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N° 40

Formaldehyde

IOMC

INTER-ORGANIZATION PROGRAMME FOR THE SOUND MANAGEMENT OF CHEMICALS

A cooperative agreement among UNEP, ILO, FAO, WHO, UNIDO, UNITAR and OECD

WORLD HEALTH ORGANIZATION

This report contains the collective views of an international group of experts and does not necessarily represent the decisions or the stated policy of the United Nations Environment Programme, the International Labour Organization, or the World Health Organization.

Concise International Chemical Assessment Document 40

FORMALDEHYDE

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The **International Programme on Chemical Safety (IPCS)**, established in 1980, is a joint venture of the United Nations Environment Programme (UNEP), the International Labour Organization (ILO), and the World Health Organization (WHO). The overall objectives of the IPCS are to establish the scientific basis for assessment of the risk to human health and the environment from exposure to chemicals, through international peer review processes, as a prerequisite for the promotion of chemical safety, and to provide technical assistance in strengthening national capacities for the sound management of chemicals.

The **Inter-Organization Programme for the Sound Management of Chemicals (IOMC)** was established in 1995 by UNEP, ILO, the Food and Agriculture Organization of the United Nations, WHO, the United Nations Industrial Development Organization, the United Nations Institute for Training and Research, and the Organisation for Economic Co-operation and Development (Participating Organizations), following recommendations made by the 1992 UN Conference on Environment and Development to strengthen cooperation and increase coordination in the field of chemical safety. The purpose of the IOMC is to promote coordination of the policies and activities pursued by the Participating Organizations, jointly or separately, to achieve the sound management of chemicals in relation to human health and the environment.

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FOREWORD

Concise International Chemical Assessment Documents (CICADs) are the latest in a family of publications from the International Programme on Chemical Safety (IPCS) — a cooperative programme of the World Health Organization (WHO), the International Labour Organization (ILO), and the United Nations Environment Programme (UNEP). CICADs join the Environmental Health Criteria documents (EHCs) as authoritative documents on the risk assessment of chemicals.

International Chemical Safety Cards on the relevant chemical(s) are attached at the end of the CICAD, to provide the reader with concise information on the protection of human health and on emergency action. They are produced in a separate peer-reviewed procedure at IPCS. They may be complemented by information from IPCS Poison Information Monographs (PIM), similarly produced separately from the CICAD process.

CICADs are concise documents that provide summaries of the relevant scientific information concerning the potential effects of chemicals upon human health and/or the environment. They are based on selected national or regional evaluation documents or on existing EHCs. Before acceptance for publication as CICADs by IPCS, these documents undergo extensive peer review by internationally selected experts to ensure their completeness, accuracy in the way in which the original data are represented, and the validity of the conclusions drawn.

The primary objective of CICADs is characterization of hazard and dose–response from exposure to a chemical. CICADs are not a summary of all available data on a particular chemical; rather, they include only that information considered critical for characterization of the risk posed by the chemical. The critical studies are, however, presented in sufficient detail to support the conclusions drawn. For additional information, the reader should consult the identified source documents upon which the CICAD has been based.

Risks to human health and the environment will vary considerably depending upon the type and extent of exposure. Responsible authorities are strongly encouraged to characterize risk on the basis of locally measured or predicted exposure scenarios. To assist the reader, examples of exposure estimation and risk characterization are provided in CICADs, whenever possible. These examples cannot be considered as representing all possible exposure situations, but are provided as guidance only. The reader is referred to EHC 170[1] for advice on the derivation of health-based guidance values.

While every effort is made to ensure that CICADs represent the current status of knowledge, new information is being developed constantly. Unless otherwise stated, CICADs are based on a search of the scientific literature to the date shown in the executive summary. In the event that a reader becomes aware of new information that would change the conclusions drawn in a CICAD, the reader is requested to contact IPCS to inform it of the new information.

Procedures

The flow chart on page 2 shows the procedures followed to produce a CICAD. These procedures are designed to take advantage of the expertise that exists around the world — expertise that is required to produce the high-quality evaluations of toxicological, exposure, and other data that are necessary for assessing risks to human health and/or the environment. The IPCS Risk Assessment Steering Group advises the Co-ordinator, IPCS, on the selection of chemicals for an IPCS risk assessment, the appropriate form of the document (i.e., EHC or CICAD), and which institution bears the responsibility of the document production, as well as on the type and extent of the international peer review.

The first draft is based on an existing national, regional, or international review. Authors of the first draft are usually, but not necessarily, from the institution that developed the original review. A standard outline has been developed to encourage consistency in form. The first draft undergoes primary review by IPCS and one or more experienced authors of criteria documents to ensure that it meets the specified criteria for CICADs.

The draft is then sent to an international peer review by scientists known for their particular expertise and by scientists selected from an international roster compiled by IPCS through recommendations from IPCS national Contact Points and from IPCS Participating Institutions. Adequate time is allowed for the selected experts to undertake a thorough review. Authors are required to take reviewers' comments into account and revise their draft, if necessary. The resulting second draft is submitted to a Final Review Board together with the reviewers' comments.

