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State of affairs 2007

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Abstract

The risks of environmentally hazardous substances in import containers
State of affairs 2007

Approximately 2.5 million containers carrying goods from all over the world arrive each year in Dutch harbours. Measurements revealed that containers may contain high concentrations of volatile organic compounds (VOCs). The presence of these substances can be explained by their use in gassing containers and/or their use in the production process of the goods being carried – as either a constituent or a solvent.

The Ministry of Housing, Spatial Planning and the Environment of the Netherlands (VROM) commissioned the National Institute for Public Health and the Environment (RIVM) to analyse the risks of the concentrations of VOCs in containers to human health and the environment. The risk assessment was based on existing data due to the need for an answer within a very short period of time. The risks to employees in their work places were not included in the assessment.

One of the conclusions of the assessment is that the concentrations of VOCs may be high enough to lead to an increased risk of acute health effects in those people in the immediate surroundings of a container when it is opened, or shortly thereafter, and who are subsequently exposed to the substances.

Consumers may also be exposed to VOCs when they use goods from gassed containers. This may occur when these substances vaporize from the goods during use in the home or when gassed food or medicines are ingested.
The information available on the concentrations of VOCs in goods and the extent of their vaporization from goods was limited and mainly derived from an earlier assessment carried out by the RIVM on a number of products made available for testing by VROM. As such, vaporization data were available on only twenty different products, and exposure data were available for only two mattresses and one pair of shoes. Based on the measurements in these specific cases, the RIVM expects that the risks will not surpass those considered to be acceptable according to currently applied public health standards. Due to the limited data available, however, it was not possible to quantify the risks or to exclude them in other cases.

In terms of the environment, serious consideration must be given to the use of methyl bromide for gassing containers worldwide as it is a potent ozone layer-depleting substance, and it is used in great amounts.

Key words:
import container, methyl bromide, 1,2-dichloroethane, fumigants, biocides, bystanders, phosphine, risk assessment

Rapport in het kort

De risico's van milieugevaarlijke stoffen in importcontainers
De stand van zaken 2007

In Nederlandse havens komen per jaar circa 2,5 miljoen containers binnen met goederen uit alle werelddelen. Uit metingen is gebleken dat in deze containers hoge concentraties van vluchtige organische stoffen kunnen voorkomen, als gevolg van het gassen van de containers, of omdat deze vluchtige organische stoffen tijdens het productieproces van de goederen als bestanddeel of oplosmiddel zijn gebruikt.

Het ministerie van VROM heeft het RIVM verzocht om inzicht te geven in de risico's die deze gassen in containers kunnen inhouden voor mens en milieu. De opdracht was om deze risicoanalyse te baseren op reeds beschikbare informatie over begassing en stofconcentraties. Het analyseren van de risico's voor de arbeidssituatie was geen onderdeel van deze opdracht.

Uit de beoordeling van de gegevens blijkt dat de concentraties van vluchtige organische stoffen in containers zo hoog kunnen zijn dat omstanders bij het openen van containers en bij blootstelling aan deze concentraties, gezondheidseffecten kunnen ondervinden.
Ook consumenten kunnen worden blootgesteld als zij de goederen uit gegaste containers gebruiken. Dit kan gebeuren wanneer de producten binnenshuis uitdampen, maar ook bij het consumeren van gegaste voedingsmiddelen en geneesmiddelen.

De beschikbare informatie over de concentratie in, en uitdamping uit goederen bleek zeer beperkt en vooral afkomstig uit eerdere onderzoeken van het RIVM aan door VROM aangeboden onderzoeksobjecten. Zo was informatie beschikbaar over de uitdamping van een twintigtal verschillende goederen en de nalevering uit twee matrassen en een paar schoenen. In deze specifieke gevallen verwachtte het RIVM geen risico's boven de grenzen die normaal in het beleid gehanteerd worden. Het is echter niet mogelijk om op grond hiervan risico's in andere gevallen te kwantificeren of uit te sluiten. Daarvoor zijn het aantal mogelijke situaties en de onzekerheden te groot.

Vanuit het oogpunt van de effecten op het milieu is vooral methylbromide van belang, omdat deze stof de ozonlaag kan aantasten en er bij het gassen van containers relatief veel van deze stof wordt gebruikt.

Trefwoorden:
importcontainer, methylbromide, 1,2-dichloorethaan, fumiganten, biociden, omstanders, fosfine, risicobeoordeling

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Summary

Dutch harbours receive about 2.5 million containers annually with goods from all parts of the world. Research has shown that these containers may contain high concentrations of volatile organic substances. These environmentally dangerous substances are put into containers to decontaminate goods and prevent their decay. Another reason why these substances occur in containers is that they have been used as components or solvents in the production process, after which they evaporate from the product.

The RIVM has investigated the risks this may cause to humans and the environment. Risks for humans may occur if people are exposed to high concentrations when the containers are opened or when the goods emit gases indoors after they have been purchased. Risks for the environment may occur because, by definition, the substances used to decontaminate containers affect living organisms and may have side-effects. Methyl bromide, for instance, is a substance that depletes the ozone layer.

Risks from the occupational viewpoint were not included in the study.

The concentrations *inside* containers may be so high that bystanders may experience health effects if they are exposed to these concentrations when the containers are opened.

To determine the risks due to evaporation from products indoors (degassing), The RIVM has determined the evaporation from different goods and assessed the health risks of the gas emission from two mattresses and a pair of shoes. The gases emitted from mattresses were methyl bromide on the one hand and 1,2-dichloroethane and a number of solvents on the other; the emissions from shoes included toluene. In these cases the RIVM does not expect risks beyond the boundaries accepted in normal policy. Of the twenty products investigated for their degassing behaviour, the RIVM regards mattresses as the worst case product in terms of potential exposure of human beings. Even so, the significance of the risk assessment based on two mattresses remains limited. After all, this number is small compared with the number of products and exposure scenarios. In practice, the issue involves a large number of very different products that are transported in containers and from which the environmentally dangerous substances may evaporate. Evaporation may lead to exposure through the respiratory tract (inhalation), through the skin (dermal exposure) or through the mouth (oral exposure). The degree of exposure is determined by the properties of the substances, the quantity, the duration of contact, the matrix properties and the distance of the consumer to the degassing product. Quantification of the potential risks is not possible due to a lack of factual data. The RIVM cannot rule out the possibility that in other situations health effects will occur.

The effects on the environment seem to be minor, as the quantities of the substances released are small compared with the national emissions. The RIVM has observed, however, that the quantity of methyl bromide used in other countries for treatment of containers, is many times higher than the total emission in the Netherlands. Methyl bromide is a substance that depletes the ozone layer. Its application for treatment of wood has been laid down in international rules, but its application for decontamination of containers is more extensive than strictly necessary.

If reduction of the risks is considered, the RIVM has identified the following options:

- Appeal to the producers' responsibility to put safe products on the market. This could involve precise specification of product requirements and agreements on the transportation of the goods. Such an approach will also reduce the risks for workers.
- Analysis of the trade chain to evaluate the policy and enforcement instruments and to identify the options to effectively improve the situation. All stakeholders, including the market parties, could be involved in this analysis.
- Consultations with importers and buyers about effective measures to prevent exposure when containers are opened. A possible option would be sampling and analysis of containers prior to opening, in conjunction with measures in case the concentrations in the container prove to be too high.

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List of abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
AEGL	Acute Exposure Guideline Levels
AMvB	Order in Council (*Algemene Maatregel van Bestuur*)
CBS	Statistics Netherlands (*Centraal Bureau voor de Statistiek*)
Ctgb	Advisory Board for the Authorisation of Plant Protection Products and Biocides (*College voor de toelating van gewasbeschermingsmiddelen en biociden*)
DCE	1,2-dichloroethane ($C_2H_4Cl_2$)
EPA	Environmental Protection Agency
GPSD	General Product Safety Directive of the European Union
LOAEL	Lowest Observed Adverse Effect Level
MAC value	Maximum Accepted Concentration for the workplace. Determination of a MAC value is based on the criterion that long-term exposure should not affect human health; however, economic criteria play a role as well.
MeBr	Methyl bromide (CH_3Br)
MTR	Maximum permissible risk level (*Maximaal Toelaatbaar Risiconiveau*)
NeR	Dutch emission guidelines (*Nederlandse Emissie Richtlijnen*)
NOAEL	No Observed Adverse Effect Level
RAPEX	EU warning system for dangerous consumer products.
RIVM	Rijksinstituut voor Volksgezondheid en Milieu
TDI	Tolerable daily intake
TEU	Twenty-foot equivalent unit containers
VWA	Food and Consumer Product Safety Authority, an agency of the Dutch Ministry of Agriculture, Nature and Food Quality (*Voedsel en Waren Autoriteit*)
VI	VROM Inspectorate
VR	Negligible risk level (*Verwaarloosbaar Risiconiveau*)
VROM	Ministry of Housing, Spatial Planning and the Environment (*Ministerie van Volkshuisvesting, Ruimtelijke Ordening en Milieubeheer*)
VRW	Informative Target Value (*Voorlichtingsrichtwaarde*)
VOC	Volatile Organic Compounds
Wms	Chemical Substances Act *(Wet milieugevaarlijke stoffen*)

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1 Subject of this report

1.1 Reason for the study

During the last few years, at the request of the VROM Inspectorate, research has been conducted on the consequences of treating containers with pesticides. Such a treatment is given to prevent the transportation of harmful organisms or to protect the products in the containers against deterioration. The substances used for this purpose are pesticides[1], and are also harmful to human beings and the environment. Methyl bromide is one of the chemicals used and admitted for this purpose. Methyl bromide is harmful to humans when inhaled and contributes to the breakdown of the ozone layer.

Research has shown that in 2002 one out of every five import containers in Rotterdam contained pesticides such as methyl bromide, phosphine and formaldehyde (Knol-de Vos, 2003). Further research revealed that these chemicals may penetrate the products transported in the containers, and that these chemicals are slowly released again (degassing). As a result, these chemicals may be released in the homes of consumers, so that citizens are exposed to them (Knol et al., 2005a and 2005b). In 2005 a risk analysis was carried out in which the RIVM concluded the following (Knol et al., 2005b): On average, the potential risk resulting from this [note: evaporation at the consumer's home] seems to be minor and acceptable in the context of traditional risk policy (below the level regarded as negligible). This should be regarded as a signal, as the analysis was based on samples from large numbers of containers and large quantities of products. Moreover, mainly the effects of methyl bromide were considered and little is known about the risks of other pesticides.

One of the recommendations from this study was that the situation be monitored to keep an eye on developments. This recommendation was followed, and in 2007 the results of this monitoring effort up to the end of 2006 were presented (De Groot, 2007). One conclusion was – translated freely – that more containers with harmful substances are being encountered in ports. Another conclusion was that not only typical pesticides were found, but also substances such as benzene and toluene, which are not used for fumigation but are used in the production process (such as solvents).

On the basis of these results the Minister of VROM promised Parliament that a risk analysis would be undertaken. The RIVM has been instructed to carry out this risk analysis; the findings are presented in this report.

After this promise (spring of 2007) the problem attracted further public attention when a bed retailer recalled mattresses from the market as they had been transported in a container in which high concentrations of pesticides and solvents were found. This publicity added to the urgency of a risk analysis.

[1] In this report we will refer to the chemicals used for fumigation as 'pesticides'. This is not entirely correct. Firstly, only *gaseous* pesticides are involved and not, for instance, powders or pellets. Secondly, in policy-making a distinction is made between agricultural use of pesticides and non-agricultural use. The former involves crop protection chemicals, the latter involves biocides. The present case concerns the use of pesticides outside agriculture, so formally biocides. This policy term is not very common, and therefore in this report we have chosen the more understandable term of 'pesticides'.

1.2 Assignment and questions to be answered

The VROM Inspectorate has instructed the RIVM to carry out a risk analysis before the end of 2007. This risk analysis should consider health, environmental and indoor environmental aspects. Occupational risks, i.e. the risks for workers, need not be taken into consideration.

On the basis of these instructions the RIVM has formulated the following questions which the study has to answer:

1. Do the substances found during the monitoring of import containers pose an acute danger to citizens who are exposed to them unexpectedly, for a short period and without protective equipment, when a container is opened?
2. To what extent do the substances found in the products during the monitoring of import containers pose a health risk to citizens? This calls for a specification of the substances for which the risk is above or below the Maximum Permissible Risk level and/or above or below the Negligible Risk level.
3. How large is the quantity of substances imported into the Netherlands in this way and how does this emission compare to the emissions known to exist in the Netherlands (according to the Dutch Emission Register)?
4. To what extent do these substances, in the quantities as determined under point 3, lead to effects on the environment, and more specifically, on nature?
5. What are the Dutch and European policies with respect to these substances for Dutch, European or non-European producers?
6. To what extent are the efforts of Dutch and European producers nullified?
7. To what extent do the goods with the observed concentrations of pesticides and production chemicals contribute to the concentrations in the indoor environment, in relation to the concentrations found in Dutch homes?
8. What future developments are to be expected on the basis of the trends observed?
9. What measures may lead to reduction of the risks?

1.3 Approach to the study

This risk analysis was carried out making use of available data. No additional research has been conducted. Although the available data were limited, as will become clear from this risk analysis, the time frame for this risk analysis was too short to allow for supplementary research.

1.4 Structure of this report

Chapter 2 of this report deals with the problem in general, and chapter 3 describes the Dutch and European policies in this field. Chapters 4 and 5 present the actual risk assessment; chapter 4 deals with the risks for humans and chapter 5 with those for the environment. The report ends with recommendations and conclusions.

2 Cause of the problem

2.1 Containers with harmful substances

Several studies carried out during the last few years have proved that maritime containers may hold high concentrations of environmentally dangerous substances. It has been found that, on the one hand, these are substances that have been put into the container to prevent the transportation of harmful organisms or to prevent decay of the goods. Such substances are popularly known as pesticides (formally: *biocides*, see footnote on page 11). On the other hand, substances are involved that are used in the production process, for instance, as solvents. We will call such substances *production chemicals*. Although this classification may seem clear, it has been found that the substances do not necessarily fall into one of these categories. Benzene, for instance, is a substance that is regarded as a typical production chemical (solvent and detergent). There are indications, however, that shoes are treated with benzene to keep them mould-free.

2.2 Fumigation to prevent transport of harmful organisms

The transportation of goods across the globe leads to the wish to prevent the spread of harmful organisms or to prevent decay of the goods.

There are no regulations that make it obligatory to treat containers with goods in order to kill harmful organisms. There are international regulations, however, which impose requirements for the packaging timber used. Decontamination of this wood may and must take place by heating or treatment with methyl bromide. A single treatment is sufficient for permanent decontamination. The use of methyl bromide for decontamination of packaging timber is an exception to the ban on methyl bromide within the European Union (VROM-Inspectie, 2005). In the Montreal Protocol (1987), a global ban on the use of methyl bromide as from 2015 was agreed at the time. The EU has advanced this ban by 10 years. Exceptions are, however, fumigation for export (quarantine treatments and pre-shipment) and ‘critical’ applications.

In practice, however, in many import containers the packaging timber is not treated separately but is decontaminated by treating the entire container including the goods. It is conceivable that this is necessary to prevent decay of the product being shipped. There are no rules for this, which may lead to the use of a variety of chemicals or substances. Earlier studies concluded that many containers are treated with pesticides, even if the cargo does not consist of perishable goods (computers and the like). Pesticides may also be used to prevent unintentional and undesirable import of insects and pests.

An example of undesirable spreading of pests is the transport of the Asian tiger mosquito (*Aedes albopictus*). The tiger mosquito originates from countries roughly around the Indian Ocean (from Japan to Madagascar), where infectious diseases such as dengue fever occur. Importation of this mosquito therefore involves the risk of introducing such tropical diseases. At the end of the previous century the mosquito spread across other continents. As the Asian tiger mosquito may also introduce other infectious diseases, establishment of the mosquito poses a risk to public health. In Italy, the Asian tiger mosquito has established itself through the import of old aircraft tyres. The mosquito probably survived as larvae in a layer of water in the tyres. In August/September 2007 people in

northern Italy became ill from the Chikungunya virus, which was introduced by someone who had been infected in India and subsequently spread by the Asian tiger mosquito.

International agreements are in preparation. Preventing the spread of this mosquito may lead to the wish to treat containers with pesticides. Input from the Netherlands in this matter may lead, on the one hand, to an effective approach to control the mosquito (not all chemicals are suitable for controlling eggs, larvae *and* mosquitoes), and on the other hand, to a reduction of the risks for consumers due to the use of these same pesticides.

In the Netherlands, too, decontamination takes place of containers designated for export. Treatment with pesticides occurs only, however, if this is prescribed by the importing country *and* if no alternative treatment method is available. In view of the risks, treatment with pesticides in the Netherlands is subject to regulations which are strictly enforced. In the Netherlands, containers are first ventilated until the pesticide has left the container and the container can be declared 'gas-free'. Only then may the container be transported.

Internationally, shipping of containers that are not yet free of pesticides is still permitted. In that case the containers should be provided with warning stickers and accompanying documents as evidence of the fumigation. In practice, only 2 % of the containers actually bear such stickers (Knol-de Vos, 2003). The strict rules for fumigation of export containers prevailing in the Netherlands, are not applicable to import containers containing pesticides.

Figure 1 Warning sticker on a fumigated container.

2.3 Production chemicals

The VROM Inspectorate has been following the developments in fumigation of maritime containers for several years now. This has included the implementation of a monitoring programme. The results of this monitoring programme were reported in 2007 (De Groot, 2007). The programme concentrated on five well-known fumigation agents. The study also included other substances such as benzene, toluene and xylenes. These are substances that are frequently used in production processes, for instance, as solvents or detergents or as a component of mixtures of substances. Analysis of the monitoring data showed that the concentration of these substances in maritime containers has increased in the last few years and that those concentrations occurred in excess of the Maximum Acceptable Concentration (MAC value) for workplace conditions. In 2006 the following substances were found in one or more containers in concentrations in excess of the MAC value: benzene, toluene, xylene, chloromethane and tetrachloromethane.

