Methane, bromo-: Environment tier II assessment

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Preface

This assessment was carried out by staff of the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) using the Inventory Multi-tiered Assessment and Prioritisation (IMAP) framework.

The IMAP framework addresses the human health and environmental impacts of previously unassessed industrial chemicals listed on the Australian Inventory of Chemical Substances (the Inventory).

The framework was developed with significant input from stakeholders and provides a more rapid, flexible and transparent approach for the assessment of chemicals listed on the Inventory.

Stage One of the implementation of this framework, which lasted four years from 1 July 2012, examined 3000 chemicals meeting characteristics identified by stakeholders as needing priority assessment. This included chemicals for which NICNAS already held exposure information, chemicals identified as a concern or for which regulatory action had been taken overseas, and chemicals detected in international studies analysing chemicals present in babies' umbilical cord blood.

Stage Two of IMAP began in July 2016. We are continuing to assess chemicals on the Inventory, including chemicals identified as a concern for which action has been taken overseas and chemicals that can be rapidly identified and assessed by using Stage One information. We are also continuing to publish information for chemicals on the Inventory that pose a low risk to human health or the environment or both. This work provides efficiencies and enables us to identify higher risk chemicals requiring assessment.

The IMAP framework is a science and risk-based model designed to align the assessment effort with the human health and environmental impacts of chemicals. It has three tiers of assessment, with the assessment effort increasing with each tier. The Tier I assessment is a high throughput approach using tabulated electronic data. The Tier II assessment is an evaluation of risk on a substance-by-substance or chemical category-by-category basis. Tier III assessments are conducted to address specific concerns that could not be resolved during the Tier II assessment.

These assessments are carried out by staff employed by the Australian Government Department of Health and the Australian Government Department of the Environment and Energy. The human health and environment risk assessments are conducted and published separately, using information available at the time, and may be undertaken at different tiers.

This chemical or group of chemicals are being assessed at Tier II because the Tier I assessment indicated that it needed further investigation.

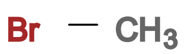
For more detail on this program please visit: www.nicnas.gov.au.

Disclaimer

NICNAS has made every effort to assure the quality of information available in this report. However, before relying on it for a specific purpose, users should obtain advice relevant to their particular circumstances. This report has been prepared by NICNAS using a range of sources, including information from databases maintained by third parties, which include data supplied by industry. NICNAS has not verified and cannot guarantee the correctness of all information obtained from those databases. Reproduction or further distribution of this information may be subject to copyright protection. Use of this information without obtaining the permission from the owner(s) of the respective information might violate the rights of the owner. NICNAS does not take any responsibility whatsoever for any copyright or other infringements that may be caused by using this information.

Acronyms & Abbreviations

Chemical Identity

Synonyms	Methyl bromide Bromomethane
Structural Formula	
Molecular Formula	CH_3Br
Molecular Weight (g/mol)	94.94

SMILES	CBr

Physical and Chemical Properties

The physical and chemical property data for this chemical were retrieved from the databases included in the OECD QSAR Toolbox, and from the OECD SIDS Initial Assessment Profile (SIAP) for the chemical (LMC, 2013; OECD, 2001).

Physical Form	Gas
Melting Point	-93.7°C (exp.)
Boiling Point	3.5°C (exp.)
Vapour Pressure	216 000 Pa (exp.)
Water Solubility	15 200 mg/L (exp.)
Ionisable in the Environment?	No
log K_{ow}	1.94 (exp.)

Import, Manufacture and Use

Australia

Methane, bromo- (or methyl bromide) is an ozone depleting substance. Ozone depleting substances are controlled under the *Ozone Protection and Synthetic Greenhouse Gas Management Act 1989* (the Ozone Act) (Cwlth) in Australia.

Under the Ozone Act, the import and manufacture of any volume of the chemical for industrial use is prohibited, unless it is to be used as an intermediate substance for the manufacture of other chemicals (feedstock use). Feedstock uses of the chemical require a permit from the Australian Government Department of the Environment, and the quantity of the chemical that is imported or manufactured must be reported on a quarterly basis. Methyl bromide is currently used on a small scale (<1 tonne per annum) as a feedstock in Australia (Australian Government Department of the Environment, 2013a; 2013b; Commonwealth of Australia, 1989).

Methyl bromide is used in Australia as a fumigant in certified quarantine and pre-shipment applications, and select critical uses (Australian Government Department of the Environment, 2013a). However, fumigant use is beyond the scope of this assessment as this is not considered an industrial use under the *Industrial Chemicals (Notification and Assessment) Act 1989*.

