Ethane, 1,1,1,2-tetrafluoro-: Environment tier II assessment

07 February 2014

CAS Registry Number: 811-97-2.

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

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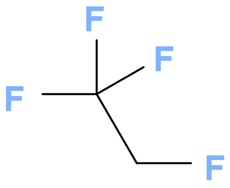
Acronyms & Abbreviations

Chemical Identity

Synonyms	HFC 134a 1,1,1,2-Tetrafluoroethane Norflurane R 134a
Structural Formula	
Molecular Formula	$C_2H_2F_4$

Molecular Weight (g/mol)	102.03
SMILES	C(F)(F)(F)CF

Physical and Chemical Properties

The physical and chemical property data for the chemical were retrieved from the databases included in the OECD QSAR Toolbox (LMC, 2013).

Physical Form	Gas
Melting Point	-101°C (exp.)
Boiling Point	-26°C (exp.)
Vapour Pressure	665 000 Pa (exp.)
Water Solubility	1000 mg/L (exp.)
Ionisable in the Environment?	No
log K_{ow}	1.06 (exp.)

Import, Manufacture and Use

Australia

Ethane, 1,1,1,2-tetrafluoro- (HFC 134a) is the most common hydrofluorocarbon (HFC) refrigerant gas used in Australia. The chemical is imported into Australia for use in commercial and domestic refrigeration and air conditioning applications. Hydrofluorocarbons are also used in foam blowing, in fire suppression applications and aerosols (Australian Government Department of Climate Change, 2013; DSEWPaC, 2013).

The chemical is commonly used to replace ozone depleting chemicals, such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), that are being phased out under the *Montreal Protocol on Substances that Deplete the Ozone Layer* (the Montreal Protocol). Import, export and manufacture of the chemical requires a licence under the *Ozone Protection and Synthetic Greenhouse Gas Management Act 1989* (Cwlth) (the Ozone Act) (Australian Government Department of Climate Change, 2013; Commonwealth of Australia, 1989).

In 2012, almost 5000 tonnes of neat HFC 134a was imported into Australia. Of this, approximately 700 tonnes was imported in pre-charged equipment, while the remainder was imported in bulk. Bulk imports of the chemical are used in mobile air conditioning systems in motor vehicles, stationary air conditioning systems, commercial chillers, commercial refrigeration and domestic refrigeration and freezers. The chemical is also imported in mixtures with other HFCs. HFC 134a is contained in the refrigerant gas mixtures HFC 404a, HFC 407a, HFC 407b and HFC 407c at concentrations of 4%, 40%, 20% and 52%, respectively. A significant volume of HFC 134a is expected to enter Australia in mixtures. For example, more than 2000 tonnes of bulk HFC 404a was imported into Australia in 2012 (AIRAH and IRHACE, 2007; DSEWPaC, 2013).

It is estimated that approximately 13 500 tonnes of HFC 134a was contained in equipment in Australia in 2012. This value is projected to continue rising until at least 2017. A small proportion of HFC 134a in Australia may be re-exported, with an additional proportion reclaimed and destroyed (DSEWPaC, 2013).

Use of the chemical has increased significantly since the commencement of the Montreal Protocol. Between 1990 and 2011, use of HFCs rose by 578% in Australia. In 2011, HFCs comprised 1.5% of Australia's greenhouse gas emissions (measured in carbon dioxide equivalents). Approximately two thirds of this value is attributable solely to HFC 134a emissions (Australian Government Department of Climate Change, 2013).

International

The majority of HFC 134a is used in air conditioning systems and commercial refrigeration (IPCC, 2005). Use of the chemical internationally has risen significantly due to the use of HFCs to replace chemicals being phased out under the Montreal Protocol. In 2005, it was estimated that the global amount of HFC 134a contained in equipment and systems was approximately equal to that already in the atmosphere (IPCC, 2005). More than 97 000 tonnes of the chemical was manufactured in the United States of America (USA) in 2012 (US EPA, 2013a).

