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The release of pesticides from container goods

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Abstract

The release of pesticides from container goods

Goods containers imported into the Netherlands are often treated with pesticides such as methyl bromide, chloropicrin and phosphine. There is always a chance that the goods will adsorb pesticides during transport and that these will be released into the air through evaporation during consumer use. This investigation, commissioned by the VROM Inspectorate, studied goods such as mattresses, footwear, bags and wooden sculptures, which were found to be prone to evaporation. This evaporation can, in turn, cause consumers to be unintentionally exposed. Furthermore, evaporation from food products and medicines can lead to oral ingestion of pesticides and perhaps even to changes in the chemical composition of food products or medicines.

Keywords: pesticides, fumigation, containers, consumers, exposure

Rapport in het kort

Nalevering van bestrijdingsmiddelen uit containergoederen

Containers met goederen die in Nederland worden ingevoerd, zijn vaak behandeld met een bestrijdingsmiddel. Veel toegepaste bestrijdingsmiddelen zijn methylbromide en chloorpicrine, en fosfine. De mogelijkheid bestaat dat deze middelen in de goederen terecht komen en uitdampen bij gebruik door consumenten.

In dit onderzoek is gebleken dat goederen zoals matrassen, schoeisel, tassen en beeldjes, nog lange tijd na begassing bestrijdingsmiddelen kunnen uitdampen. Blootstelling van consumenten kan hierdoor onbedoeld optreden. Ook is gebleken dat bij voedingsmiddelen of medicijnen de begassing kan leiden tot orale opname van bestrijdingsmiddelen en wellicht ook tot verandering van de chemische samenstelling van het voedsel of medicijn.

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

Trefwoorden: bestrijdingsmiddelen, begassing, containers, consumenten, blootstelling

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Summary

A previous study, commissioned by the VROM Inspectorate and implemented by them together with RIVM in 2002, showed that a wide range of goods that are imported into the Netherlands in goods containers are treated with a pesticide. Some of these goods do not entirely (or insufficiently) return to a gas-free condition, and pesticides (such as methyl bromide) continue to be evaporated from them for a very long time.

This current study was implemented in 2004, and focused on whether this evaporation could lead to people and/or the environment being exposed to these pesticides. This study was implemented at the request of the VROM Inspectorate, and consisted of taking samples of goods from containers that were treated with gaseous pesticides, and placing these goods in an emission chamber where the release of these pesticides was monitored. This confirmed the evaporation behaviour of the samples.

The study showed that:

1. import containers are being treated with gaseous pesticides, even when there is no legal requirement to do so;
2. consumers can be exposed to gaseous pesticides as a result of evaporation of these compounds from gassed products. These can enter the body via inhalation and via the skin;
3. methyl bromide and chloropicrin evaporate in 75% of the objects studied, following emission patterns that vary per object and per compound;
4. consumers are possibly exposed to a health risk from gaseous pesticides as a result of compounds being released from these gassed products;
5. the extent (exposure time, concentration, route, etcetera) of the possible health risk as a result of the aforementioned exposure cannot be adequately quantified as a result of this study;
6. it is not possible to define any phosphine emissions from the gassed items;
7. in addition to inhaling pesticides evaporating from these goods, inevitable adsorption can occur in goods transported in containers that are treated with pesticides. With respect to food products or medicines this can lead to oral ingestion of pesticides via food products or medicines, and possibly even to chemical changes in the composition thereof.

List of acronyms used

RIVM	National Institute for Public Health and the Environment
VROM	Ministry of Housing, Spatial Planning and the Environment

1. Introduction

The research carried out by RIVM¹ and the VROM Inspectorate in 2002 showed that at least 21% of the cargos transported in goods containers and currently being imported to the Netherlands are treated with some kind of pesticide.

Experience gained by the VROM Inspectorate has shown that the goods that are gassed cover a wide range of articles and packaging materials. In a number of cases practical tests have shown that it is very difficult, if not impossible, to return various goods and packaging to their original gas-free state. Some cargos, e.g. housing relocation items and various plastics (including children's toys), have been found that appear to have adsorbed large quantities of gas (e.g. methyl bromide), which these goods retain for several months – even up to one year – before they can be considered gas-free.

The VROM Inspectorate has insufficient insight into the risks involved, and does not know which materials form a permanent risk, both for people and for the environment, as a result of treating containers with poisonous gases. This is why the VROM Inspectorate commissioned this study, which was carried out in 2004 and is described in this report.

¹ T. Knol-deVos, Gas measurements in import containers, RIVM report 609021024, 2003

2. Objectives

The study described here aimed to define whether evaporation from pesticides in gassed items could form a risk for people and/or the environment.

This concerns goods that are imported, packed in goods containers, which are then treated with gaseous pesticides. After arrival in the Netherlands these containers cannot be returned to their original gas-free state, which can be explained by the evaporation of pesticides from the goods within the container.

This study did not focus on the question as to the timeframe required for gas-treated containers to return to their gas-free state.

3. Set-up of the study

3.1 Phasing of the study

This study was split into four phases:

1. Literature study into known data concerning the evaporation of gases, such as the most-used pesticides, from gassed materials;
2. Drawing up a list of objects that were relevant to the study, either with respect to the type of material (are certain materials more sensitive to evaporation?) or with respect to the use of the objects (does the way an item is used result in extra risk of exposure?);
3. Selection and sampling of gassed objects that meet the risk profile mentioned under 2;
4. Emission study of the sampled objects in a so-called 'emissions chamber'.

3.2 Limitations of the study

This study was limited as follows:

- type of gases and analysis methods available: the study was initially limited to the gaseous pesticides methyl bromide, phosphine, and sulfuryl fluoride. The first two are often used as pesticides in containers, and the latter is expected to be used increasingly in the future. There are field measurement methods (only recently developed for sulfuryl fluoride) available for all three gases, plus laboratory methods whereby the eventual release of these gases can be achieved in an emissions chamber. However, during the course of the study it became clear that high concentrations of chloropicrin and 1,2-dichloroethane were also being measured in the containers. Field measurements were therefore taken for chloropicrin, but there is no suitable field measurement available for 1,2-dichloroethane. This compound appears to have some cross-sensitivity to the methyl bromide detection tube. Laboratory analysis of the container air confirmed the presence of 1,2-dichloroethane;
- purpose of the objects: the selection of the study objects was partly defined by the way the objects would be used, i.e. close contact between people and the object material, or the environment and the object material;
- safety aspects of the sampling: the safety aspects, e.g. the accessibility of the goods within the container, also determined the selection of the research objects;
- size of the emissions chamber: the size of the emissions chamber (70cm x 30cm x 50cm) determined whether objects could be included in their entirety. In some cases it was possible to reduce objects to a suitable size, or place only part of the object in the emissions chamber;
- research period: the time period within which emissions from an object were measured in the emissions chamber was a maximum of 14 days. Within this timeframe researchers could at least observe which evaporation processes played a role in emitting gases from the research object;

- possible judgements as a result of an emissions study: the results of this study will allow answers to be given to questions as to whether the use of pesticides can be allowed from gassed objects if these pesticides can reach the consumer;
- gas-free status of containers: this study provides no answers to the question as to the timeframe involved before gas-treated containers return to their gas-free state. The return of large amounts of treated cargos in containers to a gas-free state depends on a number of factors, e.g. the type of load, weather conditions and the type and concentration of the pesticide used.