International

Aside from use as a fumigant, methyl bromide is used industrially as a chemical intermediate worldwide. Historically, the chemical also had industrial uses as a refrigerant, as a fire-extinguishing agent, in the de-greasing of wool and in the extraction of oils from nuts, seeds and flowers (US NLM, 2013).

Industrial uses of methyl bromide (except feedstock uses) were phased out in developed countries from 1 January 2005 under the *Montreal Protocol on Substances that Deplete the Ozone Layer* (the Montreal Protocol) (UNEP, 2012). The chemical may only be used for industrial purposes if it meets exemption criteria in accordance with Annex IV of the Seventh Meeting of the Parties to the Montreal Protocol. These include use in research and development, analytical uses and regulated applications (for example, quality control), and laboratory use (UNEP, 1995).

In the European Union, the chemical is currently only registered for intermediate use under the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) legislation (ECHA, 2013).

Environmental Regulatory Status

Australia

Methyl bromide is a scheduled substance under the Ozone Act. The Act gives effect to Australia's obligations under the Montreal Protocol by controlling the manufacture, import and export of ozone depleting substances and listing banned applications. Industrial use of the chemical is prohibited, unless it is to be used exclusively as a feedstock (Australian Government Department of the Environment, 2013a; Commonwealth of Australia, 1989). Use of the chemical as a feedstock is subject to the *Ozone Protection and Synthetic Greenhouse Gas Management Regulations 1995* (Cwlth) (Commonwealth of Australia, 1995).

United Nations

The chemical is a controlled substance as listed under Annex E of the Montreal Protocol (UNEP, 1987). The Montreal Protocol calls for the phase-out of the use of the chemical by all parties to the protocol by 1 January 2015. All 197 countries of the United Nations, including Australia, have ratified the Montreal Protocol and only a few countries are yet to ratify the last amendment of the Montreal Protocol (UNEP, 2013).

OECD

The chemical was sponsored by the United States of America (USA) under the Cooperative Chemicals Assessment Programme (CoCAP). The 13th Screening Information Data Set (SIDS) Initial Meeting Assessment (SIAM 13) in 2001 agreed that the chemical was a low priority for further work due to the control of use of the chemical under the Montreal Protocol (OECD, 2013).

Canada

The chemical is listed on Schedule 1 of the *Canadian Environmental Protection Act 1999* (the Toxic Substances List). Use is prohibited for any purpose other than in quarantine and pre-shipment applications, as a feedstock, as an analytical standard or for critical or emergency use (Environment Canada, 2013a).

The chemical has been categorised as Persistent (P), not Bioaccumulative (not B) and not Inherently Toxic to the Environment (not iT_E) by Environment Canada during the Categorization of the Domestic Substances List (DSL) (Environment Canada, 2013b).

European Union

The chemical is identified as an ozone depleting substance and is controlled under *Regulation No 1005/2009 of the European Parliament and the Council of 16 September 2009 on Substances that Deplete the Ozone Layer*. The production, trade and use of the chemical is prohibited, unless the chemical is to be used as a feedstock, process agent, an essential laboratory or analytical use, is destined for destruction or reclamation, or is for emergency purposes (European Union, 2009).

United States of America

The chemical is listed as a Class I Substance under Title VI of the *Clean Air Act 1970*. Production and use of the chemical is prohibited except for specific exceptions, including essential uses, quarantine and pre-shipment applications, and critical uses (US EPA, 2013a; 2013b; 2013c).

Environmental Exposure

The Ozone Act prohibits all industrial uses of methyl bromide in Australia, except use as a chemical feedstock (Australian Government Department of the Environment, 2013a; Commonwealth of Australia, 1989). Small emissions of methyl bromide may occur during feedstock use. However, the Australian Government Minister for the Environment must be satisfied that emissions resulting from feedstock use will be minimal (no more than 2% of the methyl bromide used) before granting a permit for use (Commonwealth of Australia, 1995). Therefore, significant releases of the chemical to the environment are not expected as a result of currently allowed industrial uses in Australia.

Environmental Fate

Partitioning

Methyl bromide is expected to partition to the atmosphere if released from currently permitted industrial uses.

