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CANADIAN ENVIRONMENTAL PROTECTION
ACT ALDEHYDES (FORMALDEHYDE,
ACETALDEHYDE, AND ACROLEIN)
AND THE FOREST PRODUCTS INDUSTRY

TECHNICAL BULLETIN NO. 874
APRIL 2004

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PRESIDENT'S NOTE

In 2000, Environment Canada and Health Canada published assessments of acetaldehyde and acrolein which concluded that both should be declared toxic under Section 64 of the Canadian Environmental Protection Act (CEPA). In 2001, they published another report that determined that formaldehyde also met the CEPA criteria of a toxic substance. Following those determinations, Environment Canada began to assess appropriate steps to reduce the risks of exposure of all three compounds. These assessments included an examination of the potential need to regulate the forest products industry.

This report summarises important information that will help both the industry and Environment Canada assess the relative importance of forest products industry CEPA aldehydes emissions. The report discusses how formaldehyde is used by the industry and how all three aldehydes may be unintentionally formed during normal production of pulp or wood products.

Earlier source inventories have been updated and expanded to include estimates of emissions from sources not previously included. It becomes clear that the forest products industry emits only a small percentage of the total CEPA aldehydes emissions.

Summarised literature documents that CEPA aldehydes have short half-lives and low octanol-water partition coefficients. Thus the compounds cannot be considered persistent or bioaccumulative, nor would they be subject to long-range transport.

Analytical methods for forest products industry air emissions are well documented, but corresponding methods for effluent or sludge need to be developed and validated. The extensive MACT testing program in the U.S. has provided reliable emission factors for air sources.

This report provides documentation that the forest products industry is not a major source of these compounds. Given that the primary reason for listing aldehydes as CEPA toxic was indoor air exposure, it is not likely that emissions from manufacturing processes are contributing significantly to the general population's exposure to these substances.

Ronald A. Yeske

April 2004

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MOT DU PRÉSIDENT

En 2000, Environnement Canada et Santé Canada publiaient deux évaluations de risques, une sur l'acétaldéhyde et une sur l'acroléine, dans lesquelles on recommandait que ces deux substances soient déclarées toxiques en vertu de l'article 64 de la *Loi canadienne de la protection de l'environnement* (LCPE). En 2001, ces deux ministères publiaient un autre rapport où on déterminait que le formaldéhyde rencontrait aussi les critères de la LCPE en matière de substance toxique. Suite à ces évaluations, Environnement Canada entreprenait d'examiner le type de mesures qui pourrait être mis en place pour réduire les risques d'exposition à ces trois substances, notamment la possibilité d'assujettir l'industrie des produits forestiers à un règlement.

Le présent rapport contient d'importantes informations qui pourront être utiles à l'industrie et à Environnement Canada pour évaluer l'importance relative des émissions aldéhydiques visées par la LCPE qui proviennent de l'industrie des produits forestiers. Le rapport traite de l'utilisation du formaldéhyde dans l'industrie et de la formation fortuite de ces trois aldéhydes durant la fabrication normale de la pâte ou des produits du bois.

Les inventaires antérieurs de ces émissions ont été mis à jour et augmentés pour inclure les émissions estimées de nouvelles sources. Il apparaît clairement que l'industrie des produits forestiers n'émet qu'un faible pourcentage du total des émissions aldéhydiques visées par la LCPE.

Le résumé d'une analyse de la littérature montre que les aldéhydes visées par la LCPE ont des demi-vies qui sont courtes et des coefficients de partage entre l'octanol et l'eau qui sont bas. En conséquence, ces composés ne peuvent être considérés comme persistants ou bioaccumulables, ni être sujet au transport à distance.

Les méthodes pour analyser les émissions atmosphériques de l'industrie des produits forestiers sont bien documentées, mais celles pour les effluents et les boues ont besoin d'être élaborées et validées. Le vaste programme d'échantillonnage MACT qui a eu lieu aux États-Unis a donné des facteurs fiables pour les sources d'émissions atmosphériques.

Le présent rapport fournit de la documentation qui montre que l'industrie des produits forestiers n'est pas une source majeure de ces composés. Étant donné que la principale raison qui a motivé l'ajout des aldéhydes à la liste des substances toxiques de la LCPE est l'exposition à l'air intérieur, il est peu probable que les émissions provenant des procédés de fabrication contribuent de façon significative à l'exposition de la population à ces substances.

Ronald A. Yeske

Avril 2004

CANADIAN ENVIRONMENTAL PROTECTION ACT ALDEHYDES (FORMALDEHYDE, ACETALDEHYDE, AND ACROLEIN) AND THE FOREST PRODUCTS INDUSTRY

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ABSTRACT

Formaldehyde, acetaldehyde, and acrolein have been declared toxic under the Canadian Environmental Protection Act (CEPA). This report summarises information related to these compounds that will provide valuable context as Environment Canada undertakes its obligations under CEPA, as well as what is known about the use and unintentional formation of these compounds by the forest products industry. It updates and expands on earlier inventories of total sources of the compounds. The environmental fate and significance of the compounds are reviewed. Their toxicologies are briefly reviewed and discussed in the context of the bases for their determinations as CEPA toxic. Analytical methods are summarised, and information on emission factors are reviewed or tabulated.

KEYWORDS

acetaldehyde, acrolein, aldehydes, analytical methods, Canadian Environmental Protection Act, CEPA, emission factors, fate, formaldehyde, persistence, toxicology

RELATED NCASI PUBLICATIONS

Technical Bulletin No. 858 (February 2003). *Compilation of 'air toxic' and total hydrocarbon emissions data for sources at kraft, sulfite and non-chemical pulp mills – An update.*

Technical Bulletin No. 774 (January 1999). *Volatile organic compound emissions from wood products manufacturing facilities, Part VII – Test methods, quality assurance/quality control procedures, and data analysis protocol.*

Technical Bulletin No. 773 (January 1999). *Volatile organic compound emissions form wood products manufacturing facilities, Part VI – Hardboard/fiberboard.*

Technical Bulletin No. 772 (January 1999). *Volatile organic compound emissions from wood products manufacturing facilities, Part V - Oriented strandboard.*

Technical Bulletin No. 771 (January 1999). *Volatile organic compound emissions from wood products manufacturing facilities, Part IV - Particleboard.*

Technical Bulletin No. 770 (January 1999). *Volatile organic compound emissions from wood products manufacturing facilities, Part III - Medium density fiberboard.*

Technical Bulletin No. 769 (January 1999). *Volatile organic compound emissions from wood products manufacturing facilities, Part II - Engineered wood products.*

Technical Bulletin No. 768 (January 1999). *Volatile organic compound emissions from wood products manufacturing facilities, Part I - Plywood.*

Technical Bulletin No. 741 (July 1997). *Volatile organic compound emissions from non-chemical pulp and paper mill sources, Part VI – Test methods, quality assurance/quality control procedures, and data analysis protocol.*

Technical Bulletin No. 694 (April 1995). *Oriented strandboard and plywood air emissions databases.*

Technical Bulletin No. 693 (April 1995) *Particleboard and medium density fiberboard air emissions databases.*

Technical Bulletin No. 684 (December 1994). *Volatile organic emissions from pulp and paper mill sources, Part X – Test methods, quality assurance/quality control procedures and data analysis protocols.*

Technical Bulletin No. 679. (October 1994). *Volatile organic emissions from pulp and paper mill sources: Part V – Kraft mill bleach plants.*

NCASI Methods Manual (1999). NCASI Method IM/CAN/WP-99.01 – Impinger/canister source sampling method for selected HAPs at wood products facilities.

NCASI Methods Manual (1998). NCASI Method CI/SG/PULP-94.02 – Chilled impinger/silica gel tube test method at pulp mill sources for methanol, acetone, acetaldehyde, methyl ethyl ketone and formaldehyde.

ALDÉHYDES VISÉS PAR LA LOI CANADIENNE DE PROTECTION DE L'ENVIRONNEMENT (FORMALDÉHYDE, ACÉTALDÉHYDE ET ACROLÉINE) ET L'INDUSTRIE DES PRODUITS FORESTIERS

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RESUME

Le formaldéhyde, l'acétaldéhyde et l'acroléine ont été déclarés toxiques en vertu de la *Loi canadienne de protection de l'environnement* (LCPE). Le présent rapport résume l'information connue sur ces substances en matière d'utilisation et de formation fortuite par l'industrie des produits forestiers. Il contient aussi de l'information qui pourra être utile au moment où Environnement Canada entreprendra de rencontrer ses obligations en vertu de la LCPE. Il met à jour les inventaires antérieurs et les augmente en y intégrant un plus grand nombre de sources pour ces composés. Il examine le devenir et l'importance de ces composés dans l'environnement. Il traite de leurs toxicologies de façon succincte et analyse ces dernières en fonction du contexte qui a amené ces composés à être déclarés toxiques en vertu de la LCPE. Il décrit brièvement les méthodes analytiques, et présente de l'information sur les facteurs d'émission ou les met sous forme de tableaux.