4. Implementation of the study

4.1 Literature study

The literature study focused on the keywords: delivery, gassing, methyl bromide, phosphine, sulfuryl fluoride, Vikane, adsorption, transport, health, for the period 1985 to 2003, over a wide range of bibliographic files from scientific literature and reports from government institutes.

4.2 Adsorption-sensitive materials

Based on the results of the aforementioned literature study, a list was drawn up of materials that, according to the literature, were less suitable for gasification, either due to the fact that gasification guidelines warned of adsorption and evaporation from the material, or because studies of these gassed materials had already observed adsorption and evaporation of pesticides. This list is included in Section 5.2.

4.3 Selection and sampling of gassed objects

4.3.1 Selection

The VROM Inspectorate first made a pre-selection of the containers during standard checks, using field measurements (see Appendix 3); these indicated that the containers were not gas-free. The VROM Inspectorate, in close collaboration with RIVM and after consulting the list of adsorption-sensitive materials, then decided whether the contents of these particular containers should be tested in the emissions chamber. Other parameters were also taken into account, such as the size of the objects in the containers, with respect to the limited space available in the emissions chamber.

4.3.2 Taking samples

Selected objects were sampled by a VROM Inspectorate member of staff. This initially consisted of taking a sample of the air inside the container. The respective container was then opened and a Vac-U-tube used to gather a sample of air in a Tedlar bag (see Appendix 2).

One or more objects from inside the container were then selected for testing in the emissions chamber. The objects, still packed in any trade packaging, were then sealed in airtight plastic foil and transported immediately to RIVM, along with the Tedlar bag(s).

If the emissions chamber was not immediately available, the objects were stored in a refrigerated room at a temperature of 6°C. Measurements have determined that no pesticides were released from the packed objects during the time they were in the refrigerated room.

4.4 Analysis of the Tedlar bags

To check the results of the field measurements, the air samples were analysed using GC-MS² analysis, both for the pesticides found during the field measurements and for any other organic components (see Appendix 4).

4.5 Emission study using the emissions chamber

RIVM developed a so-called 'emissions chamber' in order to implement the required emission study. Appendix 5 describes the emissions chamber in more detail.

The research objects were placed in this chamber and, under controlled circumstances (temperature, air humidity, ventilation fraction) the concentrations of the respective pesticides in the air were measured using a gas chromatograph with a mass-spectrometer. Appendix 6 describes the way in which the concentration of pesticides was followed online. Based on the concentration progress in the emissions chamber researchers were able to determine whether (and if so, how) these pesticides had been emitted from the sample material.

Appendix 7 describes the theory of the various emission processes that can play a role in the evaporation of gaseous components from products. The maximum testing time in the emissions chamber was 14 days. A number of objects were tested for a shorter period due to the observed concentration progress in the emissions chamber that, in some cases, soon provided the information required to allow model calculations.

4.6 Processing of the measurement data

As a result of the measured concentration progress, the following was defined for each object:

- a) whether or not the object emitted any of the pesticide present in the air inside the container;
- b) the total emission (in mg) of pesticide, per kg object;
- c) the characteristics of the emission processes that can play a role for the particular object;
- d) the half-value time³ of the emission processes.

The parameters mentioned under points b-d were calculated by entering the measurement data into an emissions model, after determining that the observed concentration progress did actually fit into the respective emissions model. Determining these parameters allowed a comparison to be made of the emissions behaviour produced by the various products tested.

² GC-MS: gas chromatography with mass spectrometry

³ Half-value time is the time it takes for half of the total present amount of pesticides to evaporate.

5. Results of the study

5.1 Literature study

The literature study resulted in a list of over 200 references; most of which concerned exposure of workers during, or shortly after, gasification, e.g. food products and soil. Only 17 references concerned observations of the presence of pesticides from gassed materials, primarily in homes, but also from plastic water pipes. None of the references described pesticide presence from consumer products, and there was no quantification found in the references.

5.2 List of adsorption-sensitive materials

Based on the limited information from the literature study, a list of materials was drawn up showing those materials that were probably sensitive to adsorption by the gaseous pesticides covered in this study. These materials are listed in Table A.

Table A: Materials that are sensitive to adsorption by gaseous pesticides

Foam rubber
Polystyrene foam
Vinyl, cellophane
Feathers and down
Leather
Wool, threads
Wood, charcoal, paper, carbon
Concrete, cinder blocks (porous)
Soil
Fruit, nuts

Apart from the type of material, the purpose of the objects also played a role in the eventual selection of test objects in the emissions chamber. The way in which these objects were to be used also affected the exposure risk: e.g. skin contact with methyl-bromide-emitting objects, or gas emissions from toys meant for young children.

Appendix 1 provides a brief description of the health aspects of exposure to methyl bromide, chloropicrin, 1,2-dichloroethane, sulfuryl fluoride and phosphine. Relevant entry routes for methyl bromide and chloropicrin are inhalation and through the skin, and for 1,2-dichloroethane, sulfuryl fluoride and phosphine inhalation forms the main entry path into the body.

5.3 Selected objects

Table B shows the objects that were selected for testing, the pesticide used and the concentrations thereof that were found in the container, as determined using the GC-MS analysis of the air samples in the Tedlar bags.

The table also indicates the ingestion route (inhalation, via the skin or mouth) that is considered the most probable, considering the type of object.

Table B: Selected objects and concentrations of pesticides in the containers

Seq.no.	Container	Object	MeBr mg/m ³	CP mg/m ³	DCE mg/m ³	SO ₂ F ₂ mg/m ³	PH ₃ mg/m ³	Main ingest.route mg/m ³
1	1	Slippers	18	n.d.	n.d.	n.d.	n.d.	Inhale/skin
2	1	Marbles	18	n.d.	n.d.	n.d.	n.d.	Inhalation
3	2	Footstool	174	1	n.d.	n.d.	n.d.	Inhale/skin
4	3	Medicines	7	0.3	0.9	n.d.	n.d.	Mouth (digestive system)
5	4	Bamboo wind chime	87	n.d.	n.d.	n.d.	n.d.	Inhalation
6	1	Shoes	18	n.d.	n.d.	n.d.	n.d.	Inhale/skin
7	3	Tablecloths	7	0.3	0.9	n.d.	n.d.	Inhalation
8	5	Mattress	115	3.9	n.d.	n.d.	n.d.	Inhale/skin
9	3	Cushions	7	0.3	0.9	n.d.	n.d.	Inhale/skin
10	6	Dried flowers	9	n.d.	n.d.	n.d.	n.d.	Inhalation
11	7	Plastic blocks	0.1	n.d.	n.d.	n.d.	n.d.	Inhale/skin
12	8	Polyresin figures	n.d.	n.d.	36	n.d.	n.d.	Inhalation
13	9	Bags	2	1.7	n.d.	n.d.	n.d.	Inhalation
14	9	Photo albums	2	1.7	n.d.	n.d.	n.d.	Inhale/skin
15	9	Decoration material	2	1.7	n.d.	n.d.	n.d.	Inhalation
16	9	Jewellery box	2	1.7	n.d.	n.d.	n.d.	Inhalation
17	10	Pistachio nuts	n.d.	n.d.	n.d.	n.d.	n.d.	Mouth (digestive system)
18	9	Candle holder	2	1.7	n.d.	n.d.	n.d.	Inhalation
19	11	Santa Claus figure	n.d.	n.d.	6.2	n.d.	34	Inhalation
20	1	Model boat	18	n.d.	n.d.	n.d.	n.d.	Inhalation
21	1	Rucksack	18	n.d.	n.d.	n.d.	n.d.	Inhalation

n.d.= not detected

MeBr = methyl bromide

CP = chloropicrin

DCE = 1,2-dichloroethane

SO₂F₂ = sulfuryl fluoride (vikane)

PH₃ = phosphine

None of the containers showed any indications (stickers, cargo documents) that the contents of the containers had been gassed during transport. Packing wood was not used in any of the containers. None of the containers were transporting goods that legally or otherwise required the use of pesticides.

