Internat. Marit. Health, 2006, 57, 1 - 4

HEALTH RISKS BY BROMOMETHANE AND OTHER TOXIC GASES IN IMPORT CARGO SHIP CONTAINERS

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Abbreviations used:

CA	California
GC	Gas chromatography
ILO	International Labour Organization
IMO	International Maritime Organization
ISPM	International standard of phytosanitary measures
MAC	Maximum workplace concentration
MS	Mass spectrometry
SIFT	Selected ion flow tube
TDS	Thermal desorption system
TEU	Twenty foot equivalent unit

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TWA	Time weighted average
VOC	Volatile organic components
WHO	World Health Organization
ZfA	Zentralinstitut fuer Arbeitsmedizin

ABSTRACT

Containers are increasingly used for the worldwide transport of all kinds of goods. Consistent with national and international regulations on pest controls, a growing proportion of these containers undergoes fumigation. Frequently, the prescribed labelling is missing. According to literature, this situation may lead to accidents and represents a significant health risk to dock workers, inspectors and custom workers. Furthermore, warehouse workers and even consumers may come in contact with these toxic fumigants. Presented measurement data underline this health risks due to bromomethane but also due to other fumigants and, surprisingly, due to further noxious gases. So far, no routine method for sensitive and specific measurements on the spot has been available. The consequences of container fumigation should always be carefully weighed up, and alternatives to pesticides, e.g. heat treatment or atmospheres with reduced oxygen and for high CO_2 concentrations should be considered. In addition, stringent international controls as well as sanctions if IMO's "Recommendations on the safe use of pesticides in ships" are disregarded are required.

INTRODUCTION

Recent reports on severe intoxications of dock workers and inspectors, some with fatal outcome, due to the contact with in-transit fumigated cargo ship containers or goods have attracted attention in several countries, e.g. New Zealand, USA, Ukraine, The Netherlands and Germany (1).

The objective of this report is to summarize available data (including those of our own studies) on measurements of bromomethane and other toxic gases present in import containers of various ports.

It should be mentioned that the use of containers for the transport of all kinds of goods, especially by sea, has worldwide strongly increased in recent years amounting to 303 million TEU in 2004 (2) and to about 400 million TEU in 2005. Due to the enforcement of ISPM 15 (The International Standards for Phytosanitary Measures

Guidelines for Regulating Material in International Trade 15), fumigation of cargo ship containers has increased since the middle of 2005.

This regulation aiming at the inhibition of the worldwide distribution of wood-damaging insects prescribes fumigation by bromomethane or heat treatment of wood and wood packaging material entering the European Community and most other western countries (3). However, heat-treatment installations are either not or only insufficiently available in ports.

METHODS

To list data on health risks due to the contact with fumigated containers the database PubMed/Medline was systematically searched for "containers + pesticides", "intoxication + containers" or "intoxication + fumigation". We retrieved 20, 64, and 25 publications respectively, and read their abstracts. Only one (4) referred to measurements of a fumigant in containers gassed in transit on cargo ships. Furthermore, respective information obtained from customs services (5) as well as a newspaper report was compiled (6).

Our own measurements aimed at the comparison of three air monitoring methods. The first one, by short- term indicator tubes, is based on chemical colour change reaction (Draeger, Luebeck, Germany). Compared to other methods it is fast, easy to handle but expensive (about 50 € per measurement). It contains a test set which measures five gases simultaneously). The second method is selected ion flow tube mass spectrometry (SIFT-MS, Voice 100, Syft, New Zealand). It is also very fast and easy to handle but not transportable and expensive (about 240,000 €). The third one is a combination of thermal desorption, gas chromatography and mass spectrometry (TD-GC-MS; TDS, Markes International Limited; GC-MS, Agilent Technologies, USA). It is the most reliable one; using two dimensions (retention time and mass spectrum) for fumigant identification and internal standards but it has a low throughput, can only be handled by skilled people and is also expensive (about 120,000 €).

RESULTS

1. Method comparison for the determination of bromomethane and chloropicrin

Using TD-GC-MS as gold standard, we assayed specificity and sensitivity of the other two methods by analyzing container air samples collected in Hamburg port. In case of bromomethane, the two versions of Draeger tubes obtained only a specificity of 21% and a sensitivity of 29% on average (n=153) (Table 1). The reason for this poor performance is unclear. SIFT-MS showed a specificity of 40% and a sensitivity of 100% (n=68).

In case of chloropicrin, Draeger colorimetric detector tubes did not obtain a meaningful outcome because of the small sample size. SIFT-MS showed a specificity of 0% and a sensitivity of 0% (n=68) (Table 1).