The chemical is registered for various uses under the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) legislation at 10 000 to 100 000 tonnes per annum in the European Union (ECHA, 2013). It is estimated that 23 600 tonnes of HFC 134a was released to the atmosphere from Europe in 2004 (IPCC, 2005). However, since then, use of the chemical for various emissive uses has been prohibited (European Commission, 2006a). Use of the chemical is further being phased out in motor vehicle air conditioning units due to its high global warming potential (GWP) (European Commission, 2006b).

As a result of the phase out of use of the chemical in mobile air conditioning units in motor vehicles in the European Union, alternative chemicals to HFC 134a are now being introduced. The hydrofluoroolefin (HFO) 2,3,3,3-tetrafluoropropene (HFO 1234yf) has been accepted for use in the European Union and the USA (European Commission, 2013; US EPA, 2012a), and is increasingly being used instead of HFC 134a in mobile air conditioning units internationally. HFO 1234yf does not contribute to ozone depletion and has a significantly lower GWP when compared to HFC 134a (US EPA, 2012a).

Recent developments have highlighted the potential for an international agreement to phase down the use of HFCs. At the Group of Twenty (G20) meeting in September 2013, 26 countries (including Australia, the USA and the European Union) agreed to support initiatives to phase down the production and consumption of HFCs. This followed proposals by the USA, Canada, Mexico and the Federated States of Micronesia in April 2013 to amend the Montreal Protocol to address HFCs (UNEP, 2013a; 2013b).

Environmental Regulatory Status

Australia

HFC 134a is a scheduled substance under the Ozone Act. A licence is required to import, export or manufacture the chemical, unless the chemical is used on board ships or aircraft which are transiting between Australia and a place outside Australia. Import and manufacture of the chemical incurs a levy under the *Ozone Protection and Synthetic Greenhouse Gas (Import Levy) Act 1995* (Cwlth) and the *Ozone Protection and Synthetic Greenhouse Gas (Manufacture Levy) Act 1995* (Cwlth), respectively. Additionally, the quantity of the chemical that is imported or manufactured must be reported on a quarterly basis to the Australian Government Department of the Environment which administers the Ozone Act (Commonwealth of Australia, 1989).

Under the *Ozone Protection and Synthetic Greenhouse Gas Management Regulations 1995* (Cwlth), only authorised personnel may carry out work on refrigeration and air conditioning equipment containing the chemical, or possess bulk volumes of the chemical. Certified personnel must operate in accordance with relevant Australian Standards and codes of practice which set out requirements for minimising leakages and gas emissions (Commonwealth of Australia, 1995).

United Nations

HFCs are listed as greenhouse gases on Annex A of the *Kyoto Protocol to the United Nations Framework Convention on Climate Change* (UNFCCC, 1998). The Kyoto Protocol calls for a reduction in emission of greenhouse gases to the environment. Of the 197 countries of the United Nations, 192 have ratified the Kyoto Protocol, including Australia (UNFCCC, 2013).

Since 2009, numerous proposals to phase-down the production and consumption of HFCs have been made annually under the Montreal Protocol. To date, there has not been consensus to negotiate any such phase-down (UNEP, 2012).

OECD

The chemical has not been sponsored for assessment under the Cooperative Chemicals Assessment Programme (CoCAP) (OECD, 2013).

Canada

The chemical is listed on Schedule 1 of the *Federal Halocarbon Regulations, 2003*. Systems intended to operate with the chemical cannot be installed without a permit. Additionally, a permit is required to use the chemical as a solvent in solvent systems. Only certified personnel may install, service, leak test or charge a refrigeration or air conditioning system, and use of the chemical is subject to exposure restrictions and reporting requirements (Government of Canada, 2003).

The chemical is also listed on Schedule 1 of the *Canadian Environmental Protection Act 1999* (the Toxic Substances List). Emissions of the chemical must be reported under the National Pollutant Release Inventory. The chemical is further subject to a Significant New Activity rule, whereby any new uses of the chemical constituting more than 1 tonne in volume (excluding use in closed loop cooling systems) must be assessed and approved before use can commence (Environment Canada, 2013b; Government of Canada, 2006).

