Methyl bromide health monitoring guidelines

Queensland Government

Methyl bromide health monitoring

Substance: methyl bromide
Synonyms: bromomethane
monobromomethane
Chemical formula: CH_3Br
CAS No.: 74-83-9
Exposure standard: 5 ppm or 19 mg/m^3 (TWA)* Skin [1]

Main uses/occupations at risk

Uses of methyl bromide and means of industrial exposure

Industry	Occupation	How used	Route of exposure
Quarantine or pre-shipment fumigation	Pest control	Fumigant	Inhalation Dermal
Horticulture, flowers, strawberries	Farmer, fumigation contractor	Soil fumigant	Inhalation Dermal
Mining	Miner	Ore extraction (bromide)	Inhalation Dermal

From 1 January 2005 all use of methyl bromide, other than for quarantine and pre-shipment or chemical feedstock applications, is prohibited in Australia. However some 'critical use exemptions' have been allowed under the Montreal Protocol on Substances that Deplete the Ozone Layer.[2] Critical use exemptions have been granted for soil fumigation in the production of strawberry runners and treatment of rice packaged in Australia for domestic use.

Quarantine applications are treatments to prevent the introduction, establishment and/or spread of quarantine pests (including diseases) and to prevent spread between different regions in Australia. Pre-shipment applications are applied within 21 days prior to export to meet the official requirements of the importing country or existing official requirements of the exporting country.[3]

The *Managing Risks of Methyl Bromide Exposure when Unpacking Shipping Containers* information sheet provides health and safety guidance to employers on how to control the risks associated with unloading of fumigated shipping containers.[4] People unloading containers that have been fumigated with methyl bromide have become ill from exposure to residual fumes. Prior to entry, fumigated shipping containers should be vented using mechanical ventilation for approximately 30 minutes, aerated for minimum of 12 hours with natural ventilation or tested for fumigant levels using suitable air testing equipment. Further information regarding fumigation is available from the Australian Department of Agriculture.[5]

Non-occupational sources

Some methyl bromide is formed naturally by algae or kelp in the ocean. Food that has been fumigated with methyl bromide or grown in methyl bromide treated-soil, especially leafy vegetables such as lettuce and spinach, can take up large amounts of bromide ion.

*Time weighted average (8-hour day)

Elevated levels can also be due to the use of common bromine-based over-the-counter pharmaceuticals such as bromopheniramine maleate (Dimetane, Dimetapp) used for colds and allergies and hyoscine hydrobromide used for travel sickness.

Methyl bromide can diffuse through plastic drinking water pipes if the surrounding soil has been fumigated with methyl bromide and can contaminate drinking water. Bromine is used as a swimming pool and spa pool water disinfectant with minimum levels of bromine to be maintained between 2 and 8 mg/L.[6] The average daily intake of bromide from normal diets is 8 mg/day for adults. Fifty per cent of manufactured methyl bromide eventually enters the atmosphere. Some diffuses upward to the stratosphere where it can react with ozone and contribute to depletion of the ozone layer, hence its inclusion in the Montreal Protocol.

Target organ/effect

Skin – skin irritation, blistering or burns, contact dermatitis, hyperpigmentation.

Nervous system, central – blurred vision, mental confusion, tremors, twitching, ataxia, respiratory paralysis, convulsions.

Nervous system, peripheral – peripheral neuropathy.

Respiratory tract – irritation, pulmonary oedema.

Eyes – severe irritation, corneal burns.

Kidney – tubular damage.

Liver – cellular damage.

Type of health surveillance required

- medical examination with emphasis on the nervous and respiratory systems and skin
- blood bromide levels – post-shift at end of work week

Biological occupational exposure limit (BOEL)

Blood bromide

- The mean for bromide in blood was 5.3 $\pm$ 1.4 mg/L (67 $\pm$ 17.7 µmol/L) in a group of 183 healthy Queenslanders with range 2.5 to 11.7 mg/L (31 to 146 µmol/L).[7]
- Blood sample collection at end of shift at end of work week (preferably after showering and changing clothes to avoid contamination).
- Recommended blood bromide BOEL is 12 mg/L (150 µmol/L).[8]

Urinary bromide

- The bromide concentration in urine is a suitable parameter for determining exposure to methyl bromide. However there is currently no recognised biological occupational exposure limit.

