics of this technique are the following:
- time-averaged and easy sampling;
- suitable for ascertaining concentrations on the order of µg m^{-3} to mg m^{-3}.

Processing and analysing the samples
A loaded active charcoal tube is opened, and the contents are emptied entirely into a 10 ml vial. depending on the quantity of charcoal (400 mg or 200 mg) 4 or 2 ml cold dichloromethane is added, respectively, after which the vial is sealed with a crimp cap. After 30 minutes, during which the vial is regularly agitated, a portion of the fluid is transferred to a 2 ml vial; analysis then takes place using GC-MS.

3.6 Sensors

In the present study, the results of the measurements with the above mentioned apparatus are compared with the results of the online monitoring apparatus (hereinafter to be called the 'OLM unit'). This apparatus was tested by ECT regarding its suitability for measuring high concentrations of fumigants, with an eye towards monitoring the area surrounding fumigated containers.
The measurements were conducted by the supplier.

Figure 5 An OLM unit near containers (photograph: Comon Invent)

One of the OLM units used here comprised four different semiconductor sensors. These sensors respond – non-specifically – to low concentrations of oxidizing and/or reducing gases. However, by using multiple semiconductor sensors together and a type of 'fingerprint' of substances, the concentration of a specific substance can be determined to a certain extent. The OLM units used were 'characterized' in this way for methyl bromide.

Characteristics
The characteristics of this measurement method are the following:
- a continuous measurement method with continuous indication of the concentration;
- rapid response to concentration changes;
- intended as a monitoring instrument;
- sensitive for other substances.

4. Project approach

4.1 Project approach in brief

The measurement programme was conducted with the aim of acquiring insight into the concentrations that occur during degassing of containers.

The research was conducted with *actively fumigated containers*, where the fumigation took place in a comparable fashion to *export containers in the Netherlands*. This study was conducted in a controlled fashion to the extent that the conditions could be influenced. In the study, three containers were fumigated with methyl bromide, three with phosphine and three with sulfuryl fluoride (Vikane) in accordance with the method used in practice. A certified fumigation company conducted these fumigations. During the degassing, concentrations of the fumigants were determined at various distances up to approximately 50 metres downwind. In order to create a worst case situation, we chose to fumigate three containers simultaneously with the same substance; the distance to where the concentrations were detected downwind, would be – under comparable weather conditions – a maximum dispersal distance. A possibly larger dispersal distance would occur only under other weather conditions.

The research with *import containers* was conducted in the situation in actual practice. During seven weeks, the time-averaged methyl bromide concentrations in a fumigation area [1] at ECT were ascertained, and on various days other measurements were conducted in order to acquire a picture of the dispersal around the containers. The research focused on the concentrations of known fumigants such as methyl bromide, phosphine, sulfuryl fluoride, 1,2-dichloroethane and chloropicrine.

4.2 Experimental design for degassing actively fumigated containers

Three sets of containers were placed on the terrain of the ECT company, which is located on the Maasvlakte near Rotterdam. These containers were rented by the VROM Inspectorate and were the type of containers normally used. The containers were empty and therefore did not contain any goods. These containers were fumigated with methyl bromide, sulfuryl fluoride and phosphine according to the standard operational method by certified fumigation companies (Holland Fumigation for methyl bromide and phosphine, SGS-Sanitec for sulfuryl fluoride). The fumigations with phosphine took place on 9 and 20 August 2006; the fumigations with methyl bromide and sulfuryl fluoride took place on 16 and 28 August 2006. The intended concentrations for each container concerned 48 g m^{-3} for methyl bromide and 65 g m^{-3} for sulfuryl fluoride. In the containers that were fumigated with phosphine, two ‘cords’

[1] A marked and fenced-off area where containers with these fumigants are degassed in such a way that people cannot be exposed to high concentrations.

Figure 6 Placement of containers in the experiment; the photograph on the left shows three containers; the photograph on the right shows one group of three opened containers.

were placed; 30 g phosphine was formed from each cord. In a 66 m^3 container, this would result in a maximum concentration of 1 g m^{-3}.

On 17 and 30 August 2006, the degassing began. This meant that the degassing began eight days after the fumigation with phosphine, one day after fumigation with methyl bromide and two days after fumigation with sulfuryl fluoride. In the containers that were fumigated with phosphine, air samples were taken on various days in Tedlar bags in order to track the progression of the concentrations in the containers. Preceding the fumigation, measures had been taken so that air samples could be taken from the containers to monitor the phosphine concentrations without having to open the containers.

During the fumigation, various measurement methods (see chapter 3) were used to measure the concentration of the fumigants downwind from the containers. Immediately before the degassing began, air samples were taken from the containers using the Tedlar bags in order to measure the concentrations in the containers. Because high concentrations were sometimes measured at the back of the containers during the first measurement series on 17 August, we began to suspect that some of the containers were leaking. Therefore, during the second measurement series on 30 August, air samples were taken at the back of the containers before the containers were opened. The sampling was conducted with the Vac-U-tube in Tedlar bags; the analysis was conducted with GC-MS.

During the degassing, the concentrations of the various substances were measured downwind. Samples of methyl bromide were taken with badges, active charcoal tubes, canisters and sensors (OLM units). Samples of phosphine and sulfuryl fluoride were taken with canisters. The sampling height ranged from 40 to 60 cm.

The measurement setup, besides being dependent on the number of available apparatus, was especially dependent on the wind direction. On 17 August, a southwest wind was expected; on 30 August a west wind was expected. The measurement setups are shown schematically in Figure 7 and Figure 8. The measurement setup on 17 August was based on an expected southeast wind. While setting up the apparatus, the measurement strategy was modified in accordance with the south wind that was ascertained at the location. During the experiment, the wind turned out to blow directly from the south.

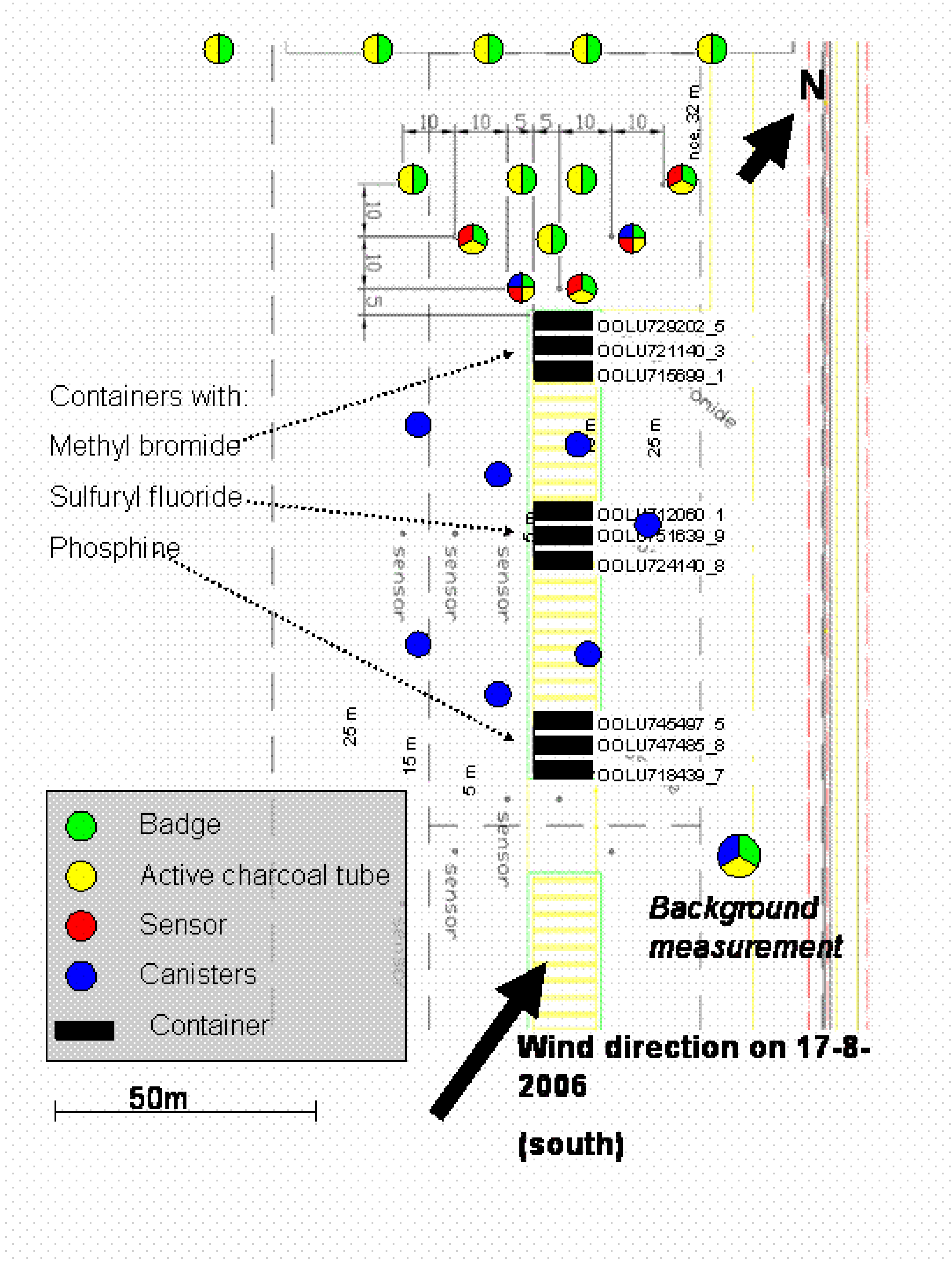


Figure 7 Setup of sampling apparatus on 17 August 2006

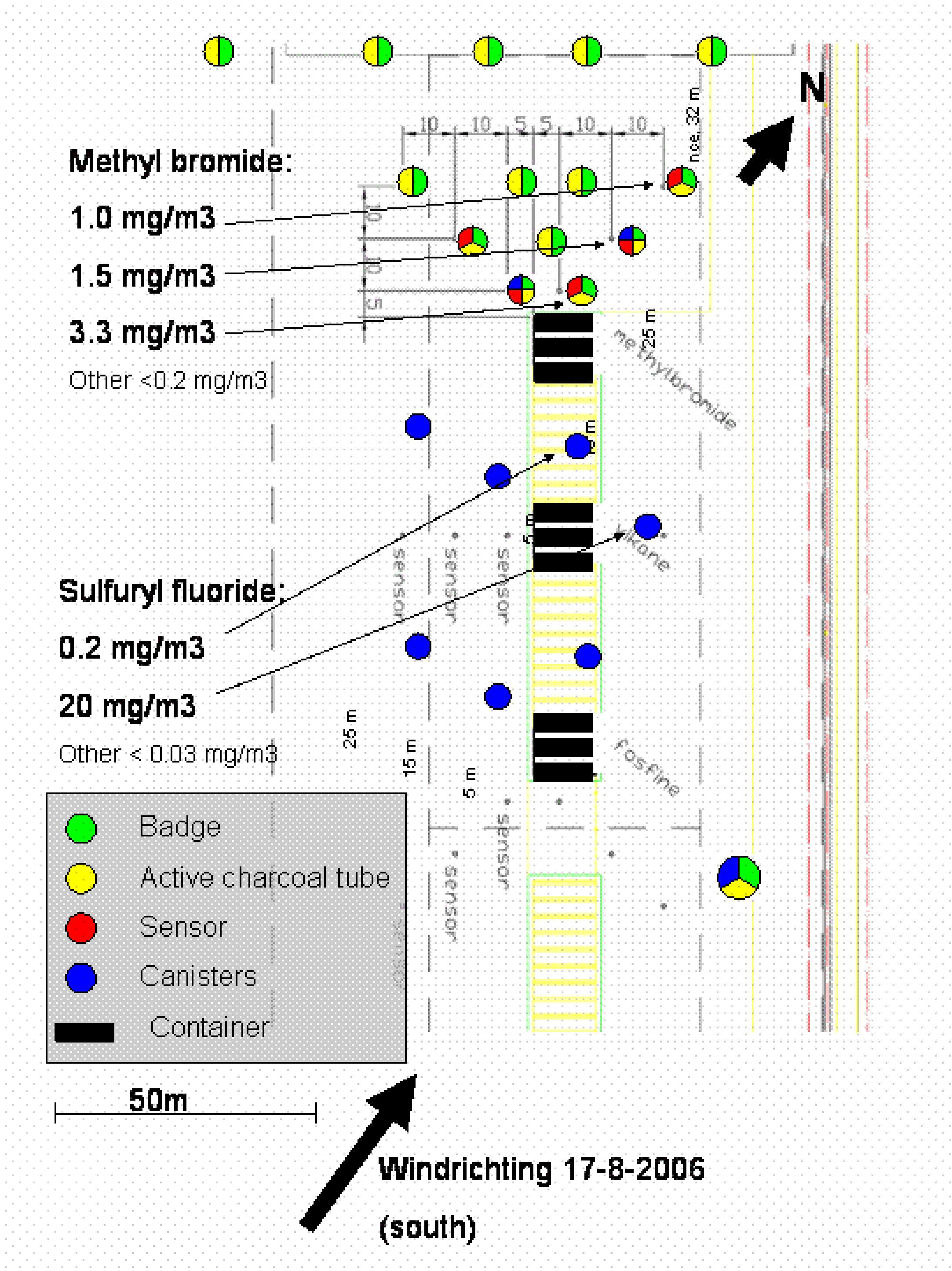


Figure 8 Setup of sampling apparatus on 30 August 2006

4.3 Experimental setup for the import containers study

The study of the import containers was carried out under the practical conditions of containers undergoing degassing as these occurred at the time. The study aimed to ascertain the general dispersal distance surrounding the import containers undergoing degassing. The study was conducted with two different measurement strategies.

Firstly, badges (see section 3.2) were placed at various distances from the containers undergoing degassing. The badges continuously sampled the air around the containers for a period of several weeks and thereby provided a picture of the average concentration of methyl bromide during the measurement period. The placement of the badges is shown in Figure 9. The measurements were conducted during two sequential periods of three and four weeks respectively: 7 through 28 September and 28 September through 27 October 2006. The badges were suspended on the fences around the degassing area (at approximately 150 cm above the ground), on tripods (50 cm above the ground) and on concrete blocks (approximately 40 cm above the ground). Funnel-shaped rain caps were suspended above the badges. This did not affect the sampling. During the sampling period, the VROM Inspectorate kept track of which containers were moved and recorded which fumigants had been used in the containers.