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, 2013a).

European Union

Use of the chemical for most applications in the European Union is controlled under *Regulation No 842/2006 of the European Parliament and of the Council of 17 May 2006 on Certain Fluorinated Greenhouse Gases*. Use of the chemical for non-confined refrigeration systems, windows, footwear, tyres, novelty aerosols and one component foams (except when required to meet national safety standards) is prohibited. Additionally, use is subject to emission restrictions (leakage prevention), training of personnel, labelling and reporting requirements (European Commission, 2006a).

The use of the chemical in motor vehicle air conditioning systems in the European Union is regulated under *Directive 2006/40/EC of the European Parliament and of the Council of 17 May 2006 relating to Emissions from Air Conditioning Systems in Motor Vehicles*. As of 1 January 2013, most systems designed to contain the chemical cannot be approved for use in the European Union in applicable vehicles (European Commission, 2006b; 2013).

The European Union is expected to adopt regulations in the foreseeable future to begin to phase-down the use of HFCs and ban the use of higher GWP HFCs in some equipment, including domestic and commercial refrigerators and air conditioning systems (European Commission, 2014).

United States of America

Servicing of refrigeration and air conditioning systems containing the chemical, including those in motor vehicles, is regulated under the *Clean Air Act 1970*. Intentional release of the chemical from an air conditioner, refrigerator, chiller or freezer is prohibited. Additionally, only trained personnel can service motor vehicle air conditioners containing the chemical, and servicing must be performed using approved refrigerant recycling equipment (US EPA, 2013b).

Environmental Exposure

HFC 134a is primarily used as a refrigerant in Australia. Although refrigerants generally operate in closed systems, the chemical may be lost through leakages. Leakage rates for HFCs used in refrigerant applications range from approximately 1% of the total volume per annum in modern domestic refrigerators to as high as 25% of the total volume per annum in refrigeration transport vehicles (DSEWPaC, 2013).

In 2011, more than 3500 tonnes of HCF 134a is estimated to have been released to the environment in Australia. The majority of this release is expected to have occurred due to leakages and losses from mobile air conditioning systems, stationary air conditioning systems, and freezers and refrigerators (Australian Government Department of Climate Change, 2013; DSEWPaC, 2013).

Environmental Fate

Partitioning

The chemical is expected to partition to the atmosphere when released from typical industrial uses.

The measured Henry's Law constant for partitioning of HFC 134a from water to air is 5070 Pa-m^3/mol at 22°C (LMC, 2013), indicating that the chemical is highly volatile from water and moist soil. Calculated organic carbon normalised adsorption coefficients (K_{OC}s) for the chemical range from 8 to 86 (US EPA, 2008), suggesting that the chemical is highly mobile in soil. However, evaporative losses are expected to dominate the partitioning and transport 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 (51%) and water (46%) compartments, with minor partitioning to soil (3%). However, with sole release to the atmosphere, the model predicts that 100% 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 this chemical to the environment.

Degradation

Degradation of the chemical in the atmosphere is slow.

The chemical has a predicted overall atmospheric lifetime of 13.4 years, based on reactions with hydroxyl radicals in the troposphere and destruction in the stratosphere (WMO, 2011). As HFC 134a is expected to partition to the atmosphere, these are expected to be the predominant degradation processes for the chemical in the environment.

The major degradation process for HFC 134a in the atmosphere is oxidation. The chemical has low reactivity towards indirect photo-oxidation by hydroxyl radicals in the troposphere, with an estimated lifetime of 14.3 years for this reaction (WMO, 2011). Due to its low reactivity, a proportion of the chemical will be transported to the stratosphere, where degradation by photo-oxidation or ultraviolet (UV) photolysis may occur. However, degradation of the chemical in the stratosphere is slow and is expected to account for less than 10% of total loss (IPCC, 2005).