The measured Henry's Law constant for partitioning of methyl bromide from water into air is 744 Pa-m^3/mol at 25°C (LMC, 2013), indicating that the chemical is highly volatile from water and moist soil. Measured organic carbon normalised adsorption coefficients (K_{OC}s) for the chemical range from 164 to 174 for a variety of soils (OECD, 2001), suggesting that the chemical is moderately mobile in soil. However, evaporative losses are expected to dominate the partitioning behaviour of the chemical in soil.

Calculations with a standard multimedia partitioning (fugacity) model assuming equal and continuous distributions to air, water and soil compartments (Level III approach) predict that the chemical will mainly partition to air (53%) and water (42%) compartments, with minor partitioning to soil (5%). However, with sole release to the atmosphere, the model predicts that 99% of the chemical will remain in the air compartment (US EPA, 2008). The latter scenario is expected to be the more likely route for release of the chemical to the environment from industrial uses.

Degradation

Methyl bromide is slow to degrade in the atmosphere, which is the main receiving compartment for emissions resulting from currently permitted industrial uses of this chemical.

The most recent estimate of the overall lifetime for the chemical in the atmosphere is 0.8 years. This lifetime takes into account all major loss mechanisms such as reactions with hydroxyl radicals, destruction in the stratosphere and uptake by oceans

(WMO, 2011). As methyl bromide released from industrial uses is expected to partition to the atmosphere, these are expected to be the predominant degradation and loss processes for the chemical if released as a result of current industrial use.

The major degradation processes for methyl bromide in the atmosphere involve oxidation and photolysis. The chemical has relatively low reactivity towards indirect photo-oxidation by hydroxyl radicals in the lower atmosphere (troposphere), with a predicted life time of 1.9 years for this reaction. Due to this long lifetime, a proportion of the chemical will be transported through the troposphere to the stratosphere, where it will be degraded by ultraviolet (UV) photolysis (OECD, 2001; WMO, 2011).

In water, methyl bromide is primarily degraded by hydrolysis. The hydrolysis half life for the chemical in water is approximately 20 days, but can range from 10 to 50 days dependent on temperature and pH (IPCS, 1995; NITE, 2010; OECD, 2001). The chemical is not rapidly biodegradable, but limited biodegradation may occur. The aerobic biodegradation of the chemical was determined to be 17% in 28 days in a study conducted in accordance with OECD Test Guideline (TG) 301 D (LMC, 2013).

The chemical has a reported half life in soil of 1 to 29 days, although the reliability of these data cannot be determined (Linders, et al., 1994; LMC, 2013). Nevertheless, hydrolysis and abiotic degradation reactions in soil are expected, with some further potential for biodegradation by various species of nitrifying bacteria (IPCS, 1995; OECD, 2001).

Bioaccumulation

The chemical is not expected to bioaccumulate in aquatic or terrestrial biota.

No specific measured bioconcentration or bioaccumulation data are available for the chemical. However, based on the measured octanol water partition coefficient (log K_{OW} = 1.94), and the rapid metabolism of the chemical in various animal models (IPCS, 1995; OECD, 2001), the chemical is expected to have a low potential for bioaccumulation in the environment.

Transport

If present in the atmosphere, the chemical will undergo atmospheric transport and is highly likely to undergo long range transport.

Methyl bromide undergoes atmospheric transport due to its persistence in the troposphere, as evidenced by the detection of the chemical at the marine boundary layer. Additionally, ice core records sampled from the Antarctic demonstrate a rise in mean atmospheric abundance of this gas since the industrial revolution. Although the chemical is released from numerous natural sources and is subsequently globally distributed, these findings strongly suggest that the chemical undergoes long-range transport in the environment (WMO, 2011).

Predicted Environmental Concentration (PEC)

Methyl bromide is not expected to be released to the environment in significant quantities due to industrial use in Australia, as industrial use (aside from feedstock use) is prohibited under the Ozone Act. Minimal releases during feedstock use are possible but are assumed to be insignificant due to the conditions placed on feedstock use permits (Commonwealth of Australia, 1995). As no significant environmental releases resulting from current industrial uses are expected, the PEC for this chemical has not been calculated.

Nevertheless, the chemical may be present in the environment due to historical use, non-industrial use and emissions from natural sources. In the period 1996 to 1998, methyl bromide was present at an abundance of 9.2 parts per trillion (ppt) in the atmosphere. This has since been reduced to 7.3 to 7.5 ppt in 2008, primarily due to the Montreal Protocol. However, over 100 000 tonnes of methyl bromide is still expected to be released to the environment globally each year from human activities and natural sources. Almost half of this amount is produced by marine organisms. Other significant natural sources include biomass burning and coastal salt marshes. These emissions are primarily to air and therefore likely to partition to the atmosphere. Approximately 14 000 tonnes is released to the environment from fumigation uses (WMO, 2011).