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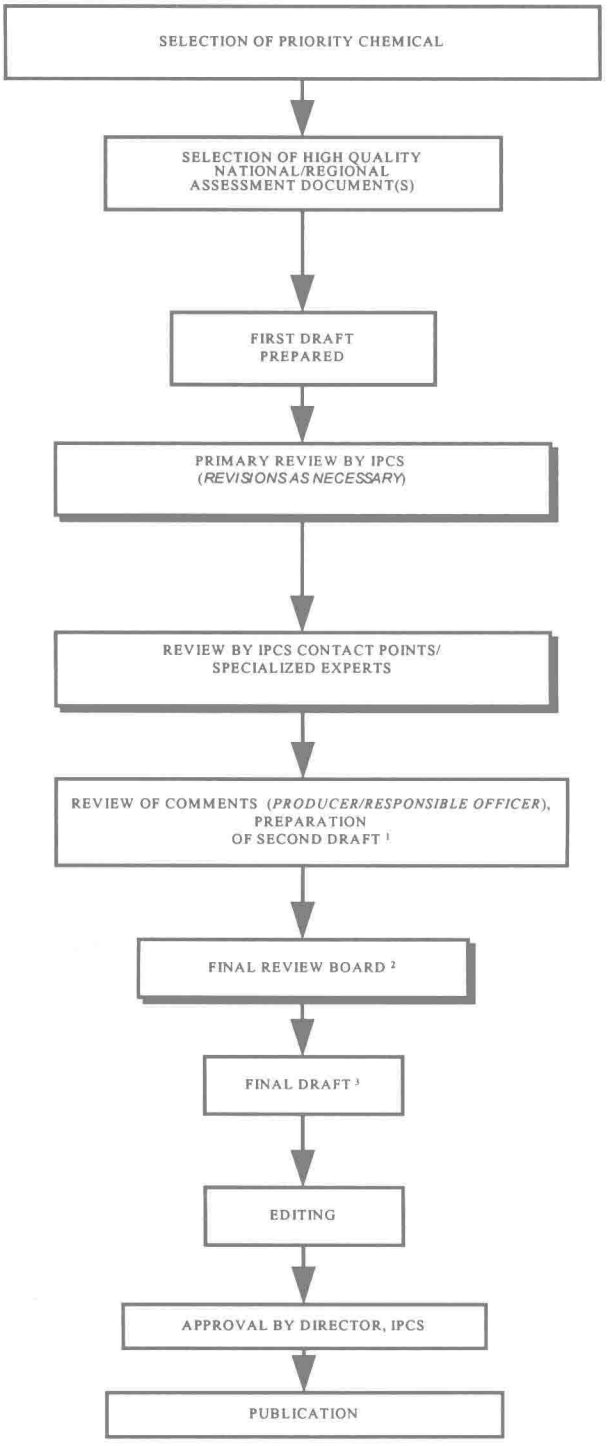
[1] International Programme on Chemical Safety (1994) *Assessing human health risks of chemicals: derivation of guidance values for health-based exposure limits.* Geneva, World Health Organization (Environmental Health Criteria 170).

CICAD PREPARATION FLOW CHART



1 Taking into account the comments from reviewers.
2 The second draft of documents is submitted to the Final Review Board together with the reviewers' comments.
3 Includes any revisions requested by the Final Review Board.

A consultative group may be necessary to advise on specific issues in the risk assessment document.

The CICAD Final Review Board has several important functions:

- to ensure that each CICAD has been subjected to an appropriate and thorough peer review;
- to verify that the peer reviewers' comments have been addressed appropriately;
- to provide guidance to those responsible for the preparation of CICADs on how to resolve any remaining issues if, in the opinion of the Board, the author has not adequately addressed all comments of the reviewers; and
- to approve CICADs as international assessments.

Board members serve in their personal capacity, not as representatives of any organization, government, or industry. They are selected because of their expertise in human and environmental toxicology or because of their experience in the regulation of chemicals. Boards are chosen according to the range of expertise required for a meeting and the need for balanced geographic representation.

Board members, authors, reviewers, consultants, and advisers who participate in the preparation of a CICAD are required to declare any real or potential conflict of interest in relation to the subjects under discussion at any stage of the process. Representatives of nongovernmental organizations may be invited to observe the proceedings of the Final Review Board. Observers may participate in Board discussions only at the invitation of the Chairperson, and they may not participate in the final decision-making process.