MOTS CLES

acétaldéhyde, acroléine, aldéhydes, devenir, facteurs d'émission, formaldéhyde, LCPE, Loi canadienne de protection de l'environnement, méthodes analytiques, persistance, toxicologie

AUTRES PUBLICATIONS DE NCASI DANS CE DOMAINE

Bulletin technique No. 858 (février 2003). *Compilation of 'air toxic' and total hydrocarbon emissions data for sources at kraft, sulfite and non-chemical pulp mills – An update.*

Bulletin technique No. 774 (janvier 1999). *Volatile organic compound emissions from wood products manufacturing facilities, Part VII – Test methods, quality assurance/quality control procedures, and data analysis protocol.*

Bulletin technique No. 773 (janvier 1999). *Volatile organic compound emissions form wood products manufacturing facilities, Part VI – Hardboard/fiberboard.*

Bulletin technique No. 772 (janvier 1999). *Volatile organic compound emissions from wood products manufacturing facilities, Part V - Oriented strandboard.*

Bulletin technique No. 771 (janvier 1999). *Volatile organic compound emissions from wood products manufacturing facilities, Part IV - Particleboard.*

Bulletin technique No. 770 (janvier 1999). *Volatile organic compound emissions from wood products manufacturing facilities, Part III - Medium density fiberboard.*

Bulletin technique No. 769 (janvier 1999). *Volatile organic compound emissions from wood products manufacturing facilities, Part II - Engineered wood products.*

Bulletin technique No. 768 (janvier 1999). *Volatile organic compound emissions from wood products manufacturing facilities, Part I - Plywood*.

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1.0 INTRODUCTION

In 2000, Environment Canada and Health Canada published assessments of acetaldehyde and acrolein which concluded that both should be declared toxic under Section 64 of the Canadian Environmental Protection Act (CEPA). In 2001, they published another report that determined that formaldehyde also met the CEPA criteria of a toxic substance. Under CEPA, once a compound has been declared toxic, Environment Canada has two years to identify an instrument to reduce amounts of the compound in the environment (either through broad or targeted regulatory or non-regulatory programs), followed by 18 months to implement that instrument. Although formaldehyde was declared toxic later than acrolein and acetaldehyde, Environment Canada chose to address it simultaneously under the earlier timeline.

This report has been compiled to provide both Environment Canada and the forest products industry with background information on what is known about these compounds in the pulp, paper, and wood products industries. It also provides the context necessary to evaluate forest products industry emissions relative to total source emissions, as well as those sources that are primarily responsible for the compounds' listings as CEPA toxics. While not intended as a comprehensive review of available information, the report attempts to present a concise summary of the most relevant information.

The literature concerning the unintentional formation of these compounds in various processes is summarised in Section 2. In the case of formaldehyde, the use of this compound by the panel board industry is discussed. Section 2 also updates and expands on earlier source inventories to put forest products industry emissions into perspective.

Section 3 reviews the environmental fate and significance of the compounds. It addresses fate and persistence in all compartments of the environment, thereby providing the basis for an assessment of the potential for long-range transfer, bioaccumulation, and environmental half-life. The section also briefly reviews the toxicology of the compounds, including the bases for their listings as toxic.

The availability, capability, and limitations of analytical methods is critical to assessing the significance of these compounds and will be important to understand as Environment Canada and the industry move forward. Section 4 reviews analytical methods for aqueous, sludge, soil, sediment, and air samples.

The literature and previous surveys of emissions of these compounds are summarised in Section 5. NCASI has had a very active program documenting air emissions in support of the U.S. industry's MACT-related work and in facilitating reporting for the Toxics Release Inventory. These data are also summarised in Section 5.

2.0   SOURCES AND FORMATION

2.1   Formaldehyde

2.1.1   *Formation in Pulping and Bleaching*

Formation of formaldehyde during pulping can occur through several different mechanisms. Under alkaline conditions, α-guaiacylglycerol-β-arylethers, β5-cyclic α-aryl ethers, and (β-1)-dilignol structures can yield formaldehyde through γ-cleavage (Sarkanen and Ludwig 1971). Under acidic conditions, α-guaiacylglycerol-β-arylethers and (β-1)-dilignol can yield formaldehyde as well (Sarkanen and Ludwig 1971). Thus, many of the common structures found in wood lignin can produce formaldehyde under conditions found in kraft and sulphite pulping. However, under alkaline or acidic conditions, some of the formaldehyde that is formed can add to aryl ether structures to form an aromatic methylol substituent or can react with propane side chain carbonyls via a Tollens reaction to form α-methylol substituted ketones (Marton et al. 1966). Thus, formaldehyde can be both formed and consumed in the pulping process. To the best of NCASI's knowledge, formaldehyde has not been identified in bleach plant effluents. However, given that both acidic and alkaline conditions can lead to formaldehyde formation if the appropriate precursors are present, it would not be surprising to find it in bleach plant filtrates.

2.1.2   *Use in Wet Strength Additives*

Thermosetting resins are added to stock to impart wet strength to certain grades of paper. Example applications include some boxes, paper towels, maps, outdoor posters, food wrap, photographic papers, filter papers, tea bags, and disposable garments and bed sheets (Biermann 1996). Two formulations of thermosetting resins commonly used for this purpose are urea-formaldehyde and melamine-formaldehyde. Between 1988 and 1993, the industry gradually moved away from the urea-formaldehyde wet strength additives to polyamide based materials. The industry now uses polyamides almost exclusively.

2.1.3   *Formation in Wood Drying (e.g., lumber and panel plants)*

Although formaldehyde has been reported in emissions from wood drying or panel board press vents (NCASI 1999a-f; Otwell et al. 2000), no mechanistic studies have yet been undertaken to definitively determine how it was formed. There has been considerable research into pyrolysis products from both wood and cellulose. Some of these studies indicate that formaldehyde can be formed from cellulose under extremely high temperature conditions (Molton and Demmitt 1977). Because these conditions are more extreme than those found in normal wood drying and pressing operations, it can only be interpreted to indicate the potential of cellulose to be the primary precursor and cannot exclude other precursors or even other mechanisms.

2.1.4   *Use in Panel Board Manufacturing (e.g., phenol-formaldehyde and urea-formaldehyde resins)*

Phenol-formaldehyde adhesives are used in manufacturing exterior panel products such as plywood, oriented strand board, and some hardboard. Phenol, resorcinol-formaldehyde adhesives are used for laminated or engineered construction materials (beams, trusses, etc.). Urea-formaldehyde resins are used for decorative and interior products, including particleboard and interior plywood. Due to concerns over formaldehyde release and contamination of indoor air, the industry has been moving towards urea-formaldehyde formulations that have reduced formaldehyde emissions in the final products. A very small amount of melamine-formaldehyde resin is used for some speciality products.

2.1.5 *Comparison with Other Sources*

Environment Canada's Priority Substance List (PSL) Assessment Report for formaldehyde (EC/HC 2000c) notes that formaldehyde can be formed through secondary reactions. It can be generated as a result of the oxidation of methane or other hydrocarbons. The World Health Organization (WHO 1989) estimated global atmospheric production of formaldehyde from methane to be 4×10^{11} kg/year versus a total industrial production of 3.5×10^9 kg/year. This did not include emissions from automobiles, which are significant. However, these estimates do point out that naturally formed formaldehyde production exceeds industrial production by two orders of magnitude.

Environment Canada's PSL Assessment Report for formaldehyde (EC/HC 2000c) also provided some estimates of total annual emissions of formaldehyde. These are summarised in Table 2.1.

Table 2.1 Canadian Estimates of Formaldehyde Releases into the Environment

Source	Tonnes/year
On road releases	11,284
Aircraft emissions	1,730
Marine emissions	1,175
Cigarette smoke	84
Coal-electric power production	0.7 – 23
Hazardous/municipal/medial waste incineration	10.6
Total industrial[a]	1,423.9

[a] based on 1997 National Pollutant Release Inventory (NPRI)

In the report, Environment Canada acknowledges that it did not address a variety of known combustion-related sources (forest fires, wood stoves and furnaces, etc.). It also makes no mention of other non-road sources such as recreational vehicles, lawnmowers, and construction equipment or trains.

In 1996, the U.S. Environmental Protection Agency (USEPA) compiled an inventory of formaldehyde releases to air (USEPA 1996a, National Toxics Inventory [NTI]). Because air emissions clearly dominate the total releases, it is useful to examine the NTI data to evaluate potential misperceptions one might encounter from an incomplete inventory. USEPA's inventory accounted for major source emissions, area and other source emission, on-road emissions, and non-road emissions. These represented 5, 41.9, 25.9, and 27.2% of the total inventory, respectively. The nonpoint source documentation report indicated that the area and other emissions category may be low because it only inventoried emissions from forest fires and prescribed burning on federal lands, not private sector or state managed lands (ERG 2002). Although exact comparisons cannot be made between the U.S. and Canadian inventories, they do help put the potential significance of sources not inventoried by Environment Canada into perspective. For instance, the U.S. non-road category overlaps with the aircraft and marine estimates incorporated into the Canadian inventory, but also goes on to include trains and recreational vehicles. If these practices are comparable in the U.S. and Canada, the Canadian inventory may be low by as much as 8000 tonnes. Because almost 42% of the U.S. inventory is in area and other sources which are not accounted for in the Canadian inventory, there could be another 15,000 tonnes left unaccounted. Together, these two omissions suggest that the Canadian inventory could be as much as 70% low.