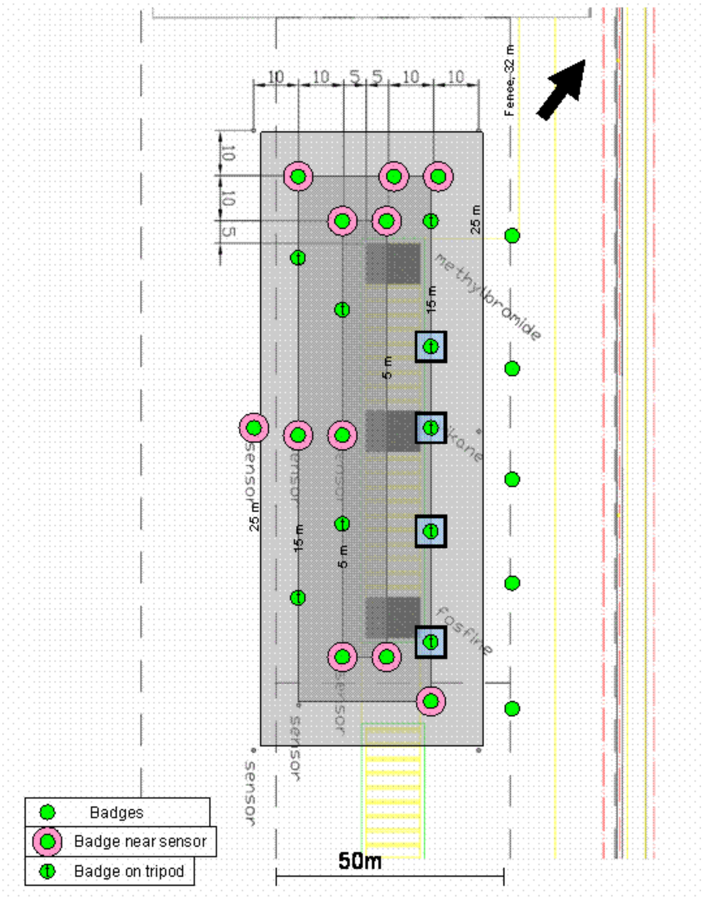


Figure 9 Placement of the badges for measuring the concentration of methyl bromide

Secondly, the concentrations of the fumigants were measured inside the fumigation area. This was done twice downwind from containers (with high concentrations of certain substances) which had just been opened and once with containers that had already been open for a few days. This concerned the following measurements:

- measurements around a container, with high concentrations of chloropicrine, undergoing degassing (19 September 2006);
- measurements around a container, with high concentrations of phosphine, undergoing degassing (30 September 2006). In this 33 m^3 container, phosphide was being transported as a mole control agent. The chemical was not adequately packaged, because high concentrations of phosphine were measured in the container;
- measurements conducted around containers undergoing degassing which had already been open for some time (27 October 2006).

The sampling for chloropicrine on 19 September and phosphine on 30 September was conducted with canisters (the only available time-averaged measurement method for these substances). During the sampling on 27 October, the active charcoal tubes were also used to detect other components. The measurement setups, together with the results, are presented in section 5.2.

5. Results

5.1 Results of the study of actively fumigated containers

5.1.1 Results of the study on 17 August 2006

Figure 10 shows the progression of the measured concentrations of phosphine in the three fumigated containers during the period 10 through 17 August. The fumigation had taken place on 9 August 2006.

The measured concentrations in the containers immediately preceding the opening are shown in Table 3.

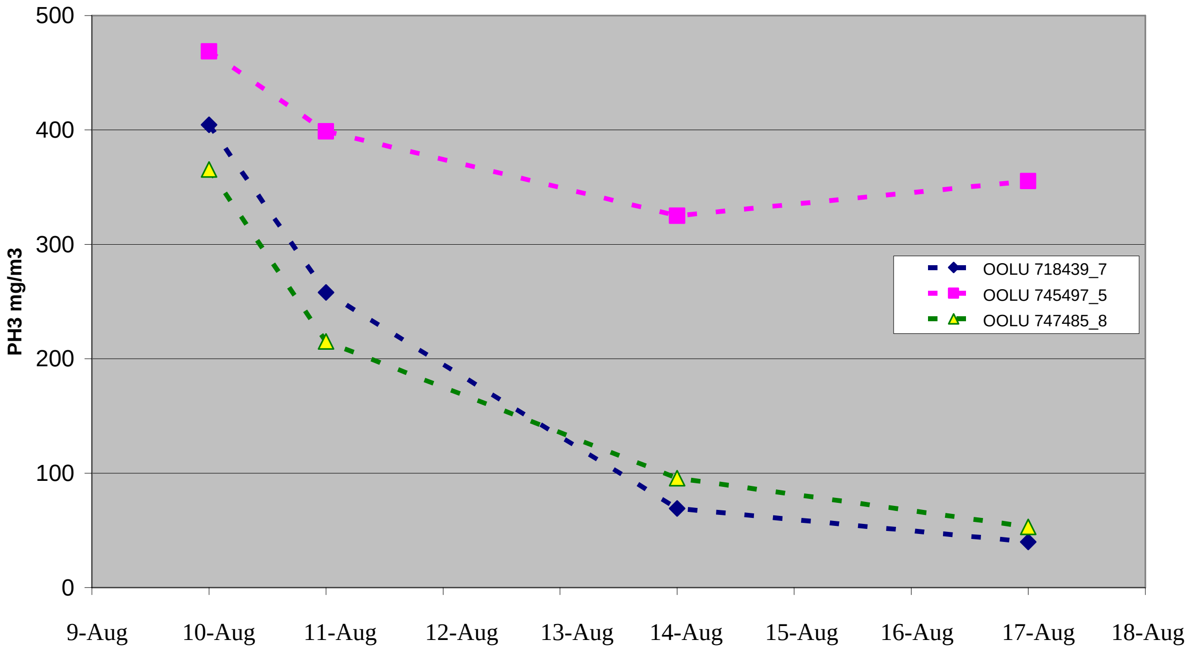


Figure 10 Progression of the measured concentrations of phosphine (in mg m^{-3}) in the fumigated containers, from the fumigation to the degassing, first series, 8-17 August 2006

Table 3 Measured concentrations in the containers on 17 August 2006 immediately before the containers were opened

Fumigated with	Container	Concentration (g m^{-3})	Total quantity in the container (66 m^3)
Methyl bromide	OOLU729202_5	69	4.6 kg
	OOLU721140_3	37	2.4 kg
	OOLU715699_1	34	2.2 kg
Sulfuryl fluoride	OOLU712060_1	28	1.8 kg
	OOLU751639_9	78	5.1 kg
	OOLU724140_8	49	3.2 kg
Phosphine	OOLU745497-5	0.05	3 g
	OOLU747485-8	0.04	3 g
	OOLU718439-7	0.36	24 g

Weather data
The weather conditions were as follows:
Wind direction : south
Wind speed : 3 Bft (4 m s^{-1})
Temperature : 22°C
Precipitation : none
Fractional cloud cover : heavily overcast (6/8 to 8/8).

Results of measurements around the containers
The sampling duration was approximately two hours for all measurement methods. Appendix 1 presents the measurements in table form. The measured concentrations are shown in Figure 11. Only the concentrations above the limit of quantification are shown.

There were three badges on which the concentrations of methyl bromide were measured above the limit of quantification (approximately 0.02 mg m^{-3}). These badges were located on a single line downwind of the containers fumigated with methyl bromide. The measured, two-hour average concentrations ranged from 3 mg m^{-3} at a distance of approximately 10 m to 1 mg m^{-3} at a distance of approximately 35 m.

At the same location where a badge measured a methyl bromide concentration of 1.5 mg m^{-3}, the canister measured a concentration of 2.6 mg m^{-3}. These measurements differ by a factor of 1.7.

None of the measurements with the active charcoal tubes showed concentrations of methyl bromide above the limit of quantification (0.02 mg m^{-3}). This led us to suspect that this was due to the sampling method and that an excessively high suction rate was used. The advantage of a high suction rate is that more of a substance can absorb onto the active charcoal, which reduces the limit of quantification. However, methyl bromide is a volatile component that possibly also desorbs. During tests where known concentrations of methyl bromide were used, it indeed turned out that excessively low concentrations were found at the suction rate of 1,000 ml min^{-1} which was used in the sampling. At a suction rate of 50 ml min^{-1}, the correct concentrations were found. This lower suction rate was used for all other experiments.

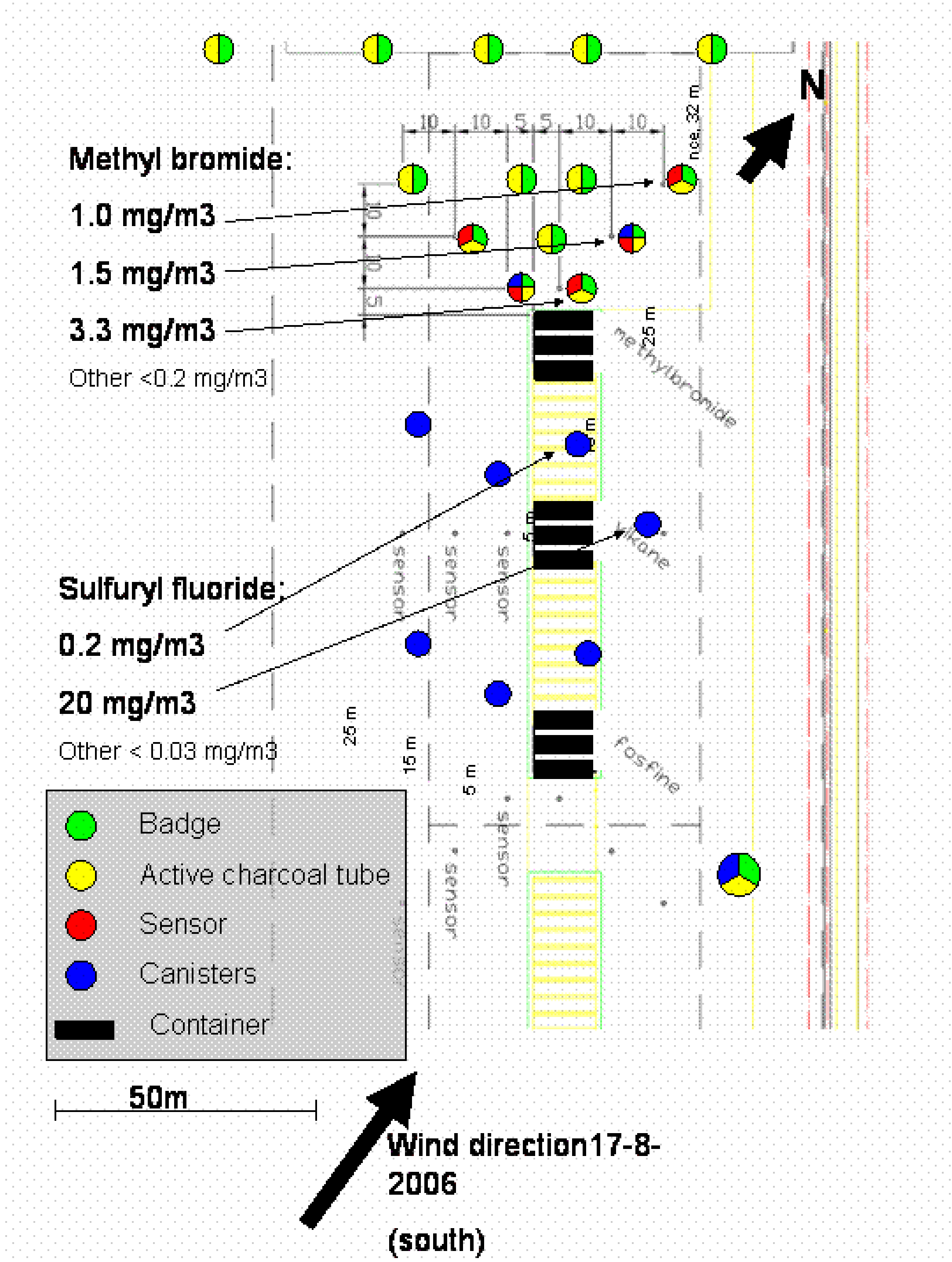


Figure 11 Measured concentrations on 17 August 2006, averaging time two hours, concentrations in mg m^{-3}

With the canisters, two locations downwind from the containers fumigated with sulfuryl fluoride were determined to be above the limit of quantification (approximately 0.02 mg m^{-3}). Immediately behind the containers, a concentration of 20 mg m^{-3} was measured; at approximately 10 m from the open doors of the container, a concentration of 0.2 mg m^{-3} was measured.

No concentrations of phosphine were shown to be above the limit of quantification (about 0.02 mg m^{-3}).

5.1.2 Results of the study on 30 August 2006

Concentrations inside the fumigated containers

The concentrations inside the containers immediately before degassing (opening the doors) are shown in Table 4. For each set of three containers an air sample in a Tedlar bag was taken behind the containers immediately before degassing. This was done because during the first measurement series taken behind the containers that were fumigated with sulfuryl fluoride, high concentrations of this substance were found. These measurements are also shown in Table 4.

Table 4 Measured concentrations in and behind the containers (in g m^{-3} in the containers and mg m^{-3} behind the containers) on 30 August 2006 immediately before opening the containers

Fumigated with	Container	Concentration in the container (g m^{-3})	Total quantity in the container (66 m^3)	Concentration behind the containers (**m**g m^{-3})
Methyl bromide	OOLU729202_5	33	2.2 kg	0.3
	OOLU721140_3	3	0.2 kg	
	OOLU715699_1	59	3.9 kg	
Sulfuryl fluoride	OOLU712060_1	15	1.0 kg	0.4
	OOLU751639_9	36	2.4 kg	
	OOLU724140_8	10	0.7 kg	
Phosphine	OOLU745497_5	0.10	7 g	0
	OOLU747485_8	0.01	1 g	
	OOLU718439_7	0.003	0 g	

Weather data

The weather conditions were as follows:

Wind direction : west
Wind speed : 3 Bft (4 m s^{-1})
Temperature : 16°C
Precipitation : none
Fractional cloud cover : heavily overcast (6/8 to 8/8).

Results of measurements with badges, active charcoal tubes and canisters

The sampling duration was approximately two hours for all measurement methods.
In Appendix 1, all measurement data are presented in table form. Table B.1.3 shows the following:

- the duplicates for the badge measurements differ by no more than 0.1 mg m^{-3};

- the methyl bromide concentrations measured by badges at distances of up to 25 metres are approximately half of the concentrations measured with active charcoal tubes. At the 50 metre distance, the concentrations are comparable;
- the methyl bromide concentrations measured with the canisters are a factor of 4 higher than the concentrations measured with the active charcoal tubes.

Figure 12 shows a map with the measured methyl bromide concentrations that globally correspond with the measurements made with the active charcoal tubes.