1. EXECUTIVE SUMMARY

This CICAD on formaldehyde was prepared jointly by the Environmental Health Directorate of Health Canada and the Commercial Chemicals Evaluation Branch of Environment Canada based on documentation prepared as part of the Priority Substances Program under the *Canadian Environmental Protection Act* (CEPA). The objective of assessments on Priority Substances under CEPA is to assess potential effects of indirect exposure in the general environment on human health as well as environmental effects. This CICAD additionally includes information on occupational exposure. Data identified as of the end of December 1999 (environmental effects) and January 1999 (human health effects) were considered in this review.[1] Other reviews that were also consulted include IARC (1981, 1995), IPCS (1989), RIVM (1992), BIBRA Toxicology International (1994), and ATSDR (1999). Information on the nature of the peer review and availability of the source document (Environment Canada & Health Canada, 2001) and its supporting documentation is presented in Appendix 1. It should be noted, as indicated therein, that the biologically motivated case-specific model for exposure–response analyses for cancer included in this CICAD was the product of a joint effort involving the US Environmental Protection Agency (EPA), Health Canada, the Chemical Industry Institute of Toxicology (CIIT), and others. The product of this collaborative effort superceded the content of a draft CICAD on formaldehyde prepared previously by the Office of Pollution Prevention and Toxics of the US EPA, on the basis of health-related toxicological information published prior to1992. Information on the peer review of this CICAD is presented in Appendix 2. This CICAD was approved as an international assessment at a meeting of the Final Review Board, held in Geneva, Switzerland, on 8–12 January 2001. Participants at the Final Review Board meeting are listed in Appendix 3. The International Chemical Safety Card for formaldehyde (ICSC 0275), produced by the International Programme on Chemical Safety (IPCS, 2000), has also been reproduced in this document.

Formaldehyde (CAS No. 50-0-0) is a colourless, highly flammable gas that is sold commercially as 30–50% (by weight) aqueous solutions. Formaldehyde enters the environment from natural sources (including forest fires) and from direct human sources, such as automotive and other fuel combustion and industrial on-site uses. Secondary formation also occurs, by the oxidation of natural and anthropogenic organic compounds present in air. The highest concentrations measured in the environment occur near anthropogenic sources; these are of prime concern for the exposure of humans and other biota. Motor vehicles are the largest direct human source of formaldehyde in the environment of the source country (Canada). Releases from industrial processes are considerably less. Industrial uses of formaldehyde include the production of resins and fertilizers.

When formaldehyde is released to or formed in air, most of it degrades, and a very small amount moves into water. When formaldehyde is released into water, it does not move into other media but is broken down. Formaldehyde does not persist in the environment, but its continuous release and formation result in long-term exposure near sources of release and formation.

The focus of the human health assessment is airborne exposure, due primarily to the lack of representative data on concentrations in media other than air and limited data on effects following ingestion.

Extensive recent data are available for concentrations of formaldehyde in air at industrial, urban, suburban, rural, and remote locations in the source country (Canada). There are fewer but still considerable data on concentrations in indoor air, which are higher. Data on concentrations in water are more limited. Although formaldehyde is a natural component of a variety of foodstuffs, monitoring has generally been sporadic and source directed. Based on available data, the highest concentrations of formaldehyde occurring naturally in foods are in some fruits and marine fish. Formaldehyde may also be present in food due to its use as a bacteriostatic agent in production and its addition to animal feed to improve handling characteristics. Formaldehyde and formaldehyde derivatives are also present in a wide variety of consumer products to protect the products from spoilage by microbial contamination. The general population is also exposed during release from combustion (e.g., from cigarettes and cooking) and emission from some building materials, such as pressed wood products.

Since formaldehyde (also a product of intermediary metabolism) is water soluble, highly reactive with biological macromolecules, and rapidly metabolized, adverse effects resulting from exposure are observed primarily in those tissues or organs with which formaldehyde first comes into contact (i.e., the respiratory and

[1] New information flagged by reviewers and obtained in a literature search conducted prior to the Final Review Board meeting has been scoped to indicate its likely impact on the essential conclusions of this assessment, primarily to establish priority for its consideration in an update. More recent information not critical to the hazard characterization or exposure–response analysis, considered by reviewers to add to informational content, has been included.

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aerodigestive tract, including oral and gastrointestinal mucosa, following inhalation or ingestion, respectively).

Sensory irritation of the eyes and respiratory tract by formaldehyde has been observed consistently in clinical studies and epidemiological surveys in occupational and residential environments. At concentrations higher than those generally associated with sensory irritation, formaldehyde may also contribute to the induction of generally small, reversible effects on lung function.

For the general population, dermal exposure to concentrations of formaldehyde, in solution, in the vicinity of 1–2% (10 000–20 000 mg/litre) is likely to cause skin irritation; however, in hypersensitive individuals, contact dermatitis can occur following exposure to formaldehyde at concentrations as low as 0.003% (30 mg/litre). In North America, less than 10% of patients presenting with contact dermatitis may be immunologically hypersensitive to formaldehyde. Although it has been suggested in case reports for some individuals that formaldehyde-induced asthma was attributable to immunological mechanisms, no clear evidence has been identified. However, in studies with laboratory animals, formaldehyde has enhanced their sensitization to inhaled allergens.