In water and soil, HFC 134a is not expected to be rapidly degraded under aerobic conditions. The aerobic biodegradation of the chemical was determined to be 3% in 28 days in a study conducted in accordance with OECD Test Guideline (TG) 301 D (ECHA, 2013).

Trifluoroacetic acid is a product of the photochemical degradation of HFC 134a in the atmosphere. Trifluoroacetic acid is a highly water soluble strong organic acid which is removed from the atmosphere primarily in rain (wet deposition). This degradation product is not rapidly degradable and has some reported toxicity to the algae *Selenastrum capricornutum* (IPCC, 2005; LMC, 2013; WMO, 2011).

Although trifluoroacetic acid is expected to be produced due to the atmospheric degradation of HFC 134a, it also occurs naturally in the environment. Based on global 2008 figures, it is predicted that degradation of HFC 134a in the atmosphere gives rise to between 9000 and 35 000 tonnes of trifluoroacetic acid per annum. However, a study in 2002 estimated that there is approximately 8×10^8 tonnes of trifluoroacetic acid which is naturally present in the world's oceans. Formation of trifluoroacetic acid as a result of degradation of HFC 134a in the atmosphere at current emission levels is therefore not expected to significantly affect overall background environmental concentrations of this fluorinated organic acid (IPCC, 2005; WMO, 2011).

Bioaccumulation

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

No specific measured bioconcentration or bioaccumulation data are available for the chemical. However, based on the measured octanol water partition coefficient ($\log K_{OW} = 1.06$), the chemical is expected to have a low potential for bioaccumulation in the environment.

Transport

The chemical will undergo atmospheric transport, and long range transport is highly likely.

Due to the long atmospheric lifetime of the chemical, HFC 134a will become mixed throughout the atmosphere through atmospheric transport (IPCC, 2005). Further, the long lifetime and volatility of the chemical is also expected to result in the chemical undergoing long range transport in the environment.

Predicted Environmental Concentration (PEC)

A PEC was not calculated for HFC 134a as there is a large body of high quality environmental monitoring data available from multiple sites around the world. As the chemical has no natural sources or significant non-industrial uses, measured environmental concentrations are expected to have resulted solely from industrial manufacture and use of the chemical. The abundance of the chemical in the air compartment in 2011 was found to be approximately 63 parts per trillion (ppt), with data showing levels increasing at a rate of around 5 ppt per year (IPCC, 2013; WMO, 2011). Emissions of HFC 134a in Australia are currently increasing at a rate of approximately 250 tonnes per annum (Australian Government Department of Climate Change, 2013).

HFC 134a is not expected to have any significant presence in the water, soil or sediment compartments due to the partitioning behaviour of the chemical, and therefore PECs have not been calculated for these compartments.

Environmental Effects

Effects on the Atmosphere

HFC 134a does not deplete the ozone layer, but it does have a high global warming potential.

Photolysis of halocarbons containing chlorine and bromine can cause depletion of the ozone layer (WMO, 2011). As HFC 134a does not contain chlorine or bromine atoms, it does not contribute to ozone depletion. However, halocarbons with long atmospheric lifetimes such as HFC 134a contribute to global warming by absorbing radiation emitted from Earth and thus trapping the energy in the atmosphere (radiative forcing) (WMO, 2011). 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; WMO, 2011). HFC 134a has a one hundred year GWP of 1300 (IPCC, 2013).

Effects on Aquatic Life

HFC 134a is not expected to cause toxic effects in aquatic organisms at low concentrations.

Acute toxicity

The following median lethal concentration (LC50) and median effective concentrations (EC50s) for model organisms across three trophic levels were reported in the Registration Dossier for HFC 134a under the European Union REACH legislation, or calculated using the Neutral Organics QSAR models available in ECOSAR v1.11 (ECHA, 2013; US EPA, 2012b):

Taxon	Endpoint	Method
Fish	96 h LC50 = 450 mg/L	Experimental *Oncorhynchus mykiss* (Rainbow trout) EU Method C.1; semi-static
Invertebrates	48 h EC50 = 980 mg/L	Experimental *Daphnia magna* (Water flea) EU Method C.2; static Decreased mobility observed
Algae	96 h EC50 = 159 mg/L	Calculated Neutral Organics; ECOSAR v1.11

The measured data were obtained from studies conducted in accordance with Good Laboratory Practice (GLP) by the Imperial Chemical Industries (ICI) Group Environmental Laboratory (Berends, et al., 1999; ECHA, 2013). Toxicity values calculated using the Neutral Organics QSAR models for fish and aquatic invertebrates showed good consistency with the measured data, which supports the assumption that the chemical has a non-polar narcotic mode of action for acute effects.