In the 1997 National Pollutant Release Inventory (NPRI) used in the CEPA PSL Assessment Inventory, the total formaldehyde releases from the Paper and Allied Industries and the Wood Industries were 47.23 and 993.38 tonnes, respectively (EC 2002). These totals might be somewhat low, as comparatively few facilities reported releases. The number of Paper and Allied Industries facilities reporting formaldehyde releases in 1999 was higher, and in that year a total of 112.54 tonnes was reported. The 1999 figure for the Wood Industries category was 1269.37 tonnes.

The 2001 NPRI reported total releases of formaldehyde to the environment of 1736.33 tonnes. Of this, the Wood Industries accounted for 82% and the Paper and Allied Industries accounted for 5%. However, when the Wood Industries and the Paper and Allied Industries releases are compared to the total emissions inventoried in Environment Canada's Assessment document, they represent only 6.3 and 0.3%, respectively. Given the significance of the sources that were not included in the Canadian inventory, these represent an overestimation of the forest products industry contribution. NCASI estimates that these percentages could drop to 4 and 0.2 % if the inventory had included other significant sources. This is a very rough estimate and is provided only to give a general sense of the importance of these sources relative to the total. A more thorough inventory should be undertaken to develop more accurate estimates.

2.2   Acetaldehyde

2.2.1   *Formation in Pulping and Bleaching*

The potential for formation of acetaldehyde in pulping has long been recognised (Adler and Haggroth 1949). It has been suggested that a possible mechanism is α–β cleavage of coniferaldehyde end groups in lignin (Sarkanen and Ludwig 1971). Bailey and Dence (1969) also showed that acetaldehyde could be released by the action of alkaline hydrogen peroxide on spruce milled groundwood lignin and spruce groundwood.

Acetaldehyde was first identified in chlorination stage filtrates by Ota, Durst, and Dence (1973). Limited ECF bleach plant filtrate analyses indicated that acetaldehyde may also be present in modern bleaching sequences (NCASI 1994a).

NCASI is not aware of any systematic studies that examine the formation of acetaldehyde as a function of pulping or bleaching process variables. All acetaldehyde found in the pulping and bleaching process is due to unintentional by-product formation. Acetaldehyde is not used as a pulping chemical nor is NCASI aware of its presence in any process additives.

2.2.2   *Formation in Wood Drying*

As was the case for formaldehyde, NCASI is not aware of any published reports that address the formation mechanism for acetaldehyde in wood drying operations. However, the same review of reaction mechanisms for the pyrolysis of cellulose lists acetaldehyde as one of the known products. Thus, it is likely that cellulose is at least one of the precursors.

2.2.3   *Comparison with Other Sources*

Environment Canada's CEPA PSL Assessment noted that acetaldehyde can be formed from a wide range of organic compounds via photochemical oxidation (EC/HC 2000a). This is of greatest significance in urban areas where precursor hydrocarbons are abundant. In California, for example, photochemical oxidation is responsible for 41 to 67% of the atmospheric acetaldehyde.

A limited acetaldehyde anthropogenic source inventory was included in the PSL Assessment Report for acetaldehyde (EC/HC 2000a). This inventory is summarised in Table 2.2 along with the total industry emissions reported in the 1996 NPRI.

Table 2.2   Canadian Estimates of Acetaldehyde Releases into the Environment – 1994

Source	Tonnes/year
On road releases	3,290
Aircraft emissions	677
Cigarette smoke	5 – 76
Coal-electric power production	28
Hazardous/municipal/medial waste incineration	2.6
Total industrial[a]	525.37

[a]   based on 1996 National Pollutant Release Inventory (NPRI)

As noted for the formaldehyde assessment document, many combustion sources (forest fires, wood stoves and furnaces, furnaces, power plants, etc.) were not included in the inventory, nor did it examine marine and other non-road emissions other than those from aircraft. Thus, it could be seriously underestimating the total acetaldehyde released into the Canadian environment.

In the 1996 NPRI (EC 2002), the total acetaldehyde releases from the Paper and Allied Industries were 193.7 tonnes. No releases were reported from the Wood Industries. These totals are probably low due to lack of information on emissions factors that early in the NPRI program. The number of Paper and Allied Industries facilities reporting acetaldehyde releases in 1999 was higher, and in that year a total of 419.61 tonnes was reported. The 1999 figure for the Wood Industries was 310.91 tonnes.

The 1996 USEPA National Toxics Inventory was again used to examine the potential for underestimating total Canadian acetaldehyde emissions. The 1996 NTI estimated total air emissions for acetaldehyde of 197,678,754 pounds. USEPA indicated that some significant sources such as prescribed burning and forest fires were underestimated because the NRI only included data from federally managed lands. The distribution among the different sources was a) major source emissions, 8.9%; b) area and other emissions, 19.9%; c) on-road emissions, 29.3%; and d) non-road emissions, 42%. Thus, by omitting the non-area emissions and only partially accounting for the non-road emissions (e.g., accounting for only the aircraft emissions), the Canadian inventory could be close to 60% low.

The 2001 NPRI (EC 2002) reported total releases of acetaldehyde to the environment of 1095.52 tonnes. Of this, the Wood Industries accounted for 32% and the Paper and Allied Industries accounted for 59%. However, when the Wood Industries releases are compared to the total emissions inventoried in Environment Canada's assessment document, they represent only 4.2%. Given the significance of the sources that were not included in the Canadian inventory, these represent an overestimation of forest products industry contributions. NCASI estimates that the contribution of the Wood Industries could drop to 3% if the inventory had included other significant sources. It was also estimated (using the 2001 NPRI data) that the Paper and Allied Industries would contribute 6% to the total emissions. This is a very rough estimate and is provided only to give a general sense of the importance of these sources relative to the total. A more thorough inventory should be undertaken to develop more accurate estimates.

2.3   Acrolein

2.3.1   *Formation in Pulping and Bleaching*

NCASI is unaware of any research that suggests a mechanism for formation of acrolein in either pulping or bleaching. An examination of information on a wide range of process additives found no evidence that acrolein is part of the formulations. Thus, NCASI believes that all acrolein releases are attributable to unintentional production during either pulping or bleaching.

2.3.2   *Formation in Wood Drying (e.g., lumber and panel plants)*

As with formaldehyde and acetaldehyde, NCASI is not aware of any published reports that address a formation mechanism for acrolein in wood drying operations. However, the same review of reaction mechanisms for the pyrolysis of cellulose lists acrolein as one of the known products. Thus, it is likely that cellulose is at least one of the precursors.

2.3.3   *Comparison with Other Sources*

The PSL Assessment Report for acrolein (EC/HC 2000b) estimated selected Canadian acrolein emission sources for 1995. The inventories sources are summarised in Table 2.3. The report acknowledges that off-road vehicle emissions (which were not included) could be greater than on-road releases. It notes, but does not inventory, other sources such as forest fires, prescribed burning, wood stoves and furnaces, natural gas furnaces, smelters, and other electric power generation plants. Acrolein is also used as a pesticide (herbicide for controlling vegetation in irrigation ditches) and is regulated under the Pest Control Products Act.

Table 2.3   Canadian Estimates of Acrolein Releases into the Environment – 1995

Source	kg/year
Road motor vehicles	209,000 – 2,730,000
Oriented strand industry	3,208 – 25,664
Pulp and paper (kraft) mills	3,747 – 18,735
Waste incineration	2,435
Coal based electric power generation	467 – 17,504

The lower numbers for oriented strand board (OSB) and pulp and paper in the table reflect reported emissions from a limited number of facilities. The larger numbers are estimates using the emissions factors of the limited reports applied to all facilities. According to the 2001 NPRI (EC 2002), Wood Industries released 120.19 tonnes of acetaldehyde and there were no reported Paper and Allied Industries releases of acrolein. The Wood Industries release reports were dominated by two major corporations, suggesting that the total may be low because not many facilities have information about their emissions. It does appear that the PSL Assessment Report for acrolein may have overestimated both OSB and pulp and paper emissions. Again, comparison of these data to the U.S. NTI data is helpful in understanding the significance of the omissions in the Canadian inventory. The 1996 NTI of air releases reported that major source emissions accounted for 0.7%, area and other sources accounted for 60.4%, on-road emissions accounted for 15.6%, and non-road emissions accounted for 23.2%.[1] As noted, the 1996 NTI report points out that area and other source emissions are low biased

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[1] The NTI background documents indicate that in some instances, AP-42 emissions factors are used to estimate releases. NCASI has not been able to assess to what extent USEPA relied on these emissions factors to

because only federal land forest fires and prescribed burning were included. If these figures are representative of the non-inventoried sources in Canada, the Canadian estimate may be close to 85% low.

Given that the assessment inventory omitted several significant sources and may have overestimated forest products industry emissions, it is difficult to compare the Wood Industries releases to a total source inventory. NCASI estimated the sources that were not inventoried by Environment Canada using the USEPA 1966 NTI ratios as a guide. The 2001 NPRI Wood Industries was then compared to that estimated total, and accounted for about 2% of the total. This is a very rough estimate and is provided only to give a general sense of the importance of this source relative to the total. A more thorough inventory should be undertaken to develop more accurate estimates.