Following inhalation in laboratory animals, formaldehyde causes degenerative non-neoplastic effects in mice and monkeys and nasal tumours in rats. *In vitro*, formaldehyde induced DNA–protein crosslinks, DNA single-strand breaks, chromosomal aberrations, sister chromatid exchange, and gene mutations in human and rodent cells. Formaldehyde administered by inhalation or gavage to rats *in vivo* induced chromosomal anomalies in lung cells and micronuclei in the gastrointestinal mucosa. The results of epidemiological studies in occupationally exposed populations are consistent with a pattern of weak positive responses for genotoxicity, with good evidence of an effect at site of contact (e.g., micronucleated buccal or nasal mucosal cells). Evidence for distal (i.e., systemic) effects is equivocal. Overall, based on studies in both animals and humans, formaldehyde is weakly genotoxic, with good evidence of an effect at site of contact, but less convincing evidence at distal sites. Epidemiological studies taken as a whole do not provide strong evidence for a causal association between formaldehyde exposure and human cancer, although the possibility of increased risk of respiratory cancers, particularly those of the upper respiratory tract, cannot be excluded on the basis of available data. Therefore, based primarily upon data derived from laboratory studies, the inhalation of formaldehyde under conditions that induce cytotoxicity and sustained regenerative proliferation is considered to present a carcinogenic hazard to humans.

The majority of the general population is exposed to airborne concentrations of formaldehyde less than those associated with sensory irritation (i.e., 0.083 ppm [0.1 mg/m^3]). However, in some indoor locations, concentrations may approach those associated with eye and respiratory tract sensory irritation in humans. Risks of cancer estimated on the basis of a biologically motivated case-specific model for calculated exposure of the general population to formaldehyde in air based on the sample exposure scenario for the source country (Canada) are exceedingly low. This model incorporates two-stage clonal growth modelling and is supported by dosimetry calculations from computational fluid dynamics modelling of formaldehyde flux in various regions of the nose and single-path modelling for the lower respiratory tract.

Environmental toxicity data are available for a wide range of terrestrial and aquatic organisms. Based on the maximum concentrations measured in air, surface water, effluents, and groundwater in the sample exposure scenario from the source country and on the estimated no-effects values derived from experimental data for terrestrial and aquatic biota, formaldehyde is not likely to cause adverse effects on terrestrial or aquatic organisms.

2. IDENTITY AND PHYSICAL/CHEMICAL PROPERTIES

Formaldehyde (CH_2O) is also known as methanal, methylene oxide, oxymethylene, methylaldehyde, oxomethane, and formic aldehyde. Its Chemical Abstracts Service (CAS) registry number is 50-00-0.

At room temperature, formaldehyde is a colourless gas with a pungent, irritating odour. It is highly reactive, readily undergoes polymerization, is highly flammable, and can form explosive mixtures in air. It decomposes at temperatures above 150 °C. Formaldehyde is readily soluble in water, alcohols, and other polar solvents. In aqueous solutions, formaldehyde hydrates and polymerizes and can exist as methylene glycol, polyoxymethylene, and hemiformals. Solutions with high concentrations (>30%) of formaldehyde become turbid as the polymer precipitates (IPCS, 1989). As a reactive aldehyde, formaldehyde can undergo a number of self-association reactions, and it can associate with water to form a variety of chemical species with properties different from those of the pure monomolecular substance. These associations tend to be most prevalent at high concentrations of

formaldehyde; hence, data on properties at high concentrations are not relevant to dilute conditions.

Values reported for the physical and chemical properties of formaldehyde are given in Table 1. Additional physical/chemical properties are presented in the International Chemical Safety Card reproduced in this document.

Table 1: Physical and chemical properties of formaldehyde reported in literature.[a]

Property	Range of reported values[b]
Relative molecular mass	30.03
Melting point (°C)	-118 to -92
Boiling point (°C, at 101.3 kPa)	-21 to -19
Vapour pressure (calculated) (Pa, at 25 °C)	516 000
Water solubility (mg/litre, at 25 °C)[c]	400 000 to 550 000
Henry's law constant ($Pa \cdot m^3/mol$, at 25 °C)	2.2×10^{-2} to 3.4×10^{-2}
Log octanol/water partition coefficient (log K_{ow})	-0.75 to 0.35
Log organic carbon/water partition coefficient (log K_{oc})	0.70 to 1.57
Conversion factor	1 ppm = 1.2 mg/m^3

[a] Because of polymerization and other reactions, care should be taken in interpreting or using reported values. See also text.

[b] Includes experimental and calculated values from Hansch & Leo (1979, 1981); Karickhoff et al. (1979); Kenaga & Goring (1980); Weast (1982–1983); Verschueren (1983); Perry & Green (1984); Dean (1985); US EPA (1985); Betterton & Hoffmann (1988); Deneer et al. (1988); Howard (1989); Sangster (1989); Zhou & Mopper (1990); Mackay et al. (1995); Staudinger & Roberts (1996).

[c] Water solubility of a chemical is defined as the maximum amount of the chemical that will dissolve in water at a specified temperature, pressure, and pH. Results such as 1 220 000 mg/litre (Dean, 1985) and 1.0×10^8 mg/litre (DMER & AEL, 1996) have been quoted. These values are pseudo-solubilities, since solutions become turbid as the polymer precipitates at concentrations of approximately 55% and greater.