Benzene and tetrachloromethane are substances included in the black list. Policy within the European Union is aimed at minimising human exposure to these substances.

Therefore, these substances are included in the risk analysis described here by the RIVM. Descriptions are given of the extent to which these chemicals have been encountered, of the policy with respect to these substances, and of the human and environmental risks of these substances.

2.4 Substances encountered in maritime containers

In 2002 a study was conducted on substances encountered in maritime containers in the port of Rotterdam (Knol-de Vos, 2003). In a random sample of 300 containers, methyl bromide, phosphine or formaldehyde was found in over 20 % of the containers. In 5 % of the containers the concentration exceeded the MAC value. A trend analysis (De Groot, 2007) presents the tendency in the period 2003 to 2006. The conclusions from this analysis are:

- there is a rising tendency in the number of containers treated with pesticides;
- of all the pesticides, methyl bromide was encountered most frequently. No change was observed in the percentage of containers treated with this chemical;
- the rise was mainly attributable to the increased number of containers treated with 1,2-dichloroethane;
- other environmentally dangerous substances were encountered as well, and over the years an increase was observed in the number of times that benzene, toluene, xylenes, chloromethane and tetrachloromethane were found.

In Germany, a comparable study was carried out on the situation in the port of Hamburg (Bauer et al., 2007). In this study more than 2000 randomly selected containers were investigated. The study focused on the substances found, the type of goods and the country of origin. The results, in terms of the pesticides encountered and their percentages, are comparable with the findings in the port of Rotterdam. In the port of Hamburg it was observed that 14 % of the containers included pesticides such as methyl bromide, phosphine, formaldehyde and 1,2-dichloroethane, and 17 % contained other environmentally dangerous substances such as benzene, dichloromethane and toluene. These substances were encountered especially in containers with textile and shoes from South-East Asia.

3 Dutch and European policies

3.1 Dutch and European environmental policies

The substances involved here belong to the class of volatile organic compounds (VOC). For various reasons environmental policy has been developed for these substances. Of special importance here are the policy developed for crop protection chemicals and biocides, the policy for volatile hydrocarbons and the substance-specific policies for different substances. A detailed description of the environmental policies is presented in Appendix 1. A summary is given below.

Policy for crop protection chemicals and biocides
The substances used for treating containers against vermin are intended to kill vermin, and this very fact makes them environmentally dangerous substances. From a policy viewpoint, these substances are called *biocides*; when used in agriculture, the same substances are called pesticides or crop protection chemicals. Many of these substances are also dangerous to humans, partly due to the high concentrations in which they are used.

In the Netherlands the use of these substances is regulated. The Ctgb (Advisory Board for the Authorisation of Plant Protection Products and Biocides) decides on the admission of crop protection chemicals and biocides on the basis of European harmonised legislation and regulations. European regulations prescribe that packaging timber and other packing material used in international transport must be treated to prevent the transport of vermin. Prescribed treatment methods are heating and fumigation with methyl bromide. In practice, the preferred option in the Far East is often the simplest and cheapest method: fumigation.

Other chemicals may be used if the objective is to protect the goods in the containers (although treated containers which did not contain perishable goods were found as well). In principle there are no international regulations for this. In the Netherlands, the Ctgb regulates which chemicals may be used for which applications.

Policy for volatile organic compounds
For volatile organic compounds, European policy is aimed at reducing emissions, because volatile organic compounds contribute to the formation of smog. Within the EU, agreements have been made on the maximum emission per country in the 'EC Directive'

Substance-specific policies
Methyl bromide depletes the ozone layer and is harmful to human beings and the environment. Its use is forbidden except for critical applications such as the treatment of dunnage and packaging timber used in international transports. Section 2.2 points out that there are international rules for treating packaging timber with methyl bromide (International Standard for Phytosanitary Measures, number 15).

The use of *phosphine* is regulated in instructions for use.

The use of 1,2-dichloroethane and chloropicrin is prohibited in the Netherlands.

Tetrachloromethane is a blacklisted substance. This substance is subject to limitations as regards marketing and use in compounds and preparations.

Benzene is a carcinogen. The European Union has set maximum values for the concentration of benzene in air to protect the population against the effects of long-term exposure.

3.2 Dutch and European product safety policies

There are not many regulations concerning the emission of specific substances from consumer products. Most of the rules on limitation of the emission of volatile organic compounds are part of the Environmental Management Act (Solvents Decree, transposition of the EU VOC Directive; Timber and Construction Companies Decree) and the Environmentally Dangerous Substances Act. In so far as anything has been put on paper for consumer products, most of the rules involve concentration requirements (for instance, in several decrees pursuant to the Consumer Goods Act, e.g. on toys, on pentachlorophenol, on formaldehyde in textiles, on azo colorants, on chipboard).

More in general, in Europe as well as in the Netherlands the safety of consumer products is regulated by the European General Product Safety Directive (GPSD).

For many products there are specific European directives, such as the Low-Voltage Directive, the Toys Directive and the Cosmetics Directive. The requirements under the GPSD are also applicable to these products in so far as these requirements are not explicitly or not sufficiently covered by the specific directives.

The essence of the GPSD is the obligation of businesses to sell safe products only. Information exchange between the governments of the EU Member States has been regulated through a rapid alert system (RAPEX). Furthermore, businesses are obliged to submit a notification for dangerous products that have been put on the market and for which measures are required to avoid risks.

Therefore, businesses bear their own responsibility for putting safe products on the market. They have to assure and assess the compatibility of their products with the statutory requirements. Furthermore, the legislation provides reference frameworks on the basis of which an assessment can be made whether a product is safe, such as the non-mandatory European and national standards.

A producer has influence on the safety characteristics of the product, a distributor usually has not. Manufacturers and their representatives within the European Union, or the first importers with the European Union, are also regarded as producers.

4 Risks for citizens

4.1 Exposure pathways

Distinction between bystanders and consumers
Containers with environmentally dangerous substances can cause risks for citizens in two ways. Firstly, persons may be present at the opening of containers as bystanders or they may enter containers, and may then be exposed to substances present in the container air. The first question to be answered by the study (see section 1.2) involves a risk assessment for bystanders.

Secondly, as consumers, persons may be exposed to dangerous substances evaporating from purchased goods that have been transported in a container with high concentrations of environmentally dangerous substances (degassing). The second question to be answered concerns these risks. This specific question mainly involves respiratory exposure (through breathing), but with some products oral (uptake through the mouth) and dermal (uptake through the skin) exposure may occur as well.

Methodology of risk assessment for bystanders
Exposure of bystanders may take place when persons come into contact with fumigation agents or solvents when containers are opened. This exposure takes place mainly through inhalation and has a short-term character (acute). In the risk assessment for bystanders we will assume exposure to the measured concentrations of the various substances in the container air. These concentrations are available for all fumigation agents and solvents. If this worst case approach leads to the conclusion that the risks are acceptable within the usual standards, then further measures will not be required. If this worst case approach leads to unacceptable risks, further detailing will be necessary. One aspects to be studied then is whether, and how often, such an exposure can actually occur.

Methodology of risk assessment for consumers
The exposure as a result of degassing from consumer products is of a (potentially) more long-term nature. Earlier studies (Knol et al., 2005a) have shown that degassing to the ambient air consists of several phases: a rapid phase, with half-life values of several hours, a slow phase with half-lives up to several days, and a very slow phase with half-lives of as much as one year The quantities of a substance released in the three phases differ from one product to another. The period of potential exposure by degassing from consumer products should be regarded, on the basis of the half-life values, as ranging from sub-acute to semi-chronic. The above study investigated the degassing behaviour of some twenty products (sculptures, clothing, consumer products). The worst case product proved to be a mattress (see next section).

The pathway of exposure by degassing depends on the product from which degassing takes place. For the vast majority of products *inhalation* is expected to be the main exposure pathway. To assess the health risks of this pathway, the intensity and period of exposure must be known. These data are affected by numerous variables. The wide variety of consumer products, each with its own physical characteristics and intended use, makes estimation of the possible respiratory exposure a complex issue. A crucial knowledge gap here is the scarcity of measurement data on evaporation of fumigation agents and solvents from consumer products at the moment the consumer comes into contact with these products (that is after removal from containers and after transport). Concentrations measured in containers cannot be used to estimate the respiratory exposure of the consumer. Some consumer

products will absorb only a small amount of the gas, other products a large amount. A mere concentration measurement in the container is not sufficient to draw any conclusions about emission of substances from consumer products during the utilisation phase.

In an earlier report (Knol et al., 2005b) the risk assessment for the consumer was concentrated on a mattress (a children's mattress), being a product that was expected to lead to the highest exposure. This expectation was based on fumigated mattresses encountered in practice, the long contact period of a consumer with a degassing mattress, the small distance between source and breathing zone, and the amount of pesticides demonstrated to be present in mattresses. For the present study, too, in comparison with other fumigated products encountered, a fumigated mattress is still the 'best' worst case situation on which the risk assessment for consumers can be based.

Dermal exposure is possible through, for instance, clothing, mattresses, shoes, furniture, cuddly toys, pillows, ornamental objects and bags. The extent to which this pathway leads to a significant burden on the body depends on the intensity and duration of the contact on the one hand and the ability of the contaminant to reach and penetrate the skin on the other. The dermal pathway will be most relevant for products that come into intensive contact with the skin in the presence of perspiration moisture. To assess this exposure, data are required on the leaching behaviour of the contaminants. At the present moment such data are lacking.

For foods and medicines, *oral* exposure will be relevant. Oral exposure due to sucking on objects may be relevant for some specific products (cuddly toys), for the vast majority of products it will be negligible compared to respiratory and dermal exposure. Available data on the possible oral exposure due to degassing from foodstuffs and medicines are all outdated. They have already been evaluated in the earlier report (Knol et al., 2005b) and will therefore be discussed only briefly here. The potential exposure due to sucking cannot be quantified owing to the lack of data.

The above shows that the available data on degassing of contaminants (pesticides and production chemicals) from consumer products are still limited. For the dermal pathway, relevant data are not available. For the oral pathway, only the data for foodstuffs are available on which Knol et al. (2005b) reported earlier. The conclusion of that report was that the available data did not point to a risk as a result of methyl bromide and bromide residues. Data on the possible oral exposure due to sucking are lacking at the moment. Therefore, we will leave the oral pathway out of consideration in the present report.

For the respiratory pathway, the data on methyl bromide from mattresses are available as evaluated earlier in Knol et al. (2005b). Degassing from this product was and is seen as the worst case in a study on degassing from different products (Knol et al., 2005a). In the following sections we will discuss new exposure data (compared with the previous risk assessment, Knol et al., 2005b) as used in the present risk assessment. A product on which supplementary investigations have been carried out is shoes from a container with high toluene concentrations. This will be included in the present risk assessment.

4.2 Exposure data

4.2.1 Exposure of bystanders

Since 2003 the VROM Inspectorate has been carrying out checks on the concentrations of pesticides and other harmful gases in containers. The origin of the substances encountered is usually not clear. Some substances may have been used for fumigation of the container, other substances may have evaporated from certain consumer products or parts thereof.

Results of measurements carried out in container air in the period 2003-2006 have recently been analysed and published (De Groot, 2007). In the present risk assessment those pesticides have been included that were found in containers: methyl bromide, phosphine, 1,2-dichloroethane and chloropicrin.

Of the production chemicals encountered, we have included benzene, toluene, xylene and chloromethane in this risk analysis because their concentrations in containers were sometimes higher than the MAC values (year 2006).

Table 1 presents the average and maximum values measured in containers for the selected substances (De Groot, 2007).

Table 1 Overview of chemicals and concentrations found in containers (all concentrations in mg m^{-3}).

Component	MAC value	2003		2004		2005		2006		Maximum value (year of occurrence)
		Av.	Med.	Av.	Med.	Av.	Med.	Av.	Med.	
Pesticides										
Methyl bromide	1	1	0.4	61	2	5	1.5	11	0.4	1,100 (2004)
Phosphine	0.1	-	-	n.a.	n.a.	*	*	*	*	0.3 (2005)
1,2-dichloroethane	7	1	0.7	7	1	12	0.6	22	2	270 (2006)
Chloropicrin	0.7	-	-	2	1	n.a.	n.a.	*	*	5 (2004)
Sulphuryl fluoride	10	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-
Other volatile organic compounds										
Benzene	3	0.3	0.1	0.8	0.09	5.8	0.1	3.2	0.3	75 (2005)
Toluene	150	5	0.6	21	0.5	19	0.5	127	1.4	650 (2006)
m/p-xylene	210	12	2	2.6	0.4	3.4	0.2	10	0.3	280 (2006)
Chloromethane (methyl chloride)	52	5.9	0.4	8.4	0.1	1.3	0.3	73	0.3	790 (2006)
Tetrachloromethane	3	*	*	0.1	0.1	*	*	*	*	4 (2006)
Chlorobenzene	23	n.a.	n.a.	0.2	0.1	n.a.	n.a.	n.a.	n.a.	23 (2003)

Av. = average concentration in positive samples

Med. = median value of positive samples

n.a. = not found; * = too few positive samples (≤ 3)

The maximum concentrations measured in the container have been used for assessing the risk for bystanders. After all, the exposure of a bystander will never be higher than the concentration in the container. The duration of this exposure will be short. As a worst case assumption we have used a

duration of one hour. In practice this will be substantially shorter, as usually the high concentrations are likely to be noticed quickly, and the concentration will diminish due to dilution/removal by wind in the open air outside the container.

4.2.2 Exposure of consumers by degassing

To allow assessment of the respiratory exposure of the consumer, information is required on the emission of substances from consumer products, preferably on the period that the consumer comes into contact with these products (that is after being removed from containers and being transported to the consumer). At the moment, emission data are available for a small number of products and substances, namely two mattresses, of which one is from an import container fumigated with methyl bromide and one from an import container fumigated with 1,2-dichloroethane. Consequently, for the present risk assessment only the emission from these two mattresses can be used, which is obviously too small a basis for drawing any risk conclusions about the overall problem. After all, only two mattresses have been studied from two containers out of a potentially large number of mattresses transported in this way and, moreover, out of a wide range of other goods transported in this way. Mattresses are indeed regarded as the worst case product, however (see section 4.1). The representativeness of the mattresses studied, in comparison with other mattresses in containers, and thus in comparison with other containers and other products, is unknown.

Methyl bromide

The results reported earlier (Knol et al., 2005b) for methyl bromide from mattresses can be summarised as follows. A calculation was made of air concentrations in a small children's room on the basis of emission chamber measurements of the evaporation pattern of a mattress that came out of a fumigated container,. On the assumption that the gas spreads reasonably quickly through the room, the model calculation predicted a maximum room concentration of about 6 $\mu g/m^3$. For this calculation a low ventilation rate was assumed (0.5 air changes per hour). After the first about 100 hours, the calculated air concentration dropped to a level of about 0.5 $\mu g/m^3$, which was then maintained for a long time. After 10,000 hours ($\approx$ 400 days) the calculated level had dropped to 0.2 $\mu g/m^3$. Of course, these concentrations would have been lower at a higher ventilation rate. With a worst-case assumption that methyl bromide keeps hanging above the mattress in an air layer of about 20 cm, the same model predicted maximum concentrations of 20 to 120 $\mu g/m^3$ in that air layer, quickly dropping to a more or less stable level of about 10 $\mu g/m^3$ after 400 hours. Obviously, the concentrations in the rest of the room were lower.

In a validation experiment carried out later, at 2 cm above a mattress treated with methyl bromide, concentrations of 300 to 450 $\mu g/m^3$ were measured. After 2 days (50 hours) this was 50-150 $\mu g/m^3$ and after 6 days (140 hours) 30 to 75 $\mu g/m^3$. On the basis of the development of the evaporation rate it was predicted that the concentrations just above the mattress in the period afterwards would drop to a range of 10 to 30 $\mu g/m^3$. The concentrations at distances larger than 2 cm from the mattress were lower (Knol et al., 2005b).

1,2-dichloroethane and solvents

During a routine inspection in spring 2007 a container was found that contained mattresses, in the air of which high concentrations of 1,2-dichloroethane and solvents were present. One of these mattresses was examined for degassing by the RIVM and for the concentrations in the mattress by the *Zentralinstitut für Arbeitsmedizin und Maritime Medizin* in Hamburg. On the basis of the degassing study by the RIVM, the air concentrations of 1,2-dichloroethane and other substances present can be estimated as they may occur in a sleeping room.

The *Zentralinstitut für Arbeitsmedizin und Maritime Medizin* took samples from the air in the interior of the mattress within several days after it had been unloaded from the ship. These air samples were studied for the concentration of volatile organic compounds. The values found are summarised in Table 2.

The substances found in the mattress are not bound to the mattress; they will evaporate quickly. As some time will lapse between the moment of unloading and the use of the mattress, it is not realistic to assume that the concentrations found are indicative of the exposure of a user of the mattress.

Table 2 Substances measured in a mattress shortly after release of the mattress from the container.

Substance	Concentration	
	(ppb)	(mg m^{-3})
1,2-dichloroethane	> 10,000	>45
Benzene	194	0.7
Toluene	1,106	4.5
Dichloromethane	5,744	22
1,2,4-trichlorobenzene	72	0.6

Degassing from mattress

The RIVM measured the emission of substances from the mattress in the emission chamber (Ganec, see Knol et al., 2005a). A section cut from the mattress (0.5 kg) was placed in the emission chamber. The emission chamber has a volume of 200 l and was ventilated at a ventilation rate of 1.33 l/min = 80 l/hour = 0.4 Air Changes (AC)/hour. The temperature in the emission chamber was set at 35 °C. In the extracted air, air samples were taken every 30-min interval and analysed for the presence of pesticides and volatile organic compounds. In this way the development of the air concentration of the substances was determined (concentration profile), as shown in Figure 2.

On the basis of the quantities emitted, the following substances were selected as the most relevant for a risk assessment: 1,2-dichloroethane, dichloromethane, benzene, toluene, trichloroethene and vinyl chloride.