Environmental Effects

Effects on the Atmosphere

Methyl bromide is an ozone depleting substance. The stratospheric ozone layer protects life on Earth by absorbing UV radiation from the sun. Depletion of ozone in the atmosphere is therefore of environmental concern, as UV radiation can be damaging to most forms of life on Earth (Australian Government Department of the Environment, 2013c).

Photolysis of methyl bromide in the stratosphere by high-energy UV radiation liberates highly reactive bromine atoms. These bromine atoms undergo reactions that destroy ozone and hence deplete the capacity of the ozone layer to absorb UV radiation. The impact of ozone depleting chemicals on stratospheric ozone is typically reported in terms of the ozone depletion potential (ODP) metric. The ODP is the ratio of the impact of the substance on ozone compared to the impact of the same mass of the chlorofluorocarbon, trichlorofluoromethane (CFC-11) (US EPA, 2010). Methyl bromide is assigned an ozone depletion potential (ODP) of 0.6 under the Montreal Protocol (UNEP, 1987)

Halocarbons with long atmospheric lifetimes such as methyl bromide also contribute to global warming by absorbing radiation emitted from Earth and thus trapping the energy in the atmosphere (radiative forcing). The amount of global warming that can be caused by a substance is typically reported in terms of the global warming potential (GWP) metric. The GWP is the ratio of the warming caused by the substance to the warming caused by the same mass of carbon dioxide, and is calculated for various time horizons (US EPA, 2010). Methyl bromide has a one hundred year global warming potential (GWP) of 5 (WMO, 2011).

Effects on Aquatic Life

Methyl bromide causes acute toxic effects at low concentrations in aquatic organisms across multiple trophic levels.

Acute toxicity

The following median lethal concentration (LC50) and median effective concentrations (EC50s) for model organisms across three trophic levels were published by Canton et al. (1980), and referenced in the OECD SIAP for methyl bromide (LMC, 2013; OECD, 2001). All studies were conducted in accordance with national test guidelines published by the Netherlands Normalisation Institute (NEN):

Taxon	Endpoint	Method
Fish	96 h LC50 = 0.7 mg/L	Experimental *Oryzias latipes* (Medaka) NEN TG 6504; semi-static, closed system
Invertebrates	48 h EC50 = 1.7 mg/L	Experimental *Daphnia magna* (Water flea) NEN TG 6501; static, closed system Increased mortality, slowed movement and paralysis observed

Taxon	Endpoint	Method
Algae	48 h EC50 = 3.2 mg/L	Experimental *Scenedesmus quadricauda* (Green algae) NEN TG 6506; static, closed system Inhibition of growth observed

The selected LC50 value for the fish *Oryzias latipes* is lower than many endpoint values available for other species of fish. However, the magnitude of the LC50 value is consistent with other toxicological data, and all available study information indicates that the referenced study was conducted under appropriate conditions. Therefore, the study is considered reliable, and the LC50 value is expected to be representative of the toxicity observed in susceptible species of fish.

Chronic toxicity

The following no-observed-effect concentration (NOEC) for a model organism was obtained by the authors of the aforementioned acute study, and referenced in the OECD SIAP and the IPCS Environmental Health Criteria for methyl bromide (IPCS, 1995; OECD, 2001):

Taxon	Endpoint	Method
Fish	91 d NOEC = 0.1 mg/L	Experimental *Poecilia reticulate* (Guppy), adults Semi-static, closed system Changes in appearance and behaviour observed

The same study found the majority of fish (*O. latipes*) embryos exposed to 1.0 mg/L of methyl bromide died before hatching (IPCS, 1995).

Effects on Terrestrial Life

Methyl bromide causes toxic effects at low concentrations in a wide range of terrestrial organisms, including various species of bacteria, fungi, nematodes and insects. Methyl bromide also has moderate toxicity to rodents and birds, and some toxic effects in plant seeds.