Pure formaldehyde is not available commercially but is sold as 30–50% (by weight) aqueous solutions. Formalin (37% CH_2O) is the most common solution. Methanol or other substances are usually added to the solution as stabilizers to reduce the intrinsic polymerization of formaldehyde (IPCS, 1989; Environment Canada, 1995). In solid form, formaldehyde is marketed as trioxane [$(CH_2O)_3$] and its polymer paraformaldehyde, with 8–100 units of formaldehyde (IPCS, 1989).

3. ANALYTICAL METHODS

Selected methods for the determination of formaldehyde in air, food, and wood are presented in Table 2 (IARC, 1995). The most widely used methods for the detection of formaldehyde are based on spectrophotometry, but other methods, such as colorimetry, fluorimetry, high-performance liquid chromatography, polarography, gas chromatography, infrared detection, and gas detector tubes, are also used. Organic and inorganic chemicals, such as sulfur dioxide and other aldehydes and amines, can interfere with these methods of detection. The most sensitive of these methods is flow injection (Fan & Dasgupta, 1994), which has a detection limit of 9 ppt (0.011 $\mu g/m^3$). Another commonly used method is high-performance liquid chromatography, which offers a detection limit of 0.0017 ppm (0.002 mg/m^3) (IARC, 1995). Gas detector tubes and infrared analysers are often used for monitoring workplace atmospheres and have a sensitivity of about 0.33–0.42 ppm (0.4–0.5 mg/m^3) (IARC, 1995).

4. SOURCES OF HUMAN AND ENVIRONMENTAL EXPOSURE

Data on sources and emissions primarily from the source country of the national assessment on which the CICAD is based (i.e., Canada) are presented here as an example. Sources and patterns of emissions in other countries are expected to be similar, although quantitative values may vary.

Formaldehyde is formed primarily by the combustion of organic materials and by a variety of natural and anthropogenic activities. Secondary formation of formaldehyde occurs in the atmosphere through the oxidation of natural and anthropogenic volatile organic compounds (VOCs) in the air. While there are no reliable estimates for releases from natural sources and for secondary formation, these may be expected to be much larger than direct emissions from anthropogenic activities. However, highest concentrations have been measured near key anthropogenic sources, such as automotive and industrial emissions (see section 6.1.1).

4.1 Natural sources

Formaldehyde occurs naturally in the environment and is the product of many natural processes. It is released during biomass combustion, such as forest and brush fires (Howard, 1989; Reinhardt, 1991). In water, it

Table 2: Methods for the analysis of formaldehyde in air and food.[a,b]

Sample matrix/preparation	Assay procedure	Limit of detection	Reference
Air			
Draw air through an impinger containing aqueous pararosaniline and sodium sulfite.	S	0.0083 ppm (0.01 mg/m^3)	Georghiou et al., 1993
Draw air through PTFE filter and impingers, each treated with sodium bisulfite solution; develop colour with chromotropic acid and sulfuric acid; read absorbance at 580 nm.	S	0.025 ppm (0.03 mg/m^3)	Eller, 1989a
Draw air through solid sorbent tube treated with 10% 2-(hydroxymethyl) piperidine on XAD-2; desorb with toluene.	GC/FID	0.25 ppm (0.3 mg/m^3)	Eller, 1989b
	GC/NSD	0.017 ppm (0.02 mg/m^3)	US OSHA, 1990
Draw air through tube that contains a smaller concentric tube made of Nafion (semipermeable) through which water flows in the opposite direction and serves to trap formaldehyde; add 1,3-cyclohexanedione in acidified ammonium acetate to form dihydropyridine derivative in flow injection analysis system.	Fluorescence (FIA)	9 ppt (0.011 µg/m^3)	Fan & Dasgupta, 1994
Draw air through impinger containing hydrochloric acid/2,4-dinitrophenylhydrazine reagent and isooctane; extract with hexane/dichloromethane.	HPLC/UV	0.0017 ppm (0.002 mg/m^3)	US EPA, 1988a
Draw air through silica gel coated with acidified 2,4-dinitrophenylhydrazine reagent.	HPLC/UV	0.0017 ppm (0.002 mg/m^3)	US EPA, 1988b
Expose passive monitor (Du Pont Pro-Tek Formaldehyde Badge) for at least 2 ppm-h. Analyse according to manufacturer's specifications.	Chromotropic acid test	0.083 ppm (0.1 mg/m^3)	Kennedy & Hull, 1986; Stewart et al., 1987
Food			
Distil sample; add 1,8-dihydroxynaphthalene-3,6-disulfonic acid in sulfuric acid; purple colour indicates presence of formaldehyde.	Chromotropic acid test	NR	Helrich, 1990
Distil sample; add to cold sulfuric acid; add aldehyde-free milk; add bromine hydrate solution; purplish-pink colour indicates presence of formaldehyde.	Hehner-Fulton test	NR	Helrich, 1990
Wood			
Large-scale chamber tests.		0.083 ppm (0.1 mg/m^3)	European Commission, 1989; ASTM, 1990; Groah et al., 1991; Jann, 1991
Formaldehyde, absorbed in distilled water, reacts specifically with a chromotropic acid–sulfuric acid solution.	2-h desiccator test	NR	National Particleboard Association, 1983; Groah et al., 1991
Small samples are boiled in toluene, and the formaldehyde-laden toluene is distilled through distilled/deionized water, which absorbs the formaldehyde; a sample of the water is then analysed photometrically by the acetylacetone or pararosaniline method.	Perforator method	NR	British Standards Institution, 1989
Formaldehyde in water is determined by adding sulfuric acid solution and an excess of iodine; the iodine oxidizes the formaldehyde, and the excess is back-titrated with sodium thiosulfate.	Iodometric method	NR	British Standards Institution, 1989

[a] From IARC (1995).