3.0   ENVIRONMENTAL FATE AND SIGNIFICANCE

3.1   Formaldehyde

3.1.1   *Environmental Fate and Persistence*

The environmental fate and persistence of formaldehyde has been reviewed and summarised by a number of different organisations (WHO1989; EC/HC 2000c; Liteplo et al. 2002; USDHHS 1999; NCASI 1999a-f). Their observations are summarised herein.

Formaldehyde in air degrades photochemically with hydroxyl radicals during the day or reacts with nitrate radicals at night. The factors that affect the half-life are time of day, sunlight intensity, temperature, and concentrations of hydroxyl and/or nitrate radicals. Daytime half-life estimates range from as short as 1.8 hours to as long as 120 hours, with a median half-life of 8.7 hours. The night-time half-life has been estimated to be 77 to 160 days. Due to these short half-lives, long-range transport of formaldehyde is not likely to be a problem. In addition, due to high water solubility, some atmospheric formaldehyde can be washed out via rain.

Formaldehyde released in either surface or ground water is subject to rapid biodegradation. Estimated half-lives range from 24 to 168 hours in surface water and from 48 to 336 hours in groundwater. Due to the Henry's Law constant, formaldehyde in water is likely to stay in the water and will not volatilise readily.

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predict emissions from particleboard plants and veneer dryers. In calculating the AP-42 factors, USEPA used a value of one-half of the detection limit for all non-detect sample runs if any acrolein was detected in the applicable source category. For example, at particleboard sanders, all runs for acrolein were non-detect and a zero value (or BDL) was placed in the AP-42 and used in this report. However, for some categories, such as veneer dryers and particleboard presses, where 10% or less of the acrolein sample runs were detectable, the use of one-half of the detection limit inflated the estimated acrolein emissions from these sources. For particleboard presses, 24 of 26 acrolein sample runs were non-detect, and for veneer dryers, 102 of 113 sample runs were non-detect. It is likely that only certain types of veneer dryers or particleboard presses emit detectable levels of acrolein. It is also possible that some of the data points are false positives and that few or perhaps none of the particleboard presses or veneer dryers emitted detectable levels of acrolein (75% of the 432 acrolein sample runs used in development of the AP-42 factors were non-detect).

It is reasonable to assume that many particleboard and softwood plywood mills will be unable to detect acrolein in their exhausts and that these mills, based on site-specific testing and modelling, will not model acrolein above health benchmarks.

Formaldehyde has a very low octanol-water partition coefficient, so it is not likely to partition onto sediment or soil solids. The low octanol-water partition coefficient also indicates that formaldehyde is not likely to bioconcentrate. Formaldehyde in soils is subject to biodegradation.

3.1.2   *Toxicology*

Basis for listing of formaldehyde as a CEPA toxic

Studies in experimental animals have shown that inhalation of formaldehyde may produce tumours in the upper respiratory tract, primarily in the nasal region. Although cytotoxicity followed by sustained regenerative proliferation has been shown to play an important role in the induction of tumours, direct interaction with DNA is also likely to be a factor. Therefore, formaldehyde is listed as a CEPA toxic under CEPA 1999 64(c), potential for harmful effects on human health.

Formaldehyde also meets the criteria for listing under CEPA 1999 64(b), danger to the environment on which life depends, because of its contribution to the formation of ground-level ozone. Formaldehyde does not meet the criteria for listing as a CEPA toxic under CEPA 1999 64(a), harmful effect on the environment or its biological diversity.

Potential for harmful effects on human health

Formaldehyde has been demonstrated to cause nasal tumours in rats exposed via inhalation. Tumours have been observed only at exposure concentrations sufficient to produce DNA-protein crosslinks and sustained cytotoxicity with resultant regenerative cellular proliferation. Although the anatomy and airflow patterns of rat and human nasal passages and respiratory tract are significantly different, it is reasonable to suspect that exposure of humans to concentrations of formaldehyde high enough to produce sustained cytotoxicity, cellular proliferation, and DNA-protein crosslinks at some site within the upper respiratory tract may present a carcinogenic hazard.

For ambient air, Health Canada has calculated a tumourigenic concentration[2] (TC_{05}) associated with a 5% increase in nasal tumour incidence based on the data from rat studies. The TC_{05} is 9.5 mg/m^3 and the lower 95% confidence limit of the TC_{05} (TCL_{05}) is 7.9 mg/m^3.

Health Canada has also calculated a tolerable concentration (TC) for non-cancer effects based on gastrointestinal effects observed in rats exposed to formaldehyde in drinking water. The drinking water TC is 2.6 mg/m^3.

Formaldehyde is known to produce ocular and upper respiratory sensory irritation in humans at ambient air concentrations above about 120 μg/m^3.

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[2] The tumourigenic concentration is calculated by applying a mathematical model called the Multi-Stage Model to data on tumour incidence and exposure levels from a study in which the experimental subjects developed cancer. The TC_{05} represents the exposure concentration at which 5% of the experimental subjects developed cancerous tumours. When the TC_{05} is calculated, a 95% confidence interval for that number is also calculated. As an added measure of conservatism, the TCL_{05}, which is the lower 95% confidence limit for the TC_{05}, is often used in regulatory decision-making. In calculating a tumourigenic concentration, the exposure level associated with a 5% increase in tumour formation is typically used because a 5% increase is the smallest increase that can be statistically differentiated from background tumour incidence levels.

Factors relevant to consideration of the significance of the contribution of forest products industry emissions of formaldehyde in relation to emissions of formaldehyde from other sources

The mean time spent outdoors by an average member of the population in a 24 hour period is 3 hours. Concentrations of formaldehyde in indoor air are consistently higher than in ambient air. In general, concentrations of pollutants in indoor air are not related to concentrations of those same substances in outdoor air. Thus, the bulk of exposures of humans to formaldehyde come from indoor sources such as cigarette smoke, building materials, consumer products, and cooking. The PSL Assessment Report for formaldehyde reported that "[t]he general population in Canada is exposed to low concentrations of formaldehyde in outdoor air and to generally higher concentrations in indoor air."

The authors of the PSL Assessment Report for formaldehyde concluded that signs of ocular and upper respiratory sensory irritation in humans are not likely to be observed at concentrations found in outdoor ambient air, but may be observed in some indoor locations.

In the same report, Environment Canada and Health Canada also concluded that "[t]he risks of upper respiratory tract cancer predicted by the biologically motivated case-specific model...are also exceedingly low...Based on this estimate of risk, priority for investigation of options to reduce exposure in relation to the carcinogenicity of formaldehyde is low." The authors further noted that this biologically motivated case-specific model "is clearly preferred as a basis for characterisation of exposure-response for cancer for formaldehyde..."

Environment Canada and Health Canada concluded that formaldehyde entering the environment in any media is not a threat to the environment or its biological diversity. In addition, in the PSL Assessment Report for formaldehyde, they stated that "[t]here is a moderate degree of certainty that consumption of drinking water does not contribute significantly to the daily intake of formaldehyde..." Therefore, air emissions are the only forest products industry emissions that have relevance to formaldehyde emissions in the context of CEPA toxics.

3.2   Acetaldehyde

3.2.1   *Environmental Fate and Persistence*

Various aspects of the environmental fate and persistence of acetaldehyde have been reviewed and summarised by a number of organisations (EC/HC 2000a; De Fouw 1995; NCASI 1999a-f). Their observations are summarised herein.

The principal degradation pathway for atmospheric acetaldehyde is photochemical reaction with hydroxyl radicals. Other minor degradation reactions are photolysis with nitrate or hydroperoxyl radicals, or reaction with ozone. Because the primary pathway involves hydroxyl radicals, it is the most important factor in determining the half-life of acetaldehyde. Other factors include time of day, sunlight intensity, and temperature. Night-time degradation is dominated by reactions with nitrate radicals. Daytime half-life estimates range from 0.7 to 19.1 hours for photochemical reactions and from 33 to 46 hours for hydroxyl reactions. The median of the reported half-lives was nine hours in daylight. Night half-lives were estimated to be approximately 59.6 hours. Due to these short half-lives, long-range transport of acetaldehyde is not significant. The high water solubility of acetaldehyde causes some of the compound to be washed out of the atmosphere by rain or fog; however, this is probably a minor mechanism for removal.

Acetaldehyde is rapidly biodegraded when released in surface waters. It can also undergo oxidation or can volatilise into the air. The estimated overall half-life in water is between 30 and 100 hours.

Acetaldehyde has a very low octanol-water partition coefficient, so it is not likely to partition onto sediment or soil solids, nor will it bioconcentrate in aquatic organisms.

3.2.2   *Toxicology*

Basis for listing of acetaldehyde as a CEPA toxic

Studies in experimental animals have shown that inhalation of acetaldehyde may produce tumours in the upper respiratory tract, primarily in the nasal region. The mechanism is uncertain, but direct interaction with DNA cannot be ruled out. Thus, acetaldehyde is listed as a CEPA toxic under CEPA 1999 64(c), potential for harmful effects on human health.