Action level

Post-shift blood bromide > 12 mg/L (150 µmol/L)

Review work practices and retest in 1 week (half-life of bromide in blood is 12 to 14 days).

Absorption/excretion pharmacology

Methyl bromide is a colourless, non-flammable gas with no taste or odour at low concentrations (odour threshold 80 mg/m^3).[9] For this reason, a lachrymatory agent such as chloropicrin (2%) is often added as a sensory warning agent.[10] Methyl bromide is usually stored as a liquid under pressure in steel cylinders or small sealed cans. The vapour is more than three times as dense as air and may collect in low spots or poorly ventilated places. Methyl bromide gas is able to penetrate many substances such as concrete, leather and rubber.

The main routes of absorption are through inhalation and the skin.

Methyl bromide is well absorbed (50%) by humans via inhalation and rapidly distributed to many tissues including the lungs, adrenal glands, kidneys, liver, nasal turbinates, brain, testes, and adipose tissue.[10] It is lipid soluble and able to penetrate the blood brain barrier with effects on the central nervous system.

Absorption by skin may readily exceed vapour inhalation exposure.

Metabolism of methyl bromide has not been elucidated. It is excreted by exhalation and in the urine.[9] The half-life of inorganic bromide is about 12 to14 days.

Summary of toxicology

Acute effects

Methyl bromide is a very toxic fumigant gas with poor olfactory warning properties. Severe poisoning and death have occurred during application due to inadvertent spread, clean-up operations and premature entry into fumigated places.[11]

Methyl bromide has local and systemic effects. Acute poisoning causes marked irritation of the eyes, skin and mucous membranes of the respiratory tract with high concentrations causing pulmonary oedema with a late onset chemical pneumonitis. Dermal exposure can cause severe irritation and corrosive injury of the skin with blisters and vesicles resembling a second-degree burn, in particular when the gas or liquid is trapped in gloves, boots or other clothing.[10]

The most important systemic effects are neurological: headache, dizziness, vertigo, slurred speech, nausea and vomiting, confusion, blurred vision, twitching and possibly convulsions and coma. Onset may be delayed from 30 minutes up to 2 days post-exposure. Ingestion is unlikely but methyl bromide is extremely poisonous if ingested.[10]

Chronic effects

Long-term exposure may produce central nervous system effects such as mental confusion, lethargy, blurred vision, loss of co-ordination and muscle weakness. Low level chronic exposure has caused polyneuropathy. Repeated skin exposure may cause contact dermatitis.[10]

Summary of epidemiology

Cases of severe poisoning with some fatalities has resulted from injection of methyl bromide into soil. Workers carried out soil disinfection with application rates ranging from 30 to 3000 ppm. Peak levels of 200 ppm persisting for a few seconds upon initial injection

with airborne levels above the soil declining to 4 ppm 5 days post-treatment were found. Tilling the soil can produce exposures of 15 ppm as long as 9 days after soil treatment.[9]

Seven cases of methyl bromide poisoning occurred amongst workers who carried out mass fumigation of timber houses in Queensland in 1958.[12] The Division of Industrial Medicine tested the gas canisters in the respirators and found none of them protected against methyl bromide for more than 30 seconds.

In March 2002, two South Australian carpenters employed by a stevedoring company were directed to retrieve timber that had been fumigated with methyl bromide 10 hours earlier. When cutting the timber inside a ship, they developed headaches, nausea, numbness and profuse sweating and were hospitalised for four days.[13]

In reported cases of intoxication by methyl bromide, blood bromide levels were around 46 to 130 mg/L (575 to 1627 µmol/L).[14] It has been suggested that values greater than 50 mg/L (626 µmol/L) in blood are indicative of potentially hazardous exposure.