Chronic toxicity

There are no suitable data available to evaluate the chronic effects of the chemical on aquatic organisms.

Predicted No-Effect Concentration (PNEC)

The PNEC for the chemical in the air compartment was not calculated as there are currently no suitable data available to evaluate the effects of this chemical on terrestrial organisms.

The PNEC for HFC 134a 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 Hazards

The categorisation of the environmental hazards of HFC 134a according to domestic environmental hazard thresholds is presented below (EPHC, 2009; NICNAS, 2013):

Persistence

Persistent (P). Based on an overall atmospheric lifetime of 13.4 years, the chemical is categorised as Persistent.

Bioaccumulation

Not Bioaccumulative (Not B). Based on a measured log K_{OW} of 1.06, the chemical is categorised as Not Bioaccumulative.

Toxicity

Not Toxic (Not T). Based on the above presented ecotoxicity data, the chemical is categorised as Not Toxic.

Summary

Ethane, 1,1,1,2-tetrafluoro- is categorised as:

- P
- Not B
- Not T

Risk Characterisation

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

HFC 134a is not an ozone depleting substance and industrial use of this chemical does not pose a risk to the ozone layer.

HFC 134a is a potent greenhouse gas and emissions of this chemical make a significant contribution to the total amount of atmospheric warming caused by the release of hydrofluorocarbon gases to the atmosphere. Analysis of use and emission estimation information for Australia indicates that significant emissions of this chemical to the atmosphere do occur. Based on domestic and international trend information, emissions of this chemical are increasing. Current industrial uses of HFC 134a are therefore increasing the risks associated with warming of the atmosphere.

The risks of ecotoxicological effects of the chemical to organisms in the water, soil and sediment compartments are expected to be low as HFC 134a is not expected to be released to, or significantly partition to, these compartments as a result of industrial use.

Key Findings

HFC 134a is used in large volumes in Australia to replace chlorofluorocarbons and hydrochlorofluorocarbons phased out of use under the Montreal Protocol. Although the chemical does not contribute to ozone depletion, it has a high global warming potential and makes a substantial contribution to the radiative forcing caused by hydrofluorocarbon gases in the atmosphere. Due to the high GWP of the chemical, and significant emissions to the atmosphere globally, HFC 134a is being replaced internationally with alternative refrigerant gases.

The Ozone Act regulates the use of the chemical in Australia to reduce emissions during technical work. However, significant emissions to the atmosphere do occur during use. Due to the significant release of the chemical to the atmosphere during use, current industrial use of HFC 134a in Australia is increasing the risks of atmospheric warming. Based on this analysis, current and projected future uses of HFC 134a are of potential concern to the environment.

In light of the environmental risks associated with cumulative emissions of hydrofluorocarbon gases from industrial uses in Australia that have been identified in this assessment, and subject to any future Australian or international regulatory action regarding these chemicals, a Tier III assessment under the IMAP framework may be warranted.

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

Recommendations

It is recommended that the Australian Government Department of the Environment review existing emission controls under the Ozone Act with a view to considering any improvements or additional actions that could be undertaken to minimise emissions of HFC 134a to the environment.

Environmental Hazard Classification

In addition to the categorisation of the environmental hazards according to domestic environmental thresholds presented above, the classification of the environment hazards of ethane, 1,1,1,2-tetrafluoro- 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	-	Not classified

There are insufficient reliable data to classify the long-term aquatic hazards of the chemical.

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