Table 1: Comparison between detection tube and SIFT-MS with TD-GC-MS in bromomethane or chloropicrin measurements

Fumigant	Bromomethane	bromometh ane	bromometh ane	Chloropicrin	chloropicrin	chloropicri n
Method	Indicator tube: multiple simultaneous test	indicator tube: single detection tube	SIFT-MS	Indicator tube: multiple simultaneous test	indicator tube: single detection tube	SIFT-MS
Sample size (n)	153	153	68	-	10	68
Specifity	13% (2 of 16)	29% (2 of 7)	40% (2 of 5)	-	n.c.	0% (0 of 19)
Sensitivity	29% (2 of 7)	29% (2 of 7)	100% (2 of 2)	-	n.c.	0% (0 of 1)

n.c. = not calculated because no positive samples among the investigated ones
Specifity and sensitivity were evaluated by TD-GC-MS as the gold standard

2. Measurements of fumigants and other noxious gases in containers of different ports

a) Rotterdam

15 out of 303 (5%) containers with missing or incorrect labels showed gaseous pesticide concentrations above the occupational limit values (MAC or TWA, time weighted average; Tables 2, 3 (7). Especially the laboratory analyses by GC-MS of bromomethane were shown to be more specific than field measurements performed by colorimetric detector tubes (Draeger). 7 containers (2%) showed bromomethane concentration above the respective MAC value. The health risk due to other hazardous gases (ammonia, toxic CO or O_2 levels, explosives) is also obvious (Table 3).

Table 2: Field measurement results and comparisons between colorimetric detector tubes (field measurements) and TD-GC-MS (laboratory analyses) in 303 import containers (7).

The listed MAC values are presently in force in the Netherlands.

Total of number containers	303								
Analysis parameter	MeBr	CH_2O	SO_2F_2	PH_3	NH_3	CO_2	CO	Ex	Ox
MAC value (ppm)	0,25	1,00	n.d	0,3	20	5000	25	40% LEL CH_4 [1])	[2])
Field measurements									
Positive result	43	19	-	28	9	12	74	2	2
Result > MAC values	22	14	-	9	0	5	41	n.a.	n.a.
Comparison between field measuremnets/laboratory analyses									
False-positive field measurement	33	15	*	*	*	*	*	*	*
Confirmed field measurement	10	4	*	6[3]	*	*	*	*	*
False-negative field measurement	9	38	*	*	*	*	*	*	*

MeBr = methyl bromide (bromomethane); CH_2O = formaldehyde
SO_2F_2 = sulfuryl difluoride
PH_3 = phosphine
NH_3 = ammonia
CO_2 = carbon dioxide
CO = carbon monoxide
Ex = risk of explosion
Ox = oxygen levels
-n.d. = not determined
- = not measured
* = no comparison possible between field measurements and laboratory analyses
n.a. = not applicable

[1]) The risk of explosion was measured as the concentration of flammable gases in the air and as the percentage of the lowest explosion level (LEL) of methane (CH_4) in air. A concentration of more than 40 % of flammable gases in air LEL CH_4 constitutes an explosion risk.
[2]) A dangerous situation exists if the oxygen levels are below 19% or above 23%.
[3]) Pesticides refer to bromomethane, formaldehyde, sulfuryl difluoride and phosphine.

Table 3: Number and percentage of risk containers, i.e. with concentrations above the respective MAC values among the 303 investigated containers (7)

Total number of containers	303								
Risk factor	MeBr	CH_2O	SO_2F_2	PH_3	NH_3	CO_2	CO	Ex	Ox
MAC value (ppm)	0,25	1,00	n.d	0,3	20	5000	25	40% LEL CH_4 [1])	[2])
Number of risk containers	7	3	0	6	0	5	41	2	2
Risk containers with regard to pesticides [3]	14 (5 %)								
Risk containers with regard to other parameters [4]	45 (15 %)								
Risk containers with regard to pesticides and other parameters	1 (0,3 %)								
Total number of risk containers	60[3] (20 %)								

MeBr = methyl bromide (bromomethane)
CH_2O = formaldehyde; SO_2F_2 = sulfuryl difluoride
PH_3 = phospine; NH_3 = ammonia
CO_2 = carbon dioxide; CO = carbon monoxide
Ex = risk of explosion; Ox = oxygen levels
-n.d. = not determined; - = not measured
* = no comparison possible between field measurements and laboratory analyses
n.a. = not applicable

1) The concentration of flammable gases in the air and the percentage of the lowest explosion level (LEL) of methane (CH_4) in air constitute an explosion risk. A flammable gas concentration in air of more than 40% LEL CH_4 constitutes an explosion risk.