Acetaldehyde does not meet the criteria for listing as a CEPA toxic under the categories described under CEPA 1999 64(a), harmful effect on the environment or its biological diversity. Acetaldehyde does, however, meet the criteria for listing under CEPA 1999 64(b), danger to the environment on which life depends, because of its contribution to the formation of ground-level ozone.

Potential for harmful effects on human health

In long-term inhalation studies in rats and hamsters, upper respiratory tract tumours developed at acetaldehyde exposure concentrations high enough to produce damage to tissues of the respiratory tract. Although limited studies indicate that the potential for other adverse health effects may exist, these effects occur only at exposure concentrations significantly higher than those shown to produce respiratory tract effects. It is reasonable to expect that similar respiratory effects may be observed in humans, although the site(s) of damage and exposure concentrations associated with such effects may be different than those observed in experimental animals.

For acetaldehyde in ambient air, Health Canada has calculated both a tolerable concentration (TC) for non-cancer effects and a tumourigenic concentration (TC_{05}) associated with a 5% increase in tumour incidence based on the data from rat studies. The TC, based on the development of non-neoplastic lesions in the nasal olfactory epithelium, is 390 μg/m^3. The TC_{05} for nasal adenocarcinomas and squamous cell carcinomas in male rats is 86 mg/m^3 and the lower 95% confidence limit of the TC_{05} (TCL_{05}) is 28 mg/m^3.

Factors relevant to consideration of the significance of the contribution of forest products industry emissions of acetaldehyde in relation to emissions of acetaldehyde from other sources

The mean time spent outdoors by an average member of the population in a 24 hour period is 3 hours. Concentrations of acetaldehyde in indoor air are consistently about ten times higher than levels in ambient air. In general, concentrations of pollutants in indoor air are not related to concentrations of those same substances in outdoor air. Thus, the bulk of exposures of humans to acetaldehyde come from indoor sources such as consumer products, cigarette smoke, building materials, and cooking.

The PSL Assessment Report for acetaldehyde concluded that "the priority for investigation of options to reduce exposure in the general population in the ambient environment is considered to be moderate only;" and "[i]n general, therefore, investigation of options to reduce exposure in the context of CEPA is not considered a high priority..."

Environment Canada and Health Canada concluded that acetaldehyde entering the environment in any medium is not a threat to the environment or its biological diversity. Furthermore, human health is not at risk from ingestion of acetaldehyde in drinking water since the levels of exposure at which health effects have been reported are orders of magnitude higher than those reported in drinking water. For that matter, the levels of acetaldehyde in fruit juices and wines are typically higher than

those reported in drinking water. Therefore, air emissions are the only forest products industry emissions that have relevance to acetaldehyde emissions in the context of CEPA toxics.

3.3   Acrolein

3.3.1   *Environmental Fate and Persistence*

Various aspects of the environmental fate and persistence of acrolein have been reviewed and summarised by a number of organisations (EC/HC 2000b; Gomes, Meek, and Eggleton 2002; Vermeire 1992; USDHHS 1999). Their observations are summarised herein.

The principal degradation pathway for atmospheric acrolein is photochemical reaction with hydroxyl radicals. Other minor degradation reactions are photolysis with nitrate or reaction with ozone. Daytime half-life estimates based on reactivity with hydroxyl radicals range from 3.4 to 33.7 hours. The overall reactivity based half-life is estimated at <10 hours. Due to these short half-lives, acrolein is not a candidate for long-range transport. The high water solubility of acrolein causes some of the compound to be washed out of the atmosphere by rain or fog; however, this is probably a minor mechanism for removal.

Acrolein released into surface waters is influenced by biodegradation, volatilisation, and a reversible hydration. Groundwater-borne acrolein is only degraded by biodegradation and hydrolysis. The range of estimated half-lives is from 30 to 100 hours for surface water and from 14 to 56 days for groundwater. Due to the relatively short half-lives, long-range transport is unlikely.

Acrolein in sediments is biodegraded, hydrolysed, volatilised, or self-oxidised. Half-lives in sediment are estimated to be 7.6 hours and 10 days for aerobic and anaerobic sediments, respectively. Similarly, acrolein in soil is degraded by biodegradation, hydrolysis, volatilisation, or irreversible sorption. Reactivity based half-life estimates are from 430 to 100 hours.

Due to the low octanol-water partition coefficient, high water solubility, and short half-life, it is highly unlikely that acrolein will accumulate in biota.

3.3.2   *Toxicology*

Basis for listing acrolein as a CEPA toxic

Acrolein has been listed as a CEPA toxic under CEPA 1999 64(c), potential for harmful effects on human health, primarily because of studies in which inhalation exposures produced non-neoplastic lesions and other histopathological changes in respiratory tract tissues of experimental animals.

Acrolein does not meet the criteria for listing as a CEPA toxic under the categories described under CEPA 1999 64(a), harmful effect on the environment or its biological diversity, or under CEPA 1999 64(b), danger to the environment on which life depends.

Potential for harmful effects on human health

In multiple acrolein inhalation exposure studies using several different species of experimental animals (rat, mouse, guinea pig, dog, monkey), degenerative changes were observed in tissues of the respiratory tract, although the specific location of these changes and the exposures required to elicit them varied between species. It is reasonable to expect that similar respiratory effects may be observed in humans, although the site(s) of damage and exposure concentrations associated with such effects may be different than those observed in experimental animals.

Health Canada has calculated a tolerable concentration (TC) for non-cancer effects based on a short-term study with rats. The TC for acrolein is 0.4 µg/m^3, based on the development of non-neoplastic lesions in nasal respiratory epithelium.

There is also some evidence that administration of acrolein in drinking water to experimental animals can produce non-neoplastic lesions in the gastrointestinal tract. A provisional TC of 1.5 µg/L for acrolein in drinking water has been developed based on preliminary data from a study with rats.

Factors relevant to consideration of the significance of the contribution of forest products industry emissions of acrolein in relation to emissions of acrolein from other sources

The mean time spent outdoors by an average member of the population in a 24 hour period is 3 hours. Concentrations of acrolein in indoor air are consistently higher than levels in ambient air. In general, concentrations of pollutants in indoor air are not related to concentrations of those same substances in outdoor air. Thus, the bulk of exposures of humans to acrolein come from indoor sources such as cigarette smoke, building materials, and cooking. The PSL Assessment Report for acrolein concluded that "[f]or the general population, the contribution of ambient air to overall exposure to inhaled acrolein is expected to be small compared with the contribution from indoor air (and cigarette smoking)."

Environment Canada and Health Canada concluded that acrolein entering the environment in any medium is not a threat to the environment or its biological diversity. In addition, in the PSL Assessment Report for acrolein, they stated that "[t]here is a high degree of certainty that consumption of drinking water does not contribute significantly to the daily intake of acrolein..." Therefore, air emissions are the only forest products industry emissions that have relevance to acrolein emissions in the context of CEPA toxics.

4.0   ANALYTICAL METHODS

Thorough reviews of published analytical procedures for various media (air, water, biota, soil, and sediment) have been performed previously (formaldehyde: Liteplo et al. 2002; USDHHS 1999; WHO 1989) (acetaldehyde: de Fouw 1995) (acrolein: USPHS 1990; Vermeire 1992). This section attempts to characterise the methods and their validation for use on forest products industry samples.

4.1   Formaldehyde

4.1.1   *Air Monitoring*

Several different test methods are available for source formaldehyde emissions testing. NCASI has used the chilled impinger train method and the DNPH method for measuring formaldehyde emissions from pulp and paper mill sources. In the chilled impinger method, the source gas is drawn through a series of midget impingers containing chilled water. The formaldehyde captured in the chilled water is reacted with acetylacetone and the coloured derivative is measured by colourimetric analysis (NCASI 1998). For the DNPH method, NCASI used sorbent tubes containing 2,4-dinitrophenyl-hydrazine-coated silica gel to capture formaldehyde. The sorbent tubes were desorbed with acetonitrile and analysed by high performance liquid chromatography (NCASI 1997). In its widely used form, the DNPH method (also called Method 0011) utilises an impinger containing 2,4-DNPH in 2N hydrochloric acid to derivatise formaldehyde. The derivative is extracted and analysed by HPLC (USEPA 1996b).

NCASI studies and data analyses have shown that different test methods can give different results when used for measuring formaldehyde emissions from wood products industry sources (Word, Elia,

and Jain 1996). In its most recent studies of wood products industry sources, NCASI used the chilled impinger/canister method for measuring formaldehyde emissions (NCASI 1999g). The method is described in the NCASI Methods Manual as Method IM/CAN/WP-99.01 (NCASI 1999h). For formaldehyde determination with this method, the source gas is drawn through a series of three chilled impingers containing water to capture formaldehyde. The formaldehyde in the impinger solution is reacted with acetylacetone and the derivative is measured by colourimetric analysis.

4.1.2   *Aqueous*

NCASI utilised USEPA Method SW-846 Method 8315 to determine formaldehyde concentrations in bleach plant filtrates (NCASI 1994a); however, no quality control or method validation work was presented or summarised. The procedure uses 2,4-dinitrophenylhydrazine to derivatise formaldehyde to its corresponding 2,4-dinitrophenylhydrazone at pH 3, followed by extraction, concentration, and analysis by HPLC using UV detection. NCASI conducted a very limited evaluation of Method 8315 compared to *Standard Methods* 20th Ed. Method 6252B and an in-house method under development. Method 6252B buffers the sample to pH 6, then derivatises the formaldehyde using o-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) at 45°C for 2 hours. The PFBHA derivatives are extracted and can be analysed by GC-ECD or by GC/MS. NCASI used GC/MS in the selected ion mode (SIM). The method under development substitutes benzyl-hydroxylamine (BHA) for the derivatisation reagent and works up the sample in essentially the same manner as Method 6252B.