5.4 Emission study

The sampled material was first weighed and then placed in the emissions chamber under controlled circumstances. From the moment the sampled material was placed in the chamber the concentration of the respective pesticide in the chamber was measured by sucking a sample of air (via a bypass) into a GC-MS every 30 minutes and analysing it carefully. This analysis, together with the known parameters of the emissions chamber, allows the following model to be calculated:

- a. the total amount of pesticide that is emitted (in mg pesticide per kg object); plus
- b. the characteristics of the emission processes that play a role for the particular object; and
- c. the half-value time for the various emission processes per object.

Table C shows the calculated results for all tested samples in a single overview. Appendix 8, in addition to showing pictures of all objects included in this study, also includes an overview of the research results per object.

Table C: Total emissions and emission processes per object, based on the measured data from the emissions chamber

Seq.no.	container number	Object	total emissions (mg/kg)					pesticide	Emission processes					
			MeBr	CP	DCE	SO ₂ F ₂	PH ₃		A (%)	T _{1/2} (h)	B (%)	T _{1/2} (h)	C (%)	T _{1/2} (h)
1	1	Slippers	2.6	0	0	0	0	MeBr	85	3	0		15	50
2	1	Marbles	8.6	0	0	0	0	MeBr	6	8	94	236	0	0
3	2	Footstool	39	0	0	0	0	MeBr	100	1	0		0	
4	3	Medicines	0	0	0	0	0	MeBr	0		0		0	
5	4	Bamboo wind chime	0.4	0	0	0	0	MeBr	64	2	36	46	0	
6	1	Shoes	3.6	13	0	0	0	MeBr	5	3	76	27	19	255
								CP	14	60	86	2080	0	
7	3	Tablecloths	0.03	1	0	0	0	MeBr	100	2	0		0	
								CP	23	9	77	108		
8	5	Mattress	11	12	0	0	0	MeBr	47	9	5	61	48	7620
								CP	60	43	40	147	0	
9	3	Cushions	1	0	0	0	0	MeBr	100	4	0		0	
10	6	Dried flowers	0.1	0	0	0	0	MeBr	8	2	92	96		
11	7	Plastic blocks	0	0	0	0	0	Nvt	nvt	nvt	nvt	nvt	nvt	nvt
12	8	polyresin figures	0	0	+	0	0	DCE	-	-	-	-	-	-
13	9	Bags	0	43	0	0	0	CP	96	4	4	65	0	
14	9	Photo albums	+	+	0	0	0	MeBr/CP	-	-	-	-	-	-
15	9	Decoration material	0	0	0	0	0	MeBr/CP	nvt	nvt	nvt	nvt	nvt	nvt
16	9	Jewellery box	0	0	0	0	0	MeBr/CP	nvt	nvt	nvt	nvt	nvt	nvt
17	10	Pistachio nuts	2.5	0	0	0	0	MeBr	100	28	0		0	
18	9	Candle holder	0	0	0	0	0	Nvt	nvt	nvt	nvt	nvt	nvt	nvt
19	11	Santa Claus figure	0	0	0.8	0	0	DCE	15	3	4	9	81	139
20	1	Model boat	0.01	0	0	0	0	MeBr	54	2	46	14	0	
21	1	Rucksack	0.08	0	0	0	0	MeBr	50	3	50	21	0	

+ = measured concentrations were too high to fit into model; no modelling possible
 - = no data available because emissions pattern did not fit into model (very fast emission)
 nvt = not applicable (no measurable emission)
 T_{1/2} = half-value time
 A = fast emission process (see Appendix 7)
 B = slow emission process (see Appendix 7)
 C = very slo emission process (see Appendix 7)

MeBr = methyl bromide
 CP = chloropicrin
 DCE =1,2-dichloroethane
 SO₂F₂=sulfurylfluoride (vikane)
 PH₃ = phosphine

6. Extra study as a result of intermediate results of the emission study

During the emission study for object number four (medicines), the emissions chamber showed no signs of gaseous compounds. There are two possible reasons for this:

- a. either there was no adsorption of pesticides;
- b. or an irreversible adsorption of pesticides had taken place.

In order to gain better insight into this phenomenon (outside the scope of the emissions study), object four was subjected to further study (see Appendix 9). The study results indicate that not only was there irreversible adsorption of methyl bromide in the medicine, but that methyl bromide had also reacted to the ingredients in the medicine. The composition of the medicine was therefore changed, and the respective product had to be removed from the market and destroyed.

As this report was being written, a container of food products was discovered by VROM Inspectorate that showed traces of methyl bromide. As a result of the aforementioned intermediate results concerning medicines, several food items (mie, chocolate biscuits, and sweets) from this container were tested for methyl bromide levels, and for emissions of methyl bromide. Appendix 10 describes this study.

The study of the food items showed that the mie (Chinese noodles), chocolate biscuits and sweets contained methyl bromide, and that contamination with chloropicrin was also possible.

7. Discussion of the results

7.1 Container study

7.1.1 General

None of the 11 containers from which the tested objects were taken, showed any indication that these containers had been treated with gaseous pesticides. This is legally required: the outer surfaces of such containers must display a description and danger symbols to indicate gasification.

Packing wood was not used in any of the containers: just as it was neither necessary nor legally required to use pesticides for the type of commercial goods in these containers.

7.1.2 Pesticides

Table D shows (per container) whether or not (and if so, which type of) pesticides were measured in the air inside the relevant container.

Table D: Gaseous pesticides per container

container pesticide	1	2	3	4	5	6	7	8	9	10	11	Total number of containers per pesticide
MeBr	+	+	+	+	+	+	+	-	+	-	-	8
CP	-	+	+	-	+	-	-	-	+	-	-	4
DCE	-	-	+	-	-	-	-	+	-	-	-	2
PH ₃	-	-	-	-	-	-	-	-	-	-	+	1
SO ₂ F ₂	-	-	-	-	-	-	-	-	-	-	-	0

+ = measured

- = not measured

MeBr = methyl bromide

CP = chloropicrin

DCE = 1,2-dichloroethane

PH₃ = phosphine

SO₂F₂ = sulfuryl fluoride

Phosphine was discovered in one container.

During the course of this study there was no sulfuryl fluoride found in the containers.

One container (number 10) of the 11 containers included in this study, was found to have given a false positive field measurement: i.e. no pesticides were found in the air inside the container, although the positive field measurement provided grounds for testing the container.

7.1.3 Combinations of pesticides

Eight of the 11 containers included in this study were treated with methyl bromide. It is remarkable that four of these containers also showed traces of chloropicrin and that one of these four containers also tested positive for 1,2-dichloroethane.