Acute toxicity

The following median lethal doses (LD50s) for terrestrial model organisms were reported in the OECD SIAP for methyl bromide and the IPCS Environmental Health Criteria for methyl bromide (IPCS, 1995; OECD, 2001). The bird study was conducted in accordance with the test guidelines required by the US Federal Insecticide, Fungicide and Rodenticide Act (FIFRA):

Taxon	Endpoint	Method
Birds	LD50 = 73 mg/kg bw	Experimental *Colinus virginianus* (Northern bobwhite) FIFRA TG 71-1; Single oral dose
Rodents	LD50 = 214 mg/kg bw	Experimental Rat (species not specified) OECD TG 401; Single oral dose
	LD50 = 302 mg/L	Experimental Rat (species not specified) Inhalation, exposed to gas for 8 h
Insects	LD50 = 0.009 mg/L	Experimental *Tibolium castaneum* (Red flour beetle), adults Inhalation, exposed to gas for 5-7 h

Methyl bromide is also lethal to most soil organisms, including numerous species of bacteria, nematodes, and various species of fungi (IPCS, 1995; OECD, 2001). However, standard ecotoxicological endpoint values were not able to be located for these taxa.

Exposure of plant seeds to methyl bromide may result in a delay in or loss of germination. This effect is dependent on moisture content, with seeds higher in moisture more susceptible to toxic effects (IPCS, 1995; OECD, 2001).

Chronic toxicity

In a study reported in the IPCS Environment Health Criteria for methyl bromide, fungi and some types of bacteria were found to have poorly recovered 87 days after exposure to lethal concentrations of the chemical, while other bacteria types showed full recovery (IPCS, 1995). These findings indicate that methyl bromide may cause chronic toxicity in some species of fungi and bacteria.

No additional chronic toxicity data were available for the chemical.

Predicted No-Effect Concentration (PNEC)

The PNEC for the chemical in the air compartment was not calculated. The current global consensus is that anthropogenic emissions of this chemical should be minimised in order to maintain the health of the ozone layer and to reduce global warming resulting from pollutants entering the atmosphere.

The PNEC for the chemical in the water, soil and sediment compartments was not calculated as the chemical is not expected to be released to, or significantly partition to, these compartments as a result of industrial use.

Categorisation of Environmental Hazard

The categorisation of the environmental hazards of methyl bromide according to domestic environmental hazard thresholds is presented below (EPHC, 2009; NICNAS, 2013):

Persistence

Persistent (P). Based on an overall atmospheric lifetime of 0.8 years, the chemical is categorised as Persistent.

Bioaccumulation

Not Bioaccumulative (Not B). Based on a measured log K_{OW} of 1.94, the chemical is categorised as Not Bioaccumulative.

Toxicity

Toxic (T). Based on the 96 h LC50 for fish (*O. latipes*) of 0.7 mg/L, the chemical is categorised as Toxic.

Summary

Methane, bromo- is categorised as:

- P
- Not B
- T

Risk Characterisation

Risk quotients (RQs) have not been calculated for this chemical.

The international consensus is that release of this chemical to the atmosphere poses a risk to the environment. However, as environmental exposure in Australia is controlled under the Ozone Act, the risk to the atmosphere resulting from current industrial uses of the chemical is low.

The risks to the water, soil and sediment compartments are expected to be low as the chemical is not expected to be released to, or significantly partition to, these compartments as a result of industrial use.

Key Findings

The release of methyl bromide to the environment is of concern due to the ozone depleting and global warming properties of the chemical. However, the manufacture, import and export of methyl bromide for industrial use in Australia are prohibited under the Ozone Act, unless the chemical is to be solely used as a feedstock. Minimal environmental release of the chemical is expected from this use. Therefore, current industrial use of the chemical is not expected to be of concern to the environment.

The chemical is not a PBT substance according to domestic environmental hazard criteria.

Recommendations

The manufacture, import and export of methane, bromo- (methyl bromide) are controlled in Australia under the *Ozone Protection and Synthetic Greenhouse Gas Management Act 1989*. The control measures implemented under the Ozone Act are expected to prevent significant environmental exposure of this chemical from industrial use. Current risk management measures are therefore considered adequate to protect the environment. No further assessment is required.

Environmental Hazard Classification

In addition to the categorisation of the environmental hazard according to domestic environmental thresholds presented above, the classification of the environment hazards of methane, bromo- according to the third edition of the United Nations' Globally Harmonised System of Classification and Labelling of Chemicals (GHS) is presented below (UNECE, 2009):

Hazard	GHS Classification (Code)	Hazard Statement
Acute Aquatic	Category 1 (H400)	Very toxic to aquatic life
Chronic Aquatic	Category 1 (H410)	Very toxic to aquatic life with long lasting effects
Ozone Layer	Category 1 (H420)	Harms public health and the environment by destroying ozone in the upper atmosphere

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