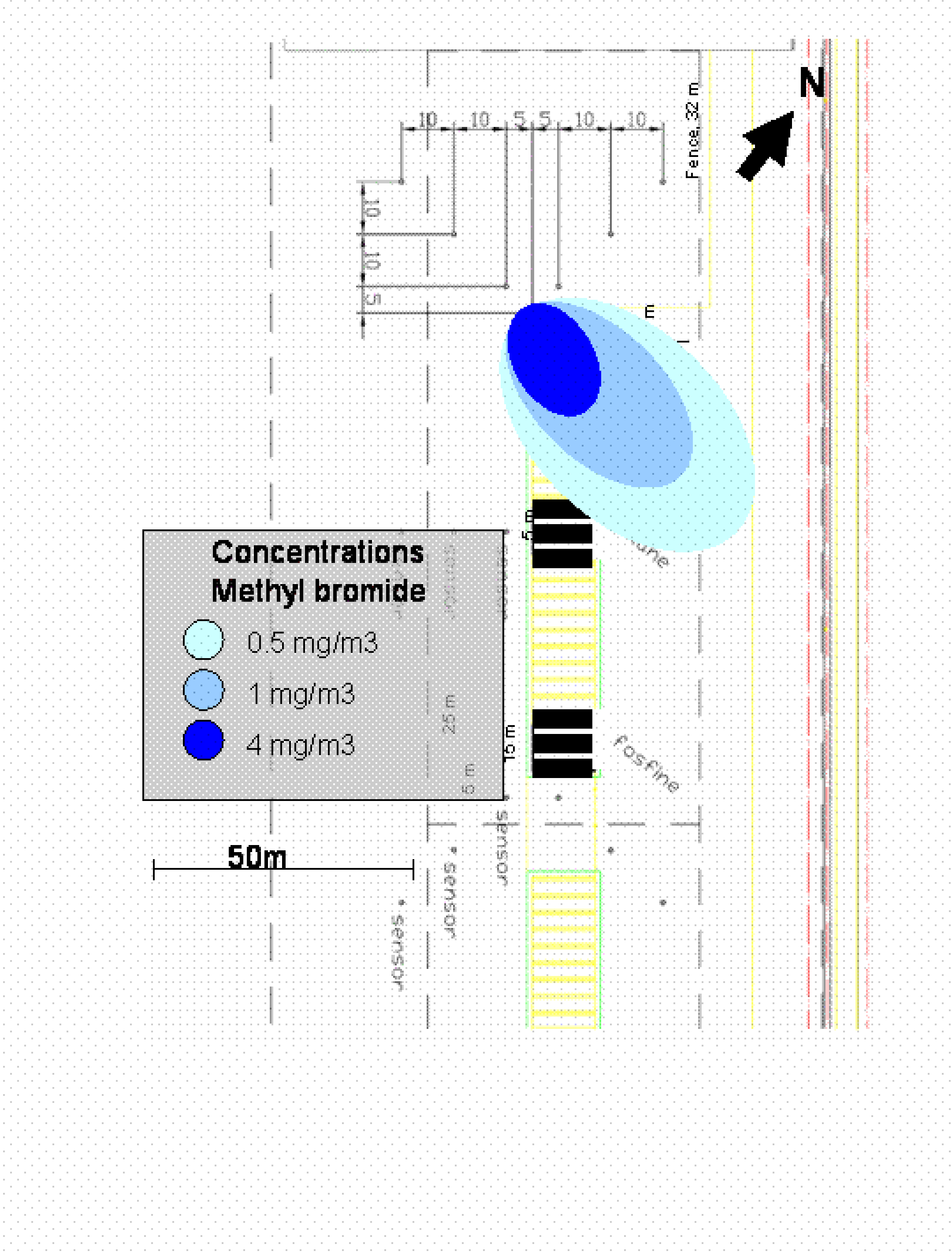


Figure 12 Measured concentrations of methyl bromide (mg m-3) on 30 August 2006, based on the results for the active charcoal tubes, two-hour average concentrations

Based on the concentrations measured with the active charcoal tubes, the following conclusions can be drawn for the two-hour average concentrations:

- up to 15 metres, the concentrations amounted to several mg m^{-3} of methyl bromide;
- at a 50 metre distance, the methyl bromide concentrations were approximately 0.5 mg m^{-3}.

Table 5 summarizes the concentrations of sulfuryl fluoride measured with the canisters. The concentrations are on the order of several mg m^{-3} for two-hour averages. No phosphine concentrations higher than 25 µg m^{-3} were ascertained.

Table 5 Two-hour average sulfuryl fluoride concentrations, measured with canisters (in mg m^{-3})

Distance to container (m)	Concentrations (mg m^{-3})
5	10
20	4
30	2

Results of measurements with OLM units

Figure 13 shows the results from one of the OLM units; the results of all units are shown in Appendix 3 (see section 3.6). The four units for which the results are listed were placed at distances of 5, 10, 15 and 20 metres downwind of the containers that were fumigated with methyl bromide. Figure 13 shows the response of the four sensors that comprise an OLM unit. The figure shows the response of the individual sensors during the time period 12:15 hrs to 12:25 hrs. The following can be seen:

- over time, the responses of the four sensors in an OLM unit are comparable;
- the signal increases rapidly beginning at 12:17 hrs (when the containers were opened) and from 12:19 hrs (2 minutes after opening) declines gradually;
- at 12:25 hrs (8 eight minutes after opening the containers) the signal is still about half of the peak value.

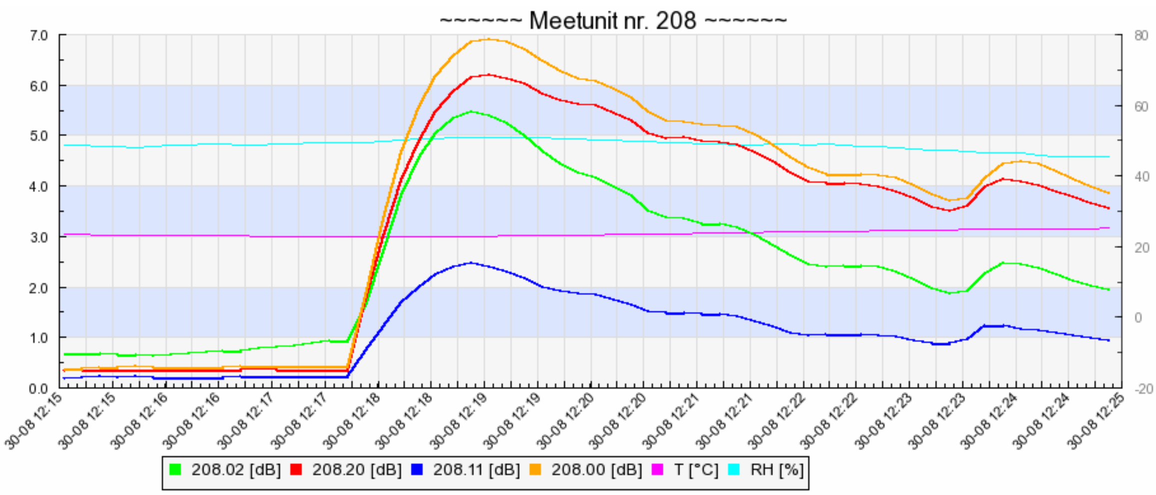


Figure 13 Result of a measurement with an OLM unit on 30 August 2006 (from 12:15 to 12:25 hrs)

Table 6 Methyl bromide concentrations as measured by the OLM units between 12:18 and 12:20 hrs (peak concentrations)

Distance to the container m	**Methyl bromide concentration**	
	mg m^{-3}	ppm
5	800	200
10	140	35
15	100	25
20	28	7

The supplier of the OLM units derived the methyl bromide concentration from the signals between 12:18 and 12:20 hrs (Bootsma, 2006). The results of this derivation are shown in Table 6. Based on these results, a two-hour average concentration from Figure 13 was ascertained by determining the average signal value in a time period, maintaining a linear correlation between signal and concentration as reported in Table 6 and then averaging. In Appendix 3, this procedure is worked out in detail. In this way, a two-hour average concentration at a 5 metre distance from the container was calculated, which was above 50 mg m^{-3}.

Figure B3.1 in Appendix 3 shows how the four OLM units displayed the same progression, where the peak level declines according to the distance to the container. Figure B3.2 in Appendix 3 shows the following:
- there was a rapid response from the sensors around the time the containers were opened (approximately 12:17 hrs);
- one hour after opening the containers, the signal from the sensors was at 20% of the peak value;
- four hours after opening the containers, the sensor signal returned to the initial value.

5.2 Results with the import containers

5.2.1 Results of the study with badges for methyl bromide

During the periods 7 September -28 September and 28 September-27 October 2006, badges were placed around degassing containers to measure the methyl bromide concentrations. The placement of the badges is shown in Figure 9. The badges were placed around the containers at distances ranging from 5 to 50 metres from the containers.

Table 7 provides a summary of the containers that were located in the fumigation area during the study. The VROM Inspectorate took samples from various containers in Tedlar bags to determine the concentration of the fumigants. Various containers that were not sampled stood in the fumigation area for less than a day. It is plausible that these containers did not contain fumigants in relevant quantities.

Table 7 Summary of degassing import containers located in the fumigation area

Container	***Date in***	***Date out***	***Number of days IN***	***Prefix Number***	***Fumigants (before the degassing began)***
1	31-8-2006	4-9-2006	4	SEAU 867270-4	Not relevant, removed before beginning the test
2	29-8-2006	6-9-2006	8	TRIU 592153-0	Not relevant, removed before beginning the test
3	4-9-2006	7-9-2006	3	UESU 456228-3	Not relevant, removed before beginning the test
4	6-9-2006	7-9-2006	1	CLHU 221301-2	Not relevant, removed before beginning the test
5	22-8-2006	14-9-2006	23	CBHU 176013-9	All components <25 ppm
6	13-9-2006	18-9-2006	5	PONU 049401-7	
7	13-9-2006	18-9-2006	5	TGHU 414266-0	
8	13-9-2006	18-9-2006	5	PONU 950569-0	
9	6-9-2006	20-9-2006	14	TTNU 314298-5	Toluene, ethyl benzene and 1-ethyl-3-methyl benzene
10	18-9-2006	20-9-2006	2	HJCU 802551-7	
11	22-9-2006	22-9-2006	0	GATU 123411-0	
12	21-9-2006	25-9-2006	4	XXXX 005647-4	
13	29-8-2006	29-9-2006	31	UESU 463584-1	Benzene and toluene
14	18-9-2006	3-10-2006	15	TCKU 254402-5	
15	18-9-2006	3-10-2006	15	YMLU 497287-4	
16	2-10-2006	5-10-2006	3	XINU 119793-4	
17	2-10-2006	5-10-2006	3	TGHU 41 0828-5	
18	4-10-2006	5-10-2006	1	EMCU 317382-0	
19	9-10-2006	9-10-2006	0	KKFU 159514-9	
20	9-10-2006	9-10-2006	0	KKFU 140337-5	
21	2-10-2006	10-10-2006	8	GSTU 432714-7	No analysis data
22	10-10-2006	14-10-2006	4	TEXU 360046-1	
23	26-9-2006	18-10-2006	22	NIOU 217725-4	No analysis data
24	26-9-2006	18-10-2006	22	CCLU 420627-0	No analysis data
25	19-10-2006	20-10-2006	1	CBHU 182163-5	
26	19-10-2006	20-10-2006	1	TRLU 466588-7	

Container	Date in	Date out	Number of days IN	Prefix Number	Fumigants (before the degassing began)
27	24-10-2006	26-10-2006	2	PONU 760679-9	
28	25-10-2006	26-10-2006	1	MSKU 283745-5	
29	25-10-2006	26-10-2006	1	KNLU 431880-8	
30	25-10-2006	27-10-2006	2	OBOU 602379-3	All components <25 ppm
31	14-9-2006	31-10-2006	47	GLDU 402540-9	Chloromethane (50 mg m^{-3}), methyl bromide (656 mg m^{-3}), tetrachloromethane (0.4 mg m^{-3}), 1,2-dibromoethane (2 mg m^{-3})

The summary shows that only a single container which contained methyl bromide (GLDU 402540-9) was placed in the fumigation area during this period. This container with methyl bromide was placed in the fumigation area on a day with an east-northeast wind. With this wind direction, only a single badge was located downwind from this container at a distance of approximately 10 metres.

Figure 14 provides a summary of the 24-hour average wind direction during this period; Appendix 5 contains a more detailed summary of the weather data. The wind direction varied normally during the study. Consequently, the badges periodically stood downwind of degassing containers.

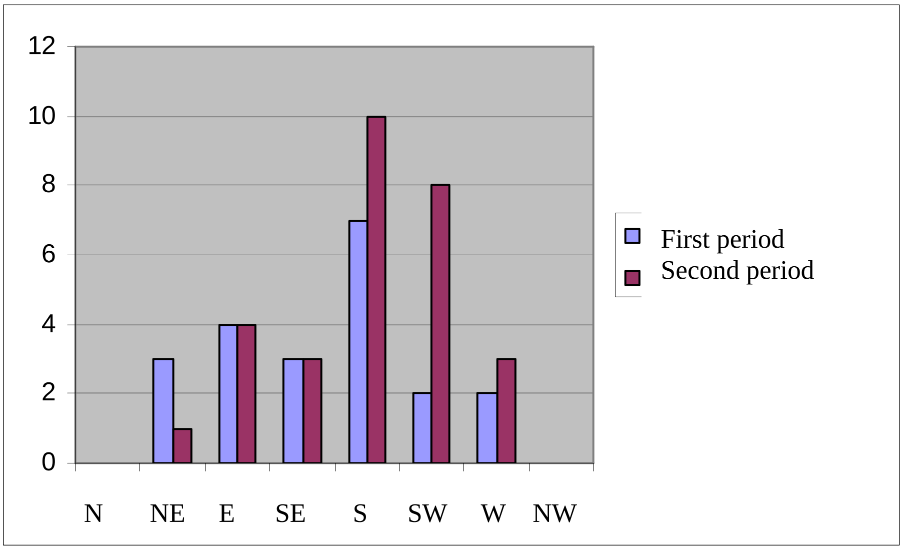


Figure 14 Number of days with a 24-hour average wind direction from the reported compass points during the first measurement period (7 – 28 September) and the second measurement period (29 September – 27 October)

Following analysis of the badges, no badges were found with methyl bromide concentrations above the limit of quantification (0.001 mg m^{-3}). Even with the badge that was located downwind from the container with methyl bromide (GLDU 402540-9), no detectable quantities of methyl bromide could be shown.

5.2.2 Results of the measurements with import containers on 19 September 2006

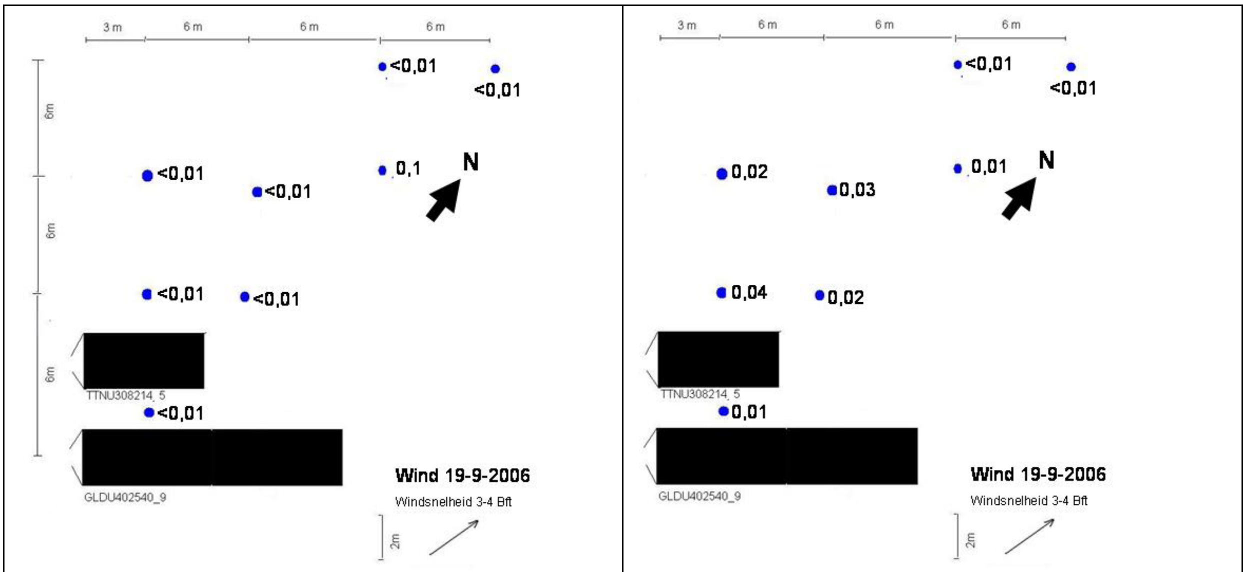
On 19 September 2006, the concentrations of methyl bromide and chloropicrine were measured near two import containers in which these substances were used (sampling with Tedlar bags). The concentrations inside the containers are shown in Table 8.