The pesticide 1,2-dichloroethane was found in two containers, both transporting so-called polyresin figures. Using 1,2-dichloroethane as a pesticide is well known, but VROM Inspectorate has, up to now, never seen its use in freight containers. In these situations it is not possible to determine whether the 1,2-dichloroethane was processed in the material from which the figures were made, and evaporated, or whether this pesticide was measurable as a result of gassing the containers.

It is certainly remarkable that standard container studies (outside the emission study) in 2004, found 1,2-dichloroethane in eight containers. There is no field method available for measuring 1,2-dichloroethane. It is therefore recommended that such a field measurement method be developed as soon as possible so that, in the future, this compound can also be measured in the field (see Recommendations).

7.2 Emission study

The emission study included objects with various exposure routes. For half of these objects (12) the main ingestion route concerned inhalation. In seven cases ingestion could also take place through the skin, and the two remaining objects could also cause exposure via the mouth. Table E shows which objects emitted one or more pesticides.

Table E: Pesticides emitted per object

Object and container gas			Gas emitted	MeBr	CP	DCE	SO ₂ F ₂	PH ₃
1	Slippers	MeBr		+	-	-	-	-
2	Marbles	MeBr		+	-	-	-	-
3	Footstool	MeBr en CP		+	-	-	-	-
4	Medicines	MeBr en CP		-	-	-	-	-
5	Bamboo wind chime	MeBr		+	-	-	-	-
6	Shoes	MeBr		+	+	-	-	-
7		MeBr en CP en DCE		+	+	-	-	-
8	Tablecloths	MeBr en CP		+	+	-	-	-
9		MeBr en CP en DCE		+	-	-	-	-
10	Mattress	MeBr		+	-	-	-	-
11		MeBr		-	-	-	-	-
12	Cushions	DCE		-	-	+	-	-
13	Dried flowers	MeBr en CP		-	+	-	-	-
14	Plastic blocks	MeBr en CP		+	+	-	-	-
15	polyresin figures	MeBr en CP		-	-	-	-	-
16	Bags	MeBr en CP		-	-	-	-	-
17	Photo albums	-		+	-	-	-	-
18	Decoration material	MeBr en CP		-	-	-	-	-
19	Jewellery box	DCE en PH ₃		-	-	+	-	-
20	Pistachio nuts	MeBr		+	-	-	-	-
21	Candle holder	MeBr		+	-	-	-	-
Total				13	5	2	0	0

+ = emission determined

- = no emission determined

MeBr = methyl bromide

CP = chloropicrin

DCE = 1,2-dichloroethane

SO₂F₂ = sulfurylfluoride

PH₃ = phosphine

Thirteen of the objects studied emitted methyl bromide. Four of these 13 cases also included chloropicrin emissions. One object emitted only chloropicrin. Two objects emitted 1,2-dichloroethane. It is not known whether this compound was used as pesticide in the container. Only one object (gassed with phosphine) was included in the emission study, where no phosphine emission was determined.

Five of the 21 objects tested emitted no pesticides; this concerned four objects that were gassed using methyl bromide and chloropicrin, and one object that was treated with phosphine. These non-emission objects vary enormously in composition: medicines, hard plastic, wood, paper, cardboard. Possible explanations for this non-emission of methyl bromide and (perhaps) chloropicrin are that:

- a. these objects did not adsorb any pesticides;
- b. there is an irreversible adsorption of pesticides.

The emission patterns of a pesticide can vary per object: e.g. methyl bromide evaporated quickly from the footstool, but showed a tendency to evaporate slowly from the dried flowers.

If several pesticides are used for a particular object, this can result in emission patterns that vary considerably. The half-value times for the emission process vary considerably, up to over 300 days for the mattress. This means that, even after being

in the Netherlands for 10 months, only half of the amount of pesticide had evaporated from the mattress studied.

7.3 Interpreting the results

This study stemmed from the question as to whether it was possible for consumers to be exposed to pesticides through using certain goods that had been imported in gassed containers.

Considering the half-value times that were determined during the course of the study, it is highly probable that consumers are indeed exposed to such risks. In addition, various products studied produced a half-value time of several months. During this period most of the objects tested would have reached consumer households via the normal trade routes.

The question then remains as to whether or not this risk factor is acceptable. This question cannot be answered by the results of this study. The working method described and followed here was generated according to the objectives of the study. This method has both advantages and disadvantages. Before the results of the study can be interpreted correctly, the following aspects should be taken into consideration. The measurement data gathered was largely determined by the practical situation. The results therefore draw a picture of what *could* happen in practice. The study provides no information as to the extent to which this risk could occur: these (gas-treated) objects were taken from containers entering the Netherlands. Out of the entire cargo of gassed objects, only one item was removed from the container and taken for testing. It is quite likely that other goods in the container might have shown greater or lesser emissions if they had been placed differently in the container, if there had been another contact pattern with the (source of the) pesticide, or if another composition of goods had been involved.

Measurements determined that the release of pesticides was indeed confirmed. The extent to which the general public is exposed was not included in the scope of this study, and cannot be judged based on the results of this study. This was not part of the study's objectives. This study only aimed to determine whether or not pesticides were evaporating in the emissions chamber. The measured concentrations are not representative of the exposure levels and are therefore not reported. In order to determine such risk to the general public, an inventory first needs to be made of the exposure routes. This will then show a wide number of variables. The products studied also show various exposure routes due to the use and circumstances surrounding the use thereof:

- shoes and clothes lead to exposure through the skin, as well as exposure through inhaling the emitted gases. Quantifying this exposure needs to take account of aspects such as long contact times through wearing, washing clothes, removal due to rain on clothes and shoes, and the effect of other clothes;
- exposure from mattresses and cuddly toys can be greater during use, due to the pressure exerted by the user, whereby air (containing pesticide) is dispersed close to the nose. In addition to inhalation there is also a certain amount of skin contact. The extent of the exposure is also partially influenced

- by the size of the room, the ventilation, clothing coverage and other (bed) materials;
- the effects determined for medicines and food products are totally different: not only can the pesticides be adsorbed into the products, these compounds also probably react to the product's components. Which reaction products are produced depends on the food product and the reaction circumstances.

Despite all the limitations of this study to judge the extent of the risk, the conclusion remains that consumers ARE exposed to pesticides through gassing of products in freight containers. In most cases this gasification is unnecessary for the products studied. Exposure takes place through inhalation, skin contact and orally. This oral exposure occurs when gassed products and medicines are swallowed, and concerns exposure to pesticides and unknown reaction products. The extent to which this risk is acceptable is a social question that is based on the amount of risk and the extent to which this risk is necessary.

8. Conclusions

1. Import containers are treated with gaseous pesticides, without any legal requirement to do so.
2. This study shows that consumers are exposed to gaseous pesticides, as a result of these compounds being emitted from gassed products. Ingestion can occur through inhalation and via the skin.
3. This study found that methyl bromide and chloropicrin evaporated from 75% of the studied objects. The emission or evaporation pattern varies per object and per compound.
4. This study found 1,2-dichloroethane being evaporated from two objects. Although it is not certain whether this was the result of previous gasification with 1,2-dichloroethane, this finding leads to the conclusion that using 1,2-dichloroethane as a pesticide leads to evaporation of this compound.
5. No phosphine emissions (from objects treated with this compound) were found during this study: only one object was studied and no phosphine emission could be detected.
6. The extent of the possible health risks as a result of the aforementioned exposure to gaseous pesticides cannot be quantified accurately on the basis of this limited study.
7. Even if no emissions of pesticides can be detected from objects transported in gas-treated containers, medicines and food products should at least be studied to discover whether pesticides have been irreversibly incorporated into these products.