According to the International Agency for Research on Cancer (IARC) evaluation [15], there is inadequate evidence in humans for the carcinogenicity of methyl bromide. There is limited evidence of carcinogenicity in experimental animals.

Overall carcinogenic evaluation: Methyl bromide is not classifiable as to its carcinogenicity to humans (Group 3).

Reference list

[1] Safe Work Australia. Hazardous Substance Information System (HSIS) [Internet]. Canberra: Safe Work Australia; [date unknown] [cited 3 February 2015]. Available from: http://hsis.safeworkaustralia.gov.au/ExposureStandards

[2] Department of the Environment. Methyl bromide [Internet]. Canberra: Department of Environment; [date unknown] [cited 3 February 2015]. Available from: http://www.environment.gov.au/protection/ozone/methyl-bromide

[3] United National Environmental Programme (UNEP). Methyl bromide: quarantine and preshipment uses. Kenya: UNEP; [date unknown] [cited 9 February 2015]. Available from: http://ozone.unep.org/new_site/en/resources.php

[4] Safe Work Australia. Managing risks of methyl bromide exposure when unpacking shipping containers. Canberra; Safe Work Australia; [in press].

[5] Department of Agriculture. Quarantine treatments and fumigants [Internet]. Canberra; Department of Agriculture; 2014 [cited 3 February 2015]. Available from: http://www.agriculture.gov.au/biosecurity/import/general-info/qtfp/treatments-fumigants

[6] Department of Human Services, South Australian Health Commission. Standard for the operation of swimming pools and spa pools in South Australia, Supplement C, Bromine disinfection of swimming pool, spa pool, hydrotherapy pool & waterslide pool water. Adelaide: South Australian Health Commission. 1992 [cited 3 February 2015]. Available from: www.eha.sa.gov.au/uploadFiles/documents/codebromine.pdf

[7] Olszowy HA, Rossieter J, Hegarty J & Geoghegan P. Background levels of bromide in human blood. J Anal Tox. 1988 May; 22(3): 225-30.

[8] Deutsche Forschungsgemeinschaft (DFG). The MAK collection for occupational health and safety – Methyl bromide [BAT value documentation, 2005]. [2005] [cited 23 February 2015]. Available from: http://onlinelibrary.wiley.com/book/10.1002/3527600418/topics

[9] ACGIH. Documentation of the threshold limit values for chemical agents – Methyl bromide. Cincinnati (OH): ACGIH; 2001.

[10] World Health Organisation, International Programme on Chemical Safety (IPCS). Health and safety guide no. 86 – Methyl bromide (bromomethane) health and safety guide [Internet]. Geneva: IPCS. 1994 [cited 5 February 2015]. Available from: http://www.inchem.org/documents/hsg/hsg/hsg86_e.htm

[11] Agency for Toxic Substances and Diseases Registry (ATSDR). Toxicological profile for bromomethane. USA: ATSDR. 1992 [cited 5 February 2015]. Available from http://www.atsdr.cdc.gov/substances/index.asp

[12] Rathus EM & Landy PJ. Methyl bromide poisoning. Brit J Indust Med. 1961;18: (53-57).

[13] Moore v Hobart Ports Corporation Pty Ltd [2004] SAIRC 85.

[14] Lauweys RR & Hoet P. Industrial chemical exposure: guidelines for biological monitoring. 3rd ed. Boca Raton: Lewis Publishers; 2001. 519 - 521 p.

[15] International Agency for Research on Cancer (IARC). IARC Monographs on the evaluation of carcinogenic risks to humans – Volume 71 - Re-evaluation of some organic chemicals, hydrazine and hydrogen peroxide. Geneva: IARC. 1999 [cited 5 February 2015]. Available from: http://monographs.iarc.fr/ENG/Monographs/PDFs/index.php