Table 8 Measured fumigants inside the import containers on 19 September 2006

	Concentrations in the containers (mg m^{-3})		Total quantities in the containers (g)	
	methyl bromide	chloropicrine	methyl bromide	chloropicrine
Container 1 (66 m^3)	54		3.6	
Container 2 (33 m^3)	320	1.5	11	0.05

Weather data during the measurements:
Wind speed : 3 Bft (4 m/s)
Wind direction : SW (225 degrees)
Temperature : 18^{o}C
Precipitation : none
Cloud cover : partly cloudy (4/8)

Figure 15 lists the measured concentrations around the containers. The two-hour average methyl bromide concentrations ranged from 0.01 to 0.04 mg m^{-3} at a distance of up to 25 m. For chloropicrine, at 25 metres a concentration of 0.1 mg m^{-3} was found; at other measuring points, no concentrations of chloropicrine higher than the limit of quantification were ascertained.



Chloropicrine concentrations (mg m^{-3}) | Methyl bromide concentrations (mg m^{-3})

Figure 15 Two-hour average concentrations of chloropicrine and methyl bromide (mg m^{-3}) downwind of degassing import containers

5.2.3 Results of the measurements with import containers on 30 September 2006

On 30 September 2006, the phosphine concentrations around an open import container were measured. This import container (33 m^3) held 56 g phosphine (1.7 g m^{-3}). This large quantity was the result of the product being carried in the container (phosphide), which had begun to leak, resulting in the formation of phosphine. This container was therefore not a fumigated container, but one with a leaking product. The concentration measurements were conducted while repackaging the product in another container. The measurements began immediately before the container was opened.

Weather data during the measurements:

Wind speed	: 3 Bft (4 m/s)
Wind direction	: SSW (200 degrees)
Temperature	: 20 ^oC
Precipitation	: none
Cloud cover	: partly cloudy (3/8)

Figure 16 lists the two-hour average phosphine concentrations. Within a radius of 5 metres, a concentration of more than 2 mg m^{-3} was measured. Up to a distance of 15 to 20 metres, the concentrations amounted to approximately 0.1 mg m^{-3}.

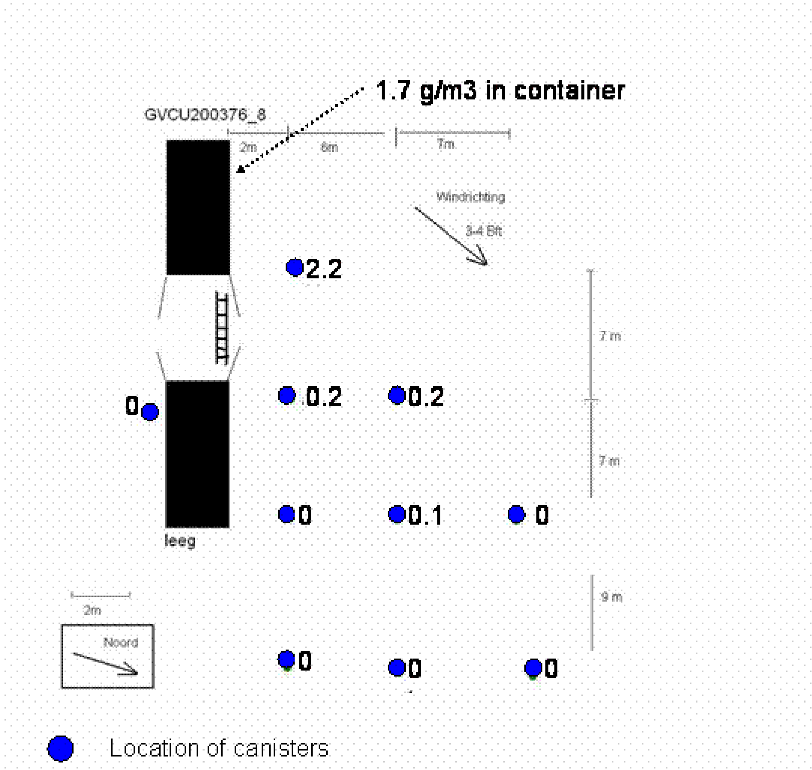


Figure 16 Two-hour average phosphine concentrations (mg m^{-3}) downwind of an open import container on 30 September 2006

5.2.4 Results of the measurements with import containers on 27 October 2006

On 27 October 2006, the concentration of various fumigants was measured around containers undergoing degassing in the fumigation area. The containers had been opened for some time before the measurements began.

Weather data:
Wind speed : 3 Bft (4 m/s)
Wind direction : WSW (245 degrees)
Temperature : 12 ^{o}C
Precipitation : none
Cloud cover : partly cloudy (4/8)

Table 9 provides a summary of the containers that were located in the fumigation area at that time, with the corresponding fumigant.

Figure 17 shows the location of the containers and the measurement apparatus. Canisters and active charcoal tubes were used for the measurements. The distance to the containers was 5 to 25 metres. The measurement duration was two hours. None of the measurement apparatus indicated concentrations for methyl bromide, phosphine, 1,2-dichloroethane and chloropicrine that were above the limit of quantification (approximately 0.02 mg $m^{-3)}$.

Table 9 Containers in the fumigation area and the fumigants encountered

Date in	Date out	Prefix Number	Fumigants encountered
		CRXU457593-2	None
		TRLU315343-8	None
		HJCU769522-1	None
		PONU815353-1	Phosphine
		TTNU308214-5	None
14-9-2006	31-10-2006	GLDU 402540-9	Chloromethane, methyl bromide, tetrachloromethane, 1,2-dibromoethane
		MSKU619728-1	Methyl chloride, methyl bromide

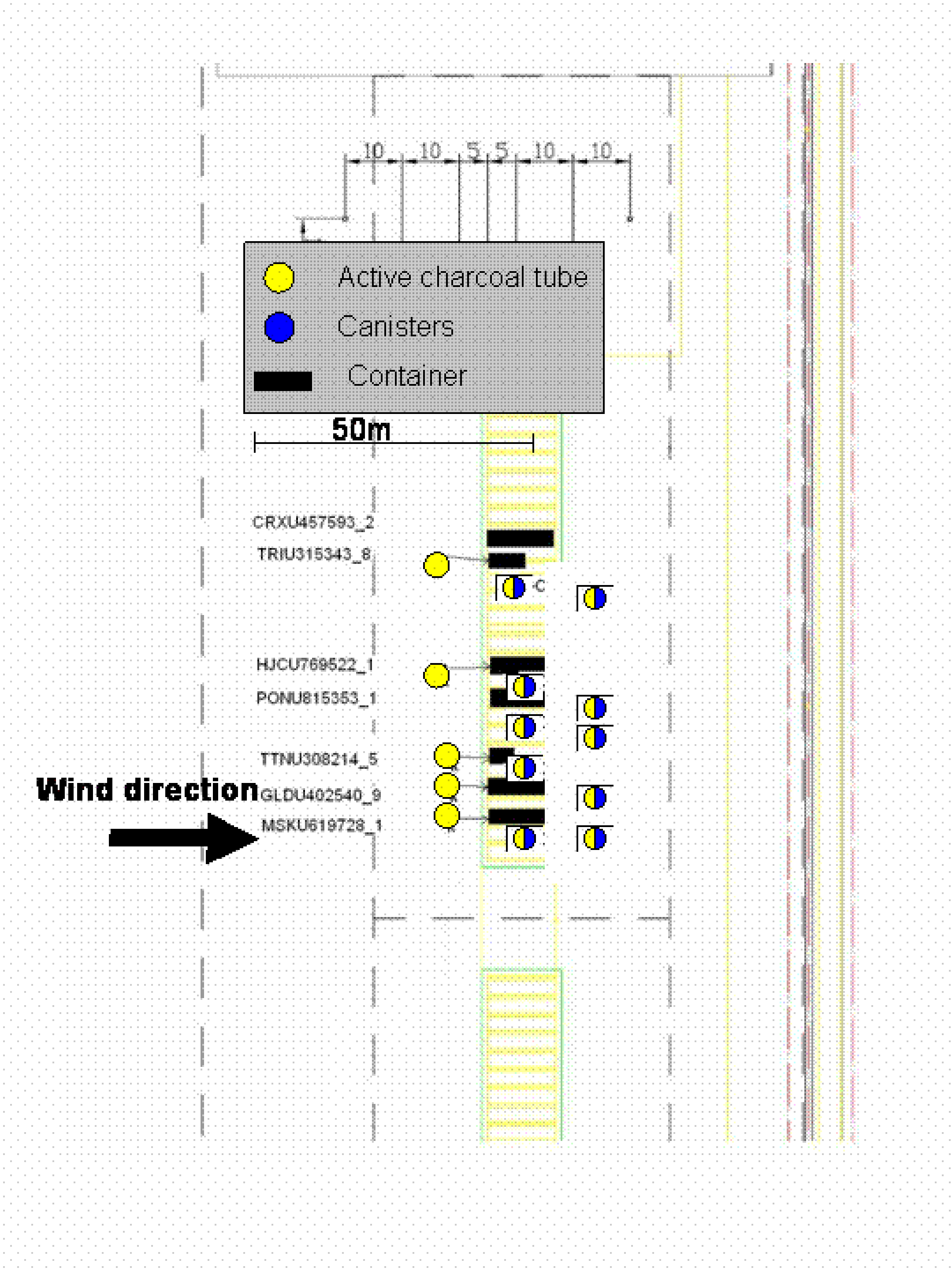


Figure 17 Measurement setup around degassing import containers on 27 October 2006

6. Interpretation and discussion

6.1 Progression of the concentrations of fumigants with the actively fumigated containers

With the containers that were actively fumigated, the fumigation procedures were considered to be successful. On 17 August (the first experiment), the average concentrations were 97% of the fumigation concentration for methyl bromide and 79% for sulfuryl fluoride. On 30 August (the second experiment), these percentages were lower: 66% and 31%, respectively. However, a normal progression of the fumigation concentration during the 24-hour waiting period is not known. There are various possible explanations for the difference between the intended and realized concentrations.

- Fumigation did not take place precisely enough, so that there was a large fluctuation around the intended fumigation concentration. This was also shown from the fact that one of the containers fumigated with methyl bromide had a nearly 50% *higher* concentration - even after standing for one full day - than the intended fumigation concentration;
- Containers can leak, as shown in previous experiments as well as in the present study. Regarding leakage, during the present experiment we noted the following: behind one of the containers that was fumigated with sulfuryl fluoride, concentrations of several mg m^{-3} were ascertained, even though the containers were still filled with gas and were closed.

Most of the fumigations with phosphine were also successful. When the containers were opened, the phosphine concentrations varied from several mg m^{-3} to several hundred mg m^{-3}. With the first fumigation, during the days when the containers were filled with gas, air samples were taken from the container and the phosphine concentration was analyzed. The concentration one day after fumigation was the highest, amounting to 500 mg m^{-3}, or 50% of the maximum concentration to be achieved.

6.2 Comparison of the measurement methods

In the present study, various measurement methods were used in order to compare the results of methods with each other. In the following section, various findings are discussed.

During the first experiment on 17 August, no methyl bromide concentrations were found with the active charcoal tubes at locations where such concentrations were expected and where concentrations ranging far above the limit of quantification were found with the other methods. An investigation into this problem indicated that the absence of methyl bromide in the charcoal tubes was the result of the suction rate that was used. This suction rate was too high, causing the volatile methyl bromide to be insufficiently absorbed onto the active charcoal. After reducing the suction rate, good results were achieved in both the laboratory and in the field.

During the experiment on 17 August (duration of measurement: 2 hours) there were two measurement points at which both badges and canisters were located. At one of these measurement points, the methyl bromide concentrations were below the limit of quantification (the wind direction turned out to be different than expected). At the other measurement point, the concentration on the badge was approximately 60% of the canister concentration (the difference was less than a factor of 2). This is an acceptable result.

During the experiment on 30 August (duration of measurement: 2 hours) various measurements were conducted with badges in duplicate. The results of these measurements were very good: the duplicate measurements differed by no more than 0.1 mg m^{-3}. The agreement with the results of the active charcoal tubes was acceptable. However, the difference with the results of the canisters was large: the measurements of the active charcoal tube and the canister differed by a factor of 4, and therefore from badge to canister there was a difference of a factor of 8. The deviation in this case appeared to be systematic. Methyl bromide is a heavy gas and therefore a higher concentration is expected closer to the ground than higher above the ground. The difference in sampling height - as with the experiment on 17 August - was less than 30 cm. Possibly there was an effect due to the humidity, for which the active charcoal tubes and the badges are susceptible, but which did not affect the sampling of the canisters. No other reasons could be found to explain the differences.

During the measurements in the vicinity of the import containers, badges were suspended for several weeks around the degassing containers. None of the badges showed concentrations above the limit of quantification. This can be largely explained by the fact that during the period of seven weeks, only a single container with a high methyl bromide concentration was placed in the fumigation area. A badge was located at 10 metres downwind from this container. No methyl bromide was found in this badge either. An explanation could be that this badge was not positioned in line with the container at the time when the largest quantities of methyl bromide were released. This could not be determined; the available data did not contain sufficient details.

The available measurements for the OLM units indicate the following:

- immediately after opening the containers, there was a rapid change in the sensor output, which can be related to a change in the methyl bromide concentration;
- based on the estimated concentration for the peak and the graph for the progression of the concentration on 30 August (Figure B3.2), a two-hour average methyl bromide concentration for OLM unit 208 was estimated, which is approximately a factor of 25 higher than the concentration measured by the badges and canister (see Appendix 3).

The sensors appeared to quickly track the changes in concentration. The absolute measured concentration levels deviated strongly from the results with the other methods. The RIVM did not investigate whether the lower measurement range was sufficient to warn for exceedances of relevant norms, and did not look at the response to other components.