9. Recommendations

1. This study has shown that objects transported in gassed containers do emit these pesticides, whereby consumers can be exposed to these compounds in their own home. Considering the set-up and scope of this study it is not possible to determine the extent of the exposure risk to dangerous concentrations of pesticides. It is therefore recommended that further practical research should be carried out, whereby the exposure route via the skin should not be neglected.
2. Now that it has been determined that pesticide emissions lead to exposure by the general public, it is recommended that, for example, the Health Council should be asked to advise on the desirability of this situation, partly considering the possibility to avoid such exposure (the current lack of any legal obligation or necessity for gasification) and considering the question of whether there is any health risk.
3. This study has shown that irreversible adsorption of methyl bromide and chloropicrin can occur in food products. It is not known whether this also applies to phosphine. It is therefore recommended that further study should be undertaken into:
 - the adsorption of phosphine in food products;
 - risks of ingesting phosphine-retaining food products;
 - risks of ingesting methyl bromide or chloropicrin in food products;
 - food products that are gassed with various gases.
4. Further research into any (or increased) use of 1,2-dichloroethane as a pesticide in containers is also recommended. This is a compound for which no standard detection measurements are carried out by gasification companies, and for which there are currently no field measurement methods available.
5. It is also recommended that a field measurement method should be developed for detecting 1,2-dichloroethane in the air, so that in the future containers can also be checked for the presence of this compound.

Appendix 1: Health Aspects of methyl bromide, chloropicrin, 1,2-dichloroethane, sulfuryl fluoride and phosphine

Methyl bromide

Methyl bromide is poisonous if inhaled, and can lead to narcotic effects even in small concentrations. Symptoms after exposure include: dizziness, headache, nauseousness, equilibrium disturbances, and irritation of the airways. Methyl bromide can also affect the central nervous system and, in high concentrations, even lead to death as a result of respiratory failure.

Norms

The ATSDR (Agency of Toxic Substances and Disease Registry) has determined a minimum risk level (MRL) of 0.05 ppm (50 ppb) for acute and sub-chronic exposure (i.e. up to a maximum of one year). For chronic exposure the MRL is a factor of 10 lower, i.e. 5 ppb. In both cases the MRL applies to exposure over seven days per week and 24 hours per day. Note that methyl bromide is also adsorbed via the skin, but this is dependent on aspects such as circulation, humidity and coverage of the skin. With a relatively large body surface/weight ratio (e.g. in babies) it is possible that skin adsorption would contribute substantially to the impact on the body. This contribution is impossible to define (or model) based on the current limited data available.

A MAC value (for methyl bromide) has been defined for employees, at which concentration an employee may be exposed for eight hours per day, for a maximum 40-hour week, and must be able to continue his/her working life without experiencing health problems. This MAC value is 0.250 ppm methyl bromide.

References:

Anon. (2001) Evaluated OECD data on methyl bromide.

Hertel R.F. and Kielhorn T. (1995) Methyl bromide. Environmental Health Criteria 166. IPCS/WHO.

Norman K.N.T. (2000) The persistence of methyl bromide residues in rice, dried fruits, seeds and nuts following laboratory fumigation. *Pest manag Sci* 56: pp. 154-158.

Norman K.N.T., Scudamore K.A., Matthews W.A. and Wilson M.F. (1995) Determination of methyl bromide residues in stored foods using automated headspace gas chromatography. *Pest Sci* 44: pp. 309-316.

Chloropicrin

Chloropicrin is a volatile compound that, when inhaled, causes considerable irritation of the eyes, nose, throat and respiratory tract. The 'tear generation' process is also remarkable. The use of chloropicrin as insecticide goes back to the beginning of the 20th century. During the Second World War chloropicrin was used as a weapon of war. Inhalation of chloropicrin leads to the aforementioned irritation and also to nausea and vomiting. Lung damage occurs primarily in medium-sized and small bronchial tubes, and lung oedema is usually the cause of death. Exposure can also lead to inhalatory sensitisation.

Norms

There are no oral limits available for chloropicrin. Inhalation limits only concern acute values for calamity situations. These so-called disaster intervention values are:

VRW (an information guideline): 0.2 mg/m³ (eye irritation)

AGW (alarm limit value): 2 mg/m³ (eye irritation)

LBW (life-threatening limit): 10 mg/m³ (animals will die)

These maximum values apply for single exposures of one hour. The only known maximum value for longer exposure is the work-toxicological MAC value. This is 0.7 mg/m³. This value is based on very limited data (American TLV (threshold limit value) evaluation).

References:

ACGIH (1991) Documentation of the Threshold Limit Values and Biological Indices and Biological Exposure Indices. Sixth Edition, Volume 1.

BCPC (2002) The Pesticide Manual 2002-2003. Twelfth Edition, British Crop Protection Council.

ERPG (1999) Emergency Response Guidelines Chloropicrin, dated 1999.

GGD (2000) Beknopte stofdocumenten interventiewaarden gevaarlijke stoffen: Chloorpicrine (versie 2000, pagina 76). GGD Rotterdam.

WHO (2003) Chloropicrin in drinking-water: Background document for development of WHO Guidelines for Drinking-Water Quality. WHO/SDE/WSH/03.04/52.

1,2-dichloroethane

This pleasant-smelling volatile solvent damages various organ systems after a single or repeated exposure, e.g. liver, kidneys, nervous system, cardiovascular system, and the immune system. Observed symptoms from human intoxication include suppression of the central nervous system, nausea and vomiting, respiratory effects, as well as liver and kidney damage. In the case of lethal intoxications, the presumed cause of death was usually heart rhythm dysfunction. Toxicological studies into longer-term exposure show genotoxicity (damage to inherited material), carcinogenicity and damage to the reproduction system and pregnancy.

Norms

In 2001 the RIVM recommended chronic maximum values for air (TCL) of 48 µg/m³ and a chronic oral maximum value (TDI) of 14 µg /kg body weight/day (both based on the genotoxic-carcinogenic process). There are no specific maximum values for short-term exposure.

References:

ATSDR (2001) Toxicological Profile for 1,2-dichloroethane. Agency of Toxic Substances and Disease Registry, US Department of Health and Human Services.

RIVM (2001) Re-evaluation of human-toxicological Maximum Permissible Risk levels. RIVM report no. 711701025, dated March 2001.

Sulfuryl fluoride

Sulfuryl fluoride is a colourless gas that works by suppressing the nervous system. Intoxication symptoms consist of drowsiness, slow coordination and speech, nauseousness, vomiting, stomach ache, a feeling of drunkenness, itching and convulsions. High concentrations can cause irritation of the respiratory tract or respiratory failure. Skin contact is not dangerous, but contact with the liquid form can cause pain reactions as a result of fast evaporation. The long-term effects are the same as those for fluoride, i.e. damage to the bone structure and teeth.

Norms

There are no known health-based norms for this substance.

References:

EXTOXNET (Extension Toxicology Network). Pesticide Information Profiles: sulfuryl fluoride. <http://extoxnet.orst.edu/pips/sulfuryl.htm>

Phosphine

Phosphine is a poison that generally focuses on the metabolism: it damages important enzymes in the respiratory system of body cells, resulting in internal asphyxiation.