The following can be said about the extrapolation of the concentration profiles to a realistic exposure. Firstly, the ventilation in the emission chamber roughly corresponds to that of a moderately ventilated room. Furthermore, the air concentration will be proportional to the amount of mattress and inversely proportional to the volume of the room in which the mattress is located.

$$C_{room} \approx C_{Emission\ chamber} \times \frac{M_{total\ mattress}}{M_{sample\ mattress}} \times \frac{V_{emission\ chamber}}{V_{room}} = C_{Emission\ chamber} \times F_{scale}$$

For a mattress of, for instance, 20 kg, on the basis of this extrapolation one would expect a similar concentration in a room of 8 m^3, which is of the same order of magnitude as a small room. The concentration profiles can therefore be used as a rough estimate of the concentrations that may occur in an actual exposure situation and to which a consumer may be exposed. It is emphasised that this should be regarded as an indication of the potential level of exposure.

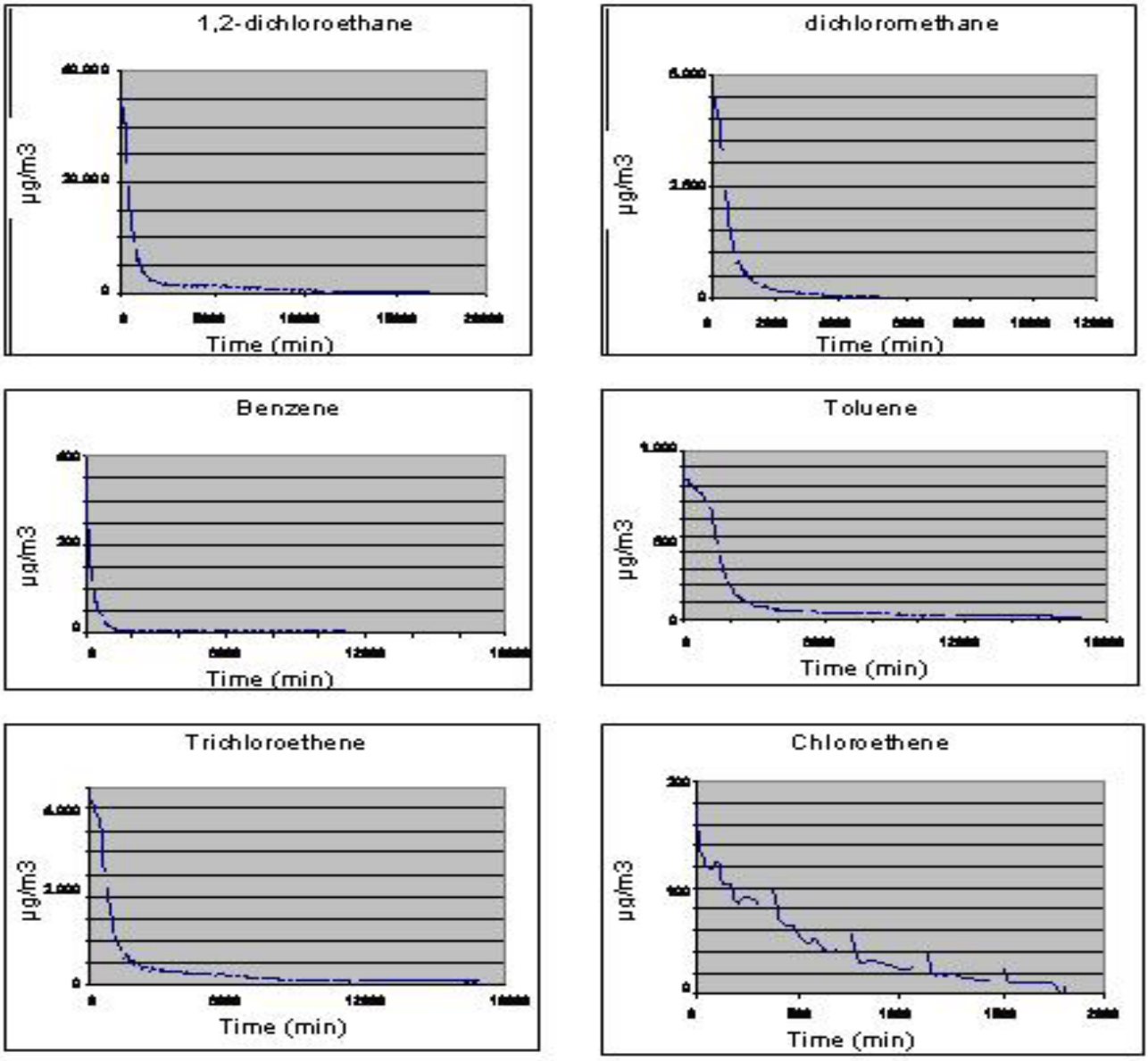

Figure 2 Air concentrations of substances (µg m^{-3}) due to emissions from a mattress.

The following comments can be made on the use of concentration profiles: this simulation does not take account of the fact that the emission in the emission chamber is likely to proceed more quickly than under typical indoor conditions, in view of the relatively high temperature used in the experiments. Another factor not taken into account is that the indoor air is not mixed homogeneously, and that concentrations just above the mattress are likely to be higher than the average in the room. Without additional experiments it is not possible to say how these two effects affect the end result. It can be expected that especially the long-term concentrations will be higher than predicted by the estimate described above, because the evaporation will proceed more slowly.

Furthermore, these mattresses were take from the container and immediately placed in a cold (4 °C) room. As a result, the quantity evaporating during transport and storage will be lower than in the practical situation, so the emission will be higher than in the practical situation.

Another source of uncertainty is the fact that only one piece was taken from the mattress. Without additional data it is not possible to say how representative this piece is of all mattresses (and possibly other consumer products) to which exposure can take place.

Toluene in shoes
In September 2007 the VROM Inspectorate found a container with a high concentration of toluene in the container air (over 1,500 mg m^{-3}). The container was used to transport shoes, which were analysed by the Food and Consumer Product Safety Authority (VWA) for the concentration of this substance. The result was an extractable concentration (extraction agent: pentane) in the shoe material of 170 to 260 mg/kg. The weight of the shoes was 220 g (two shoes).

It is unknown how much toluene will evaporate from the shoes and at what rate, and what increase in concentration this would cause in occupied rooms. It is also unknown how high the dermal load may be as a result of leaching towards the skin and the watery matrix of sweat that may be present on the skin.

On the basis of the total toluene content the maximum possible body load has been calculated and compared with a relevant toxicological standard. This means assessment of the maximum exposure that is possible as a result of respiratory and dermal uptake.

4.3 Toxicological risk assessment

4.3.1 Explanatory notes

Toxicological information about various substances is presented in Appendix 2. For each of the selected substances we will give a brief overview of the relevant toxicological information, with emphasis on a description of the critical health effects in case of acute, sub-acute and semi-chronic respiratory exposure and available toxicological reference values (limit values) for such exposures. Dermal and oral toxicity will be dealt with briefly.

As usual, we will base the risk assessment on limit or reference values with respect to health. In Dutch environmental policy, the limit value of the ‘Maximum Permissible Risk’ (MPR) for chemical substances plays an important role. This limit value is used to assess, from different viewpoints, to what extent reduction of exposure is necessary or desirable. The MPR concerns long-term exposure and is less suitable for short-term exposure, as is the case here for bystanders. As explained in previous sections, we assume a maximum acute exposure time of bystanders of one hour.

MAC values were limit values for occupational situations, applicable to long-term exposure of employees. In the mean time the policy has been changed, the MAC values have been replaced by a more limited set of public limit values, and employees and employers have to make agreements on safe values to work with. In this report we will fall back on the former MAC value, despite the fact that the elements ‘long-term’ and ‘employee’ cause the MAC values to be less suitable for assessment of the risk for bystanders.

The most suitable limit values for bystanders are the acute limit values as derived in other contexts. Here, too, some caution may be necessary, for instance when these limit values are applicable to acute exposure in calamity situations. Safety margins in such limit values have intentionally been kept small, so these values cannot be used directly for different types of exposure situations.

If acute or short-term limit values are not available, the available dose-response relationship of the substance in question can be used to make the best possible estimate of the likelihood of harmful effects for the bystander.

As explained in section 4.2.1, the assessment for the bystander concentrates on the following substances: methyl bromide, phosphine, 1,2-dichloroethane, chloropicrin, benzene, toluene, xylene and chloromethane.

For degassing and the resulting exposure of the consumer, on the basis of the concentration profiles as presented in section 4.2.2, account should be taken of a short-term high exposure for a few hours up to several days, followed by a possible period of several weeks of lower exposure (sub-acute to sub-chronic). In view of the importance of the MPR in the environmental policy, it is relevant to identify cases in which this chronic limit value is exceeded. Furthermore, we will give the best possible indication of the likelihood of health effects for the consumer due to exceedance of the MPR, making use, as customary, of the acute or short-term limit values as a tool or, if such limit values are lacking, falling back on the available toxicological information on the dose-response relationship. As explained in section 4.2.2, the assessment for the consumer concentrates on the following substances: 1,2-dichloroethane, dichloromethane, benzene, toluene, trichloroethene and vinyl chloride. The selection criterion here was exceedance of the MPR for air.

In the following sections we will assess successively the exposure of bystanders and the exposure of consumers, on the basis of the available data. Toxicological information on the substances will only be discussed very briefly.

4.3.2 Risk assessment for bystanders

Methyl bromide

The most sensitive toxicological effect of methyl bromide by inhalation is neurotoxicity. For acute exposure (one hour) the Ministry of VROM uses a limit value of 10 mg/m^3 (MPR hourly average). The MPR annual average is 100 μg/m^3.

For methyl bromide a highest average value of about 61 mg/m^3 has been found in containers (year 2004) and a maximum of 1,146 mg/m^3. A 1-hour exposure to the latter concentration corresponds with the level of a 1-hour threshold for mortality (AEGL-3, see Appendix 1) of 1,185 mg/m^3. An acute limit value for irreversible harmful effects (AEGL-2) of 816 mg/m^3 would be exceeded, which means that at the maximum found, actual neurological effects (clinical symptoms) are to be expected. The average of 61 mg/m^3 is well above the acute 1-hour limit value of 10 mg/m^3 used by the Ministry of VROM. The probability of occurrence of actual intoxication symptoms at such a concentration would seem to be limited, in view of, for instance, the fact known from toxicological literature that humans have been reported to exhibit symptoms after the use of methyl bromide only at concentrations exceeding 390 mg/m^3 (and moreover, we do not expect that the bystander will be exposed for one hour, see section 4.2.1).

It is concluded that for bystanders there is a clear risk of acute effects if they inhale the methyl bromide concentrations encountered *in* containers.

Phosphine
This substance is a respiratory poison. Phosphine disturbs the respiratory system of cells and thus induces internal suffocation. For a 24-hour exposure period, the RIVM has derived a limit value of 20 μg/m^3. For chronic exposure through air, a limit value (MPR) of 7.5 μg/m^3 has been proposed.

For phosphine it is not possible to derive an average value from the available data, because the number of positive samples was too small. The maximum concentration measured in fumigated containers amounts to 300 μg/m^3.

A 1-hour exposure to the latter concentration means exposure to a concentration in excess of the RIVM limit value of 20 μg/m^3 for exposures of up to 24 hours. However, the concentration is well below the estimated 1-hour threshold for serious acute toxicity (AEGL-2) of 2.8 mg/m^3. This suggests that the exposure will not lead to an actual health effect. Comparison with the reported NOAEL in humans of 3.3 mg/m^3/hour points in the same direction.

For bystanders it is concluded that there is no risk of acute effects if they inhale the phosphine concentrations as encountered in containers. Longer-term effects are not likely for phosphine.

1,2-dichloroethane
Acute inhalation of high concentrations of this substance affects the nervous system, the liver and the kidneys. As a warning value for exposure during calamities, a 1-hour threshold of 200 mg/m^3 is known, based on the odour of the substance. For long-term exposure through air the MPR amounts to 48 μg/m^3, based on the genotoxic and carcinogenic properties of the substance.

For 1,2-dichloroethane a highest average value of about 22 mg/m^3 has been found in containers (year 2006) and a maximum of 270 mg/m^3 (2006). A 1-hour exposure to the latter concentration is well below the estimated 1-hour threshold for mortality in the human population of 2,000 mg/m^3 (life-threatening value for calamity situations). Death or serious intoxication therefore do not appear likely at the maximum found. Whether any toxic symptoms may occur at this level cannot be concluded with any certainty, because of the scarcity of toxicological data on the acute dose-response relationship. The level of the NOAEL in short-duration studies on laboratory animals (430 mg/m^3) suggests only a small toxic risk. With regard to the carcinogenic risk, both the average and the maximum values found represent substantially higher concentrations than the MPR as life-long average (risk level of one in ten thousand per lifetime). Owing to the short duration of these concentrations above the MPR value, the actual extra risk of cancer in a lifetime as a result of this exposure is negligible (less than one in a million per lifetime).

It is concluded that the concentrations exceed the MPR value for a short period. The extra risk of cancer due to inhalation of the maximum concentrations found will be in the negligible range, however. Serious toxic effects are not to be expected at the maximum values found. However, due to the scarcity of data on the threshold for minor acute effects, such toxic effects cannot be ruled out altogether.

Chloropicrin
This substance is known for its highly irritating effect on eyes, nose and respiratory tract. On the basis of an observed threshold of 2 mg/m^3 for the lacrimal effect in humans (10-min exposure), a 1-hour threshold for calamity situations has been established of 200 μg/m^3 (Informative Target Value). An

MPR is not available for this substance. The only known limit value for long-term exposure is 0.4 μg/m^3, derived by the Californian EPA.

For chloropicrin a highest average value of about 1.9 mg/m^3 has been found in containers (year 2005) and a maximum of 5.6 mg/m^3 (2004). Exposure for one hour to the latter concentration remains below the estimated 1-hour threshold for mortality in the human population of 10 mg/m^3 (life-threatening value for calamity situations). At the maximum found, death is therefore not likely. The estimated 1-hour threshold for serious eye irritation of 2 mg/m^3 (set as the Warning Limit Value) is exceeded, however. At the average of 1.9 mg/m^3, lacrimation is to be expected as well. On the basis of toxicological information available, long-term effects on bystanders due to chloropicrin are not to be expected.

It is concluded that at the measured chloropicrin concentrations, irritation of eyes, nose and respiratory tract is to be expected. Other effects are not expected.

Benzene
This substance is known as a human carcinogen on the basis of occupational epidemiological studies in which chronic respiratory exposure resulted in an increased incidence of leukaemia. From the genotoxic and carcinogenic effect, the RIVM has derived an MPR of 20 μg/m^3. In accordance with the definition of the MPR, this limit value corresponds with an extra risk of cancer of one in ten thousand per lifetime at lifelong exposure. As regards acute toxicity, the neurological effects are the most sensitive. For serious neurological effects a 1-hour threshold of 2,590 mg/m^3 is known (AEGL-2) and for minor neurological effects a threshold of 168 mg/m^3 (AEGL-1).

For benzene a highest average value of about 5.8 mg/m^3 was found in containers (year 2005) and a maximum of 75 mg/m^3 (2005). A 1-hour exposure to this concentration remains well below the estimated threshold for minor neurological effects in the human population (168 mg/m^3).

It is concluded that the given maximum concentrations are not expected to lead to acute health effects in bystanders. With regard to the carcinogenic risk, both the average and the maximum values found represent substantially higher concentrations than the MPR value as life-long average. Owing to the short duration of these concentrations above the MPR value for life-long exposure, the actual extra risk of cancer in a lifetime as a result of this exposure is negligible (less than one in a million per lifetime).

Toluene
Toluene is also neurotoxic after acute inhalation. Lethal concentrations cause death due to serious nervous system depression. For a 1-hour exposure, the estimated threshold for mortality in the human population is 10,875 mg/m^3 (AEGL-3), while the threshold for minor neurological effects (based on observations in volunteer studies) is 750 mg/m^3 (AEGL-1). The MPR for toluene in air is 0.4 mg/m^3, based on neurological observations in occupational toxicological studies with chronic exposure. Generally speaking, toluene is much less toxic than the haemato-toxic and carcinogenic substance benzene.

For toluene a highest average value of about 127 mg/m^3 has been found in containers (year 2006) and a maximum of 649 mg/m^3 (2006). Exposure for one hour to this concentration remains well below the estimated threshold for minor neurological effects in the human population (750 mg/m^3).

It is concluded that the given maximum concentrations are not expected to lead to acute health effects in bystanders. The concentrations are substantially higher than the MPR value for a short period, but do not pose an acute health risk. Long-term effects are not expected.

Xylene
The acute toxic effect of xylene is similar to that of toluene. Lethal concentrations cause serious central nervous system depression followed by death. For xylenes the estimated 1-hour threshold for mortality in the human population is 4,000 mg/m^3 (AEGL-3). In contrast with toluene, xylenes also have an irritating effect on the respiratory tract at relatively low concentrations. The estimated 1-hour threshold for this effect in the human population is equal to 560 mg/m^3 (AEGL-1). The MPR for xylenes is 0.87 mg/m^3, a value derived from a Lower Observed Adverse Effect Level (LOAEL) of 870 mg/m^3 for behavioural changes in offspring in a laboratory animal study in rats (short-term exposure). As the derivation is based on a study of short duration, this MPR should be interpreted as a short-term value.

For xylene a highest average value of about 12 mg/m^3 has been found in containers (year 2003) and a maximum of 276 mg/m^3 (2006). Exposure for one hour to this concentration remains well below the estimated 1-hour threshold for minor eye irritation in the human population (560 mg/m^3).

It is concluded that the given maximum concentrations are not expected to lead to acute health effects in bystanders. For a short period the concentrations are substantially higher than the MPR value, but they do not pose an acute health risk. Long-term effects are not expected for xylene either.

Chloromethane
Acute inhalation of chloromethane leads to neurological effects. For serious neurological effects, the 1-hour threshold for the human population is estimated at 1,035 mg/m^3 (AEGL-2). The corresponding threshold for minor neurological deviations amounts to 207 mg/m^3 (AEGL-1). For chloromethane no MPR for air has been derived. The only available chronic limit value for air is 0.09 mg/m^3, derived from a NOAEL of 104 mg/m^3 from a short-duration study on mice for brain damage due to the substance. Similar to the MPR for xylene, this value should also be interpreted as a short-term value.