6.3 Measured concentrations in relation to distance and norms

6.3.1 Measurements on 17 August 2006

During the experiment on 17 August, the wind direction turned out to behave differently than expected. Therefore, at the experimental setup around the containers fumigated with methyl bromide, concentrations above the limit of quantification were found only at the outermost measurement points. The measured concentrations were in the order of mg m^{-3}. The nearest measurement points to these were approximately 10 m away. This indicates that a narrow plume formed which passed over several measurement points, and passed alongside the other points. The measurement duration was two hours, which means that with a constant emission and a usual variation in wind direction, a portion of the released methyl bromide should also have passed over other measurement points. Our conclusion is that the largest quantity must have been released in a short time period. This conclusion is supported by the measurement data from the OLM units in the experiment on 30 August, which indicated the release of a large quantity from the containers within half an hour after they were opened.

For methyl bromide, the ascertained concentrations could be compared with the public health norm for the maximum hourly average. With the data from the OLM unit – for the experiment on 30 August – it was concluded that the two-hour average concentration was determined for 90% by the concentrations during the first hour (see Appendix 3). This means that the average concentration during the first hour was 1.8 times the two-hour average concentrations. At a distance of approximately 10 metres, this means that there was a one-hour average concentration of 6 mg m^{-3} and at a 30 metre distance, 2 mg m^{-3}. Related to the norm for the maximum hourly average concentrations of 10 mg m^{-3}, this means that these were high concentrations (60% and 20% of the norm, respectively), but they did not exceed the norm.

In comparison with the MAC value, the two-hour average concentrations can be divided by four, because the MAC value applies to eight-hour averages. This means that at a 10 metre distance, the concentration was near the MAC value (1 mg m^{-3}) and at a 30 metre distance it was 25% of the MAC value, without taking account of the small contribution of the remaining six hours.

For sulfuryl fluoride, no public health norms are available. The concentration of sulfuryl fluoride at 10 metres downwind from the container amounted to 0.2 mg m^{-3} and was a factor of 10 below the MAC value (without converting the two-hour average concentration into an eight-hour average concentration). The concentration immediately behind the container (20 mg $m^{-3)}$ was comparable to the MAC value, without taking the duration of exposure into consideration. This high concentration was attributed to a leak in one or more of the containers. If there was a leak, then the ascertained concentration around the container could occur for as long as the container was undergoing fumigation.

The measured phosphine concentrations near the actively fumigated containers were below the norms. The limit of quantification of the measurement method is approximately equal to the public health norm for the 24-hour limit value. The container with leaking phosphide, around which measurements were conducted on 30 September, contained more phosphine than the actively fumigated containers. Around this container, concentrations near the limit value were measured at distances up to 20 metres (see section 6.3.4)

The dilution of the quantity of methyl bromide in the three containers (9.2 kg) at a 10 metre distance downwind amounted to $0.4x10^{-6}$ (see note [2]). For sulfuryl fluoride (10,2 kg) the dilution amounted to $0.02x10^{-6}$ and for phosphine more than $0.7x10^{-6}$ (could not be determined with precision).

6.3.2 Measurements on 30 August 2006

During the second experiment, more measurement data became available because the wind direction behaved as predicted. The dispersal around the containers fumigated with methyl bromide was comparable with the results of the experiment on 17 August: based on the results for the active charcoal tubes, concentrations around 4 mg m^{-3} were found at a distance of approximately 10 m and concentrations around 1 mg m^{-3} were found at a 30 metre distance. The difficulty with this interpretation is that the results for the badges were lower (within acceptable limits) and for the canisters they were higher (by a factor of 4).

The measurements with the OLM units indicate that the degassing took place during a short period: immediately after opening, there was a large peak of several hundred mg m^{-3} (to a distance of 15 metres). After one hour, slightly higher concentrations were still being observed, and after four hours the sensor signal returned to the baseline. Averaged over time, the OLM units indicated higher methyl bromide concentrations than the other measurement methods.

The downwind concentrations of sulfuryl fluoride varied from approximately 10 mg m^{-3} at a 5 metre distance to 2 mg m^{-3} at a 30 metre distance. Also on 30 August, concentrations above 0 were measured behind the closed containers. However, the concentrations were lower than those measured on 17 August (0.4 compared to 20 mg m^{-3}).

Once again, no phosphine concentrations were measured, due to the low quantity in the containers.

The dilution of the quantity of methyl bromide in the three containers (6.3 kg) at a 10 metre distance downwind amounted to $0.6x10^{-6}$ (a concentration of approximately 4 mg m^{-3}). For sulfuryl fluoride (4 kg) the dilution amounted to $2.5x10^{-6}$ and for phosphine more than $2.5x10^{-6}$ (could not be determined with precision).

6.3.3 Measurements with badges around import containers

The measurements with badges of methyl bromide concentrations around the import containers did not provide any usable results. During the seven week period of the study, there was only one container with high methyl bromide concentrations that was placed in the fumigation area. When this container was opened, only a single badge was located more or less downwind. This badge was located at a 10 metre distance. Considering the other experiments, this badge should have shown methyl bromide if it was downwind from the container. However, no methyl bromide was shown. An explanation for this could be that during this degassing, large quantities of methyl bromide were released during a short time and passed alongside the badge.

[2] Mass of 9.2 kg x dilution factor = concentration of 3.3 mg m^{-3}

6.3.4 Measurements on 19 and 30 September 2006 and 27 October 2006

During the experiment on 19 September, methyl bromide concentrations higher than 0.01 mg m^{-3} were ascertained within a radius of 25 metres around the container. These values are below the norms for acute to sub-chronic exposure (see Table 1). The two containers together held approximately 14 g of methyl bromide.

For chloropicrine, a concentration of 0.1 mg m^{-3} was found at 25 metres. The container held approximately 0.1 g of chloropicrine. At smaller distances to the container, no concentrations above the limit of quantification (0.02 mg m^{-3}) were found. The measured concentration is a factor of 10 higher than the measured value for methyl bromide at the same point, even though there was a factor of 100 less chloropicrine in the container than methyl bromide. These results therefore cause the validity of this measurement to be doubted, although no unusual aspects emerged during analysis. If the value is correct, then it is near the 'information guideline value' in the case of calamities, if the measurement duration and the one-hour averaging time with these alarm limit values are taken into account.

During the experiment on 30 September, there was one container which held 56 g phosphine which resulted from a leaking product. In this container, phosphine was formed and released continuously from the packaged phosphide. In this regard, the source differs from those in the other experiments. At a short distance to the container (approximately 5 metres), phosphine concentrations of several mg m^{-3} were measured and at 20 metre, concentrations of approximately 0.1 mg m^{-3}. These values are close to or above the limit value for 24-hour exposure and are on the order of the alarm limit values.

The weather conditions were slightly unstable (Pasquill class B) at the time of measurement. With more neutral or stable weather types, the distance to where high concentrations were measured would increase.

The experiment on 27 October was conducted with containers that had been undergoing degassing for more than one day. In this experiment, no concentrations of various fumigants were ascertained above the limit of quantification. This confirms the impression that the concentrations immediately after opening the container have the greatest effect on the exposure of people in the surroundings.

6.4 Modelling the dispersal

Based on the data from the experiment on 30 August, the dispersal around the containers was modelled. The calculations were conducted with the PHAST (DNV, 2004) model. At the distances relevant to this case (dispersal within 100 metres and around obstacles), calculation models only indicate the order of magnitude of the expected concentrations. These calculations should be used only to provide a general indication of the dispersal. In this case, data about the emission quantities and the meteorology were entered as basis data. We first looked at which modelling parameters for the obstacle produced results that approached the measured results at 10 metres from the containers. We then calculated the dispersal under different weather conditions.

Figure 18 shows the results of the modelled dispersal that corresponded with the results of the actual experiment. The input data are listed in Appendix 4. At a short distance (< 20 metres) from the containers (which are 12 metres long), the modelled concentration is approximately 4 mg m^{-3} (1 ppm). At 80 metres, the concentration is 4 times lower, and at 300 metres, it is 20 times lower.

Figure 19 and Figure 20 show the dispersal for two other weather types: stability class A with a wind speed of 3 m s^{-1} and stability class D with a wind speed of 6 m s^{-1}. More stable weather types were not chosen (stability classes E and F) because the available information indicates that degassing does not take place in the evening and at night. The two other weather types were chosen for the following reasons. Stability class D in combination with this wind speed occurs frequently; stability class A was added in order to also understand the dispersal during unstable conditions.

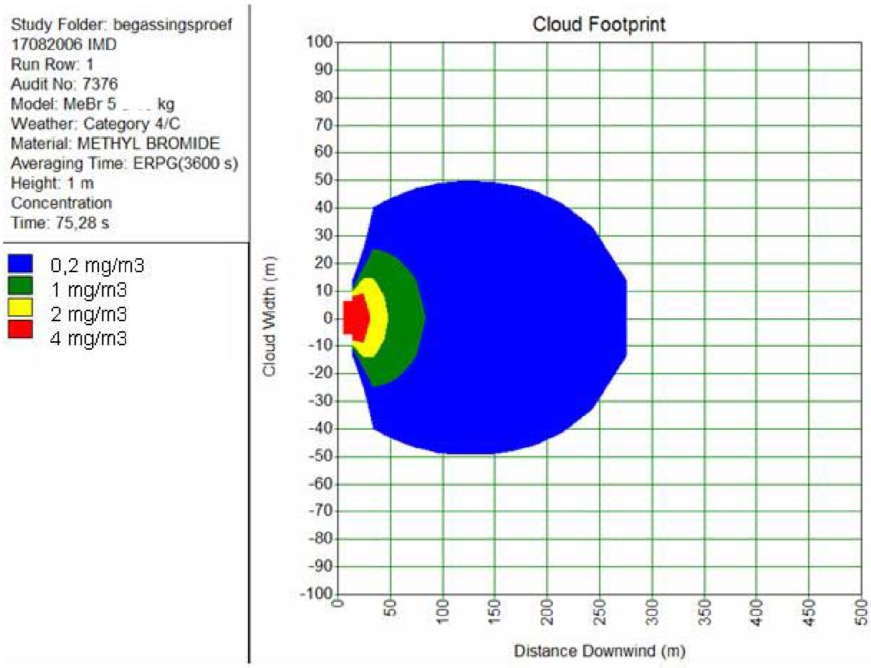


Figure 18 Calculated dispersal fitted to measurement data (stability class C and wind speed 4 m s^{-1}, concentrations in mg m^{-3})

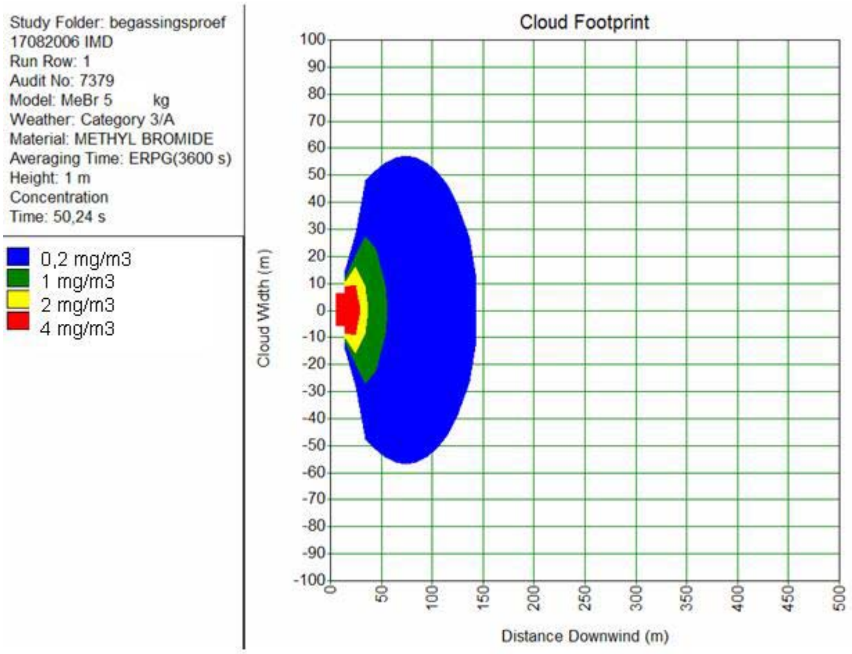


Figure 19 Dispersal at stability class A and wind speed 3 m s^{-1} (concentrations in mg m^{-3})

It can be seen that the dispersal during stability class A weather leads to shorter distances for the maximum concentrations, and that stability class D weather leads to longer distances.

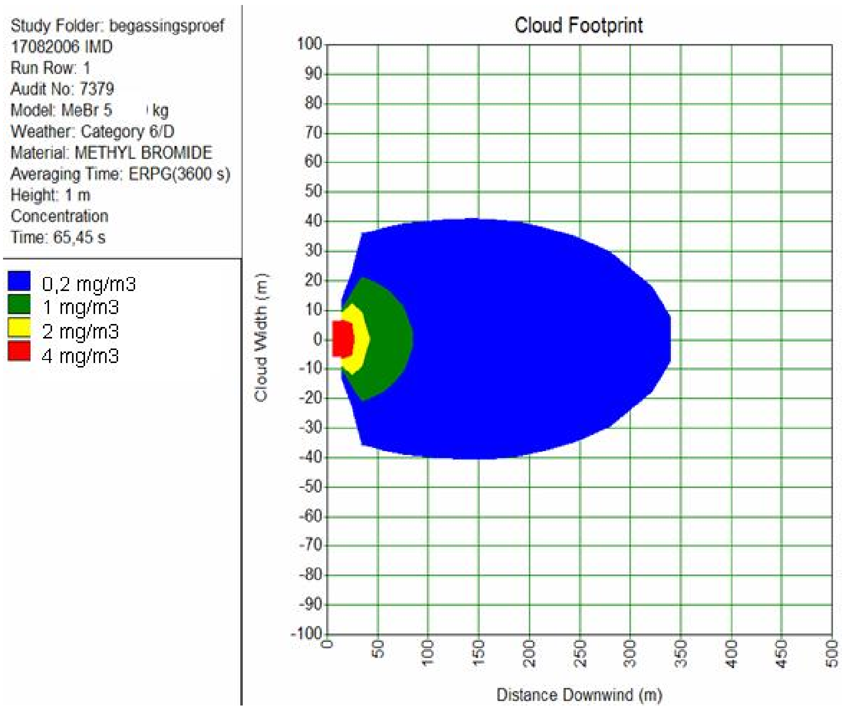


Figure 20 Dispersal at stability class D and wind speed 6 m s^{-1} (concentrations in mg m^{-3})

Table 10 lists the distances to which specific concentrations of methyl bromide occurred downwind of containers during various weather types. The distances become larger as the stability of the atmosphere increases. For the stable weather types not included in the calculations (class E and class F), the distances would be larger.