2) A dangerous situation exists at oxygen levels below 19% or above 23%.

3) Pesticides refer to bromomethane, formaldehyde, sulfuryl difluoride and phosphine.

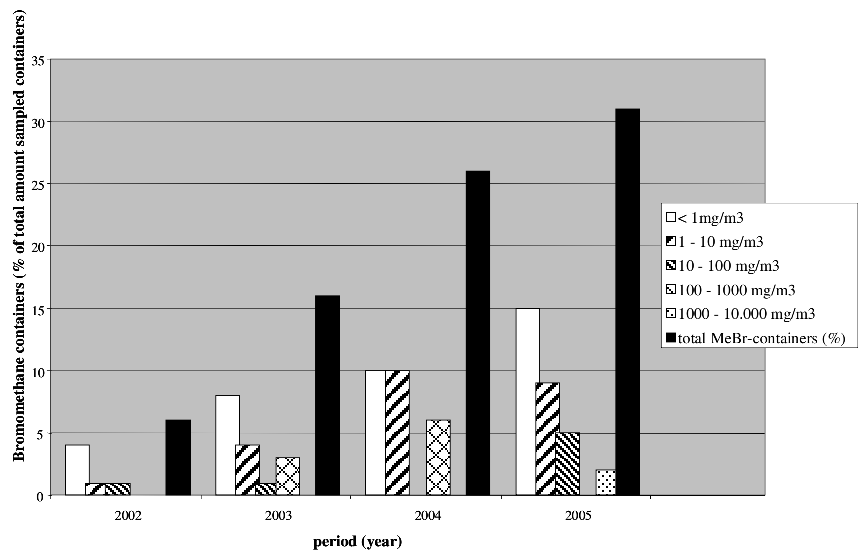
4) Other parameters refer to ammonia, carbon dioxide, carbon monoxide, explosion risk and oxygen levels.

5) The total number of risk containers is lower than the number of individual parameter- specified risk containers. This is due to an overlap of risk factors.

Follow-up measurements of fumigants in imported containers in Rotterdam port showed an increase in positive bromomethane results from 6% in 2002 to 31% in 2005.

It is interesting that not only the number of positive findings but also the concentrations of bromomethane have increased in recent years (Fig. 1).

Fig. 1: Bromomethane concentrations in import containers during the years 2002 – 2005 in Rotterdam port. Each year a random sample of 150 containers was measured.



b) Other ports

Detailed reports on 134 containers imported from Shanghai in Long Beach (CA, USA) harbour exhibited bromomethane concentrations above 5 ppm in eight cases (6%; (4)).

A similar figure was found by the Australian Customs Service (5) and by first informative measurements in Hamburg port (8) where predominantly bromomethane and phospine were identified in undeclared fumigated import containers.

3. Reports on dock workers intoxicated by fumigants

The New Zealand maritime union is backing an inquiry concerning bromomethane used for the fumigation of timber in New Zealand ports (9). The widows of six former dock workers raised the alarm after their husbands contracted degenerative brain disorder motor neurone disease (6, 9). Five of the affected workers died after working in confined spaces where the gas had been used. An investigation was initiated to find out whether the cases of motor neurone disease are linked with bromomethane poisoning. Furthermore, precautionary blood testing of workers in New Zealand ports were performed (6, 9).

An unknown number of non-reported accidents in ports – some with fatal outcome – occurred due to the exposure to high concentrations of fumigants in containers or their goods. The authors are aware of incidental cases from various ports in Europe, North America and South Africa.

4. Emission studies

Detailed investigations in Rotterdam port were related to emissions from fumigated goods. 75% of food emitted fumigants. In some food and medicaments, fumigation had an effect on the composition of products (7).

DISCUSSION AND CONCLUSIONS

According to the presented literature (1, 7) and our own measurements, gaseous pesticide concentrations and other toxic gases in undeclared freight containers represent an increasing health risk during transportation, inspection and unloading. Recent investigations in different countries have shown at least 5% of all import containers to have concentrations of bromomethane, phosphine and/or other fumigants above the respective TWA/MAC.

The predominant one was bromomethane classified by the "Montreal Protocol on Substances that Deplete the Ozone Layer and the Clean Air Act" as an ozone-depleting substance. It was scheduled for complete phaseout by January 1, 2005. However, the Critical Use Exemption is designed to allow the further production and import of bromomethane after phaseout if no technically and economically feasible alternatives are available. According to the Montreal Protocol Meeting in 2005, 16 nations were allowed to use 16,050 metric tons of bromomethane for "critical use exemptions" (10). Quarantine, shipment and critical emergency uses are exempted from the Montreal Protocol; it has to be assumed that these indications led to the use of a similar quantity.