For chloromethane a highest average value of about 73 mg/m^3 has been found in containers (year 2006) and a maximum of 785 mg/m^3 (2006). A 1-hour exposure to this concentration exceeds the estimated threshold for minor neurological effects in the human population (207 mg/m^3) and approaches the threshold for serious neurological effects (1,035 mg/m^3). The highest average remains below the two thresholds mentioned above and is therefore not linked to an acute toxicological risk. Chloromethane has been shown to produce reproduction-toxic effects at relatively low concentrations (NOAEL: 310 mg/m^3). For development toxicity, and more in particular the induction of cardiac disorders in mice, the NOAEL is 206 mg/m^3. It cannot be ruled out that a single exposure to the above maximum, in the scenario as defined for bystanders, poses a risk for these endpoints.

It is concluded that the highest concentrations found cause neurological disorders, probably of a moderately serious to serious nature. Furthermore, effects on development and reproduction cannot be ruled out altogether. Thus the observed maximum concentration in containers poses a health risk.

Summary
Table 3 presents a summary of the effects in bystanders.

Table 3 Summary of the risk assessment for bystanders.

Substance	Measured concentrations in containers*	Assessment
Methyl bromide	Maximum 1,100 mg/m^3	Health effects possible (value lies between AEGL-2 and AEGL-3)
	Average 61 mg/m^3	Above limit value for one hour, but no health effects to be expected
Phosphine	Maximum 300 µg/m^3	Below effect levels, so no unacceptable health risk expected
1,2-dichloroethane	Maximum 270 mg/m^3 Average 22 mg/m^3	No serious health effects to be expected. Minor, acute effects cannot be excluded
Chloropicrin	Maximum 5.6 mg/m3 Average 1.9 mg/m^3	Irritation of eyes, nose and respiratory tracts
Benzene Toluene Xylene		No acute or long-term health risk to be expected
Chloromethane	Maximum 785 mg/m^3 Average 73 mg/m^3	Health effects possible

* where the average concentration is given, this is the average concentration in containers in which the substance has been found, being the highest average concentration over four separate years (see Table 1)

4.3.3 Risk assessment for consumers by degassing from mattresses

As explained in section 4.1, for only two mattresses usable data are available. Mattresses have been selected as the most plausible worst case products as regards exposure. For methyl bromide, measurements were carried out in 2005 in one mattress, followed by a validation experiment. For 1,2-dichloroethane and solvents, measurements were carried out in 2007 on one mattress.

Methyl bromide

The available results for this substance were assessed earlier by Knol et al. (2005b). Model calculations indicated concentrations of 0.02 to 0.12 mg/m^3 in the air layer immediately above the mattress (see section 4.2.2), decreasing to a more or less stable level of about 0.1 mg/m^3 in 400 hours. Validation measurements pointed at slightly higher initial concentrations of 0.3 to 0.45 mg/m^3 immediately above the mattress, decreasing to 0.05 to 0.1 mg/m^3 after two days and to 0.01 to 0.03 mg/m^3 in the period after six days. The MPR for methyl bromide in air amounts to 0.1 mg/m^3. The concentrations found by calculations and measurements exceed this MPR value for about two days. For a brief period the concentrations are also higher than the semi-chronic limit value for air for methyl bromide of 0.3 mg/m^3; in view of the short duration, this is not significant from a health viewpoint.

It is concluded that the modelled and measured concentrations suggest values which temporarily exceed the MPR value, but that this does not lead to an unacceptable health risk (Knol et al., 2005b).

1,2-dichloroethane

The concentration profile for this substance from the mattress sampled in 2007 (section 4.2.2) shows an initial concentration of about 35 mg/m^3. Over a period of about one day this concentration decreases to a level below 5 mg/m^3. Subsequently, it drops further to less than 3 mg/m^3 in a day and a

half, and to less than 0.7 mg/m^3 in seven days. The available toxicological data for acute to sub-acute exposure are limited. Limit or threshold values for such exposure times are lacking. The data indicate that liver effects are the most sensitive. For such effects in laboratory animals a NOAEL of 400 mg/m^3 is known. In view of this value, the occurrence of toxic effects at concentrations of 5 to 35 mg/m^3 for one or several days, as roughly indicated by the concentration profile, should be regarded as unlikely. The estimated concentrations are higher than the MPR value of 0.048 mg/m^3 for 1,2-dichloroethane. This implies an extra risk of cancer, in view of the genotoxic and carcinogenic properties of this substance. This extra risk of cancer due to this exposure is in the negligible range, however, as shown by calculations.[2]

It is concluded that the concentrations of 1,2-dichloroethane resulting from degassing for several days are higher than the MPR value. This is not expected to lead to actual toxic health damage. The estimated extra risk of cancer due to the elevated exposure is in the negligible range.

Dichloromethane
The concentration profile for this substance (section 4.2.2) shows an initial concentration of about 4.5 mg/m^3. Over a period of about one day this concentration decreases to below 1 mg/m^{3}and to below 0.3 mg/m^3 in a day and a half. The MPR for air is 3 mg/m^3. This MPR is based on carbon monoxide binding to the haemoglobin (formation of COHb), the critical effect of this substance. The MPR indicates the level that will produce an increase by 0.1 % COHb, which is a very small increase given the normal variation of this parameter as a result of all kinds of normal exposures. For non-smokers it is known that exposure to about 13 mg/m^3 for 8 hours leads to a 0.1 % increase in COHb. In the light of this information, inhalation of the current concentrations (1 to 4.5 mg/m^3 for up to one day) will only lead to a marginal increase in COHb concentration (less than 0.1 %) and will therefore not be linked to a health risk. Dichloromethane is not genotoxic or carcinogenic, and therefore no long-term effects are expected from this substance.

It is concluded that the concentrations occurring as a result of degassing of dichloromethane for less than one day are in excess of the MPR value. This is not expected to lead to actual health damage due to toxic effects. Long-term effects are not expected.

Benzene
The concentration profile for this substance shows an initial concentration of about 0.3 mg/m^3. Over a period of about one day this concentration decreases to below 0.02 mg/m^3, the MPR level for benzene. Comparison with available sub-acute NOAEL values in laboratory animals for benzene of 32 and 129 mg/m^3 for the critical effects of toxicity on the haematogenic system and the development before birth, respectively, shows that the margins are wide so that the occurrence of such effects should be regarded as highly unlikely. As benzene is a genotoxic carcinogen, the increased exposure poses an extra risk of cancer. This extra risk of cancer due to this exposure is in the negligible range, however, as shown by calculations.[3]

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[2] The extra risk of cancer for the time-integrated exposure, that is the area below the time-concentration curve as shown in section 4.2.2, can be calculated on the basis of the risk-specific concentration for one in ten thousand per lifetime of 0.048 mg/m^3 (= MPR). The result is an estimated extra risk of about two in one million per lifetime.

[3] Analogous to 1,2-dichloroethane (see previous footnote), the extra risk of cancer can be calculated for the time-integrated exposure (the area below the time-concentration curve as shown in section 4.2.2) on the basis of the risk-specific concentration for one in ten thousand per lifetime of 0.020 mg/m^3 (=MPR). The result is an estimated extra risk of about two in one hundred million per lifetime.

It is concluded that the concentrations are in excess of the MPR value for a short time. The calculated extra risk of cancer is negligible.

Toluene
The concentration profile for this substance shows an initial concentration of about 0.8 mg/m^3. Over a period of about one day this concentration decreases to well below 0.4 mg/m^3, the MPR for toluene. Toluene has been studied in several short-term volunteer studies, which resulted in 150 mg/m^3 as the NOAEL for neurological effects (the most sensitive effect at short-term exposure). A limit value for exposure times up to two weeks based on this amounted to 3.8 mg/m^3. This limit value is not exceeded within the concentration profile found (up to 0.8 mg/m^3). Therefore, on the basis of the concentrations observed for the mattress involved, which exceed the MPR value, for a short period, no health effects are expected.

Trichloroethene
The concentration profile for this substance shows an initial concentration of about 4.5 mg/m^3. Over a period of about a day and a half, this concentration decreases to about 0.5 mg/m^3. The MPR for air for trichloroethene of 0.2 mg/m^3 is reached in about 4 days. The MPR for trichloroethene is based on liver effects and nervous system depression, for which a NOAEL of 200 mg/m^3 was derived in laboratory animal studies. Trichloroethene has also been the subject of several volunteer studies with short-term exposure. It was found that minor neurological effects occur at concentrations of 1,074 mg/m^3 and higher. From this level, a limit value for exposure times up to two weeks has been derived of 10.8 mg/m^3. This limit value is not exceeded within the concentration profile found (up to 4.5 mg/m^3), and therefore no health effects are expected.

It is concluded that concentrations of trichloroethene occur that exceed the MPR value for several days. This not considered to pose an actual health risk, however.

Chloroethene (vinyl chloride)
The concentration profile for this substance shows an initial concentration of about 0.16 mg/m^3. Over a period of about one day this concentration decreases to about 0.1 mg/m^3 and subsequently over a period of several hours to even lower levels, around the MPR for air of this substance of 0.0036 mg/m^3. Vinyl chloride is a proven human carcinogen, and similar to benzene and 1,2-dichloroethane its MPR corresponds to an extra risk of cancer of one in ten thousand per lifetime. As vinyl chloride is genotoxic and carcinogenic, the estimated exposure to this substance from the mattress poses an extra risk of cancer. This extra risk falls entirely in the negligible range, however, as shown by calculations.[4] The risk of toxic health damage due to concentrations exceeding the MPR value for a short period (non-carcinogenic effect) is regarded by us as low. Effects on liver, kidneys and nervous system, as are common for chlorinated aliphates, occur only at very high concentrations after short-term exposure to vinyl chloride. Effects on prenatal development may occur at much lower concentrations, however. From a NOAEL for foetotoxicity of 130 mg/m^3 in mice, a limit value for exposure periods of up to two weeks has been derived of 1.3 mg/m^3. This limit value is not exceeded within the concentration profile found (up to 0.16 mg/m^3), and therefore no toxic health effects are expected. As stated above, the calculated extra risk of cancer due to degassing of vinyl chloride from the mattress studied is negligible.

[4] Analogous to 1,2-dichloroethane and benzene (see previous footnotes), the extra risk of cancer can be calculated for the time-integrated exposure (the area below the time-concentration curve as shown in section 4.2.2) on the basis of the risk-specific concentration for one in ten thousand per lifetime of 0.036 mg/m^3 (= MPR). The result is an estimated extra risk of about five in one hundred million per lifetime.

Summary
Table 4 presents a summary of the effects in consumers.

Table 4 Summary of the risk assessment for consumers due to degassing.

Substance	Assessment
Methyl bromide 1,2-dichloroethane Dichloromethane Benzene Toluene Trichloroethene Vinyl chloride	Measured value briefly above substance-specific MPR value (for life-long exposure). The exposure is short-term, the standard is related to life-long exposure, and therefore the cases considered do not constitute an unacceptable health risk.

4.3.4 Risk assessment for consumers by degassing of shoes

Toluene
The maximum concentration in the shoes amounted to 260 mg/kg. Assuming a total utilisation period of the shoes (weight 250 g) of six months, the maximum daily body dose for a person of 60 kg is 0.006 mg/kg body weight/day[5]. This is a worst case estimate, as obviously the major part of the evaporating toluene escapes to the surroundings.

For toluene the RIVM uses a chronic oral limit value (MPR) of 0.223 mg/kg body weight/day. Considering the high oral absorption, this MPR can also be regarded as body dose (internal dose).

It is concluded that the maximum possible body dose due to the wearing of these contaminated shoes remains well below the MPR, and therefore we do not expect any health risk from such shoes.

4.4 Influence of degassing on the indoor environment

Evaporation of volatile organic compounds included in consumer products will occur partly indoors. This will influence the concentrations in the indoor environment. The RIVM has derived recommended values for health purposes. Recommended values are available for substances such as 1,2-dichloroethane, benzene, toluene and xylenes. No such values are available for common fumigation agents such as methyl bromide, chloropicrin and phosphine, and not for chloromethane either.

For a risk assessment of the substances in consumer products in relation to the indoor environment, two aspects are especially relevant. Firstly, for the substance studied most extensively (methyl bromide) no reference is available in the form of a recommended value. However, ample toxicological information is available for methyl bromide (see Appendix 2) and there are standards that allow immediate testing of the exposure of people. In the previous sections this has been done as best possible, and a discussion of the concentrations of methyl bromide in the indoor environment will not yield new information of any significance.

[5] 260 mg/kg means 260/4 mg in a pair of shoes of 250 g. Dividing this by a body weight of 60 kg and 183 days (six months) results in an exposure of 0.006 mg/kg body weight/day.

Secondly, it is not very well possible to calculate accurately concentrations in the indoor environment on the basis of the measured emissions of only a very small number of products. The concentration in the indoor environment is determined by the total of all sources in the house. At the moment, it is not known what sources (products or other sources) may contribute. Any attempt to estimate the concentration in the indoor environment would therefore be speculative.

In the previous risk assessment (Knol et al., 2005b) a risk characterisation was made for cuddly toys obtained from the shelves of wholesalers. It was found that the risk for consumers due to evaporation was negligible. A weak point of this study was that it was unclear whether the cuddly toys studied (obtained from wholesalers) had ever been in fumigated containers. This study was therefore not focused on a worst case situation.

In 2005 a report was published on the degassing properties of different products (Knol et al., 2005a). Data on the amount of methyl bromide in the materials are available for different products, such as slippers, sculptures, marbles and bags. The largest quantity per kg of product was found in a hassock (39 mg of methyl bromide per kg of product); the largest absolute quantity was found in a mattress (11 mg of methyl bromide per kg of product). Several products also contained chloropicrin in addition to methyl bromide. Furthermore, two of the products investigated contained 1,2-dichloroethane.

These data can be used for a risk assessment for the indoor environment. The hassock had a half-life of 1 hour. The influence of this on the concentrations in the indoor environment is negligible, as the period between unloading from the container to sale and placement in the home is much longer.

The risk assessment of mattresses for consumers is described in section 4.3.3, which presents a description of the concentrations to be expected in the indoor environment.

It is conceivable, and has also been observed in practice, that all the household goods of immigrants are transported in a container that is fumigated. In the previous risk assessment (Knol et al., 2005b) this group of people was identified as a risk group. Scenarios to calculate the actual influence on the indoor environment are speculative, and therefore such calculations have not been made.

4.5 Risk characterisation of foods and medicines

A report on the risks of fumigated foods and medicines has been published earlier (Knol et al., 2005b). Since then no reports of studies in this field have appeared. The earlier conclusions with respect to foods and medicines were, that it was demonstrated that fumigated foods contain pesticide residues and that changes in the composition of the medicines occur. Immediate health risks by the methyl bromide and bromine contents are not to be expected. It is unknown what the effect is of other pesticides and what effects (reactions) the pesticides have on, for instance, medicines.

5 Risks for the environment

5.1 Influence on the environment

The substances found in containers affect the environment in different ways, and through the environment they have effects on humans and/or nature. Volatile organic compounds contribute to the formation of smog, the pesticides have effects on nature and some substances deplete the ozone layer (methyl bromide). In this chapter we will outline these effects. The policies with respect to these substances and the recorded emissions in the Netherlands are described in Appendix 1.

5.2 Extra emissions on Dutch territory

According to data from the Statistics Netherlands, in 2006 about 2.5 million loaded containers arrived by sea at Dutch ports (CBS, 2007). This corresponds to about 5 million twenty-foot equivalent units containers (1 TEU container is 33 m^3)[6].

In 2002 a study was carried out on the occurrence of the different substances in containers. This study involved 300 containers in the port of Rotterdam. In 2003 the VROM Inspectorate set up a monitoring programme in which annually about 100 containers were selected for determination of the concentrations of the different substances. The selection method has remained unchanged over the years. Selection was performed by the customs on the basis of non-environmental criteria. In 2007 a trend analysis was carried out on these containers (De Groot, 2007). In this trend analysis the percentage of containers was determined that contained the substances (pesticides and other volatile organic compounds). As the same selection method was used, conclusions can be drawn about trends, but the absolute value does not allow conclusions about the total number of containers. The percentage of containers with methyl bromide in concentrations above the MAC value was 2 % in 2002. During the non-random sampling in the years 2003 - 2006 higher percentages were found, namely 7 %, 20 %, 13 % and 11 %, respectively. It is unknown to what extent a rising trend can be distinguished (2002 compared with other years) or what the influence is of the selection method.

The trend analysis included detailed data on the number of containers in which the different substances were found and in what concentrations. These data were used to make the estimate given below of the resulting emissions in the Netherlands. As the selection method was not random, the calculated emissions are probably an overestimate of reality. Other factors were also chosen so as to overestimate the emissions. For instance, no correction was made for the volume of goods in the containers. If it is concluded that the emission does not contribute substantially to the emissions from other sources, then there is no problem. If the emission proves to be relatively high, then a closer study is desirable.

On the other hand, this calculation method underestimates the quantities entering the Netherlands. After all, only the concentration in the air is taken into account. No account is taken of the quantities included in the products and released later on. For pesticides that have been put in for decontamination

[6] The data from the CBS also specify the number of containers in TEU. In practice, the conversion factors prove to be about 2. A container of 1 TEU has a length of 20 feet and a capacity of 33.1 m^3.

and are absorbed by products, it might be possible to estimate an upper limit for this quantity as an order of magnitude. For methyl bromide the quantity used has been estimated in section 5.3.3, and obviously this is the upper limit of what may have been absorbed by products. Other volatile organic compounds, e.g. benzene, toluene and xylenes, are included in products or are used, for instance, as solvents. For these substances, data on concentrations in the products are lacking, so that the quantity cannot be calculated.

Table 5 shows in how many containers the various volatile organic compounds were found and what the average concentration was. On the basis of these data it was calculated what load entered the Netherlands in this way. We assume that this load has been emitted in the Netherlands. The above CBS data on numbers of containers used for this calculation are given in the table. A sample calculation has been worked out in a footnote[7].