Table 10 *The distances to where the reported 1-hour average concentrations occurred around degassing containers holding 5 kg of fumigant agent*

Concentration	Stability A Wind speed 3 m s^{-1}	Stability C Wind speed 3 m s^{-1}	Stability D Wind speed 6 m s^{-1}
10 mg m^{-3}	<20 metres	<20 metres	<20 metres
4 mg m^{-3}	<20 metres	20 metres	20 metres
2 mg m^{-3}	30 metres	50 metres	50 metres
1 mg m^{-3}	60 metres	80 metres	90 metres
0.2 mg m^{-3}	150 metres	280 metres	350 metres

We have included the following remarks with the picture established by the model:

- The distances shown in Table 10 apply during the dispersal of 5 kg of methyl bromide. This quantity can be present in a single container that is fumigated for export, see the results in Table 3 and Table 4. Sulfuryl fluoride can also be present in a quantity of 5 kg in a container fumigated for export (see Table 3).
- The concentrations in Table 10 can be related to the norm for the maximum hourly average concentration of methyl bromide. Concentrations above or equal to the norm appear to occur only near the containers. At 20 metres, the concentrations are less than about 40% of this norm and at 50 metres about 20%.
- For sulfuryl fluoride, there is a norm of 12 mg m^{-3} for short-term exposure. Based on this value, the situation is comparable with that for methyl bromide.
- The quantity of phosphine in the fumigated containers is lower (60 g). During the experiments with actively fumigated containers, no concentrations above the limit of quantification were ascertained. Data are available from the experiment on 30 September, during which a container was fumigated with 56 g of phosphine. Formally speaking, this was not a fumigated import container, but a container with leaking product that led to the formation of phosphine. During the weather conditions at that time - which were unstable - the concentrations at 20 meters from the container were near the limit value for the 24-hour average concentrations. This could mean that the concentrations would fall to 20% of the norm at 50 metres from the container during more neutral weather conditions (class D).
- For chloropicrine, few suitable norms are available for this situation. The norms that have been established for chloropicrine (MAC value and intervention values for calamities) are in the same order of magnitude as those for phosphine. Chloropicrine is not used in the Netherlands as a fumigant and only occurs in the import containers. The quantity used is no more than 5% of the quantity of methyl bromide. Although the norm specifies lower concentrations than those for methyl bromide, the quantity used is smaller. These two

opposite effects result in the norms being exceeded at similar distances as with methyl bromide.

- The model calculations were conducted only under good dispersal conditions. It is known that model calculations are not possible for modelling dispersal during windstill weather (wind speeds lower than 0.5 m s^{-1}). In these cases, it is conceivable that ‘clouds’ with high concentrations of fumigants do not move in a clear direction and can spread over a larger distance than reported in the table without much dilution. This is an undesirable situation.
- The reported concentrations are one-hour averages. The experiments have shown that these concentrations occur due to a high peak immediately after opening a container, followed by a gradual decline. During the experiment on 30 August, for one to two minutes after opening, the concentration was 8 to 10 times higher than the one-hour average value. This is an essentially different situation than a one-hour average concentration that results from a constant source and a fluctuating wind. However, most norms are based on the latter situation.
- At 20 metres, the concentrations were less than 40% of the norms for methyl bromide and sulfuryl fluoride and were approximately equal to the norm for phosphine. This means that the concentrations resulting from a quantity 10 times as small in the container would be less than 20% of the relevant norms at less than 20 metres. This statement is somewhat uncertain because at these short distances, there could be unusual wind currents around the containers. In addition, it has been ascertained that containers can leak, and with containers that are up to 12 m long, at these shorter distances this could also influence the concentrations.

7. Conclusions and recommendations

7.1 Conclusions

The RIVM has drawn the following conclusions about the research questions:

With respect to degassing export containers:

What concentrations of fumigants occur, especially downwind, of export containers that are undergoing degassing? (research question 1)
Two experiments were conducted concerning the dispersal around containers that were fumigated for export in the usual fashion. Together, the containers held 5 to 10 kg of fumigant; the maximum quantity in a single container was approximately 5 kg. In the area between 5 and 30 metres from the containers, high concentrations of methyl bromide and sulfuryl fluoride were ascertained for several minutes (on the order of 10-50 mg m^{-3}); one-hour average concentrations were ascertained on the order of several mg m^{-3}.
We expect that these are worst case results because:
- measurements were conducted on sets of three containers;
- the calculations were based on the maximum quantity found in one container;
- the containers were empty, so no goods could absorb the gas.

Due to this last effect, we expect that the initially released quantity in the experiment was larger (leading to a higher maximum concentration) and that the lag effect was smaller (the containers became ‘gas free’ more quickly) than is the case in the actual practice of degassing.

Are there observable differences in the dispersion of various types of fumigants? (research question 2)
In this study, various dilution factors were found for the various fumigants at approximately equal distances. Measurements at different heights provide indications that methyl bromide spreads as a heavy gas, which is expected. However, the location of a measurement point has turned out to be very critical. Depending on its location, a measurement apparatus could sample a high concentration or just miss it. In summary, there is too little support to make statements about differences in the dispersal of the various fumigants.

How do the concentrations relate to the available and applicable public health norms (research question 3) and at which distances are the concentrations below these norms, given the weather conditions at the time of the measurements? (research question 4)
Most of data concerned methyl bromide. The measured concentrations were related to the norm that is available for the maximum one-hour average concentration for this substance (10 mg m^{-3}). Concentrations at the level of this norm occurred only near the containers (<20 metres). Model calculations for these substances indicated concentrations during different weather types greater than 2 mg m^{-3} - this is 20% of the norm for methyl bromide - up to 50 metres from the containers. When considering the possible effects, it is important to also take account of the very high concentrations during several minutes after opening a container.

These results apply to containers with methyl bromide in a quantity of approximately 5 kg. Containers can be fumigated with a comparable quantity of sulfuryl fluoride. Consequently, the concentrations for these substances that occur downwind are the same. The norm for sulfuryl fluoride is comparable with the norm for methyl bromide, so that the distances at which the norm is exceeded are also comparable.

For a container with phosphine in the quantities that can occur with export fumigation, concentrations near the limit value were measured at distances of up to 20 metres. At 50 metres, the concentrations fell to below 20% of the norm.

Are the results collected under the conditions that occurred in practice usable for making an estimate of the situation during other weather conditions and for a representative part of the time? (research question 5)
For methyl bromide, model calculations indicated that the concentrations during other weather conditions would also not exceed the norm for one-hour averages at distances greater than 20 m from the containers. At 50 metres, the concentrations would be 20% of this norm or lower (depending on the type of weather), assuming that degassing does not take place during windstill weather, in the evening or at night. The dispersal in the evening and the night (when there are more stable atmospheric conditions) was not examined because – according to our information – no degassing takes place at these times. In addition, the dispersal during windstill weather cannot be modelled and it is conceivable that ‘clouds’ with high concentrations could then spread over large distances. Degassing during windstill weather is therefore undesirable.
For phosphine, concentrations equal to the norm for the 24-hour average were measured at 20 metres. At a 50 m distance, the concentrations were no more than 20% of the norm.

An additional remark is that significant concentrations have been ascertained near closed containers ‘undergoing fumigation’. Containers can therefore leak, which has also been ascertained in previous studies. Leakage of containers ‘undergoing fumigation’ results in concentrations on the order of magnitude of relevant norms. The RIVM expects that the total quantity is small due to the pressure-free dispersal; the concentration will therefore be significantly lower at some distance (‘several tens of meters’).

With respect to degassing import containers The RIVM has drawn the following conclusions:

Which concentrations of fumigants occur in the situation in practice on the company terrain of Europe Container Terminals (ECT) around and in the vicinity of import containers undergoing degassing, and how do the concentrations relate to the available and applicable norms for public exposure? (research questions 6 and 7)
Little measurement data was provided about the concentrations near degassing containers. This lack of data is attributed to 1) the low number of import containers fumigated with methyl bromide that were placed in the fumigation area during the seven-week study period, and 2) of the three individual containers studied, one fumigated import container was not taken into consideration because it held a leaking product.

It has become clear that the quantities in the actively fumigated export containers were much higher (by a factor of 100) than the quantities in the *fumigated import* containers, and that the concentrations during degassing were consequently higher for the actively fumigated containers.

At which distances are the concentrations below these norms, given the weather conditions that occurred during the measurements, and are the results that were collected under the conditions in practice usable for making an estimation of the situation during other weather conditions and for a representative part of the time? (research questions 8 and 9)
As reported previously, few measurements near the import containers turned out to be usable. Based on the study of actively fumigated containers, the following conclusion can be derived. If the import containers are fumigated with 5 kg of methyl bromide, 5 kg of sulfuryl fluoride or 60 g of phosphine, then the concentrations at 20 metres do not exceed the currently available public health norm. If the quantity is a factor of 10 smaller, then the concentrations will be 10% of the norm.

A separation distance of less than 20 metres is unadvisable for the following three reasons:
- at shorter distances, the local wind currents around the containers must be taken into account (obstacle flows);
- leakage of the containers is possible and can lead to high concentrations near the containers;
- the degassing of import containers also takes place during the night and therefore during more stable weather conditions.

Are the results of the various sampling and analysis techniques for methyl bromide comparable with each other? (research question 10)
During the studies, differences in the concentrations measured by the various methods were ascertained. During the first experiment, the measurements with the active charcoal tubes were unsuccessful. After modification of the suction rate, the active charcoal tubes and the badges showed comparable results within a factor of 2. This is an acceptable difference for field studies with various measurement techniques. In the first experiment, the results with the canister were comparable, and in the second experiment the canisters systematically indicated higher concentrations than those measured with the active charcoal tubes. The explanation for this difference is possibly the influence of humidity or the difference in sampling height (although small, this difference may have had an effect).

The OLM sensors indicated much higher concentrations. We expect that the sensors responded well to the changing concentrations and we have therefore used these results to support the conclusions. Based on the comparison with other, more validated methods, the experiment has shown that the sensors indicated an excessively high methyl bromide concentration. A relevant consideration concerning the use of sensors for monitoring is that the highest concentrations passed by in narrow plumes, and that for monitoring purposes a finely meshed network of sensors is therefore necessary.

7.2 Recommendations

This research was conducted based on the need to simplify the safety enforcement near fumigated containers. The differing provisions for each fumigant and the exceptions to the rules turned out to be difficult to enforce in practice. The underlying question is whether a single separation distance requirement can be defined for containers undergoing degassing, and if this is the case, what is that distance? (research question 11)
When considering this question, at least two distinct aspects emerge: the weather type and the relationship between the quantity of fumigant in the containers, the concentrations in the environment and the norms.

Regarding the weather type, there are weather conditions during which spreading is poor. This is especially the case with windstill weather. During such weather, degassing is not advisable because ‘clouds’ with high concentrations can spread in a virtually undiluted state. We therefore recommend a ban on degassing during windstill weather (average wind speed lower than 0.5 m s^{-1}, or 0 on the Beaufort scale).

Regarding the quantity of fumigants and the norms, we note that the quantities in export containers are a factor of 100 or more higher than those in fumigated import containers, and that the substances have effects in very different concentrations. The latter can be seen in the differences in the norms that have been proposed for other concentrations. It does not seem logical to pursue the same separation distance requirement for such differences. There are certainly differences[3] between export and import containers, but the exposure of people essentially comes down to which substances have been used in which quantities and the weather conditions for the dispersal. The RIVM proposes to base the separation distance requirement on the substance and the quantity that is in the container.

The RIVM makes the following recommendation:

Total quantity in containers to undergo degassing (maximum concentration, if this quantity is used in a single 66 m^3 container)	Distance from the container(s) within which people are forbidden without personal protection equipment, until the container is declared to be ‘gas free’
methyl bromide to 1 kg (15 g m^{-3}) or sulfuryl fluoride to 1 kg (15 g m^{-3}) or phosphine to 10 g (0.2 g m^{-3})	20 metres
methyl bromide to approximately 5 kg (75 g m^{-3}) or sulfuryl fluoride to approximately 5 kg (75 g m^{-3}) or phosphine to approximately 60 g (1 g m^{-3})	50 metres
methyl bromide more than 10 kg (>150 g m^{-3}) or sulfuryl fluoride more than 10 kg (>150 g m^{-3}) or phosphine more than 100 g (>1.5 g m^{-3})	Degassing can take place only in consultation with and under supervision of the VROM Inspectorate

The degassing cannot begin during windstill weather (wind speed 0 on the Beaufort scale).

The RIVM bases its recommendation on the following considerations:

1. The degassing process is characterized by extremely high concentrations occurring several minutes after the beginning, followed by a gradual decline. As part of the derivation of the norms, this non-normal variation in the one-hour average was not taken into account. A toxicological investigation of these transient peak concentrations is recommended and may possibly lead to a modification of the separation distance.
2. In view of the uncertainties and the high concentrations immediately following the beginning of the degassing process, we have based the recommendation on 20% of the limit values for public health protection. This was done in an analogous fashion to the frequently used action level of 20% of the MAC value to protect employees. Above the action level, measures are taken to protect employees from exposure that exceeds the MAC value.
3. Of course, there are uncertainties in the measurement values. As with every field experiment, different measurement methods resulted in different measurement values.

[3]Export containers that are fumigated in the Netherlands contain higher concentrations of known and permitted substances. Import containers that have been fumigated contain lower concentrations of many different kinds of substances.

When making our recommendations, we used measurement values that were on the high side, such as the measurement values from the active charcoal tubes on 30 August. These values were higher than the measurement values derived from the badges. However, the values were significantly lower than the measurement values derived from the canisters and the OLM sensors.

4. Leakage can occur with closed containers, which leads to high concentrations near the containers. Exposure of the public to high concentrations is prevented by applying the minimum distance of 20 metres to closed containers as well.

Reducing the separation distance after several hours can be considered because during the experiments the largest quantity was released during a brief period. However, the experiments were conducted with empty containers, and it is possible that the release will take place more slowly and last longer with containers that are filled with goods. The time period after which the distance could be reduced should be investigated.

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Appendix 1 Summary of the measurement results

Summary of measurement results 17 August 2006

Table B.1.1 Measured concentrations of methyl bromide (mg m^{-3}), sampled with badges, 17 August 2006

	Concentration
Badge 1	*< 0.2*
Badge 2	*< 0.2*
Badge 3	3.3
Badge 4	*< 0.2*
Badge 5	*< 0.2*
Badge 6	1.5
Badge 7	*< 0.2*
Badge 8	*< 0.2*
Badge 9	*< 0.2*
Badge 10	1
Badge 11	*< 0.2*
Badge 12	*< 0.2*
Badge 13	*< 0.2*
Badge 14	*< 0.2*
Badge 15	*< 0.2*

Based on the sampling duration, no concentrations lower than 200 µg m^{-3} could be shown.

None of the active charcoal tubes sampled concentrations of methyl bromide above the limit of quantification (15 µg m$^{-3)}$.