Although not conclusive, it appears that Method 6252B and the BHA method under development have the potential to create formaldehyde (as an analytical artefact) during the derivatisation procedure, thus leading to a high bias. This preliminary observation requires further study and confirmation, but care should be taken in interpreting any formaldehyde data (especially any produced using Method 6252B) until a method can be fully tested and validated.

NCASI is not aware of any other procedures being applied to the determination of low level formaldehyde in forest products industry samples.

Formaldehyde determinations are highly prone to field and laboratory contamination due to the ubiquitous nature of formaldehyde. Thus, the limiting factor in analytical sensitivity is often the ability of a laboratory to control this spurious contamination. In the comparative study described herein, the lower calibration limits and reliable reporting levels (e.g., above background/blank levels) were 20 μg/L and 10 μg/L for Method 8315 and Method 6252B, respectively.

Given that formaldehyde is readily biodegraded, some form of sample preservation or storage stability needs to be studied.

4.1.3   *Solids – Sludge, Soil, and Sediment*

NCASI is not aware of any procedures being applied or validated for determination of low level formaldehyde in forest products industry sludge, soil, or sediment samples. However, Elia and Messmer (1996) reported on a comparison of chromotropic acid, 2,4-dinitrophenylhydrazine, and acetylacetone analysis procedures for formaldehyde resin-containing wood dust. They found that the aggressive conditions of the 2,4-dinitrophenylhydrazine and chromotropic acid procedures tended to release formaldehyde from the resin (thus leading to a high bias), while the acetylacetone method appeared to measure just the free formaldehyde found in the samples.

4.2   Acetaldehyde

4.2.1   *Air Monitoring*

NCASI has developed and used two methods for measuring acetaldehyde emissions from pulp and paper mill sources. These include a) NCASI Method CI/SG/PULP-94.02 – Chilled Impinger/Silica Gas Tube Test Method at pulp and paper mill sources for methanol, acetone, acetaldehyde, methyl ethyl ketone, and formaldehyde; and b) NCASI Dilution Probe/Ambient Temperature Canister Method for Source Sampling (NCASI 1997). The chilled impinger/silica gel method absorbs acetaldehyde in the impinger water and on the silica gel tube. The impinger water is analysed on a GC/FID through direct injection. The silica gel sorbent is desorbed with n-propanol and analysed for acetaldehyde using GC/FID. In the dilution probe/ambient canister method, the sample is extracted from the source, diluted with air, and captured in an evacuated SUMMA canister. The canister gases are cryogenically preconcentrated and analysed for acetaldehyde using a GC equipped with a mass selective detector.

For wood products mills and panel plant sources, NCASI has developed the impinger/canister source sampling method for selected HAPs at wood products facilities (NCASI 1999h). In this method, the source gas is drawn through a series of three chilled impingers containing water. A portion of the gas exiting the vacuum pump is drawn into an evacuated stainless steel canister. The impinger contents are analysed for acetaldehyde on a GC equipped with an FID. The canister contents are analysed by cryogenic preconcentration followed by injection into a GC equipped with a mass selective detector.

4.2.2   *Aqueous*

NCASI reported the determination of acetaldehyde in bleach plant filtrates by Method 8315 but, as noted, no supporting QC or method validation data were provided (NCASI 1994a). The Method Detection Limit (MDL) published by USEPA is 43.7 µg/L, but this is probably a high biased estimate due to the high spiking level used in the MDL study.

NCASI also examined USEPA SW-846 Method 5031 followed by GC/FID analysis. Because the scope of the NCASI evaluation fell short of a full validation but proved promising and potentially useful, the method is included in the NCASI Methods Manual as NCASI Method MD-99. The acetaldehyde Method Detection Limit as determined by the procedure described in 40 CFR 136 Appendix B was 45.4 µg/L.

NCASI is not aware of any other analytical procedures being applied to the analysis of acetaldehyde in forest products industry wastewaters.

No acetaldehyde analytical procedures are currently fully validated for application to forest products industry wastewater analyses, nor are there any published storage time or sample preservation procedures.

4.2.3   *Solids – Sludge, Soil, and Sediment*

NCASI is unaware of any procedures being applied or validated for determination of low level acetaldehyde in forest products industry sludge, soil, or sediment samples.

4.3   Acrolein

4.3.1   *Air Monitoring*

NCASI has used a number of methods for measuring acrolein emissions from pulp and paper mill sources. These include the heated SUMMA canister method and the dilution probe/ambient canister

method. In the heated canister method, the source gas is collected in an evacuated, heated canister and analysed using a GC equipped with an FID. A mass selective detector is used for confirming the presence of the analyte (NCASI 1994b). The details of the dilution probe/ambient canister method are included in NCASI Technical Bulletin No. 741 (NCASI 1997). In this method, the sample gas is extracted from the source, diluted with air, and captured in an evacuated SUMMA canister. The canister contents are cryogenically preconcentrated and analysed for acrolein using a GC equipped with a mass selective detector.

NCASI has used the impinger/canister method for measuring acrolein emissions from wood products sources and panel plants. The details of this method are provided in the *NCASI Methods Manual* (NCASI 1999h). In this method, the source gas is drawn through a series of three chilled impingers containing water. A portion of the gas exiting the vacuum pump is drawn into an evacuated stainless steel canister. The impinger contents are analysed on a GC equipped with an FID. The canister contents are analysed by cryogenic preconcentration followed by injection into a GC equipped with a mass selective detector.

4.3.2 *Aqueous*

NCASI reported the determination of acrolein in bleach plant filtrates by Method 8315 but, as noted, no supporting QC or method validation data were provided (NCASI 1994a). USEPA did not include acrolein in the analyte list for Method 8315, so it did not report a Method Detection Limit.

NCASI examined the applicability of NCASI Method MD-99 for the analysis of acrolein in pulp mill wastewaters. However, due to generally poor precision and variable and low recovery of matrix spikes, acrolein was not included in the final analyte list of the proposed method.

During the data gathering phase of the Cluster Rule, USEPA utilised its Office of Water Method 1624B to analyse for acrolein. This method is an isotope dilution, purge and trap GC/MS procedure. Unfortunately, USEPA does not routinely perform laboratory duplicates or matrix spike recoveries, so the performance of this procedure is unknown. Due to the limited availability and high cost of the labelled standards required, this is a very expensive procedure and few laboratories offer to perform it.

4.3.3 *Solids – Sludge, Soil, and Sediment*

NCASI is unaware of any procedures being applied or validated for determination of low level acrolein in forest products industry sludge, soil, or sediment samples.

5.0 EMISSION FACTORS

5.1 Formaldehyde

5.1.1 *Pulp and Paper Mills*

Air

Trace amounts of formaldehyde may be emitted from several sources in a typical pulp and paper mill. This section provides an estimate for typical emissions of formaldehyde from an example bleached kraft pulp mill.

Example bleached kraft pulp mill: A kraft mill produces 1100 ADTUBP/d which is then bleached after O_2 delignification to produce 1000 ADTBP/d. The pulping process generates 1.65 t BLS per ADTUBP, and 0.275 t CaO is regenerated in the lime kiln per ADTUBP. The final product is

1000 ADT/d of bleached paper. The mill operates a 540 GJ/hr wood-fired boiler and two DCE recovery furnaces.

Table 5.1 shows the vast majority of the formaldehyde emitted from operations at this example mill as estimated using average reported emissions in an NCASI report (NCASI 2003). Total emissions are estimated to be 5557 kg/yr, or about 0.015 kg/ADTBP for a 1000 ADTBP/day mill operating 365 days a year. Trace amounts of formaldehyde may also be released from the secondary waste treatment system in a bleached kraft pulp mill due to volatilisation (estimated at $<1.9 \times 10^{-4}$ kg/ADTBP).

Table 5.1 Emissions of Formaldehyde from Example Bleached Kraft Pulp Mill

Process Unit	Average Emission Rate (A) and Units	Factor to Convert to kg/ADTUBP (B)	Total Emitted $(A \times B \times C)^a$ kg/yr
BLO tank	3.7E-04 kg/t BLS	1.65 t BLS/ADTUBP	245
Brownstock washers	8.0E-04 kg/ADTUBP	1.0	321
Deckers	7.5E-04 kg/ADTUBP	1.0	301
Lime kilns	2.8E-03 kg/t CaO	0.275 t CaO/ADTUBP	309
Paper dryer	3.2E-03 kg/ADTFP	0.91^b	1,168
DCE recovery furnaces	4.8E-04 kg/t BLS	1.65 t BLS/ADTUBP	318
Smelt dissolving tank	1.8E-03 kg/t BLS	1.65 t BLS/ADTUBP	1,192
Wood-fired boilers	3.6E-04 kg/GJ	11.78^c	1,703
Total Emitted – Stack/Point Releases			***5,557***

NOTES: ADT – air dry metric tonne; FP – finished product; UBP – unbleached pulp; BLS – black liquor solids
[a] where C = 1100 ADTUBP/d x 365 d/yr
[b] (1000 ADTFP / 1100 ADTUBP) = 0.91
[c] (540 GJ/hr x 24 hr/d) / (1100 ADTUBP/d) = 11.78 GJ/ADTUBP

Effluent

NCASI is not aware of any surveys of pulp and paper mill effluent formaldehyde concentrations. NCASI has done some exploratory method development work (see Section 4.1.2) which suggests that effluent concentrations may be in the 20 to 120 µg/L range, but this work was extremely limited in scope.