Table 5 Quantities of substances in containers.

Substance	Found in containers	Average concentration	Load*	Year	Total emission in the Netherlands (in 2004)**
	(percentage)	mg m^{-3}	kg		kg
Benzene	54 %	3.2	283	2006	2,983,000
Toluene	85 %	127	17,866	2006	7,857,000
Xylene	70 %	9.7	1,124	2006	
Chloromethane	35 %	73	4,229	2006	
	33 %	1.3	71	2005	
Tetrachloromethane	9 %	0.066	1	2004	
Chlorobenzene	9 %	0.07	1	2006	
Methyl bromide	28 %	10.9	505	2006	6,400
1,2-dichloroethane	33 %	22.2	1,212	2006	38,000
Chloropicrin	8 %	1.9	25	2004	

* the estimate of the load is only based on the concentration in air. The quantity of a substance absorbed in the goods may be much larger, especially with respect to substances also used for production purposes, such as benzene and toluene. These quantities may also be released on Dutch territory.
** see Appendix 1.

5.3 Effects of these emissions

5.3.1 Load of volatile organic compounds

The emission of volatile organic compounds (VOC) in the Netherlands amounted to 171,000 tonne in 2005 (Emissieregistratie, 2007). The emission of volatile organic compounds estimated here amounts to 20 to 30 tonne, or 0.02 %. Therefore the contribution of volatile organic compounds to environmental effects is very small. The estimate is probably on the low side, however, because some volatile organic compounds will evaporate from the products. This effect is not quantifiable, especially for the substances that are originally included in products or semi-finished products or

[7] The methyl bromide load has been calculated as follows. In 2006, methyl bromide was found in 28% of the containers, at an average concentration of 10.9 mg/m^3. The number of maritime containers entering the Netherlands was 5 million TEU containers. A TEU container has a volume of 33 m^3. The load follows from: number of TEU containers * volume of TEU container * percentage of containers with methyl bromide * average concentration * unit correction factors.

which are used in the production process. If the quantity in products is by 100 times larger, this would lead to a contribution of 1 to 2 %, but data on the quantities included in products compared with the quantities in air are lacking.

The emissions on a local level, for instance, in the Rijnmond area, are presented in Table 6. Also in comparison with the local emissions, the load from containers is negligibly small (0.2 %). The emission of hydrocarbons by seagoing ships in the port of Rotterdam is estimated at 400 tonne in the year 2000 (EC, 2002).

Table 6 Emissions to air by large companies in the Rijnmond area (data from DCMR, 2007).

Industry	Emission (tonne per year)
Chemical	2,832
Refineries	7,671
Storage and handling	4,789
Energy	245
Waste	6
Total	15,542

5.3.2 Load of benzene and toluene

The quantities of benzene and toluene imported into the Netherlands are 0.28 and 18 tonne per year, respectively. This will be an underestimation of reality, as these substances are probably included in the products and will evaporate afterwards. The ratio between the quantity in the product and the concentration in the air is unknown and will depend on the type of product. Most of the evaporation of this unknown quantity will be spread out over the Netherlands.

The benzene emission in the Netherlands is almost 3,000 tonne (data from the Dutch Emission Register, see Appendix A1.8), with the target group 'Traffic and Transport' accounting for about 65 % of the emission. The calculated contribution to this from containers (0.28 tonne) is negligible.

For benzene there are air quality requirements as well. The emission from containers is spread out over the various sea ports of the Netherlands. The contribution to the local air quality will be small compared with the contribution from local traffic. In the residential environment, a substantial elevation of the local concentrations due to the containers arriving at the port is not to be expected.

The emission of toluene in the Netherlands is about 8,000 tonne (see Appendix A1.9), the major emitters being the target groups 'Traffic and Transport' (55 %) and 'Industry' (20 %). The calculated load of toluene of 18 tonne per year is less than 0.5 %. In view of the other sources of toluene, the emission from containers, will not lead to a noticeable increase in local concentrations in the industrial environment in which containers are handled.

5.3.3 Load of methyl bromide

Within the group of selected containers, methyl bromide was found in 28 % of the cases in 2006. This would seem to be an overestimation of the actual figure. In 2002, in a random sample a percentage of 6 % was found (Knol-de Vos, 2003); in Hamburg (Baur et al., 2007) a similar percentage was found. At a percentage of 6 %, an average concentration as shown in Table 5, and 2.5 million loaded containers, the total amount of methyl bromide being brought into the Netherlands is 50 kg, not

including the quantity that may evaporate afterwards from products. At 28 % this quantity is 500 kg. This is 1 to 10 % of the emission in the Netherlands (see Appendix A1.2).

Methyl bromide is intentionally put into containers for fumigation purposes. During fumigation such a quantity of methyl bromide is put in that a concentration of 40 to 50 g/m^3 is created. If 6 % of the containers - the percentage of the random sample - that enter the Netherlands have been treated with methyl bromide, this represents a methyl bromide consumption of:
6 % * 5 million TEU containers * the volume of a TEU container (33 m^3) * 45 g =
300 tonne of methyl bromide.

This means that the transport of containers to the Netherlands causes 50 times more emission than the current emission in the Netherlands. Even the emission in the Netherlands before a stringent methyl bromide policy was instituted (71 tonne in 1990) is a factor four smaller than the quantity currently used to decontaminate products for the Netherlands.

Methyl bromide is a substance that depletes the ozone layer, on which agreements have been made (such as the Montreal Protocol) to reduce the emissions. Its application for treatment of dunnage and packaging timber is excluded from this protocol. Considering, however, that containers are treated as a whole, whereas the dunnage needs to be treated only once, this consumption (and therefore these emissions) can largely be avoided.

5.3.4 Load of 1,2-dichloroethane and chloropicrin

The emissions of 1,2-dichloroethane to the air in the Netherlands total 38 tonne per year (see Appendix A1.4). The release of air from containers could add 1 tonne per year (2 to 3 %) to this. It is not expected that these emissions will cause problems with the air quality standards.

For chloropicrin there are no data on environmental quality or standards with which the estimated emission can be compared.

6 Conclusions and recommendations

On the basis of available data on the substances and concentrations in import containers, the RIVM has evaluated the data and used them for a risk assessment for humans and the environment. the RIVM was not assigned to analyse the occupational risks, i.e. the risks for workers, and therefore these have not been included in this risk assessment.

The conclusions of the RIVM with respect to the questions to be answered are as follows.

6.1 Risks for bystanders

Question 1: Do the substances found during the monitoring of import containers pose an acute danger to citizens who are exposed to them unexpectedly, for a short period and without protective equipment, when a container is opened?

Conclusion: The present risk assessment indicates that the high concentrations of pesticides in containers form an acute health risk to citizens who are exposed to them. People run this risk if they enter, or stay very close to, a recently opened container. The exposure can be unexpected and high, partly because containers treated with pesticides are not labelled as such. Only 2 % of the treated containers have labels (Knol-de Vos, 2003).

As a worst case scenario for exposure of bystanders to the concentrations occurring in containers, for methyl bromide we expect acute neurological symptoms, for 1,2-dichloroethane light acute neurological disorders may occur (cannot be determined with complete certainty), for chloropicrin we expect irritation of eyes, nose and respiratory tracts, and for chloromethane we expect neurological disorders, probably of a moderately serious to serious nature, and possibly an effect on development and reproduction.

For benzene, toluene and xylenes we do not expect effects for bystanders on the basis of the maximum values found.

6.2 Risks for consumers

Question 2: To what extent do the substances found in the products during the monitoring of import containers pose a health risk to citizens? This calls for a specification of the substances for which the risk is above or below the Maximum Permissible Risk level and/or above or below the Negligible Risk level.

Conclusion: The available data on degassing from consumer products are very limited. For the *oral* pathway, the data evaluated earlier (Knol et al., 2005b) do not indicate a health risk for the methyl bromide and bromide ion residues found. For other products and other substances, various data on the extent of this type of exposure are lacking. For some products, sucking could be a relevant pathway of oral exposure. Due to a lack of data, conclusions on the actual risk occurring in this way are not possible.

The same applies to the *dermal* pathway, which may be relevant for some products that come into intensive contact with the perspiring skin.

As indicated in the earlier report by Knol et al. (2005b), we regard mattresses as a 'worst case product' deserving further study in view of the intensive and long-term potential exposure. For mattresses, too, the available data with regard to the actual exposure are limited. Only two mattresses from the large quantity of imported mattresses have been studied for degassing. The representativeness of these mattresses is unknown. Final conclusions on the risks due to evaporation indoors at the consumer's home are therefore not possible in the present report.

The possible health risk due to degassing of methyl bromide from a mattress has been assessed in the earlier report by Knol et al. (2005b). For that mattress, as the worst case product, the conclusion was that health risks were not to be expected at the measured degree of degassing. This conclusion was drawn on the basis of only one mattress sampled. New data are limited to one other mattress obtained from a container featuring high concentrations of 1,2-dichloroethane and several solvents. On the basis of the measurements carried out, as worst case, we estimate that for six contaminants present in this mattress, the concentrations in the room where the mattress is located, will exceed the Maximum Permissible Risk value (MPR) for several days. This applies in particular to the concentrations of 1,2-dichloroethane. Further toxicological assessment of this revealed that health effects are not to be expected because the duration of the high exposure is relatively brief. The calculated extra risk of cancer per lifetime for 1,2-dichloroethane was in the range of what is regarded as the negligible risk level in standard risk policy. For other contaminants found, the conclusion was also that no actual health risk was expected due to degassing from the sampled mattress.

The assessment of the two mattresses sampled indicates that degassing from consumer products coming from contaminated/fumigated containers may lead to concentrations in the indoor air that are well in excess of the MPR value. As the exposure duration is brief in comparison with the time period to which the MPR applies, health risks exceeding the negligible risk level are not to be expected for these two mattresses. It is uncertain whether this conclusion can be extrapolated to mattresses in general and to other fumigation agents and solvents. For more certainty on this issue additional research will be required. The necessity of, and options for, additional research will be addressed by the RIVM in the recommendations (section 6.9).

6.3 Extra emissions in the Netherlands

Question 3: How large is the quantity of substances imported into the Netherlands in this way and how does this emission compare to the emissions known to exist in the Netherlands (according to the Dutch Emission Register)?

Conclusion: On the basis of the quantities found *in container air* it can be stated that the load of volatile organic compounds that enters the Netherlands in this way is small compared with national and local emissions. Especially for substances used in production processes, quantification of the amounts contained in these products and slowly evaporating from them was not possible. These quantities may be much larger than the quantities in the air. Adequate data on this are lacking. The amount included in the products would have to be a 100 times as high as in the air if the extra quantity of volatile organic compounds is to become a few percent of the existing emission.

6.4 Environmental effects by emissions

Question 4: To what extent do these substances, in the quantities as determined under point 3, lead to effects on the environment, and more specifically, on nature?

Conclusion: On the basis of the number of containers in which *methyl bromide* has been found, the amount of methyl bromide used for treatment of the containers has been quantified. For the containers entering the Netherlands, the quantity of methyl bromide used for fumigation is many times larger than the national emission at this moment (300 tonne compared with 6 tonne). Methyl bromide is a substance that depletes the ozone layer; its use is restricted by the Montreal Protocol. Treatment of dunnage and packaging timber is a permitted application, but the way in which this is done internationally leads to extra emissions. The wood needs to be treated only once, and it is not necessary to treat whole containers.

The release of other substances from the containers is not expected to cause any effects, in view of their quantities compared with the national emissions and the place where they are released (industrial environment).

6.5 Dutch and European policies

Question 5: What are the Dutch and European policies with respect to these substances for Dutch, European or non-European producers?

Conclusion: In Europe as well as in the Netherlands the safety of consumer products is regulated by the European General Product Safety Directive. The essence of this directive is the obligation of businesses to sell safe products only. Therefore, businesses are responsible for putting safe products on the market. They have to assure and assess the compatibility of their products with the statutory requirements. Furthermore, legislation provides reference frameworks on the basis of which an assessment can be made whether a product is safe, such as the non-mandatory European and national standards. A producer has influence on the safety characteristics of the product, a distributor usually has not. Manufacturers and their representatives within the European Union, or the first importers with the European Union, are regarded as producers.

The policy as regards the treatment of packaging timber and dunnage has been laid down in International Standard for Phytosanitary Measures (ISPM) No. 15. This standard states that such wood must have undergone a heat treatment or a treatment with methyl bromide to prevent international transport of pests.

6.6 Efforts that are nullified

Question 6: To what extent are the efforts of Dutch and European producers nullified?

Conclusion: Measures from the past against substances whose use is undesirable or even dangerous from a health or environmental viewpoint, may be undermined by the lack of a comparable regulation or self-regulation system for producers in other parts of the world. During the past period there have been incidents indicating that there may be a wider problem with the safety of import products due to contamination during production processes, partly related to the use of substances that have been

phased out in western countries. Furthermore, substances may be used for unforeseen applications, such as the suspected immersion of shoes in toluene, as referred to earlier in this report. A systematic analysis of this problem is lacking, however, so that the scope of the problem is as yet unknown.

6.7 Consequences for the indoor environment

Question 7: To what extent do the goods with the observed concentrations of pesticides and production chemicals contribute to the concentrations in the indoor environment, in relation to the concentrations found in Dutch homes?

Conclusion: Not enough data are available for a comparison with observed concentrations in the indoor environment or the recommended values for these concentrations. There are a few data on evaporation of methyl bromide from a number of products, but information on the representativeness of these data for similar or other products is lacking. Furthermore, calculation of the situation in the indoor environment would require the availability of scenarios about the sources to be considered. Such scenarios are not available and would not yield much supplementary information compared with the analysis of the effects of degassing under Question 2.

6.8 Developments to be expected

Question 8: What future developments are to be expected on the basis of the trends observed?

Conclusion: The trends indicate that the developments are not predictable. No extensive research has been carried out on the question why the concentrations of volatile organic compounds have increased. No obvious reasons have been identified either, and it seems that sometimes one substance is preferred, and sometimes another. In spite of the small samples, the data obtained from containers in the ports of Rotterdam and Hamburg are remarkably similar.

On the basis of the monitoring data, the RIVM concludes that the situation may change in a short time span (order: a few years). It seems that since 2006 more solvents or production chemicals have been put into containers, without apparent reason. The substances also seem to change without apparent reason.

The RIVM observes that a discussion is ongoing about the tiger mosquito in containers. The tiger mosquito may transmit tropical diseases among human beings. The mosquito or its larvae or eggs may survive in containers in a watery environment. RIVM's recommendation to the Dutch Ministry of Health, Welfare and Sport is that if international bodies undertake negotiations on measures against the spread of the tiger mosquito and fumigation is being considered, the Ministry should provide these bodies with information about the possible consequences of fumigation. The objective would be to arrive at good practices to prevent the spread of the tiger mosquito without secondary effects.

6.9 Options to reduce the risks

Question 9: What measures may lead to reduction of the risks?

Conclusion: the RIVM observes that health risks occur during the opening of containers. Furthermore, the exposure to environmentally dangerous substances due to evaporation (degassing) from import products is increasing. Health risks as a result of this have not been demonstrated, but the RIVM cannot rule out such risks either. Several options to reduce exposure are given below.

Option: reduction at the source, to start with an analysis of the trade chain
The most practical approach may be to take measures at the source. Measures at the source affect the entire chain and would lead to reduced exposure of citizens as well as employees. The option is therefore to analyse the trade chain for possibilities to come to an agreement with producers and importers to reduce the use of environmentally dangerous substances. After all, they are in a position to set requirements to the substances used for decontamination of containers or in production.

The recommendation to appeal to producers to reduce the use of such substances has been made before (Knol et al., 2005b). In view of the increasing trend, it must be concluded that this does not have sufficient effect. The RIVM has not investigated where the bottlenecks are located in the chain. Possibly the policy pursued offers insufficient instruments to address the situation. After all, no unacceptable risks have been demonstrated for individual products, so there is not much ground to appeal to producers to take their responsibility to put safe products on the market. Possibly, there is a lack of knowledge of the problem and dissemination of information is necessary, or there are other (economic) obstacles. An analysis of the trade chain, focusing on an evaluation of the policy and enforcement instruments, for instance using methods such as the '11 Times Table' method (Van Reenen, 2000), will probably reveal this type of obstacles.

Option: measures in the short term
The option described above may lead to improvements in the longer term. It is not likely to lead to improvements in the short term. Health risks will occur especially when citizens enter containers and are exposed to the sometimes high concentrations. There are different options to address this situation.

In 2007 the RIVM published a report on *zones* to be used during the opening of import containers, which only persons wearing breathing protection would be allowed to enter (Schols and Van Putten, 2007). This could be made applicable to situations in which citizens are present during the opening of containers. Excepts could be made for containers of which it is certain that they have not been treated with decontaminants. It should be noted that this can only be ascertained by measurements at the moment. Exposure to high concentrations of evaporating production chemicals or components is still possible then, but these have not yet been proven to pose acute risks.

Another option is to *intensify the checking* of containers, by private companies or by government bodies. The RIVM observes, however, that the problem involves large numbers of containers, a wide variety of goods and a constantly changing situation. Research into differentiation of high-risk containers on the basis of the nature of the goods or the origin of the container, has not yielded any results. More intensive inspection of containers may prevent a few incidents, but a major effort will be required to control the risks.

Option: monitoring of developments
To identify trends and determine the effectiveness of any future agreements with producers and importers, monitoring would be an option. This can be implemented by taking random samples. Monitoring would have to focus not only on a well-defined number of substances, but also on trends in the use of new substances. Cooperation on a European level, for instance with the authorities in Hamburg, would be a good option.

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Appendix 1 Environmental policy with respect to specific substances

The information that is available on the Dutch and European policies, standards and emissions for the substances involved in this study is described separately below for each substance. To ensure consistency, the description starts with information on the policy on volatile organic compounds (VOC), the category to which these substances belong. Part of this information has been taken from the factsheets of the substances occurring on the list of Dutch priority substances (RIVM, 2007). The specific characteristics and problems with regard to fumigation, for which a number of substances are used, are described separately in section A1.11.