Above all, inhalation can result in a local effect of the respiratory tract. The symptoms (lethal concentrations) include: low blood pressure and collapse. Slightly lower concentrations cause lung oedema, which can also be lethal. Acute intoxications can also cause serious deviations to the brain, heart, liver and kidneys.

Norms

The maximum toxicological values were set by RIVM in 1996 for the general public's exposure to phosphine. For exposure of up to 24 hours, RIVM set a maximum value for the general public of 20 µg/m³. For exposure to phosphine of up to two weeks, RIVM set this maximum value at 17 µg/m³. For chronic exposure (up to life-long exposure) RIVM set a maximum value for the general population of 0.25 µg/m³.

References:

RIVM (1996) Containerontsmettingen met fosfine - Afleiding van inhalatoire grenswaarden. Ad hoc recommendations RIVM/CSR, dated April 1996.

RIVM (2000) Toxicologisch profiel voor Fosfine. Ad hoc recommendations RIVM/CSR, dated 20 September 2000.

Appendix 2: Sampling in Tedlar bags using the Vac-U-Tube

Figure 2.1 shows a picture of the Vac-U-Tube.

Figure 2.1: Vac-U-Tube



The Vac-U-Tube works as follows:

An empty Tedlar bag is inserted into the cylinder of the Vac-U-tube. A plunger is then used to create a vacuum in the cylinder, whereby the Tedlar bag expands and fills with air from the atmosphere being tested. The Tedlar bag is then sealed and removed from the cylinder. The bag is labelled with a sample code and transported (at ambient temperature) to the laboratory for further analysis.

Appendix 3: Field methods used in the emission study

- Detection tubes

Detection tubes work according to the colouring theory. The compound to be detected reacts to the substance(s) in the detection tube and changes colour. The intensity of the colour change indicates the extent of the concentration of this compound in the air sampled.

Detection tubes were used in this study to measure methyl bromide, chloropicrin and sulfuryl fluoride. A certain cross-sensitivity exists in using detection tubes, where a colouring can occur as a result of the presence of another substance in the air; in this case methyl bromide, chloropicrin or sulfuryl fluoride. The colouring can (but may not necessarily) deviate from the usual colouring, as a result of the presence of methyl bromide, chloropicrin or sulfuryl fluoride.

- Electrochemical cells

Molecules of the (to be determined) substance generate a voltage difference in an electrochemical cell, equal to the concentration of this substance in the air. Depending on the (to be detected) component, the specific electrochemical cell is more or less sensitive to interference from other substances.

This study used an electrochemical cell to measure phosphine.

Appendix 4 Laboratory analysis of air samples in tedlar bags

In order to analyse methyl bromide, chloropicrin and sulfuryl fluoride in air, a 50 ml air sample from a Tedlar bag was analysed using a gas chromatograph with a mass spectrometer. The sample was thus separated in a capillary column in the gas chromatograph and detected using a mass spectrometer in the 'electron impact' mode. The full scan range is 29-300 m/z. Quantification occurs with respect to a 0.5 ppm sulfuryl fluoride standard and 0.1 ppm methyl bromide standard in a Tedlar bag, and a 0.24 ppm chloropicrin standard in a canister.

The other components were identified using the NIST (National Institute of Standards and Technology) library (120,000 components) and the AMDIS (Automatic Mass Spectrum Deconvolution and Identification System) deconvolution technique. Hydrocarbons that are part of the TO-14 standard (including 1,2-dichloroethane) are quantified with respect to these standard concentrations.

Appendix 5 The emissions chamber – measurement equipment used to determine gases in materials

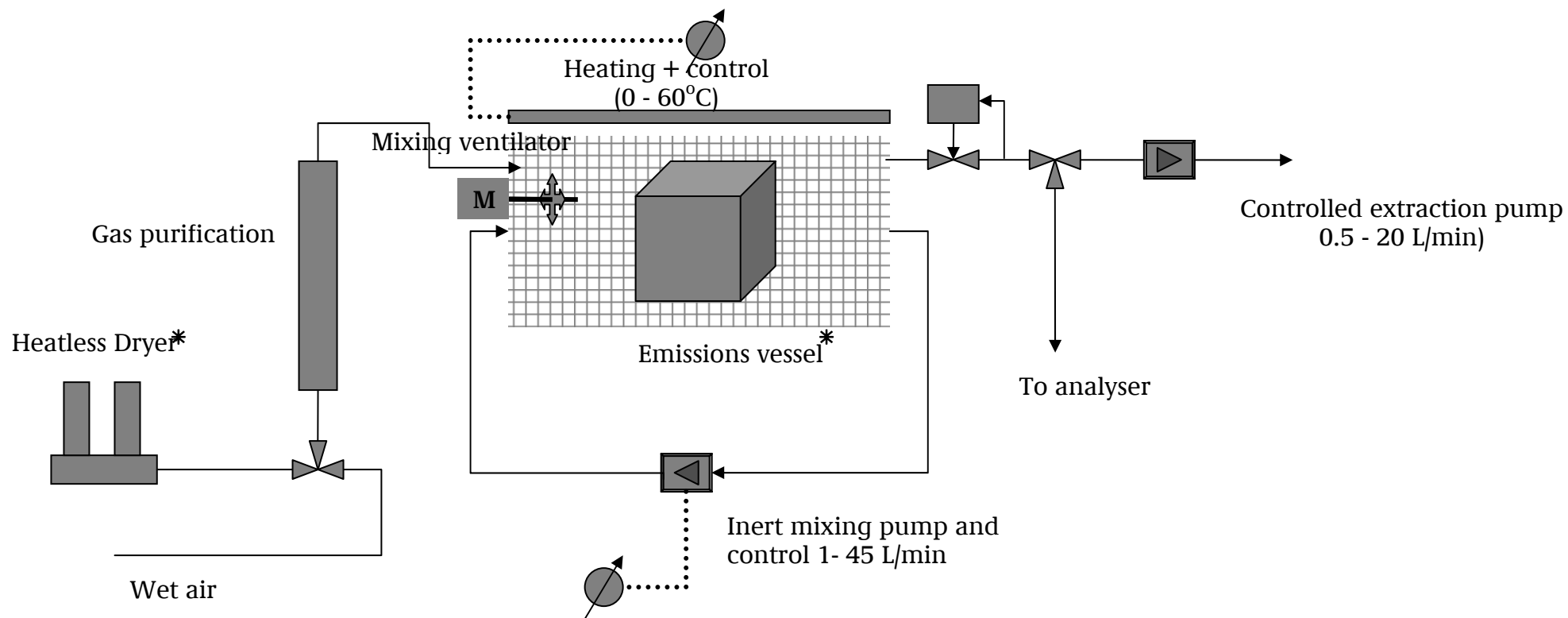
The materials studied were placed in an emissions vessel with a volume of around 200 litres that was rinsed with pure outside air at a regulated rate (up to 45 litres/minute, controlled using mass flow controllers). A sample was taken from this airflow every 30 minutes). A second circuit ensured optimum mixing of the clean air input and the emitted gases. The temperature was held stable at 30°C (see following illustration of the empty emissions chamber).

Figure 5.1: Emissions chamber



A diagram of the equipment used is shown on the following page.