[b] Abbreviations used: GC/FID = gas chromatography/flame ionization detection; GC/NSD = gas chromatography/nitrogen selective detection; FIA = fluorescence immunoassay; HPLC/UV = high-performance liquid chromatography/ultraviolet detection; NR = not reported; PTFE = polytetrafluoroethylene; S = spectrometry.

is also formed by the irradiation of humic substances by sunlight (Kieber et al., 1990).

As a metabolic intermediate, formaldehyde is present at low levels in most living organisms (IPCS, 1989; IARC, 1995). It is emitted by bacteria, algae, plankton, and vegetation (Hellebust, 1974; Zimmermann et al., 1978; Eberhardt & Sieburth, 1985; Yamada & Matsui, 1992; Nuccio et al., 1995).

4.2 Anthropogenic sources

Anthropogenic sources of formaldehyde include direct sources such as fuel combustion, industrial on-site uses, and off-gassing from building materials and consumer products.

Although formaldehyde is not present in gasoline, it is a product of incomplete combustion and is released, as a result, from internal combustion engines. The amount generated depends primarily on the composition of the fuel, the type of engine, the emission control applied, the operating temperature, and the age and state of repair of the vehicle. Therefore, emission rates are variable (Environment Canada, 1999a).

Based on data for 1997 reported to the National Pollutant Release Inventory, on-road motor vehicles are the largest direct source of formaldehyde released into the Canadian environment. Data on releases from on-road vehicles were estimated by modelling (Mobile 5C model), based on assumptions outlined in Environment Canada (1996). The amount estimated by modelling to have been released in 1997 from on-road motor vehicles was 11 284 tonnes (Environment Canada, 1999b). While Environment Canada (1999b) did not distinguish between gasoline-powered and diesel-powered vehicles, it has been estimated, based on emissions data from these vehicles, that they account for about 40% and 60% of on-road automotive releases, respectively. Aircraft emitted an estimated 1730 tonnes, and the marine sector released about 1175 tonnes (Environment Canada, 1999b). It can be expected that the rates of release of formaldehyde from automotive sources have changed and will continue to change; many current and planned modifications to automotive emission control technology and gasoline quality would lead to decreases in the releases of formaldehyde and other VOCs (Environment Canada, 1999b).

Other anthropogenic combustion sources (covering a range of fuels from wood to plastics) include wood-burning stoves, fireplaces, furnaces, power plants, agricultural burns, waste incinerators, cigarette smoking, and the cooking of food (Jermini et al., 1976; Kitchens et al., 1976; Klus & Kuhn, 1982; Ramdahl et al., 1982; Schriever et al., 1983; Lipari et al., 1984; IPCS, 1989; Walker & Cooper, 1992; Baker, 1994; Guski & Raczynski, 1994). Cigarette smoking in Canada is estimated to produce less than 84 tonnes per year, based on estimated emission rates (IPCS, 1989) and a consumption rate of approximately 50 billion cigarettes per year (Health Canada, 1997). Canadian coal-based electricity generating plants are estimated to emit 0.7–23 tonnes per year, based on US emission factors (Lipari et al., 1984; Sverdrup et al., 1994), the high heating value of fuel, and Canadian coal consumption in 1995 (D. Rose, personal communication, 1998). A gross estimate of formaldehyde emissions from municipal, hazardous, and biomedical waste in Canada is 10.6 tonnes per year, based on measured emission rates from one municipal incinerator in Ontario (Novamann International, 1997; Environment Canada, 1999a).

Industrial releases of formaldehyde can occur at any stage during the production, use, storage, transport, or disposal of products with residual formaldehyde. Formaldehyde has been detected in emissions from chemical manufacturing plants (Environment Canada, 1997b,c, 1999a), pulp and paper mills, forestry product plants (US EPA, 1990; Fisher et al., 1991; Environment Canada, 1997b, 1999a; O'Connor & Voss, 1997), tire and rubber plants (Environment Canada, 1997a), petroleum refining and coal processing plants (IARC, 1981; US EPA, 1993), textile mills, automotive manufacturing plants, and the metal products industry (Environment Canada, 1999a).