A1.1 Environmental policy for volatile organic compounds (VOC)

For volatile organic compounds there are European agreements on the reduction of emissions to be attained by each country. The reduction is to be achieved partly by product policy and partly by emission policy. Examples of regulations aimed at achieving this reduction are: the Solvents Decree (VOC Directive 1999/13/EC), the Decree on organic solvents in paints and varnishes (EC Paint Products Directive 2004/42/EC) and the European directive on the control of volatile organic compounds (VOC) emission resulting from storage of petrol and its distribution from terminals to service stations (94/63/EC). The latter directive has been implemented in the Netherlands through the Decree on environmental management at service stations, the Regulation on environmental management during storage, handling and distribution of petrol, and the Regulation on petrol transport in mobile tanks. Furthermore, VOC measures are included in the '8.40 AMvBs' (Order in Council under the Environmental Management Act).

An important part of the measures is implemented through covenants with the target groups and through the permitting system, making use of the emission requirements as laid down in the NER (Dutch emission guidelines).

In 1999, an agreement in the UN-ECE framework was signed in Göteborg about national emission ceilings for SO_2, NO_x, NH_3 and VOC, to be achieved in 2010. For the Netherlands this included a maximum VOC emission of 191 million kg. Subsequently, in 2001 the NEC Directive was adopted, which included a VOC emission ceiling for the Netherlands of 185 million kg as from 2010 (Directive 2001/81/EC).

A1.2 Environmental policy on methyl bromide

Policy
In accordance with the Montreal Protocol (1987), in 2001 the use of methyl bromide had been reduced by at least 50 % compared with 1991, and as from 2005 it is prohibited, except for critical applications.

Directive 2037/2000 concerning ozone depleting substances is a supplement to the Montreal Protocol. It contains agreements on the production, import, export, use, and exception for critical applications. Critical applications include applications for storage and transport of goods. For instance, Commission Decision 2001/219/EC stipulates that wood originating from certain countries must be treated against pests. This treatment may take place through heating or fumigation. The latter method is cheaper.

The admission of methyl bromide as a biocide and pesticide falls under the Crop Protection Chemicals and Biocides Act (the successor of the Pesticides Act). All admissions for methyl bromide were cancelled in December 2001 and replaced by a new admission (admission No. 6476 N). The admissions concern pre-shipment applications (export applications), quarantine applications (import applications) and the critical applications according to the criteria of the Montreal Protocol and EC Directive 2037/2000.

Standards and emissions
Environmental quality standards for methyl bromide are not available. They are expected to become available shortly.

In the Netherlands, data on emissions to air due to the use of methyl bromide are collected through the Emission Register programme. In 2003, the consumption was about 5 tonne per year (target group of Trade, services and other). The VROM Inspectorate expects that the use for quarantine applications during storage of goods and transport in (container) ships, and for fumigation of ship cargo holds, will increase during the coming years to an emission level of up to 30 tonne per year (VROM-Inspectie, 2005).

Tabel A1.1 Emissions of methyl bromide to air in the period 1990-2004 in tonne per year.

Target group	1990	2001	2002	2003	2004
Industry (chemical and other)	6.9	6.4	3.9	1.4	1.7
Trade, services and other	64	6.0	4.1	5.0	4.5
Total	71	12	8.0	6.4	6.4

A1.3 Environmental policy on phosphine

Policy
The admission of phosphine as a biocide and crop protection chemical in the Netherlands comes under the Crop Protection Chemicals and Biocides Act. The following laws and regulations apply to phosphine:

- the statutory directions for use concerning the delivery and utilisation of Degesch Plates (admission number 8418 N),
- the statutory directions for use concerning the delivery and utilisation of Magtoxin Pellets (admission number 8420 N),
- the statutory directions for use concerning the delivery and utilisation of Detia gas-Ex-B (admission number 9485 N).

Phosphine appears on the 'Non-limitative list of toxic and extremely toxic substances' in policy rule Arbo/AIS 0174663 of the Working Conditions Act.

Standards and emissions
In so far as known there are no environmental quality and emission data available for phosphine.

A1.4 Environmental policy on 1,2-dichloroethane

Policy
1,2-Dichloroethane is a blacklisted substance (76/464/EG), and in the Netherlands it falls under the regulation on environmental quality requirements (hazardous substances) for surface waters of the Environmental Management Act, and under the Water Framework Directive (2000/60/EC).

Discharges of waste water with this substance are subject to Directive 90/415/EEC.

Marketing and application of 1,2-dichloroethane as a crop protection chemical or biocide is prohibited or limited under Directive 87/181/EEC.

Standards and emissions
The environmental quality standards of 1,2-dichloroethane are presented in Table A1.2.

Tabel A1.2 Environmental quality standards for 1,2-dichloroethane.

Air		Water		Soil
Maximum Permissible Risk (ng/m^3)	Target Value (ng/m^3)	Maximum Permissible Risk (µg/l)	Target Value (µg/l)	Target Value (mg/kg)
100	1	700	7	0.02

Emissions of 1,2-dichloroethane take place to all compartments and originate almost entirely from the target group Industry. The emission to air in 2004 was about 38 tonne (see Table A1.3).

Tabel A1.3 Emissions of 1,2-dichloroethane to air in the period 1990-2004 in tonne per year.

Target group	1990	2001	2002	2003	2004
Industry (chemical)	1 228	60	76	53	37
Trade, services and other	18	1	1	1	*1*[1]
Total	1 246	60	77	54	38

1) *Expected value on the basis of the emission in 2003*

A1.5 Environmental policy on chloropicrin

Policy
The use of chloropicrin as a biocide is not permitted in the Netherlands. The substance is mentioned in Regulation (EC) No. 2032/2003, in which the requirements for marketing of biocides are laid down.

Standards and emissions
In so far as known, no environmental quality and emission data are available for chloropicrin.

A1.6 Environmental policy on chloromethane

Policy
Chloromethane is a volatile organic compound that is subject to the policy described in section A1.1. There is no specific national or international policy for chloromethane.

Standards and emissions
In so far as known, no environmental quality and emission data are available for chloromethane.

A1.7 Environmental policy on tetrachloromethane

Policy
Tetrachloromethane is a blacklisted substance (76/464/EC), and in the Netherlands it falls under the Regulation on environmental quality requirements (hazardous substances) for surface waters of the Environmental Management Act and under the Water Framework Directive (2000/60/EC).

Since 1st January 1995 the use of tetrachloromethane has been restricted within the European Union in accordance with the Montreal Protocol. It should be noted, however, that tetrachloromethane obtained by recycling may still be used after this date (EC Regulation 3093/94). If the indispensability of this substance for a production process can be demonstrated, dispensation may be granted (EC Regulation 2037/2000).

Tetrachloromethane falls under Directive 76/769/EEC concerning restrictions on the marketing and use of certain dangerous substances and preparations. The substance must not be used in concentrations of 0.1 % by mass or more in substances and preparations put on the market for sale to the general public and/or for applications in which the substances in question will evaporate, such as surface cleaning and cleaning of textiles. Substances and preparations with more than 0.1 % by mass of these substances must be labelled on the packaging with: ‘For use in industrial installations only’. This last regulation does not apply to medicines and cosmetic products (94/60/EC; 96/55/EC).

The provisions of Directive 94/60 concerning chlorinated hydrocarbons have been transposed into Dutch national regulations by means of an amendment to the Regulation on chemical product safety under the Consumer Goods Act. By the transposition of Directive 96/55 the relevant rules for these substances were transferred to the Decree on implementation of the EEC substances directive under the Chemical Substances Act (in 1998 renamed to Decree on implementation of the EC prohibitory directive under the Chemical Substances Act).

Standards and emissions
The environmental quality standards of tetrachloromethane are presented in Table A1.4.

Tabel A1.4 Environmental quality standards for tetrachloromethane.

Air		Water		Soil
Maximum Permissible Risk ($\mu g/m^3$)	Target Value ($\mu g/m^3$)	Maximum Permissible Risk ($\mu g/l$)	Target Value ($\mu g/l$)	Target Value (mg/kg)
60	1	1100	11	0.4

Emissions of tetrachloromethane take place mainly to air and are mainly produced by the target group Industry, see Table A1.5.

Tabel A1.5 Emissions of tetrachloromethane to air in the period 1990-2004 in tonne per year.

Target group	1990	2001	2002	2003	2004
Industry	307	12	5.6	2.8	3.1
Trade, services and other	6				
Total	313	12	5.6	2.8	3.1

A1.8 Environmental policy on benzene

Policy
Benzene is a volatile organic compound that is subject to the policy described in section A1.1. On the European level, increasingly stringent requirements are set on the composition of fuels (for instance, their aromatics content and the emission of these substances). These requirements are set in the emission regulations for new light vehicles (passenger cars and light business vehicles), which have been laid down in Directive 70/220/EEC.

On the basis of the EU Air Framework Directive, in November 2000 a daughter directive (2000/69/EC) became effective, with an annual average limit value of 5 $\mu g/m^3$ for benzene, to be achieved in 2010.

Under Directive 82/806, toys or parts of toys cannot be put on the market in EU Member States if the concentration of free benzene exceeds 5 mg/kg. In addition, Directive 89/677 stipulates that benzene is not allowed in concentrations equal to or higher than 0.1 % by weight in substances and preparations that are put on the market, with the exception of fuels and waste materials, as well as

substances and preparations intended to be used in industrial processes in which benzene emissions cannot exceed the values provided for in existing legislation.

The requirements with respect to benzene in toys from Directive 82/806 are included in the Toys Decree issued under the Consumer Goods Act. The provisions concerning benzene from Directive 89/677 have been transposed into Dutch legislation through an amendment of the Decree on the implementation of the EEC substances directive under the Chemical Substances Act (current name: Decree on implementation of the EC prohibitory directive under the Chemical Substances Act). This transposition was not carried out on time, partly as a result of uncertainty about the interpretation of one of the provisions of the Directive.
Benzene is included in Annex I of Directive 67/548/EEC concerning the classification, packaging and characteristics of dangerous substances. Benzene also falls under the Water Framework Directive (2000/60/EC), in which requirements are set on the maximum permitted concentrations in surface water and sediment.
On the national level, in the KWS-2000 project (*Hydrocarbons 2000*) agreements have been made on emission reduction within the petroleum chain (storage and handling of petroleum and fuels) and in the graphics industry (reduction of the use of aromatics).

Standards and emissions
The environmental quality standards for benzene are presented in Table A1.6.

Tabel A1.6 Environmental quality standards for benzene.

Air		Water		Soil
Maximum Permissible Risk (µg/m³)	Target Value (µg/m³)	Maximum Permissible Risk (mg/l)	Target Value (mg/l)	Target Value (mg/kg)
30	1	240	2	0.01

Most of the emissions are caused by the target groups Traffic, Industry, Consumers and Trade, services and other (see Table A1.7).

Tabel A1.7 Emissions of benzene to air in the period 1990-2004 in tonne per year.

Target group	1990	2001	2002	2003	2004
Traffic and transport	5,830	2,384	2,221	2,116	1,956
Consumers	703	540	527	514	513
Trade, services and other	605	81	94	97	156
Industry	940	137	126	135	148
Marine shipping	64	75	77	80	80
Energy sector	39	49	21	28	50
Agriculture	44	38	38	38	38
Refineries	203	19	20	18	33
Waste disposal companies	11	11	7	6	9
Construction	2	1	2	2	1
Drinking-water companies	0	0	0	0	0
Total	**8,442**	**3,336**	**3,133**	**3,034**	**2,983**

A1.9 Environmental policy on toluene

Policy
Toluene is a volatile organic compound that is subject to the policy described in section A1.1.

Toluene is mentioned in Annex I of Directive 67/548/EEC concerning the classification, the packaging and the characteristics of dangerous substances. Both at national and international levels there is the will to reduce emissions and to invest in this, but a specific policy is not in place.

Standards and emissions
The environmental quality standards of toluene are presented in Table A1.8.

Tabel A1.8 Environmental quality standards for toluene.

Air		Water		Soil
Maximum Permissible Risk (µg/m³)	Target Value (µg/m³)	Maximum Permissible Risk (µg/l)	Target Value (µg/l)	Target Value (mg/kg)
300	3	730	7	0.01

The total emission of toluene in the year 2004 was almost 8,000 tonne, of which 55 % was emitted by the target group Traffic and transport, see Table A.1.9.

Tabel A1.9 Emissions of toluene to air in the period 1990-2004 in tonne per year.

Target group	1990	2001	2002	2003	2004
Traffic and transport	14,565	5,503	5,026	4,736	4,325
Industry	18,436	2,100	2,619	1,493	1,696
Consumers	1,374	602	597	543	568
Trade, services and other	2,913	486	506	471	485
Construction	1,482	462	453	369	332
Waste disposal companies	189	119	112	105	101
Marine shipping	47	55	56	58	58
Energy sector	108	39	45	65	47
Agriculture	44	38	38	37	37
Refineries	1,330	355	151	240	20
Drinking-water companies	0	0	0	0	0
Total	**40,488**	**9,759**	**9,605**	**8,118**	**7,857**

A1.10 Xylene

Policy
The isomers of xylene are volatile organic compounds that are subject to the policy described in section A1.1.

Standards and emissions
Environmental quality standards for xylenes are not available.

The main emission sources are the target groups Construction and Traffic and transport, see Table A1.10.

Tabel A1.10 Emissions of xylenes to air in the period 1990-2004 in tonne per year.

Target group	1990	2001	2002	2003	2004
Traffic and transport	9,409	3,753	3,490	3,300	3,027
Construction	4,252	1,506	1,469	1,132	1,001
Consumers	3,045	881	795	568	695
Trade, services and other	2,065	440	489	497	499
Other industry	3,188	269	386	273	407
Chemical industry	534	111	117	90	106
Marine shipping	64	75	77	80	80
Waste disposal companies	0	0	0	0	4
Energy sector	2	0	1	0	0
Agriculture	0	0	0	0	0
Refineries	2	0	0	0	0
Total	**22,562**	**7,035**	**6,823**	**5,940**	**5,817**

A1.11 Use of chemicals for fumigation

Fumigation chemicals can be used both for decontamination of transports and for decontamination of spaces where foodstuffs and/or goods are stored. The release of these chemicals is recorded in the Emission Register as emission to the air. In the Emission Register these substances come under the heading Emissions from stores and public warehouses. These emissions are not caused by fumigation but are probably related to the storage of these chemicals at storage and handling companies. This probably also applies to the emissions of 1,2-dichloroethane and tetrachloromethane, which are known to be used together for decontamination of foodstuffs (such as cereals and nuts).

As regards decontamination of transports, only methyl bromide emissions are recorded in the Emission Register. Emissions of phosphine for decontamination purposes are not included in the Emission Register. Neither does the Emission Register include recent emission data for phosphine from other sources. Emissions for decontamination of transports are only reported for methyl bromide. In 1990 the emitted quantity of methyl bromide was about 65,000 kg. In 2004 this had been reduced to 4,500 kg.

Tabel A1. 11 Emissions of substances according to the Emission Register of the target group to which the activity Fumigations applies (kg per year).

Substance	Stores and public warehouses (SBI 63.1)		Decontamination of transports	
Year	1990	2004	1990	2004
Benzene	400,630	74,988		
Methyl bromide			64,470	4,500
1,2-dichloroethane	17,816			
Formaldehyde	0.1			
Tetrachloromethane	5,879			
Toluene	1,576,923			
Xylenes	21,011			

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Appendix 2 Toxicological profiles

A2.1 Toxicological properties of methyl bromide

Methyl bromide has been investigated for its acute, sub-acute and semi-chronic and chronic toxicity in many studies. Data are also available about genotoxicity, carcinogenity, reproductive toxicity and teratogenity. These data were assessed by the RIVM (1987) and ATSDR (1992), and more recently by OEHHA (1999) and US-EPA/AEGL (2004). The two latter assessments were made to achieve acute limit values for air. At the time, a major evaluation for the substance as a pesticide (fumigant) is being performed in an EU framework.

For methyl bromide inhalatory LC_{50} values were reported of 300 to 480 ppm (4 or 8-hour exposure) (1,185 to 1,896 mg/m^3) in rats and mice. The research on acute toxicity has revealed a very steep dose-response curve for mortality, which means that there is a sharp transition from concentrations without any effect, to concentrations that cause a 100- % mortality. The main symptoms in laboratory animals have a neurological nature. In addition, the substance also induces damage to the respiratory tract, especially to the olfactory mucous of the nose.

The literature describes a large number of cases of methyl bromide intoxication. These cases refer to accidental inhalation of high methyl bromide concentrations by bystanders or employees of enterprises where the substance was used (according to present-day criteria, this is to be considered improper use). These data provide an overall impression of the dose-effect relationship for methyl bromide in humans. Mortality among humans has occurred at concentrations of 33,000 mg/m^3 and more (unknown exposure time). These fatal intoxications result in tissue damage in the brains. Other symptoms of intoxication can show at even much lower concentrations. In humans, symptoms have been reported at concentrations from 390 mg/m^3. The most important toxic effects here occur in the nervous system (lethargy, tremors, epileptic fits, coordination problems), lungs (irritation, oedema, inflammation) and kidneys. Also eye and nose irritation and harmful effects on the vision have been reported. Symptoms can manifest themselves with a certain delay: the harmful effects of the exposure do not become manifest until after a number of hours which were still free of disorders. For the mortality endpoint US-EPA/AEGL (2004) calculated a threshold of 300 ppm (1,185 mg/m^3) at a 1-hour exposure as a value at which the entire human population is protected (AEGL-3 value). In the same assessment a 1-hour threshold to protect against serious adverse effects on the nervous system (AEGL-2) of 210 ppm (817 mg/m^3) was proposed, based on a NOAEL of 200 ppm for neurotoxicity in rats and mice at a once-only exposure for 4 hours.

In case of acute inhalation neurotoxicity is the most sensitive effect. The actual MTR hourly average of 10 mg/m^3 as used by the Ministry of VROM is based on a marginal effect level for neurological effects of 70 mg/m^3 in a 4-week inhalation experiment with rats, as referred to in RIVM (1987). In the more recent OEHHA assessment (1999) a LOAEL for neurological effects (anorexia, dizziness, headaches) of 35 ppm from a labour-toxicological study in humans was used in the derivation of a 1-hour limit value of 3.9 mg/m^3.