Diagram of emissions vessel set-up



Appendix 6 Measuring the concentrations of pesticides in the emissions chamber

- Methyl bromide, chloropicrin, 1,2-dichloroethane and sulfuryl fluoride

In order to trace the concentration process of compounds (methyl bromide, chloropicrin, 1,2-dichloroethane and sulfuryl fluoride) in the air inside the emissions chamber, an air sample (50 ml) was taken from the emissions chamber every 30 minutes using a suction pump in a gas chromatograph with a mass spectrometer. The air sample was then immediately analysed (see Appendix 4 for the analysis method).

- Phosphine

The phosphine concentration in the air inside the emissions chamber was traced via another method. An air sample (62.5 ml) was taken every 30 minutes from the emissions chamber using a Thermosorption tube (Air Toxic tube). This tube was then analysed via a gas chromatograph with mass spectrometer and thermodesorption sampler, using a blank tube and with respect to two phosphine standards (28 ppb and 500 ppb).

Appendix 7 Theoretical background to the emission measurements in the emissions chamber

In determining the amount of fumigant present in the materials to be tested, it is assumed that fumigant stored in the material is released in such a way that a number of characteristics can be derived from this process.

The basis is a well-controlled environment in which the material can be placed and the airflow in which the desorbed fumigant is transported. By keeping the temperature of the material and the speed of the airflow within certain margins, the process whereby the fumigant is released from the material can be kept constant.

It is assumed that under these circumstances the release process can only be determined by the amount of fumigant that is present in the material. Since the amount of fumigant released is reduced over a period of time, this release process will also be reduced. By taking regular measurements of the concentration in the air around the material this release process becomes visible, and therefore also the characteristics of the release process.

The type of release process cannot be determined from these characteristics. This study focused on three release processes: a fast process (A), a slow process (B) and a very slow process (C). These processes will further consist of desorption (a relatively fast process), plus diffusion and migration (slow processes). This approach involves making a number of assumptions that were verified using the model approach, which allows the characteristics of the processes to be calculated. Based on these characteristics, the total amount of fumigant present can be calculated, as released by each of these processes, plus the speed with which this occurs under controlled circumstances (as determined by the half-value time).

The development of the emissions chamber and the method of emission measurement from goods items is described in the RIVM report (not yet completed) entitled Assessment of emission of fumigants from consumer products, written by H.J.T. Bloemen, M.R. Ramlal, J.W. Uiterwijk, and E.M. van Putten.

Appendix 8 List of all objects involved in the study

The results of the emission study are shown alongside the picture of each object. Three processes are defined in the release pattern; the results clearly show which processes (and the extent to which these processes) played a role for the particular object.

Object 1: Slippers

**Total compound released:**

Methyl bromide: 2.6 mg/kg

Release pattern:

Methyl bromide:

85% quickly, $T_{1/2}$ = 3 hrs

15% very slowly, $T_{1/2}$ = 3 hrs

Object 2: Marbles

**Total compound released:**

Methyl bromide: 8.6 mg/kg

Release pattern:

Methyl bromide:

6% quickly, $T_{1/2}$ = 8 hrs

94% slowly, $T_{1/2}$ = 236 hrs

Object 3: Footstool

**Total compound released:**

Methyl bromide: 39 mg/kg

Release pattern:

Methyl bromide:

100% quickly, $T_{1/2}$ = 1 hr

Object 4: Medicines

Total compound released:
No release

Release pattern:
Not applicable

Object 5: Bamboo wind chime

Total compound released:
Methyl bromide: 0.4 mg/kg

Release pattern:
Methyl bromide:
64% quickly, $T_{1/2}$ = 2 hrs
36% very slowly, $T_{1/2}$ = 46 hrs

Object 6: Shoes

Total compound released:
Methyl bromide: 3.6 mg/kg
Chloropicrin: 13 mg/kg

Release pattern:
Methyl bromide:
5% quickly, $T_{1/2}$ = 3 hrs
76% slowly, $T_{1/2}$ = 27 hrs
19% very slowly, T = 255 hrs
Chloropicrin:
14% quickly, $T_{1/2}$ = 60 hrs
86% slowly, $T_{1/2}$ = 2080 hrs

Object 7: Tablecloths

Total compound released:
Methyl bromide: 0.03 mg/kg
Chloropicrin: 1 mg/kg

Release pattern:
Methyl bromide:
100% quickly, $T_{1/2}$ = 2 hrs
Chloropicrin:
23% quickly, $T_{1/2}$ = 9 hrs
77% slowly, $T_{1/2}$ = 108 hrs

Object 8: Mattress**Total compound released:**

Methyl bromide: 11 mg/kg

Chloropicrin: 12 mg/kg

Release pattern:

Methyl bromide:

47% quickly, $T_{1/2}$ = 9 hrs5% slowly, $T_{1/2}$ = 61 hrs48% very slowly, $T_{1/2}$ = 7620 hrs

Chloropicrin:

60% quickly, $T_{1/2}$ = 43 hrs40% slowly, $T_{1/2}$ = 147 hrs**Object 9: Cushions****Total compound released:**

Methyl bromide: 1mg/kg

Release pattern:

Methyl bromide:

100% quickly, $T_{1/2}$ = 4 hrs**Object 10: Dried flowers****Total compound released:**

Methyl bromide: 0.1 mg/kg

Release pattern:

Methyl bromide:

8% quickly, $T_{1/2}$ = 2 hrs92% slowly, $T_{1/2}$ = 96 hrs**Object 11: Plastic blocks****Total compound released:**

No release

Release pattern:

Not applicable

Object 12: Polyresin figures

**Total compound released:**

Dichloroethane: very high

Release pattern:

Dichloroethane

Release data did not fit into model

Object 13: Bags

**Total compound released:**

Chloropicrin: 43 mg/kg

Release pattern:

Chloropicrin:

96% quickly, $T_{1/2}$ = 4 hrs4% slowly, $T_{1/2}$ = 65 hrs

Object 14: Photo albums

**Total compound released:**

Methyl bromide: very high

Chloropicrin: very high

Release pattern:

Methyl bromide:

Release data did not fit into model

Chloropicrin:

Release data did not fit into model

Object 15: Decoration material

**Total compound released:**

No release

Release pattern:

Not applicable

Object 16: Jewellery box



Total compound released:
No release

Release pattern:
Not applicable

Object 17: Pistachio nuts



Total compound released:
Methyl bromide: 2.5 mg/kg

Release pattern:
Methyl bromide:
100% quickly, $T_{1/2}$ = 28 hrs

Object 18: Candle holder



Total compound released:
No release

Release pattern:
Not applicable

Object 19: Santa Claus figure



Total compound released:
Dichloroethane: 0.8 mg/kg

Release pattern:
Dichloroethane:
15% quickly, $T_{1/2}$ = 3 hrs
4% slowly, $T_{1/2}$ = 9 hrs
81% very slowly, $T_{1/2}$ = 139 hrs

Object 20: Model boat

Total compound released:
Methyl bromide: 0.01 mg/kg

Release pattern:
Methyl bromide:
54% quickly, $T_{1/2} = 2$ hrs
46% slowly, $T_{1/2} = 14$ hrs

Object 21: Rucksack

Total compound released:
Methyl bromide: 0.08 mg/kg

Release pattern
Methyl bromide:
50% quickly, $T_{1/2} = 3$ hrs
50% slowly, $T_{1/2} = 21$ hrs

Appendix 9: Study into gassed medicines

On 13 April 2004 a sample of medicines was taken from a gas-treated container. A sample of the air from inside this container was also taken in a Tedlar bag. Analysis of the air sample showed a methyl bromide concentration of 7 mg/m³, and a chloropicrin concentration of 0.27 mg/m³, plus a number of other chlorinated hydrocarbons. On the basis of these analysis results, researchers concluded that the container was treated with methyl bromide and chloropicrin. Chloropicrin is often added to methyl bromide to give it a better fragrance.