Total environmental releases in Canada from 101 facilities were 1423.9 tonnes in 1997, with reported releases to different media as follows: 1339.3 tonnes to air, 60.5 tonnes to deep-well injection, 19.4 tonnes to surface water, and 0 tonnes to soil. From 1979 to 1989, about 77 tonnes were spilled in Canada as a result of 35 reported incidents. Releases of formaldehyde to groundwater from embalming fluids in bodies buried in cemeteries are expected to be very small based on groundwater samples and the estimated loading rates of six cemeteries in Ontario (Chan et al., 1992). In the USA in 1992, total releases of formaldehyde to environmental media from certain types of US industries were approximately 8960 tonnes, of which approximately 58%, 39%, 2%, and 1% were released to the atmosphere, to underground injection sites, to surface water, and to land, respectively (TRI, 1994).

Formaldehyde has been detected in the off-gassing of formaldehyde products such as wood panels, latex paints, new carpets, textile products, and resins. While emission rates have been estimated for some of these sources, there are insufficient data for estimating total releases (Little et al., 1994; NCASI, 1994; Environment Canada, 1995). In some countries, there have been regulatory and voluntary initiatives to control emissions from building materials and furnishings, since these are recognized as the major sources of elevated concentrations of formaldehyde in indoor air.

4.3 Secondary formation

Formaldehyde is formed in the troposphere by the photochemical oxidation of many types of organic

compounds, including naturally occurring compounds, such as methane (IPCS, 1989; US EPA, 1993) and isoprene (Tanner et al., 1994), and pollutants from mobile and stationary sources, such as alkanes, alkenes (e.g., ethene, propene), aldehydes (e.g., acetaldehyde, acrolein), and alcohols (e.g., allyl alcohol, methanol, ethanol) (US EPA, 1985; Atkinson et al., 1989, 1993; Grosjean, 1990a,b, 1991a,b,c; Skov et al., 1992; Grosjean et al., 1993a,b, 1996a,b; Bierbach et al., 1994; Kao, 1994).

Given the diversity and abundance of formaldehyde precursors in urban air, secondary atmospheric formation frequently exceeds direct emissions from combustion sources, especially during photochemical air pollution episodes, and it may contribute up to 70–90% of the total atmospheric formaldehyde (Grosjean, 1982; Grosjean et al., 1983; Lowe & Schmidt, 1983). In California, USA, Harley & Cass (1994) estimated that photochemical formation was more important than direct emissions in Los Angeles during the summertime days studied; in winter or at night and in the early morning, direct emissions can be more important. This was also observed in Japan, where the concentrations of formaldehyde in the central mountainous region were not associated directly with motor exhaust but rather were associated with the photochemical oxidation of anthropogenic pollutants occurring there through long-range transport (Satsumabayashi et al., 1995).

4.4 Production and use

Formaldehyde is produced commercially from methanol. The primary methanol oxidation processes use metal catalyst (silver now, previously copper) or metal oxide catalyst (ATSDR, 1999). Similar methods of production are used in many countries worldwide. Table 3 shows the production of formaldehyde by selected countries, with the highest amounts originating from the USA and Japan.

In 1996, the domestic production of formaldehyde in Canada was approximately 222 000 tonnes (Environment Canada, 1997bc); in 1994, domestic production in the USA was 3.6 million tonnes (Kirschner, 1995). The production of formaldehyde worldwide in 1992 was estimated at approximately 12 million tonnes (IARC, 1995).

Total Canadian domestic consumption of formaldehyde was reported at about 191 000 tonnes for 1996 (Environment Canada, 1997b). Formaldehyde is used predominantly in the synthesis of resins, with urea-formaldehyde (UF) resins, phenolic-formaldehyde resins, pentaerythritol, and other resins accounting for about 92% of Canadian consumption. About 6% of uses were related to fertilizer production, while 2% of the formaldehyde was used for various other purposes, such as preservatives and disinfectants (Environment Canada, 1997b). Formaldehyde can be used in a variety of industries, including the medical, detergent, cosmetic, food, rubber, fertilizer, metal, wood, leather, petroleum, and agricultural industries (IPCS, 1989), and as a hydrogen sulfide scavenger in oil operations (Tiemstra, 1989).

Table 3: Production of formaldehyde in selected countries.[a]

	Production (kilotonnes)[b]		
Country or region	**1982**	**1986**	**1990**
Brazil	152	226	N/A
Canada	70	117	106
China	286	426	467
Former Czechoslovakia	254	274	N/A
Denmark	N/A	3	0.3
Finland	N/A	5	48
France	79	80	100
Germany	630	714	680
Hungary	13	11	N/A
Italy	125	135	114
Japan	N/A	1188	1460
Mexico	83	93	N/A
Poland	219	154	N/A
Portugal	N/A	70	N/A
Republic of Korea	N/A	122	N/A
Spain	N/A	91	136
Sweden	N/A	223	244
Taiwan	N/A	204	215
Turkey	N/A	21	N/A
United Kingdom	107	103	80
USA[c]	2185	2517	3048
Former Yugoslavia	108	99	88

[a] From IARC (1995).
[b] N/A = not available.
[c] 37% by weight.

Formaldehyde is often added to cosmetics, in which it acts as a preservative and an antimicrobial agent. Its use in cosmetics is regulated or voluntarily restricted. In Canada, for example, formaldehyde is acceptable for use in non-aerosol cosmetics, provided the concentration does not exceed 0.2% (R. Green, personal communication, 1994). It is also included in the Cosmetic Notification Hot List, with the recommendation to limit its concentration in cosmetics to less than 0.3%, except for fingernail hardeners, for which a maximum concentration of 5% applies (A. Richardson, personal communication, 1999).