Table B.1.2 Measured concentrations of fumigants, sampled with canisters

	Concentrations (mg m^{-3})		
	Sulfuryl fluoride	MeBr	Phosphine
canister 1	0.2	*< 0.03*	*< 0.03*
canister 2	*< 0.03*	*< 0.03*	*< 0.03*
canister 3	*< 0.03*	*< 0.03*	*< 0.03*
canister 4	20	*< 0.03*	*< 0.03*
canister 5	*< 0.03*	*< 0.03*	*< 0.03*
canister 6	*< 0.03*	2.7	*< 0.03*
canister 7	*< 0.03*	*< 0.03*	*< 0.03*
canister 8	*< 0.03*	*< 0.03*	*< 0.03*
canister 9	*< 0.03*	*< 0.03*	*< 0.03*
canister 10	*< 0.03*	*< 0.03*	*< 0.03*

Summary of measurement results 30 August 2006

Table B.1.3 Measured concentrations of methyl bromide (mg m^{-3}) on 30 August 2006

Measurement point	Measurement method: Badges First / Second badge (Duplicate measurement)	Measurement method: Active charcoal tubes	Measurement method: Canisters
5m1	0.7 / 0.6	1.1	
5m2	2.4 / 2.4	4.2	17
5m3	*< 0.2 / < 0.2*	*< 0.015*	
15m1	*<0.2 / < 0.2*		
15m2	0.6 / 0.7	1.4	
15m3	0.7 / 0.6	1.2	5
15m4	*< 0.2*		
25m1	*< 0.2 / < 0.2*	1.4	
25m2	0.4 / 0.4	1.7	6
25m3	*< 0.2 / < 0.2*	0.3	
25m4	*< 0.2*	*<0.015*	
50m1	0.7	0.6	
50m2	0.2	0.1	
50m3	*< 0.2*		
50m4	*< 0.2*		
Blank	*< 0.2*	*< 0.015*	
Blank field		*< 0.015*	

Based on the sampling duration, concentrations lower than 0.2 mg m^{-3} (badges) and 0.015 mg m^{-3} (active charcoal tubes) could not be measured.

Table B.1.4 Measured concentrations of fumigants, sampled with canisters, 30 August 2006

	Concentrations (mg m^{-3})		
Measurement point	Sulfuryl fluoride	MeBr	Phosphine
canister 1	*< 0.03*	*< 0.03*	*< 0.03*
canister 2	*< 0.03*	17	*< 0.03*
canister 3	10	*< 0.03*	*< 0.03*
canister 4	*< 0.03*	*< 0.03*	*< 0.03*
canister 5	*< 0.03*	5	*< 0.03*
canister 6	3.6	*< 0.03*	*< 0.03*
canister 7	*< 0.03*	*< 0.03*	*< 0.03*
canister 8	*< 0.03*	6	*< 0.03*
canister 9	1.7	*< 0.03*	*< 0.03*
canister 10	*< 0.03*	*< 0.03*	*< 0.03*

Appendix 2 Methyl bromide: toxic for people and the environment

Introduction

Methyl bromide (CH_3Br) is sold as a liquid gas. At room temperature, it is a colourless and odourless gas. As part of pest control procedures and the protection of stored commodities, a vaporizer is used to introduce the substance into a gas-tight space (grain silo, hold of a ship). The duration of such a fumigation (the period that the gas remains in the space) varies from approximately 5 hours to several days. After the fumigation, the gas is let out of the space by opening windows, doors and ventilation shafts. In this way, the methyl bromide concentration declines until the space can be declared gas-free.

During the fumigation, the concentration in the fumigated space is extremely high. During most fumigation procedures, the concentration is higher than 10,000 mg/m^3 (milligrams per cubic metre). For controlling rats in ship holds, somewhat lower concentrations are adequate (4000 mg/m^3).

Health risk

Information about the toxicological properties of methyl bromide originates from experimental research with animals and from occupational toxicity research with humans.

The relevant literature contains descriptions of many cases of poisoning with methyl bromide. These cases involve the accidental inhalation of high concentrations of methyl bromide by employees of companies where this substance is used or by people living in the vicinity (this concerns improper use with respect to current standards). These data provide only a rough picture of the dosage-effect relationship for methyl bromide.[4] With humans, mortality occurs at concentrations of 33,000 mg/m^3 and higher (duration of exposure unknown). During these fatal episodes, tissue damage occurs in the brain. Other toxicity symptoms can occur at much lower concentrations. With humans, symptoms have been reported at concentrations as low as 390 mg/m^3. The most important toxic effects involve the nervous system (numbness, tremors, seizures, coordination disturbances), the lungs (irritation, oedema, inflammation) and the kidneys. In addition, eye and nose irritation and vision damage can occur. The onset of symptoms can be delayed: the harmful consequences may not become apparent until several hours after exposure. Moreover, inhalation of methyl bromide is not the only important form of exposure. Cases are known where skin contact with methyl bromide has led to serious toxicity symptoms with humans.

The findings with research animals support the human data. The general conclusion that can be drawn from the animal research data is that the immediate effects (acute effects) of methyl bromide are the critical factor for this substance. Long-term effects such as cancer are not expected. The 1-hour LC_{50} in experimental animals[5] is ≥4680 mg/m^3. Acute toxicity research

[4] The dosage-effect relationship is a central concept in toxicology. The hazardous effect of chemicals depends on the dosage. Regarding inhalation, the dosage is determined by the inhaled concentration and the inhalation time (duration of exposure). The dosage-effect relationship indicates how the intensity of the toxic reactions increases with higher dosages. A steep dosage-effect relationship means that a relatively small increase in the inhaled concentration (and duration of exposure) is sufficient to cause severe toxic reactions. As explained in the text, methyl bromide has a steep dosage-effect relationship.

[5] LC_{50} is is a standard for acute toxicity in experimental animals. LC_{50} is the concentration where 50% of the treated animals die when they inhale the test substance during a specified period – in this case 1-hour inhalation.

has shown that methyl bromide has a very steep dosage-response curve, i.e. there is a sharp transition from concentrations that do not produce any effects to concentrations that cause 100% mortality.[6] The most important symptoms in experimental animals, like humans, were neurological effects. The division between benign and harmful concentrations (and exposure durations) is not known precisely.[7] With rats, no effect was observed from the inhalation of 63 mg/m^3 during a period of 8 hours (however, there was an effect with 122 mg/m^3). Continuous exposure to 20 mg/m^3 for three weeks did not lead to any neurological effects in rats (these effects did occur at 40 mg/m^3).

Based on the available toxicological information (for humans and experimental animals), organizations such as the RIVM have derived toxicological limit values. Such a limit value is an estimate of the concentration which one can say with great certainty that it is safe. When deriving a limit value, a significant safety margin is always included. This margin results from extrapolation steps that are required to go from a level that does not cause any harmful effects under the controlled conditions of the experimental animal study to a safe limit value for the entire human population (including susceptible groups). For methyl bromide, the following toxicological limit values for the general population are known:

– maximum exposure, 1-hour average: 10 mg/m^3
– maximum exposure for several weeks: 0.7 mg/m^3
– maximum exposure for an entire year: 0.1 mg/m^3.

The MAC value, the limit value for occupational situations (40 hours/week during 40 years) is 1 mg/m^3.

Comparing the concentrations that are necessary for pest control (≥10,000 mg/m^3) with the levels that cause toxic reactions in humans and experimental animals shows that people work with concentrations in practice that can lead to significant negative health effects in cases of accidental exposure during improper use. The steep dosage-effect curve for methyl bromide – i.e. the narrow margin between the concentration where only mild effects occur and the concentrations where very serious, life-threatening effects occur – makes the enforcement of safety regulations an urgent necessity to prevent accidents.

Environmental risk

In the Montréal Protocol from 1992, methyl bromide was placed on the list of substances that are damaging to the ozone layer. As part of the same Protocol, agreements were also made about limiting the worldwide production of methyl bromide.

Methyl bromide is used primarily as an insecticide – therefore to control insects. Insects are also a sensitive group. The immediate harmful effects caused by *short-term* exposure of other animals are variable: For example, methyl bromide is moderately toxic for birds, toxic for algae

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[6] In rats, for example, 0% mortality occurred after 4 hours of exposure to 2720 mg/m^3, but there was 100% mortality at 3110 mg/m^3.

[7] This is not an exceptional situation in toxicology. In experimental animal studies, three or more concentrations are always tested with separate groups of animals. The concentrations are maintained at a constant level during the test. The results of the study provide a ‘no observed adverse effect level’ (NOAEL): this is the highest test level at which no harmful effects occurred. As a result of this method, there is always a certain margin between the NOAEL and the lowest level at which the first effects are observed, which is known as the ‘lowest observed adverse effect level’ (LOAEL). As stated in the text, for one-time exposure to methyl bromide for 8 hours, the NOAEL is 63 mg/m^3 and the LOAEL is 122 mg/m^3; for longer exposure, these values are 20 mg/m^3 and 40 mg/m^{3,} respectively.

and water fleas and extremely toxic for fish, small mammals and earthworms. Tests with *longer-term* exposure – which are usually conducted with the bromine ion as the most important decomposition product of methyl bromide – generally indicate a relatively low toxicity: the residues therefore appear to be less toxic than the initial substance.

Methyl bromide is toxic for plants.[8] Lettuce is especially susceptible. After being made gas-free, the concentration in the immediate vicinity of a fumigated space or a special fumigation installation must be below 400 mg/m^3. However, in the Netherlands a separation distance requirement of 100 metres is maintained within which no residential spaces, or spaces with susceptible plants such as a garden allotment, may be located. Problems with the surrounding vegetation are therefore unlikely to occur.

Assuming compliance with the statutory regulations for using methyl bromide in enclosed spaces or in special fumigation installations, harmful effects to flora and fauna are unlikely. Due to improper or illegal use, however, problems can occur. In such situations, harmful effects to flora and fauna can occur due to the acute toxicity of methyl bromide (for example, in cases of direct disposal, draining toxic condensation to surface waters or non-compliance with the separation distance requirement).

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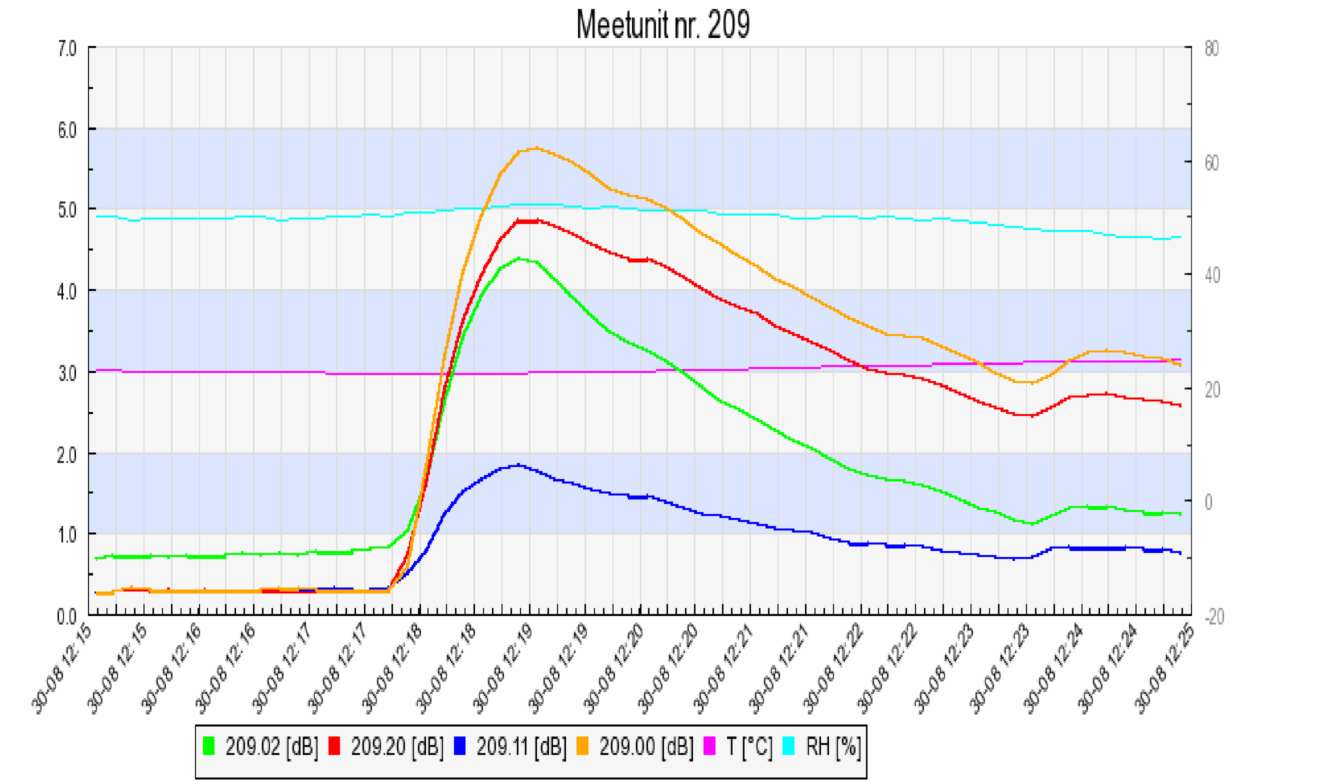
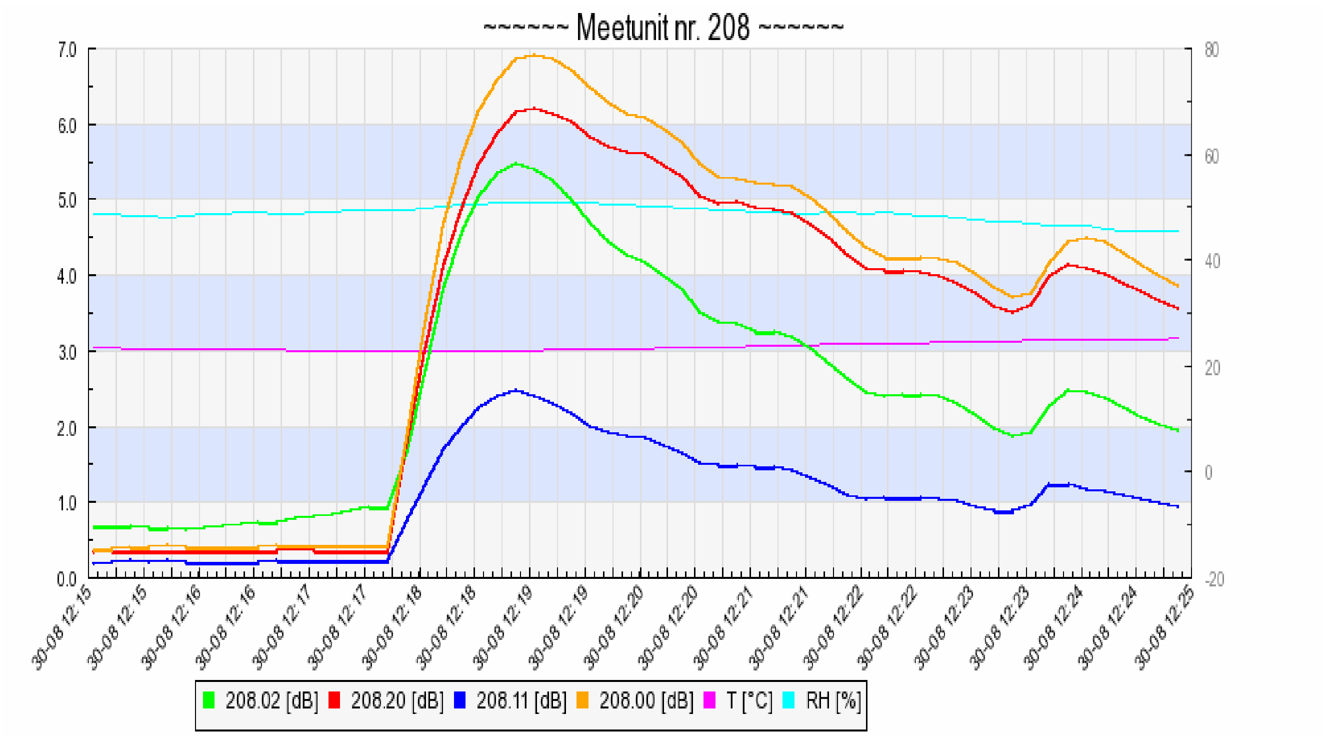
Drs. B.J.W.G. Mensink
Centre for Chemicals and Risk Evaluation,
RIVM, Bilthoven
RIVM/CSR, 21 April 2000

Supplement:
The norm for methyl bromide of 10 mg m^{-3} is based on acute public health effects. The MAC value of 1 mg m^{-3} is based on chronic effects for employees and applies as the statutory limit value for an average exposure during eight hours. During exposure of one individual to 9 mg m^{-3} of methyl bromide for one hour, the norm for acute effects is not exceeded, but the MAC value is exceeded. A one-time exceedance of the MAC value will not lead to negative health effects because for methyl bromide the effects are based on chronic exposure, the maximum one-hour average concentration is not exceeded and the average concentration during a working life is lower than the reported norm value.