Solid wastes

NCASI is not aware of any data characterising levels of formaldehyde in pulp mill solid wastes. Given the low octanol-water partition coefficient, there is no reason to believe that significant levels of formaldehyde will partition onto solids. Although formaldehyde might be an intermediate in the microbial breakdown of pulp and paper mill solids (e.g., primary and/or secondary sludge), the short estimated soil half-life of 24 to 168 hours (EC/HC 2000c) suggests that it is unlikely that a significant concentration will build up in solid wastes.

5.1.2   *Wood Products Facilities*

Air

Trace amounts of formaldehyde may be emitted from several sources in a typical wood products facility. This section provides estimates for typical "uncontrolled" and "controlled" emissions of formaldehyde from an example particleboard mill.

Example particleboard mill (no controls): A particleboard mill presses 100 million square feet of particleboard (¾ inch basis) per year (MMSF ¾/yr). The amount of wood processed through the dryers is 150,000 tons per year (oven dry basis). The mill has a board cooler on site and a 100 x 10⁶ Btu per hour wood-fired boiler operating 8000 hours per year. Half of the mill's wood furnish has a moisture content less than 30% (dry basis), the other half is green sawdust with a moisture content greater than 30% moisture (dry basis).

Table 5.2 shows the amounts of "uncontrolled" formaldehyde emissions from several major operations at this example particleboard mill as estimated using average reported emissions (NCASI 1995a, 1999a-f, 2003, and Mill File information). Total emissions are estimated to be 34,413 lb/yr (15,609 kg/yr), or about 0.344 lb/MSF ¾.

Table 5.2   Uncontrolled Emissions of Formaldehyde from Example Particleboard Mill

Process Unit	Average Emission Rate and Units[a]		Production Rate	Total Emitted lb/yr
Green (sawdust) dryer	9.7E-02	lb/ODT	75,000 ODT/yr	7,275
Dry (planer shavings) dryers	2.2E-02	lb/ODT	75,000 ODT/yr	1,650
Press	2.3E-01	lb/MSF ¾	100,000 MSF/yr	23,000
Wood-fired boiler	3.6E-04	lb/10⁶ Btu	100 x 10⁶ Btu/hr	288
Board cooler	2.2E-02	lb/MSF ¾	100,000 MSF/yr	2,200
Total Emitted – Stack/Point Releases				***34,413***

[a] lb/ODT – lb per oven dry ton of wood; lb/MSF – lb per thousand square feet of veneer dried (based on a single surface); lb/MSF ¾ – lb per thousand square feet of product dried adjusted to thickness of ¾ inch

Example particleboard mill (with RTO on press vent gases): In the same particleboard mill the gases from the press are routed to a regenerative thermal oxidiser (RTO). It is assumed that the destruction efficiency of the RTO for formaldehyde is 90%.

Formaldehyde emitted from press (90% destruction across RTO) = 23,000 x (1 − 0.90) = 2300 lb/yr

In this case, total emissions of formaldehyde are estimated to be:

7275 + 1650 + 2300 + 288 + 2200 = 13,713 lb/yr (6220 kg/yr), or about 0.137 lb/MSF ¾

Solid wastes (e.g., log yard debris, sawdust, trim)

NCASI is not aware of any data characterising levels of formaldehyde in solid wastes from wood products facilities. Given the low octanol-water partition coefficient, there is no reason to believe that significant levels of formaldehyde will partition onto solids. Although formaldehyde might be an intermediate in the microbial breakdown of woody debris, the short estimated soil half-life of 24 to 168 hours (EC/HC 2000c) suggests that it is unlikely that a significant concentration will build up in solid wastes.

5.2   Acetaldehyde

5.2.1   *Pulp and Paper Mills*

Air

Trace amounts of acetaldehyde may be emitted from several sources in a typical pulp and paper mill. This section provides an estimate for typical emissions of acetaldehyde from an example bleached kraft pulp mill.

Example bleached kraft pulp mill: A kraft mill produces 1100 ADTUBP/d which is then bleached after O_2 delignification to produce 1000 ADTBP/d. The pulping process generates 1.65 t BLS per ADTUBP, and 0.275 t CaO is regenerated in the lime kiln per ADTUBP. The final product is 1000 ADT/d of bleached paper. The mill operates a 540 GJ/hr wood-fired boiler and two DCE recovery furnaces.

Table 5.3 shows the vast majority of the acetaldehyde emitted from operations at this example mill as estimated using average reported emissions in an NCASI report (NCASI 2003). Total emissions are estimated to be 23,239 kg/yr, or about 0.064 kg/ADTBP for a 1000 ADTBP/day mill operating 365 days a year. Small amounts of acetaldehyde may also be released from the secondary waste treatment system (WTS) in a kraft pulp mill due to volatilisation. Typical estimates obtained by applying WTS models to kraft pulp mills range from a low of about 0.015 kg/ADTP for an unbleached kraft mill with steam strippers to a high of about 0.039 kg/ADTBP for a bleached kraft pulp mill with "hard-piping" of foul condensates to the WTS.

Table 5.3   Emissions of Acetaldehyde from Example Bleached Kraft Pulp Mill

Process Unit	Average Emission Rate (A) and Units		Factor to Convert to kg/ADTUBP (B)	Total Emitted (A x B x C)[a] kg/yr
BLO tank	1.1E-02	kg/t BLS	1.65 t BLS/ADTUBP	7,287
Brownstock washers	7.5E-03	kg/ADTUBP	1.0	3,011
Deckers	1.2E-03	kg/ADTUBP	1.0	482
Oxygen delignification	6.5E-03	kg/ADTUBP	1.0	2,610
Paper dryer	1.7E-02	kg/ADTFP	0.91[b]	6,205
DCE recovery furnaces	5.5E-03	kg/t BLS	1.65 t BLS/ADTUBP	3,644
Total Emitted – Stack/Point Releases				*23,239*

NOTES: ADT – air dry metric tonne; FP – finished product; UBP – unbleached pulp; BLS – black liquor solids
[a]   where C = 1100 ADTUBP/d x 365 d/yr
[b]   (1000 ADTFP / 1100 ADTUBP) = 0.91

Effluent

Acetaldehyde has never been an analyte of concern to the USEPA Office of Water, so it has not been measured as part of any regulatory development program. NCASI is not aware of any Canadian surveys of acetaldehyde wastewater discharges. An estimate of typical pulp and paper mill discharge concentrations was obtained by using the annual mill-specific surface water discharge releases reported in the NPRI and daily wastewater flows obtained from the 2003 update of the Fisher Pulp and Paper Worldwide™ database (Fisher International, Inc. 2001). Only 36 of the approximately 150 Canadian pulp and/or paper mills with biological treatment systems reported acetaldehyde releases;

of those, 35 reported releases to surface water. The others presumably had releases below the reporting threshold or no detectable acetaldehyde releases. The range of concentrations calculated from the mills with biological treatment systems that reported surface water releases was ND to 50 µg/L, with a median of 18 µg/L.

Solid wastes

NCASI is not aware of any data characterising levels of acetaldehyde in pulp mill solid wastes. Given the low octanol-water partition coefficient, there is no reason to believe that significant levels of acetaldehyde will partition onto solids, and NCASI has no reason to believe acetaldehyde is formed by microbial means.

5.2.2   Wood Products Facilities

Air

Trace amounts of acetaldehyde may be emitted from several sources in a typical wood products facility. This section provides estimates for typical "uncontrolled" emissions of acetaldehyde from an example oriented strandboard (OSB) mill and an example "dry/dry" process hardboard mill.

Example OSB mill: An OSB mill presses 200 million square feet of OSB (3/8 inch basis) per year (MMSF 3/8/yr). The mill uses a pine furnish and processes 125,000 tons per year (oven dry basis) through the dryers. The mill has a 100 x 10^6 Btu per hour wood-fired boiler on site, operating 8000 hours per year.

Table 5.4 shows the amounts of uncontrolled acetaldehyde emissions from several major operations at this example OSB mill as estimated using average reported emissions (NCASI 1995b, 1999a-f, 2003, and Mill File information). Total emissions are estimated to be 14,978 lb/yr (6794 kg/yr), or about 0.075 lb/MSF 3/8.