On behalf of the previous interim report on methyl bromide, the semi-chronic inhalatory toxicity of methyl bromide was assessed by the RIVM (Knol-de Vos, 2005a). In the studies available two effects appeared most sensitive: damage to the mucous membrane of the nose, a local effect, and neurotoxicity, a systemic effect. From a NOAEL for the two effects of 233 mg/m^3 from a 13-week study with rats, a semi-chronic limit value of 0.3 mg/m^3 for humans was derived.

The studies available do not show any carcinogenic effect of methyl bromide. Genotoxicity data do indicate a possible risk for this endpoint (RIVM, 1987, US-EPA/AEGL, 2004).

In research on the inhalatory chronic toxicity the effect on the mucous membrane of the nose appeared to be critical. The lowest test concentration value of 11.7 mg/m^3 was the marginal effect level. On this basis, the RIVM (1987) proposed a chronic limit value of 0.1 mg/m^3. The Ministry of VROM has fixed this value as the annual average MTR.

To methyl bromide a MAC value of 1 mg/m^3 applies. This value has been derived from a chronic NOAEL of 11.7 mg/m^3. This is the same NOAEL as the value on which the annual average MTR of 0.1 mg/m^3 is based.

In oral studies (semi-chronic, chronic) hyperplasia in the vestibulum gastro-oesophageale appeared to be the critical effect. For this, a semi-chronic NOAEL of 1.4 mg/kg body weight/day is available. On this basis the RIVM has proposed a semi-chronic limit value of 0.014 mg/kg body weight/day (RIVM, 2005).

No data from animal experiments are available for the dermal pathway. Data for humans indicate that accidental dermal contact with very high concentrations can bring about irritation of the skin, especially on spots where perspiration occurs (armpits, groins, genitals, below belt). Further data are not available.

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A2.2 Toxicological properties of phosphine

The toxicology of phosphine has been investigated in many studies. The resultant data were assessed by the RIVM (1987, 1996), US-EPA (1995) and US-EPA/AEGL (2007). Phosphine (synonym: hydrogen phosphide) is a gas with a strong respiratorily toxic effect. The oral toxicity of the substance has not been investigated.

Phosphine is a primary metabolic poison: it has an adverse effect on major enzymes in the respiratory system of body cells, resulting in internal asphyxia. Furthermore, if inhaled, a local effect on the respiratory tract may be expected.

In laboratory animals the acute toxicity of phosphine has been examined relatively much. The 4-hour LC_{50} in rats amounts to 15.5 mg/m^3. In the 1960s a series of experiments were performed in several animal species to investigate the connection between mortality and exposure time (dose-response relationship). Concentrations larger than 7 mg/m^3 revealed a linear decrease in lethal concentration when the exposure time was extended. With concentrations lower than 7 mg/m^3, however, no mortality was found to occur, irrespective of the duration of the exposure. The symptoms with lethal concentrations are: a lower blood pressure and collapse. With somewhat lower concentrations pulmonary oedema occurs, which also may be lethal. Furthermore, acute intoxications can cause serious anomalies in the brain, heart, liver and kidneys. For the mortality endpoint, US-EPA/AEGL (2007) derived a limit of 5.1 mg/m^3 at a 1-hour exposure at which the human population is protected (AEGL-3 value).

The data available on toxic effects in humans also contain case studies of intoxications and a few labour toxicological studies. It is not exactly known, at what concentrations (and exposure times) the initial acute symptoms in humans will occur. Reports on intoxication cases in humans after the use of phosphine as a storage protection product suggest that acute respiratory problems can occur, even at low concentrations (1.1 to 1.4 mg/m^3). The reliability of these data is limited, however. In 1994 in labour toxicological research among employees who had been working with phosphine for many years, no health effects were found at concentrations up to 3.3 mg/m^3/hour (8-hour exposure per day). For acute exposures to phosphine for at most 24 hours, the RIVM (1996) derived a limit value of 0.02 mg/m^3 for the general population. This value is based on the NOAEL level of 3.3 mg/m^3/hour of the above study among employees. Calculated on the basis of continuous exposure this NOAEL level amounted to 0.2 mg/m^3. Next, the value of this concentration was divided by a factor 10 for the protection of susceptible groups in the population.

The toxicity data available indicate that acute toxicity is the critical factor for phosphine. As far as - in case of repeated exposure - toxic effects were found, these effects can be attributed to the mechanism that is also responsible for the acute toxic effect. The only effect in a 13-week study with mice (exposure for 6 hours/day, 5 days/week) was growth retardation at a concentration of 6.3 mg/m^3 (the highest concentration in the test), whereas no deviations were found at 1.4 mg/m^3. This reduced growth was likely to be brought about by phosphine acting as a cell poison. In a sub-chronic experiment with rats using test concentrations up to 4.2 mg/m^3 (exposure for 6 hours/day, 5 days/week for 13 weeks) not any harmful effect could be observed. In a chronic experiment with rats, also using 4.2 mg/m^3 as the highest test concentration (exposure for 6 hours/day, 5 days/week for two years), no harmful effects were found, either. In special research into the effects on embryonic development in rats, effects were only observed at the highest test concentration of 10.4 mg/m^3 (mortality among mother animals as well as embryonic resorption) whereas there were not any harmful effects at 7.0 mg/m^3 and less. The genotoxicity research performed with laboratory animals (*in vivo*) does not indicate any toxic effect on the genetic material. Special research into the effects on the nervous

system (13-week study with rats) did not show any effect at concentrations up to 4.2 mg/m^3 (highest test concentration).

For exposure to phosphine for at most two weeks the RIVM derived a limit value of 0.017 mg/m^3 for the general population. This value is based on a NOAEL that results from a short-term animal experiment (teratogenity study with rats). This NOAEL amounted to 7 mg/m^3. When this value is converted to 24 hours, for 7 days/week, this NOAEL equals 1.7 mg/m^3. Subsequently, this concentration was divided by a factor of 100, being 10 for extrapolation from laboratory animal to human and 10 for protection of sensitive groups in the population.

For cases of chronic exposure to phosphine (up to life-long) the RIVM has determined a limit value for the general population of 0.00025 mg/m^3, which is based on a NOAEL of 1.4 mg/m^3 as derived from the 13-week experiment with mice (above-mentioned study). When converted to continuous exposure, the NOAEL equals 0.25 mg/m^3. This concentration was then divided by a factor of 1000 (10 for extrapolation from laboratory animal to human, 10 for protection of sensitive groups in the population, 10 for the limited duration of the study). When this limit value was set, the results of the chronic study with rats were not yet known. The NOAEL resulting from this latter study provides a better basis for the derivation of a chronic limit value and would bring about a higher limit value of 0.0075 mg/m^3.

The MAC value for phosphine is 0.4 mg/m^3 (8-hour average), with an accompanying 15-min peak value of 1.5 mg/m^3. This value is based on the estimated no-effect levels for acute toxicity in laboratory animals.

References

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WGD (1984) Werkgroep van deskundigen van de Nationale MAC-Commissie. Rapport inzake grenswaarde FOSFINE [*Expert group of the national MAC Commission. Report on limit values for PHOSPHINE*], Report No. 1/80.

A2.3 Toxicological properties of 1,2-dichloroethane

The toxicity of 1,2-dichloroethane (ethylene dichloride) has been investigated in a number of studies with laboratory animals, which were mainly dedicated to the inhalation exposure pathway. Exposure data for humans are relatively scarce. Toxicological assessments have been made by Gezondheidsraad (1997), WHO (1998), IARC (1999), WHO (2000), RIVM (2001) and ATSDR (2001).

Target organs in case of acute inhalation of very high concentrations are the nervous system, the liver and the kidneys. In laboratory animals LC_{50} values were found of ≥ 1,060 mg/m^3 (6 or 7-hour exposure). In rats, rabbits, guinea pigs, dogs and pigs, after inhalation of sub-mortal concentrations for 6 days (7 hours/day) degeneration and necrosis occurred in liver and kidneys, accompanied by haemorrhages in lungs and adrenal glands (WHO, 1998, 2000). For 1,2-dichloroethane for the mortality endpoint a Dutch intervention value for calamities has been derived from 2,000 mg/m^3 (1-hour exposure) (VROM, 2005).

Which effect is most sensitive in case of acute inhalation, does not become entirely clear from the inhalation data available. A limit value (VRW) of 200 mg/m^3 based on odour was proposed (1-hour exposure) (VROM, 2005) in the Dutch assessment to achieve intervention values for calamity situations.

As from 730 mg/m^3, effects on liver and kidneys occurred in short-term inhalation tests with rats, mice and guinea pigs. In these studies no more harmful effects were observed at a concentration of 430 mg/m^3. A 1-year to 1½-year limited inhalation experiment with rats revealed changes indicating liver toxicity at a concentration of 602 mg/m^3 (no effect at 202 mg/m^3). WHO (2000) concluded that all in all these studies indicate a NOAEL of 400 mg/m^3 and a LOAEL for liver effects of 700 mg/m^3. From this LOAEL, WHO (2000) derived a limit value for air of 700 µg/m^3. ATSDR (2001) proposed a chronic limit value for air of 3,000 µg/m^3 on the basis of a NOAEL for liver effects of 250 mg/m^3 from a limited 2-year experiment with rats (only one test concentration).

IARC's assessment (1999) of carcinogenity data for 1,2-dichloroethane resulted in this substance to be classified in group 2B (possibly carcinogenic to humans). Oral studies with rats and mice revealed increased tumour incidences, such as in the vestibulum gastro-oesophageale, lungs, liver and lymph nodes. Available inhalation studies had limitations. Genotoxicity data indicate activity, both *in vitro* and *in vivo*. As has been concluded by organisations such as Gezondheidsraad (1997) and the RIVM (2001), 1,2-dichlorethane is to be considered carcinogenic with genotoxic action. For air these two organisations made cancer risk estimates on the basis of the oral exposure experiment with rats. In this way, the RIVM (2001) proposed a risk-specific concentration of one in ten thousand (MTR) of 48 µg/m^3 based on life-long exposure.

In oral exposure experiments, liver toxicity was the critical effect. Semi-chronic experiments revealed increased liver weights at doses of ≥ 49-82 mg/kg body weight/day (WHO 1998). On the basis of an oral exposure experiment with rats the RIVM (2001) calculated a risk-specific dose of one in ten thousand (MTR) of 14 µg/kg body weight/day for the oral pathway.

The MAC value for 1,2-dichloroethane amounts to 7 mg/m^3 (8-hour average). This value is based on a quantitative cancer risk estimate on the basis of an oral exposure study with rats (Gezondheidsraad, 1997).

Suitable toxicity data for the dermal pathway are absent.

References

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Gezondheidsraad (1997) 1,2-Dichloroethane: Health-based calculated occupational cancer risk values. Report of the Dutch Expert Committee on Occupational standards, report No. 1997/01 WGD, Rijswijk, the Netherlands.

IARC (1999) IARC Monographs on the evaluation of carcinogenic risks to humans – Vol. 71.

RIVM (2001) Re-evaluation of human-toxicological Maximum Permissible Risk levels. RIVM report 711701025

VROM (2005) Interventiewaarden Gevaarlijke Stoffen [*Intervention values for dangerous substances*] – 2006. VROM Stafafdeling Crisismanagement

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WHO (2000) Air Quality Guidelines for Europe – Second edition. http://www.euro.who.int/document/aiq/5_6dichloroethane.pdf (consulted on 09/10/2007).

A2.4 Toxicological properties of chloropicrin

The toxicity of chloropicrin has been investigated in a number of animal experiments. Anecdotal human data are available as this highly irritating substance was used as a combat gat in the First World War. Toxicological assessments were made by OEHHA (1999, 2001), ERPG (1999) and WHO (2003).

Chloropicrin is a volatile substance with a strongly irritating effect on eyes, nose, throat and respiratory tract. A remarkable feature is the lacrimal effect. Inhalation of chloropicrin may also cause nausea and vomiting. Lung damage will occur especially in the medium and small bronchi; in most cases pulmonary oedema is the cause of death. Exposure can also result in inhalatory sensibilisation. For rats and mice LC_{50} values are known of 96 and 66 mg/m^3, respectively. For mortality ERPG (1999) has derived a 1-hour threshold value of 10 mg/m^3. Inhalation of this concentration is likely to cause very serious irritation without being fatal (ERPG, 1999).

For the lacrimal effect of chloropicrin a threshold value of 2 mg/m^3 (10-min exposure) is estimated. To establish the Dutch intervention value for chloropicrin (VRW) it was estimated on the basis of this value that eye irritation would be minimal at a level of 200 µg/m^3 (1-hour exposure) (GGD, 2000). On the basis of the same estimated threshold value of 2 mg/m^3 ERPG (1999) proposed a 1-hour threshold of 2 mg/m^3 for serious eye irritation in the human population.

The chronic and semi-chronic inhalation toxicology of chloropicrin has been investigated in rats and mice. In these studies irritation of bronchial tubes was the most sensitive effect, with a NOAEL in both rats and mice of 0.67 mg/m^3 (LOAEL: 3.4 mg/m^3). In the experiments on chronic effects no indication of carcinogenity was found. From a $BMDL_{05}$ of 2.8 mg/m^3, which was achieved in these studies, OEHHA (2001) derived a chronic limit value for air of 0.4 µg/m^3 (OEHHA, 2001). For chloropicrin, no MTR has been determined.

For the dermal pathway no data are available.

For chloropicrin a MAC value of 700 µg/m^3 used to apply (underpinned by ACGIH). as from 1/1/2007 this value no longer applies.

References

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OEHHA (1999) Determination of Acute Reference Exposure Levels for Airborne Toxicants March 1999: Chloropicrin *(trichloronitromethane; nitrochloroform; nitrochloromethane)* CAS Registry Number: 76-06-2.

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

A2.5 Toxicological properties of benzene

The toxicological properties of benzene have been investigated in all of the very many studies. Assess-ments of the large amount of data were made by OEHHA (1999), RIVM (2001), US-EPA (2003), US-EPA/AEGL (2003) and ATSDR (2005).

The critical effect of acute benzene inhalation is neurotoxicity. Irritation of eyes and mucous membranes will only occur at higher concentrations. For benzene LC_{50} values are known of $\geq$ 31,000 mg/m^3 (4 to 6-hour exposure). This indicates a relatively low acute inhalatory toxicity for this substance. For the mortality endpoint US-EPA/AEGL (2003) proposed a 1-hour threshold of 12,990 mg/m^3 as a value at which the human population is protected (AEGL-3 value). For serious neurotoxicity (AEGL-2) the same organisation estimated a 1-hour threshold value of 2,590 mg/m^3 based on the absence of serious nervous system depression at 12,960 mg/m^3 in laboratory animals for a 4-hour exposure.

Benzene is known for its toxic effect on the blood-forming system of the body. This effect can manifest itself already after a short-term inhalatory exposure. ATSDR (2005) mentions 10 ppm

(32.4 mg/m^3) as the lowest concentration at which this effect starts appearing in mice (exposure for 6 hours/day, 6 days). Short-term inhalation of benzene may also interfere with the *in utero* development. For this effect OEHHA (1999) derived a NOAEL in rats of 40 ppm (129 mg/m^3) (exposure for 6 hours/day, 5 days).

In case of lengthy exposure the most important harmful effect of benzene is on blood formation. The substance disturbs the function of bone marrow, which results in serious blood disorders. This will cause leukaemia (cancer of the blood). An increased occurrence of this type of cancer has been shown among industrial employees who were exposed to high benzene concentrations. Therefore, the World Health Organisation has classified benzene as an established carcinogen for human beings. The quality of human data available was insufficient to allow for a quantitative cancer risk assessment. The RIVM (2001) calculated a risk-specific concentration for one in ten thousand (MTR) of 20 µg/m^3 based on life-long exposure.

The toxicological properties for the oral pathway are relatively scarce. It is expected that the systemic effects for benzene indicated after inhalation (hematotoxicity, genotoxicity, carcinogenity) will also occur after oral exposure. On the basis of the inhalatory MTR of 20 µg/m^3, the RIVM (2001) proposed a temporary oral MTR of 3.3 µg/kg body weight/day.

For the dermal pathway it is known that high benzene concentrations can cause irritation of the skin. The data on the dose-response relationship for this effect, however, are very limited (ATSDR, 2005).

The MAC value for benzene amounts to 3.25 mg/m^3 (8-hour average). This value is based on a quantitative cancer risk assessment on the basis of an epidemiological study with inhalatory exposure (SER, 1994).

References

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US-EPA/AEGL (2003) Acute Exposure Guideline Levels (AEGLs) for Benzene (CAS Reg. No. 71-43-2). NAC/AEGL proposed 1: October 2003.

A2.6 Toxicological properties of toluene

The toxicology of toluene has been investigated in a large number of studies with laboratory animals and humans. The most recent evaluations are those by OEHHA (1999), ATSDR (2000), RIVM (2001) US-EPA/AEGL (2002), EU-RAR (2003) and US-EPA (2005).

Toluene is neurotoxic after acute inhalation. Lethal concentrations will lead to death after serious central nervous system depression. For rats 2-hour NOAEL mortality figures of 5,000 and 6,250 ppm (18,750 and 23,400 mg/m^3) are known. On the basis of these values, US-EPA/AEGL (2002) proposed a 1-hour threshold of 10,875 mg/m^3 for the mortality endpoint as a value at which the human population is protected (AEGL-3 value). On the basis of human volunteer studies a 1-hour threshold value of 750 mg/m^3 (AEGL-1) was estimated for minor neurological effects.

With toluene a large number of human volunteer studies with short-term inhalatory exposure has been performed. In these studies neurotoxicity appeared to be the critical effect, whether or not accompanied by minor sensory irritation. OEHHA (1999), ATSDR (2000) and EU-RAR (2003) concluded that 40 ppm (150 mg/m^3) resulted as the 6-hour NOAEL value from these studies. On the basis of this NOAEL value, ATSDR (2000) proposed a 2-week limit value of 3.8 mg/m^3.