This gasification could possibly lead to pesticides being adsorbed by the medicinal products inside the container. A study into the release of pesticides from the medicines in the emissions chamber resulted in immeasurable concentrations of methyl bromide and chloropicrin.

This could mean that:

- a) the pesticides did NOT penetrate through to the medicines; or
- b) the pesticides were irreversibly adsorbed by the medicines.

These conclusions led to the following study into the composition of the gassed medicines.

Objective:

To determine whether medicines had become contaminated as a result of gasification (using methyl bromide) of the container in which the medicines were transported.

Research material

The research material consisted of medicines (brand name Haloperidol) that contained the ingredient butyrofenon. Before being used in this contamination study, the research material was first tested in the emissions chamber. Testing in the emissions chamber showed no measurable concentrations of methyl bromide or chloropicrin. According to the medical supplier, Haloperidol does not contain any bromine-based compounds.

Implementation of the study

Screening for total amount of bromine

In order to obtain an indication of any possible traces of methyl bromide in the medicines sampled, the total bromine content was first determined using XRF (X-ray fluorescent) analysis. The results of this indicative study gave cause for a quantitative determination of the methyl bromide concentrations in medicines.

Determining the extent of the methyl bromide

There was no validated analysis method available for the quantitative determination of the methyl bromide levels in medicines. Therefore a 'purge and trap' method was used, whereby volatile organic substances (including methyl bromide) are retrieved from the sample and held in a suitable adsorbent. This is then analysed after thermal desorption, using GC-MS for volatile organic compounds.

Results of the study

Table 1 shows the results of the screened XRF determination for bromine in two samples of medicines (Haloperidol). The average amount found is 30 mg of bromine per kg of medicine.

Table 9.1: Results of the XRF determination for total bromine content

Sample	Total bromine content (mg Br/kg product)
A	28.8
B	30.7
Average total bromine content	30

The quantitative determination of the methyl bromide content in Haloperidol showed that this product does not contain methyl bromide.

Discussion of the results

It is possible that the bromine content of 30 mg/kg (determined through XRF analysis) found in the Haloperidol, which according to the supplier does not contain bromine, was caused by adsorption of the methyl bromide with which the container was gassed. However, this compound was not found in the medicine. It is possible that the methyl bromide had started a reaction with one of the ingredients in the medicine (butyrofenon): further study, using proton NMR (proton-Nuclear Magnetic Resonance) showed contamination of the medicine that, in theory, could be caused by methylation of the butyrofenon.

Conclusion

The medicine Haloperidol, sampled from one of the gassed containers, was probably contaminated with methyl bromide. The contaminant possibly caused a reaction with one of the ingredients in the medicine, whereby the composition of the medicine was changed.

Appendix 10: Study into gassed food products

On 19 November 2004 three food products were sampled from a gassed container. The air in this container was also sampled via a Tedlar bag. Analysis of the air sample showed a methyl bromide concentration level of 0.186 mg/m³. Chloropicrin was not above the detection limit of 0.025 mg/m³.

On the basis of these analysis results researchers concluded that the container had been gassed with methyl bromide. The addition of chloropicrin to the methyl bromide could not be confirmed. A previous study showed that methyl bromide can be irreversibly adsorbed by gassed products and can possibly react with components of these products (see also Appendix 9 of this report). It was therefore considered necessary to conduct further research into possible contamination of the sampled gassed food products.

Objective

To determine any contamination of food products as a result of gasification using methyl bromide.

Research material

Three food products were sampled for this study:

- 1 pack of mie (thin Chinese noodles), sample code FSCU 767919-2 A
- 12 plastic toy beakers filled with sweets, sample code FSCU 76919-2 B
- 1 box of chocolate biscuits, sample code FSCU 76919-2 C

The samples are shown in the illustrations, Figures 10.1, 10.2 and 10.3.



Figure 10.1: mie (FSCU 767919-2A)



Figure 10.2: Beakers full of sweets (FSCU 767919-2B)



Figure 10.3: Chocolate biscuits (FSCU 767919-2C)

Implementation of the study

Screening for total concentrations of bromine and chlorine

In order to gain an indication of any methyl bromide and/or chloropicrin released in the sampled food products, the total bromine and chlorine content was determined using XRF analysis.

Determining the methyl bromide and chloropicrin levels

Parallel to the screening of the sample food products, composition analyses were undertaken using 'headspace' analysis. These are purely indicative analyses, as there are currently no validated analysis methods available for these compounds in solid materials. In order to complete the headspace analysis, sample material was transferred into a sealed gastight vessel, which was then placed in an oven at 80 °C. After balance analysis in the gas phase and in the solid material phase, part of the volume of the headspace was analysed using GC-MS.

Results of the study

Table 10.1 shows the results of the screened XRF determination for bromine and chlorine of the three food products.

Table 10.1: Results of the XRF determination of total bromine and chlorine content

Sample code (description)	Total bromine content (mg/kg product)	Total chlorine content (mg/kg product)
FSCU 76919-2 A (mie)	12	72
FSCU 76919-2 A (mie)	11	93
FSCU 76919-2 B (sweets)	3	227
FSCU 76919-2 B (sweets)	3	212
FSCU 76919-2 B (sweets)	3	109
FSCU 76919-2 C (biscuits)	4	156
FSCU 76919-2 C (biscuits)	4	206
Blank mie	<1	6

Table 10.2 shows the results of the headspace analysis of the three food products sampled.

Table 10.2: Results of the headspace analyses for methyl bromide and chloropicrin in food products

Sample code (description)	Methyl bromide ($\mu\text{g}/\text{kg}$ product)	Chloropicrin ($\mu\text{g}/\text{kg}$ product)
FSCU 76919-2 A (mie)	0.1	< DL
FSCU 76919-2 B (sweets)	2.8	< DL
FSCU 76919-2 C (biscuits)	29.3	< DL

Discussion of the results

XRF analysis showed that the samples of food products contained bromine and chlorine. The measured content of maximum 12 mg/kg of bromine and 227 mg/kg of chlorine form an indication of the presence of methyl bromide and chloropicrin in the food products. A comparable product was taken for the mie sample, which was studied as a blank sample, and in which bromine and chlorine were only found at minimum detection level. Headspace analysis showed the presence of bromine and chlorine in all three sampled food products. Chloropicrin was not measured above the detection level for this measurement method. Considering the measured higher total chlorine levels, this could be explained by the fact that chloropicrin has been irreversibly adsorbed into the products, or that a reaction has been caused with ingredients in the product. Contamination of the food products with methyl bromide is therefore confirmed, and contamination with chloropicrin cannot be ruled out.

Conclusion

Contamination with methyl bromide of the three food products from a gassed contained treated with methyl bromide has been confirmed. Contamination of these food products with chloropicrin, which is often added to methyl bromide, is not confirmed but, on the basis of the results of this study, cannot be ruled out.