In the agriculture industry, formaldehyde has been used as a fumigant, as a preventative for mildew and spelt in wheat, and for rot in oats. It has also been used as a germicide and fungicide for plants and vegetables and as an insecticide for destroying flies and other insects. In Canada, formaldehyde is registered as a pesticide under the *Pest Control Products Act*; about 131 tonnes are applied annually for pest control. Approximately 80% of the slow-release fertilizer market is based on UF-containing products (ATSDR, 1999; HSDB, 1999). In Canada, there are currently 59 pest control products containing formaldehyde registered with the Pest Management Regulatory Agency. Formaldehyde is present as a formulant in 56 of these products, at concentrations ranging from 0.02% to 1% by weight. Formaldehyde is an active ingredient in the remaining three products, at concentrations ranging from 2.3% to 37% in the commercially available products (G. Moore, personal communication, 2000).

Formaldehyde is also used as an antibacterial agent in processing of foodstuffs. For example, the *Food and Drugs Act* allows up to 2 ppm (i.e., 2 mg/kg) formaldehyde in maple syrup resulting from the use of paraformaldehyde to deter bacterial growth in the tap holes of maple trees in Canada (M. Feeley, personal communication, 1996). Formaldehyde is also registered as a feed under the *Feed Act* in Canada.

5. ENVIRONMENTAL TRANSPORT, DISTRIBUTION, AND TRANSFORMATION

The sections below summarize the available information on the distribution and fate of formaldehyde released into the environment. More detailed fate information is provided in Environment Canada (1999a).

5.1 Air

Formaldehyde emitted to air primarily reacts with photochemically generated hydroxyl radicals in the troposphere or undergoes direct photolysis (Howard et al., 1991; US EPA, 1993). Minor processes include reactions with nitrate radicals, hydroperoxyl radicals, hydrogen peroxide, ozone, and chlorine (US EPA, 1993). Small amounts of formaldehyde may also transfer into rain, fog, and clouds or be removed by dry deposition (Warneck et al., 1978; Zafiriou et al., 1980; Howard, 1989; Atkinson et al., 1990; US EPA, 1993).

Reaction with the hydroxyl radical is considered to be the most important photooxidation process, based on the rate constants and the concentrations of the reactants (Howard et al., 1991; US EPA, 1993). Factors influencing the atmospheric lifetime of formaldehyde, such as time of day, intensity of sunlight, temperature, etc., are mainly those affecting the availability of hydroxyl and nitrate radicals (US EPA, 1993). The atmospheric half-life of formaldehyde, based on hydroxyl radical reaction rate constants, is calculated to be between 7.1 and 71.3 h (Atkinson, 1985; Atkinson et al., 1990). Products that can be formed from hydroxyl radical reaction include water, formic acid, carbon monoxide, and the hydroperoxyl/formaldehyde adduct (Atkinson et al., 1990).

Photolysis can take two pathways. The dominant pathway produces stable molecular hydrogen and carbon monoxide. The other pathway produces the formyl radical and a hydrogen atom (Lowe et al., 1980), which react quickly with oxygen to form the hydroperoxyl radical and carbon monoxide. Under many conditions, the radicals from photolysis of formaldehyde are the most important net source of smog generation (US EPA, 1993). When the rates of these reactions are combined with estimates of actinic radiance, the estimated half-life of formaldehyde due to photolysis is 1.6 h in the lower troposphere at a solar zenith angle of 40° (Calvert et al., 1972). A half-life of 6 h was measured based on simulated sunlight (Lowe et al., 1980).

The nighttime destruction of formaldehyde is expected to occur by the gas-phase reaction with nitrate radicals (US NRC, 1981); this tends to be more significant in urban areas, where the concentration of the nitrate radical is higher than in rural areas (Altshuller & Cohen, 1964; Gay & Bufalini, 1971; Maldotti et al., 1980). A half-life of 160 days was calculated using an average atmospheric nitrate radical concentration typical of a mildly polluted urban centre (Atkinson et al., 1990), while a half-life of 77 days was estimated based on measured rate constants (Atkinson et al., 1993). Nitric acid and formyl radical have been identified as products of this reaction. They react rapidly with atmospheric oxygen to produce carbon monoxide and hydroperoxyl radicals, which can react with formaldehyde to form formic acid. However, because of this rapid back-reaction, the reaction of nitrate radicals with formaldehyde is not expected to be a major loss process under tropospheric conditions.

Overall half-lives for formaldehyde in air can vary considerably under different conditions. Estimations for atmospheric residence time in several US cities ranged from 0.3 h under conditions typical of a rainy winter night to 250 h under conditions typical of a clear summer night (assuming no reaction with hydroperoxyl radicals) (US EPA, 1993). During the daytime, under clear sky conditions, the residence time of formaldehyde is determined primarily by its reaction with the hydroxyl

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