The study results do not reveal any carcinogenic effect of toluene. Genotoxicity data indicate that there is no activity for this endpoint (EU-RAR 2003).

Neurotoxicity is also the critical effect in case of chronic inhalatory exposure. In labour toxicological studies variable NOAEL/LOAEL values were found for neurological modifications after exposure to toluene. In the most recent analysis of all these studies US-EPA came to the conclusion that the average NOAEL amounted to 34 ppm (128 mg/m^3). After making a correction for the limited duration of the exposure in the study and applying a safety factor of 10, a chronic air criterion of 5,000 µg/m^3 was achieved (US-EPA 2005). Before that, the RIVM had proposed a chronic limit value for air of 400 µg/m^3, based on a LOAEL of 332 mg/m^3, which originated from a labour toxicological study.

For the oral pathway far less data are available than for the inhalatory pathway. Critical effects that present themselves in animal experiments are kidney and liver toxicity. An increased liver and kidney weight was found in an oral study on the semi-chronic effects at dosages as from 223 mg/kg body weight/day (LOAEL). On the basis of this LOAEL, the RIVM (2001) proposed a total daily intake of 223 µg/kg body weight/day.

For the dermal pathway there are only few data. In a qualitative sense it is known that high toluene concentrations can have an irritating effect on the skin. Further data on the dose-response relationship for this effect are lacking, however.

The MAC value for toluene amounts to 40 ppm (150 mg/m^3) (8-hour average). This value is based on labour toxicological studies (no further details available) (SER, 1994).

References

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A2.7 Toxicological properties of xylene

The toxicology of xylenes (3 isomers) has been investigated in a number of laboratory animal and human volunteer experiments. The most recent assessments of the data are those made by WHO (1997), OEHHA (1999), US-EPA/AEGL (2000), RIVM (2001), US-EPA (2003) and ATSDR (2005).

Acute inhalatory exposure of laboratory animals and human beings to high xylene concentrations appeared to cause neurotoxicity and irritation of the respiratory tract. Lethal concentrations bring about serious central nervous system depression (narcosis), leading to death. LC_{50} values of 3,900 ppm (16,960 mg/m^3) and higher (4 or 6-hour exposure) have been published for rats and mice. On the basis of a concentration of 2,800 ppm (12,150 mg/m^3) (4-hour exposure) that causes serious central nervous system depression in rats, US-EPA/AEGL (2000) has proposed a 1-hour threshold of 4,000 mg/m^3 for the mortality endpoint as a value at which the human population is protected (AEGL-3).

In a large number of volunteer experiments, the effect of short-term xylene inhalation has been investigated. Irritation of the respiratory tract appeared to be the critical effect in these experiments. Neurological effects, if not entirely absent, were only of a very minor nature. For minor eye irritation US-EPA/AEGL (2000) has given a LOAEL of 400 ppm (1,736 mg/m^3) at a 30-min exposure. On this basis, this organisation has estimated a 1-hour threshold of 560 mg/m^3 for minor irritation effects in the human population (AEGL-1). For an exposure up to two weeks ATSDR (2005) selected a LOAEL of 50 ppm for minor irritation and light neurological symptoms on the basis of a volunteer experiment on acute effects (exposure up to 2 hours). From this level ATSDR derived a 2-week limit value of 2 ppm (8.68 mg/m^3).

Long-term inhalation of xylene has caused increased frequencies of neurological complaints among employees. For this, ATSDR (2005) has identified a LOAEL of 61 mg/m^3 on the basis of a labour toxicological study. Another effect of xylene inhalation that can be observed is a disorder of embryonic development. As from 500 mg/m^3, a reduced foetal weight and retarded bone formation were seen in rats. In a follow-up study where pregnant rats were exposed to 870 mg/m^3, behavioural modifications were observed in their descendants. On the basis of this LOAEL, WHO (1997) proposed a chronic limit value of 870 μg/m^3. The RIVM (2001) has adopted this approach.

The studies available do not show any carcinogenic effect for xylene. Genotoxicity data indicate the absence of activity for this endpoint (RIVM, 2001; US-EPA, 2003).

Oral exposure of xylene will induce damage to kidneys and liver and, in high dosages, also neurotoxicity. No comprehensive chronic study is available so that the information on the oral pathway is limited. On the basis of a marginal LOAEL of 150 mg/kg body weight/day, which was achieved in a 90-day study where a gastric tube was used, the RIVM (2001) has proposed a chronic oral limit value of 150 µg/kg body weight/day.

Undiluted xylene has an irritating effect on the skin, which is experienced in the industrial use of the substance as a solvent and in animal experiments. For this effect there is no further information on the dose-response relationship, however.

To xylene a MAC value of 210 mg/m^3 50 ppm (8-hour average) applies. This value is based on short-term volunteer studies from which a NOAEL of 100 ppm was derived and divided by 2 because of the larger breathing volume per hour in the work environment (WGD, 1990).

References

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OEHHA (1999) Determination of Acute Reference Exposure Levels for Airborne Toxicants. March 1999 C - 354 – Xylenes (technical xylene (o-, m-, p-), xylol) (o-xylene, ortho-xylene, 1,2-dimethylbenzene, 2-xylene) (m-xylene, meta-xylene, 1,3-dimethylbenzene, 3-xylene)(p-xylene, para-xylene, 1,4-dimethylbenzene, 4-xylene) CAS Registry Numbers: 1330-20-7 (technical), 95-47-6 (o-), 108-38-3 (m-), 106-42-3 (p-). http://www.oehha.ca.gov/air/acute_rels/pdf/XylenesA.pdf (consulted on 17/10/27).

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WHO (1997) Environmental Health Criteria No. 190 – Xylenes. WHO, IPCS.

A2.8 Toxicological properties of chloromethane

Toxicological assessments for this substance have been performed by ATSDR (1998), IARC (1999), WHO (2000), US-EPA (2001) and US-EPA/AEGL (2003). The only assessment made by the RIVM dates back from 1988 (RIVM 1988).

Acute inhalatory exposure of chloromethane (also called methyl chloride) in sufficiently high concentrations will cause neurological disorders. The only LC_{50} values that are available, are for mice, but this species might not be representative of humans, as was suggested by US-EPA/AEGL (2003). This is because of the higher breathing volume and the higher glutathione levels in mice (the neurotoxicity of methyl chloride is related with glutathione conjugation, as was found in mechanistic research). In case of a 5-day exposure (6 hours/day) the NOAEL for mortality in rats was 5,000 ppm, as was concluded by US-EPA/AEGL (2003). For the mortality endpoint this organisation estimated a limit value of >2,000 ppm (4,140 mg/m^3) to be the threshold above which the human population is jeopardised in a 1-hour exposure (AEGL-3 value). For serious neurological effects for the human population a 1-hour threshold of 500 ppm (1,035 mg/m^3) (AEGL-2) was estimated.

Concentrations up to 200 ppm were tested in several short-term inhalation studies with volunteers. In these studies no indications for neurological or other effects were revealed. On the basis of these studies US-EPA/AEGL (2003) proposed a 1-hour threshold of 100 ppm (207 mg/m^3) (AEGL-1). On the other hand, to derive a 2-week limit value for air ATSDR used a NOAEL from an experiment with mice. The mouse being a sensitive species, especially where continuous exposure is concerned, was considered a suitable model for man. On the basis of a NOAEL of 50 ppm for motor coordination and cell damage in the brain, ATSDR proposed a 2-week limit value of 0.5 ppm (1,035 mg/m^3) (ATSDR (1998).

In case of long-term exposure too, the nervous system is the target organ of methyl chloride. In a chronic inhalation experiment with mice histopathological damage occurred in the spinal marrow from 50 ppm, as was indicated by WHO (2000). In that study degeneration of the cerebellum did only occur after a level of 1,000 ppm had been reached. US-EPA (2001) comes to the conclusion that damage in the cerebellum is the critical effect of methyl chloride and that the strain of mice in this chronic study is relatively resistant to that effect. Therefore, they use a NOAEL of 50 ppm as was found in an 11-day experiment with another strain of mice (LOAEL: 100 ppm) to determine a chronic inhalation standard. This is the very study used by ATSDR to determine the 2-week limit value. In this way, US-EPA (2001) calculated a chronic limit value for air of 90 µg/m^3.

Methyl chloride is toxic for reproduction and disturbs development, as has been indicated in animal studies. At 1,000 ppm (2,064 mg/m^3) in a chronic experiment with rats damage to the testes occurred. As to reproduction toxicity a NOAEL is known of 150 ppm (310 mg/m^3). In experiments with mice where methyl chloride was applied during gestation, it appeared to cause heart disorders in their descendants. The NOAEL for development toxicity amounted to 100 ppm (206 mg/m^3) (WHO, 2000).

As far as carcinogenity is concerned, in the chronic studies available for rats and mice, tumours were only found in the renal cortex of male mice, in combination with hyperplasia and karyomegaly in the renal cortex. Genotoxicity data indicate an evident activity *in vitro*, but *in vivo* data indicate not more than a weak potency (WHO, 2000).

There are no adequate data on oral toxicity for methyl chloride (US-EPA, 2001). Methyl chloride is not irritating on the skin. Contact with the liquid, however, may cause skin damage due to local freezing (DECOS, 1995).

The MAC value for methyl chloride amounts to 52 mg/m^3 (8-hour average), but this value is no longer valid as per 1/1/2007. The basis for this value is a chronic NOAEL of 224 ppm (464 mg/m^3) for rats and mice (DECOS, 1995).

References

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A2.9 Toxicological properties of trichloroethene

The toxicology of trichloroethene has been investigated in numerous studies with laboratory animals and human volunteers. Assessments were performed by ATSDR (1997), RIVM (2001) and US-EPA/AEGL (2002).

Acute inhalatory exposure to trichloroethene has a neurotoxic effect. Inhalation of very high concentrations can cause serious central nervous system depression, ending in narcosis and coma and finally death. US-EPA/AEGL (2002) concluded that 4,600 ppm (24,700 mg/m^3) was the NOAEL for mortality in laboratory animals (4-hour exposure). On the basis of this NOAEL this organisation proposed a 1-hour threshold for mortality in the human population of 3,800 ppm (20,400 mg/m^3). A once-only exposure to lower concentrations resulted in lighter effects on the nervous system. To determine the 1-hour threshold for serious acute effects (AEGL-2), US-EPA/AEGL (2002) used the result of a volunteer study on acute effects where dizziness and lethargy were observed at 1,000 ppm (2-hour exposure). On this basis the estimated 1-hour threshold was 450 ppm (2,400 mg/m^3) (AEGL-2). For light neurological effects the volunteer studies achieved an acute NOAEL of 300 ppm (2-hour exposure). From this level a 1-hour threshold for light neurological effects in the human population of 130 ppm (700 mg/m^3) was derived (EPA/AEGL (2002). In an inhalatory volunteer study in which

exposure was for 7 hours/day over a 5-day period, the LOAEL amounted to 200 ppm (1,074 mg/m^3). On this basis ATSDR (1997) proposed a limit value for 14-day exposures of 10.8 mg/m^3.

On the basis of carcinogenity and genotoxicity research, trichloroethene is considered a genotoxic carcinogen, though for the specific genotoxic activity that it causes (numerical chromosome aberrations) an action threshold is assumed (RIVM, 2001).

The effects on the nervous system and liver were the most sensitive in prolonged inhalation studies with laboratory animals. For this, the RIVM (2001) derived a LOAEL of 200 mg/m^3. The chronic limit value (MTR) for air that was proposed on this basis amounted to 200 µg/m^3 (RIVM, 2001).

The effects on the liver are the most sensitive for the oral pathway. As a result, the sub-chronic NOAEL is 50 mg/kg body weight/day. On this basis a chronic oral limit value (MTR) of 0.05 mg/kg body weight/day has been determined (RIVM, 2001).

Only limited data are available for the dermal pathway. The undiluted substance is irritating on skin and eyes. In the cases reported of labour intoxications with trichloroethene, dermal contact with undiluted liquid contributed to the internal exposure. There are no further data (ATSDR, 1997).

References

ATSDR (1997) Toxicological Profile for Trichloroethylene. September 1997.

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A2.10 Toxicological properties of chloroethene (vinyl chloride)

The toxicology of vinyl chloride has been investigated in experiments with laboratory animals and human volunteers. Assessments have been performed by the RIVM (2001), US-EPA/AEGL (2004) and ATSDR (2006).

Vinyl chloride is especially known for its carcinogenic action in humans (induction of angiosarcomas of the liver in employees in the PVC industry). The effects of acute exposure to high concentrations of the substance are comparable with those of other chloroaliphates that affect liver, kidneys, nervous system and heart (cardial sensibilisation). Acute exposure in laboratory animals caused narcotic effects, cardial sensibilisation and hepatotoxicity. In laboratory animals, from a NOAEL of 50,000 ppm (5-min exposure) for mortality after treatment with nor-epinephrine (cardial sensibilisation test) a 1-hour threshold for mortality was derived in the human population of 4,800 ppm (12,000 mg/m^3). The 1-hour threshold for serious effects (AEGL-2) was based on pre-narcotic effects as observed in human volunteer studies. AEGL-2 of 1,200 ppm (3,100 mg/m^3) (1-hour exposure) was achieved on the basis of a LOAEL of 12,000 ppm. The 1-hour threshold for light effects (AEGL-1) was based on a concentration of 491 ppm which caused volunteers to report a slight headache after they had been exposed to it for 3.5 or 7.5 hours. The estimated 1-hour threshold amounted to 250 ppm (650 mg/m^3) (US-EPA/AEGL, 2004). Critical for sub-acute exposure is the effect on the progeny, as was concluded by ATSDR (2006). From a NOAEL of 50 ppm (130 mg/m^3)

for the induction of retarded embryonic development in mice, a limit value of 0.5 ppm (1.3 mg/m^3) was derived for exposure for at most 14 days (ATSDR, 2006).

As was stated before, vinyl chloride is an established human carcinogen. The genotoxicity studies performed indicate a genotoxic action mechanism. A quantitative estimate of the carcinogenic risk resulted in a risk level of one in ten thousand per lifetime (= MTR) of 3.6 µg/m^3 for the inhalatory pathway. For the oral pathway an MTR of 0.6 µg/kg body weight/day was estimated (additional cancer risk of one in ten thousand per lifetime).

For the dermal pathway only very few data are available. The undiluted substance has a strong irritating action on the skin and the eyes. There are no further data (ATSDR, 2006).

References

ATSDR (2006) Toxicological Profile for Vinyl Chloride. September 2006.

RIVM (2001) Re-evaluation of human-toxicological Maximum Permissible Risk levels. RIVM report 711701025.

US-EPA/AEGL (2004) Acute exposure guideline levels (AEGLs) for vinyl chloride (CAS Reg. No. 75-01-4). PROPOSED 2: 03/2004.

A2.11 Toxicological properties of dichloromethane

The toxicology of dichloromethane (methylene chloride) has been investigated in a large number of experiments with laboratory animals and humans. Assessments were made by ATSDR (2000), the RIVM (2001) and US-EPA/AEGL (2005).

Dichloromethane has a neurotoxic effect in case of acute inhalatory exposure. In addition, as a consequence of metabolic conversion, the substance induces the formation of COHb (carbon monoxide bond to haemoglobin). The latter effect is the same as occurs in case of carbon monoxide poisoning.

Inhalation of very high concentrations may result in serious central nervous system depression, causing narcoses and coma and finally death or cardiac arrest due to the formation of COHb. US-EPA/AEGL (2005) concluded that 11,000 ppm (38,830 mg/m^3) was the NOAEL for mortality in laboratory animals (4-hour exposure). On the basis of this NOAEL, this organisation proposed a 1-hour threshold of 24,375 mg/m^3 for mortality in the human population. Once-only exposure to lower concentrations caused milder effects on the nervous system and COHb. For the 1-hour threshold for serious acute effects (AEGL-2), US-EPA/AEGL (2005) used an acceptable 4- % increase in COHb. A model was used to calculate the level of inhalatory exposure at which this COHb was reached, both for normal individuals and for the sensitive group of *non-conjugators*. The result was an estimated 1-hour threshold of 560 ppm (1,977 mg/m^3) (AEGL-2). In a previous assessment, the RIVM (1997) proposed an acute limit value for 4-hour exposures of 25 mg/m^3, based on an observation from labour toxicological studies that an 8-hour exposure to about 13 mg/m^3 brings about a 0.1- % increase in COHb in non-smokers. The MTR for dichloromethane is also based on an accepted 0.1- % COHb increase. The MTR was extrapolated from the labour toxicological outcome that an exposure of

employees to 90 mg/m^3 for 7.5 hours brought about a 1- % increase in COHb. The result was an MTR of 3 mg/m^3 (RIVM, 2001).

On the basis of research carried out as to carcinogenity and genotoxicity, dichloromethane is not considered a genotoxic carcinogen (RIVM, 2001).

As far as the oral pathway is concerned, effects on the liver are most sensitive. The chronic NOAEL for this amounts to 6 mg/kg body weight/day. On this basis a chronic oral limit value (MTR) of 0.06 mg/kg body weight/day was established (RIVM, 2001).

For the dermal pathway only very limited data are available. The undiluted substance is irritating skin and eyes. In the reported cases of labour intoxications with dichloromethane dermal contact with the undiluted liquid contributed to the internal exposure. There are no further data (ATSDR, 2000).

References

ATSDR (2000) Toxicological Profile for Methylene Chloride. September 2000.

RIVM (1997) Dichloormethaan - reactie op door industrie geleverde gegevens. Brief van Dr. W.H. Könemann (RIVM/CSR) aan Ir. M. Bovenkerk [*Dichloromethane - reaction on data supplied by the industry. Letter from W.H. Könemann (RIVM/CSR) to M. Bovenkerk*] (VROM), dated 15th January 1997.

RIVM (2001) Re-evaluation of human-toxicological Maximum Permissible Risk levels. RIVM report 711701025.

US-EPA/AEGL (2003) Acute exposure guideline levels (AEGLs) for methylene chloride (CAS Reg. No. 75-09-2). NAC/AEGL Proposed 1: 01/2005.

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