[8] When fumigating seeds, seedlings and bulbs, plants and parts of plants, the harmful effects of methyl bromide on flora are taken into account.

Appendix 3 Results of the OLM measurements on 30 August 2006





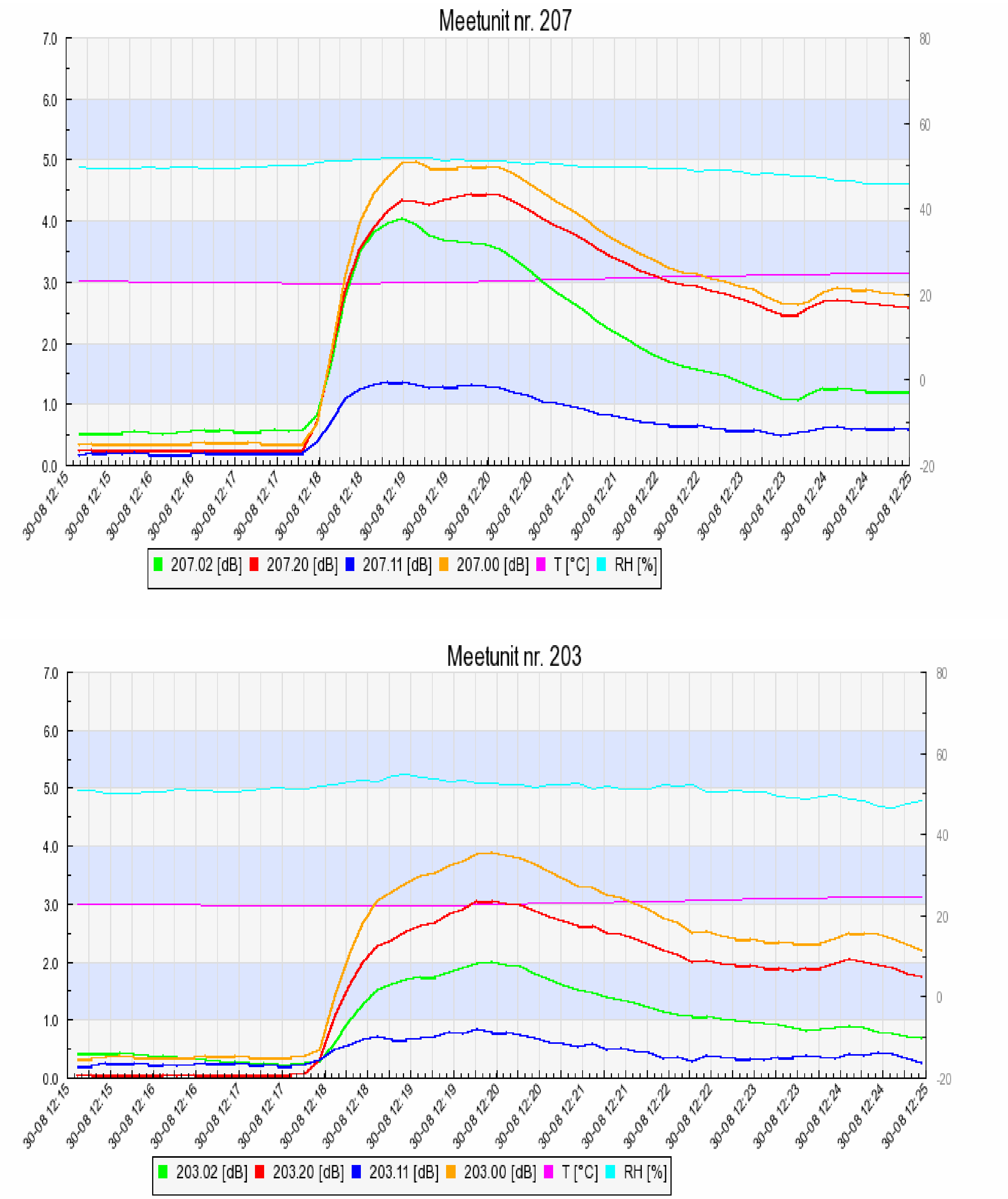


Figure B3.1 Results from four OLM units located downwind of the containers fumigated with methyl bromide (30 August from 12:15 to 12:25 hours)

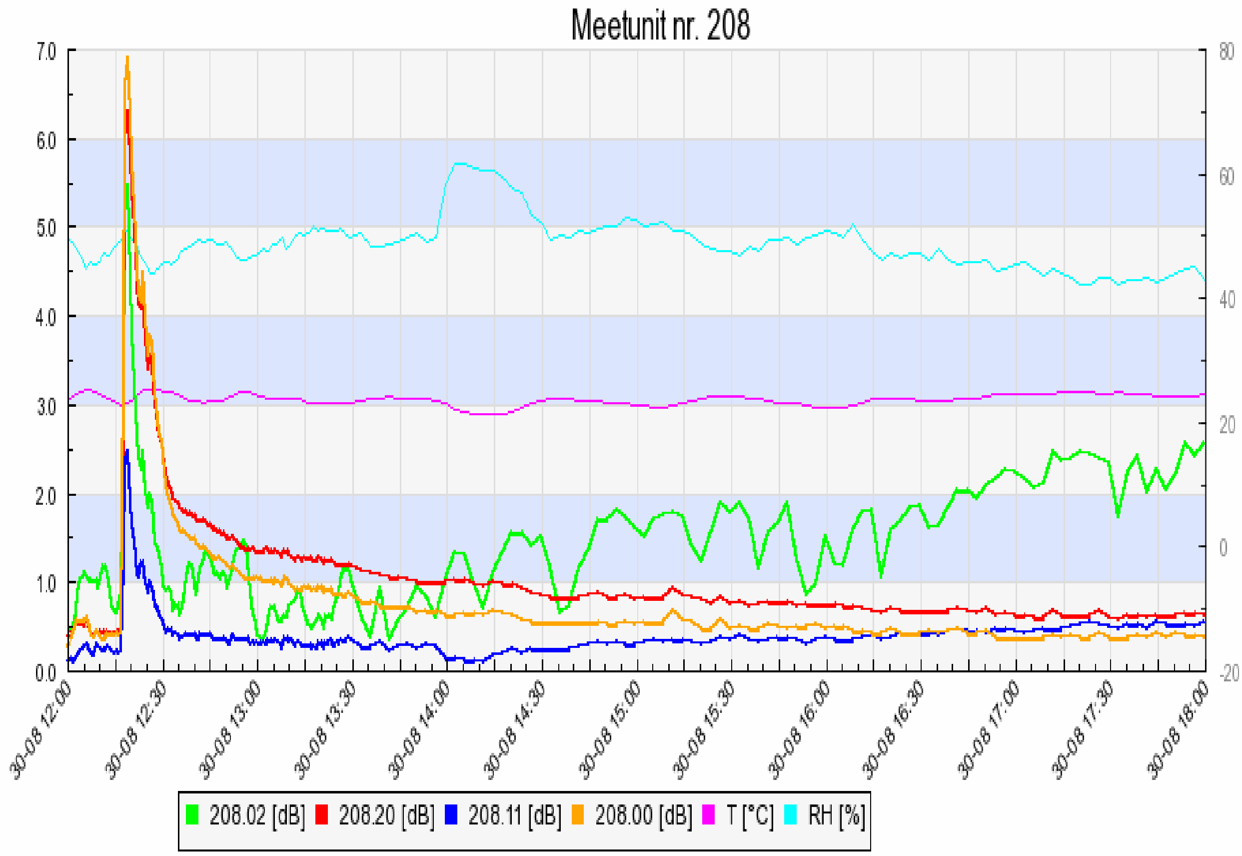


Figure B3.2 Response from OLM unit 208 on 30 August 2006 from 12:00 hours 18:00 hours (source: Comon Invent, website 16 November 2006)

Based on Figure B3.2, the average concentration in the period was estimated as follows 12:15 to 14:15 hours:

Time from	Time to	Signal reading from measurement unit 208	Concentration based on signal (mg m^{-3})	Duration in minutes	Concentration contribution to 2-hour average (mg m^{-3} min)
12:18	12:20	67	800	2	1600
12:20	12:22	52	621	2	1242
12:22	12:24	41	380	2	760
12:24	12:30	30	170	6	1021
12:30	13:00	17	43	30	1295
13:00	14:18	11	7	78	553
			TOTAL:	120 minutes	Average concentration: 54 mg m^{-3}

Appendix 4 Model input data

MeBr 5 kg, Base Case

Data		
\fumigation experiment 17082006 IMD\Study\MeBr 5 a 10 kg		
Material		
Material Identifier	METHYL BROMIDE	
Type of Vessel	Pressurized Gas	
Pressure Specification	Pressure specified	
Discharge Pressure (gauge)	0.01	bar
Discharge Temperature	22	degC
Mass Inventory of material to discharge	5	kg
Scenario		
Type of Event	Fixed duration release	
Phase	Vapour	
Building Wake Option	Roof/Lee	
Duration for fixed duration scenario	1800	s
Location		
Elevation	2	m
Dispersion Concentration of Interest	0.05	ppm
Averaging time associated with Concentration	User-defined	
ERPG selection	ERPG is set	
User Defined Averaging	User defined averaging time supplied	
User-Defined Average Time	3600	s
Bund		
Status of Bund	No bund present	
[Type of Bund Surface	Concrete]	
[Bund Height	0	m]
[Bund Failure Modelling	Bund cannot fail]	
Indoor/Outdoor		
Building Height	4	m
Building Length	12	m
Building Width	12	m
Building Angle	0	deg
Wind Angle	0	deg
Outdoor Release Direction	Vertical	
Flammable		
Method to use for explosions	TNT	
Jet Fire Method	Shell	
Dispersion		
Ignition Location	No ignition location	
Mass Inventory of material to Disperse	5	kg
Fireball Parameters		
[Mass Modification Factor	3]	
[Calculation method for fireball	DNV Recommended]	
[Temperature of fireball	1727	degC]

[Note: Data in square brackets are defaulted values]

Appendix 5 Weather data during the experiment with import containers

Source: Data KNMI, summary 24-hour average weather data, Rotterdam station

	Tavg	Tmax	Tmin	Fractional cloud cover	Rain quantity	Rain duration	Wind direction		Wind speed
	°C	°C	°C	Eighths	mm	hour	compass point	degrees	m/s
7-Sep	16.6	20.2	12.1	4	0.2	0.5	NNW	332	5
8-Sep	14.4	19.4	9.8	1	0	0	NNE	23	2.7
9-Sep	14.6	20.6	7.6	0	0	0	E	87	4.3
10-Sep	16.6	23.2	10.1	0	0	0	E	89	2.3
11-Sep	19	27	11	0	0	0	E	88	1
12-Sep	20	28	13	0	0	0	SE	129	2
13-Sep	22	26	16	0	0	0	SSE	161	3
14-Sep	22	27	18	5	0	0	SE	141	3
15-Sep	21	27	16	2	0	0	NE	52	3
16-Sep	20	26	15	1	0	0	NNE	34	2
17-Sep	17	19	14	6	0	0	WNW	285	2
18-Sep	18	22	14	6	0	0	SW	233	3
19-Sep	16	19	13	4	3	3	SW	226	5
20-Sep	17	22	12	0	0	0	S	185	5
21-Sep	20	25	14	0	0	0	SE	138	5
22-Sep	20	25	18	4	0	0	SSE	163	5
23-Sep	18	22	15	6	3	2	E	80	2
24-Sep	20	23	17	8	0	1	SSE	157	3
25-Sep	18	22	17	7	1	3	S	190	4
26-Sep	16	20	12	6	1	1	W	268	3
27-Sep	16	20	13	6	0	0	S	192	4
28-Sep	18	22	15	7	0	0	SSW	199	4
29-Sep	19	22	15	6	0	0	S	183	5
30-Sep	17	21	12	3	0	0	SSW	197	4
1-Oct	17	21	14	7	3	1	S	192	5
2-Oct	15	17	13	8	30	12	SSW	212	8
3-Oct	15	18	12	7	10	4	WSW	247	4
4-Oct	13	16	8	6	10	3	WSW	250	3
5-Oct	14	17	9	6	10	8	SSW	209	6
6-Oct	16	17	14	8	15	8	SSW	211	9
7-Oct	14	16	12	6	1	0	W	262	6
8-Oct	14	18	11	3	0	0	S	187	4
9-Oct	14	18	9	3	0	0	S	183	4
10-Oct	16	19	10	7	1	1	ESE	108	3
11-Oct	16	20	13	2	0	0	ESE	113	3
12-Oct	14	18	7	5	1	0	W	262	2
13-Oct	13	18	6	2	0	0	NE	48	2
14-Oct	13	17	8	5	0	0	ENE	69	4
15-Oct	10	13	7	2	0	0	E	67	5
16-Oct	11	16	5	0	0	0	E	103	3
17-Oct	13	17	8	2	0	0	SSE	150	3
18-Oct	14	16	12	8	3	3	S	171	3
19-Oct	15	18	13	7	2	1	SSE	158	5
20-Oct	15	17	13	8	0	1	S	187	6
21-Oct	15	17	14	6	1	1	SSW	197	6

	Tavg	Tmax	Tmin	Fractional cloud cover	Rain quantity	Rain duration	Wind direction		Wind speed
	°C	°C	°C	Eighths	mm	hour	compass point	degrees	m/s
22-Oct	15	17	12	7	18	7	S	184	6
23-Oct	15	18	11	7	13	4	SW	213	5
24-Oct	13	16	7	6	2	2	SW	233	5
25-Oct	12	15	8	6	2	1	SE	132	5
26-Oct	18	21	14	7	0	0	SSW	212	7
27-Oct	12	15	9	4	0	0	WSW	245	4

Tavg = average 24-hour temperature
Tmax = maximum 24-hour temperature
Tmin = minimum 24-hour temperature