Nearly all import containers with detectable levels of fumigants did not display the required IMO warning sticker. According to the IMO Recommendation for the Safe Use of Pesticides in Ships (IMO 267E; (11), fumigated containers or cargo transport units (CTUs) and ship cargoes have to be labelled and appropriately certified.

This omission may not only concern dock workers but also to consumers because present investigations (12) aiming at pesticide emissions from goods imported in fumigated containers indicate that many goods absorb pesticides in a reversible process, leading to the emission of pesticides with half lives lasting hours and in extreme situations up to 300 days. Pesticides and other toxic gases in some goods may even reach the consumer. This risk has not been recognized adequately so far and requires investigations in more detail.

The comparison of different analytical methods revealed that routine measurements of fumigants are still problematic. Quickly responding colorimetric detector tubes were shown to be not sufficiently specific and sensitive. SIFT-MS produced unsatisfactory results for bromomethane specificity and was not able to measure chloropicrin. This has changed in the meantime as reported by the manufacturer and proved by our latest measurements (publication in preparation). Furthermore, both methods are rather expensive. TD-GC-MS which can be regarded as gold standard requires a well-equipped lab and a well-trained lab technician; in addition, it is time-consuming.

The development of new transportable, specific, sensitive, and cost-effective devices for routine measurements of fumigants are required in order to reach reliable risk assessment on the spot. Further, we recommend regular controls of less sophisticated and especially new devices by a standardized method such as TD-GC-MS in independent labs. Results of respective comparative studies should be published.

In order to further reduce the health risks by fumigated import containers it is exigent to coordinate initiatives of international institutions (ILO, IMO, WHO) in order to enforce the correct labelling and shipment (13). Moreover, environment-protecting procedures such as heat treatment, CO_2 gassing with reduced oxygen atmospheres etc. should be promoted in order to reduce the evident health hazards due to fumigants in import containers and to protect the ozone layer.

REFERENCES

1. Low A, Hüsing UP, Preisser A, Baur X. Regulations and control of in-transit fumigated containers as well as of fumigated cargo ships. Int Marit Health 2003; 54; 77-85
2. United Nations Conference on Trade and Development. Review of maritime transport, 2005. United Nations New York, Geneva, 2005. (UNCTAD/RMT/2005)

3. New import requirements for wood and wood packaging material (including dunnage) entering the European Community – ISPM15 http://www.forestry.gov.uk/forestry/INFD-6ADJGL 02/10/2006
4. Barak AV, Hamilton B, Wang YJ, Wang X, Chen Z. Fumigation as a quarantine treatment for solid wood packing (SWP). http://mbao.org/2003/083%20barakafumigation%20swp%20mbao%202003%20summary..pdf#search=%22barak%20wang%20%22fumigation%20as%20a%20quarantine%22%22 02/10/2006
5. Woo, K. Personal communication. information@customs.gov.au
6. Port workers to be tested for methyl bromide levels. The New Zealand Herald 18.11.2004
http://www.nzherald.co.nz/category/print.cfm?c_id=204&objectid=3611289 02/10/2006
7. Knol-de Vos T. Measuring the amount of gas in import containers. National Institute for Public Health and the Environment, Bilthoven, Netherland; 2002 http://www.rivm.nl/bibliotheek/rapporten/609021025.pdf´ 02/10/2006
8. Yu F. Begasungsmittel-Biomonitoring und Analytik im ZfA. In: Jahresbericht 2004 des ZfA mit HPHC. ZfA Hamburg, 2005: 44-45. ISSN 1860-2789
9. The Maritime Union is supporting calls for an inquiry into the toxic gas methyl bromide, used as a timber fumigant in New Zealand ports. http://www.worksafereps.org.nz/news/1101077963_8454.html 02/10/2006
10. United Nations Environment Programme. Over $400 million in ozone support to developing countries
http://www.unep.org/Documents.Multilingual/Default.asp?DocumentID=459&ArticleID=5088&l=en 02/10/2006
11. International Maritime Organization. Recommendations on the safe use of pesticides in ships. IMO London, 2002. (IMO 267E).
12. Risico’s van stoffen http://www.rivm.nl/rvs/ 02/10/2006
13. Baur X. Handling of gassed import containers and their goods. Zbl Arbeitsmed 2005; 55; 82-93.