Table 5.4   Uncontrolled Emissions of Acetaldehyde from Example OSB Mill

Process Unit	Average Emission Rate and Units[a]		Production Rate	Total Emitted lb/yr
Dryer	1.1E-01	lb/ODT	125,000 ODT/yr	13,750
Press	5.5E-03	lb/MSF 3/8	200,000 MSF/yr	1,100
Wood-fired boiler	1.6E-04	lb/10^6 Btu	100 x 10^6 Btu/hr	128
Total Emitted – Stack/Point Releases				*14,978*

[a] lb/ODT – lb per oven dry ton of wood; lb/MSF – lb per thousand square feet of veneer dried (based on a single surface); lb/MSF 3/8 – lb per thousand square feet of product dried adjusted to thickness of 3/8 inch

Example "dry/dry" process hardboard mill: A "dry/dry" process hardboard mill with a tempering oven produces 300 million square feet of hardboard per year at 1/8 inch thickness (MMSF 1/8/yr). Wood-fired blow-line-blend tube dryers at the mill process 100,000 tons per year of hardwood furnish. Phenol-formaldehyde resin is applied at the blow line. Linseed oil is applied to the boards prior to tempering. The mill operates a 100 x 10^6 Btu per hour wood-fired boiler for an average of 8000 hours per year.

Table 5.5 shows the amounts of uncontrolled acetaldehyde emissions from several major operations at this example hardboard mill as estimated using average reported emissions (NCASI 1995a, 1999a-f, 2003, and Mill File information). Total emissions are estimated to be 39,828 lb/yr (18,058 kg/yr), or about 0.133 lb/MSF 1/8.

Table 5.5 Uncontrolled Emissions of Acetaldehyde from Example Hardboard Mill

Process Unit	Average Emission Rate and Units[a]		Production Rate	Total Emitted lb/yr
Dryer	1.3E-01	lb/ODT	100,000 ODT/yr	13,000
Press	1.3E-02	lb/MSF 1/8	300,000 MSF/yr	3,900
Wood-fired boiler	1.6E-04	lb/10^6 Btu	100 x 10^6 Btu/hr	128
Tempering oven	7.6E-02	lb/MSF 1/8	300,000 MSF/yr	22,800
Total Emitted – Stack/Point Releases				*39,828*

[a] lb/ODT – lb per oven dry ton of wood; lb/MSF – lb per thousand square feet of veneer dried (based on a single surface); lb/MSF 1/8 – lb per thousand square feet of product dried adjusted to thickness of 1/8 inch

Solid wastes (e.g., log yard debris, sawdust, trim)

NCASI is not aware of any data characterising levels of acetaldehyde in solid wastes from wood products facilities. Given the low octanol-water partition coefficient, there is no reason to believe that significant levels of acetaldehyde will partition onto solids, and NCASI has no reason to believe acetaldehyde is formed by microbial means.

5.3   Acrolein

5.3.1   *Pulp and Paper Mills*

Air

Trace amounts of acrolein may be emitted from several sources in a typical pulp and paper mill. This section provides an estimate for typical emissions of acrolein from an example bleached kraft pulp mill.

Example bleached kraft pulp mill: A kraft mill produces 1100 ADTUBP/d which is then bleached after O_2 delignification to produce 1000 ADTBP/d. The pulping process generates 1.65 t BLS per ADTUBP, and 0.275 t CaO is regenerated in the lime kiln per ADTUBP. The final product is 1000 ADT/d of bleached paper. The mill operates a 540 GJ/hr wood-fired boiler and two DCE recovery furnaces.

Table 5.6 shows the vast majority of the acrolein emitted from operations at this example mill as estimated using average reported emissions in an NCASI report (NCASI 2003). Total emissions are estimated to be 566.1 kg/yr, or about 0.00155 kg/ADTBP for a 1000 ADTBP/day mill operating 365 days a year. Trace amounts may also be released from the secondary waste treatment basin in a pulp mill due to volatilisation. However, available data for untreated effluents from seven bleached kraft mills and one sulphite mill all showed non-detect levels (<50 µg/L) of acrolein.

Table 5.6 Emissions of Acrolein from Example Bleached Kraft Pulp Mill

Process Unit	Average Emission Rate (A) and Units		Factor to Convert to kg/ADTUBP (B)	Total Emitted (A x B x C)[a] kg/yr
BLO tank	1.3E-06	kg/t BLS	1.65 t BLS/ADTUBP	0.9
Brownstock washers	1.3E-04	kg/ADTUBP	1.0	52.2
Deckers	4.1E-05	kg/ADTUBP	1.0	16.5
Oxygen delignification	2.6E-05	kg/ADTUBP	1.0	10.4
Paper dryer	8.0E-04	kg/ADTFP	0.91[b]	292.3
DCE recovery furnaces	1.4E-05	kg/t BLS	1.65 t BLS/ADTUBP	9.3
Wood-fired boilers	3.9E-05	kg/GJ	11.78[c]	184.5
Total Emitted – Stack/Point Releases				***566.1***

NOTES: ADT – air dry metric tonne; FP – finished product; UBP – unbleached pulp; BLS – black liquor solids
[a] where C = 1100 ADTUBP/d x 365 d/yr
[b] (1000 ADTFP / 1100 ADTUBP) = 0.91
[c] (540 GJ/hr x 24 hr/d) / (1100 ADTUBP/d) = 11.78 GJ/ADTUBP

Effluent

USEPA surveyed eleven U.S. pulp mills for three days and eight U.S. pulp mills for a total of seventeen days (weekly samples for nine weeks during the summer and eight weeks during the winter) as part of the data gathering and survey work upon which the Cluster Rule was based (USEPA 1993). USEPA utilised Method 1624, which has a Minimum Level of 50 μg/L acrolein, in all the surveys. Throughout the entire program, acrolein was detected at only one mill, at a concentration of 59 μg/L. USEPA determined that because it was detected at only one facility, this was not a compound of concern and it was not regulated in the final effluent guidelines.

NCASI is not aware of any Canadian surveys which included acrolein. No Canadian mills reported acrolein releases to surface water in the 2001 NPRI. All evidence suggests that acrolein is not present in biologically treated wastewaters at current analytical detection limits.

Solid wastes

NCASI is not aware of any data characterising levels of acrolein in pulp mill solid wastes. Given the low octanol-water partition coefficient, there is no reason to believe that significant levels of acrolein will partition onto solids, and NCASI has no reason to believe acrolein is formed by microbial means.

5.3.2   *Wood Products Facilities*

Air

Trace amounts of acrolein may be emitted from several sources in a typical wood products facility. This section provides estimates for typical "uncontrolled" emissions of acrolein from an example oriented strandboard (OSB) mill and an example "wet/wet" process hardboard mill.

Example OSB mill: An OSB mill presses 200 million square feet of OSB (3/8 inch basis) per year (MMSF 3/8/yr). The mill uses a hardwood furnish, PF/MDI resin, and processes 125,000 tons per year (oven dry basis) through the dryers. The mill has a 100 x 10^6 Btu per hour wood-fired boiler on site, operating 8000 hours per year.

Table 5.7 shows the amounts of uncontrolled acrolein emissions from several major operations at this example OSB mill as estimated using average reported emissions (NCASI 1995b, 1999a-f, 2003, and Mill File information). Total emissions are estimated to be 9741 lb/yr (4418 kg/yr), or about 0.049 lb/MSF 3/8.

Table 5.7   Uncontrolled Emissions of Acrolein from Example OSB Mill

Process Unit	Average Emission Rate and Units[a]		Production Rate	Total Emitted lb/yr
Dryer	7.3E-02	lb/ODT	125,000 ODT/yr	9,125
Press	2.8E-03	lb/MSF 3/8	200,000 MSF/yr	280
Wood-fired boiler	4.2E-04	lb/10^6 Btu	100 x 10^6 Btu/hr	336
Total Emitted – Stack/Point Releases				***9,741***

[a]   lb/ODT – lb per oven dry ton of wood; lb/MSF – lb per thousand square feet of veneer dried (based on a single surface); lb/MSF 3/8 – lb per thousand square feet of product dried adjusted to thickness of 3/8 inch

Example "wet/wet" process hardboard mill: A "wet/wet" process hardboard mill produces 300 million square feet of hardboard per year at 1/8 inch thickness (MMSF 1/8/yr). Linseed oil is added to the fibre at the wet end of the process. The direct-fired mill conveyor dryers process 100,000 oven dry tons of fibre per year. The mill applies linseed oil to the hardboard panels prior to tempering. The tempering oven processes 200 million square feet of hardboard per year. The mill operates a 100 x 10^6 Btu per hour wood-fired boiler for an average of 8000 hours per year.

Table 5.8 shows the amounts of uncontrolled acrolein emissions from several major operations at this example hardboard mill as estimated using average reported emissions (NCASI 1995a, 1999a-f, 2003, and Mill File information). Total emissions are estimated to be 10,546 lb/yr (4783 kg/yr), or about 0.035 lb/MSF 1/8.

Table 5.8   Uncontrolled Emissions of Acrolein from Example Hardboard Mill

Process Unit	Average Emission Rate and Units[a]		Production Rate	Total Emitted lb/yr
Dryer	3.7E-02	lb/ODT	100,000 ODT/yr	3,700
Press	5.7E-03	lb/MSF 1/8	300,000 MSF/yr	1,710
Wood-fired boiler	4.2E-04	lb/10^6 Btu	100 x 10^6 Btu/hr	336
Tempering oven	2.4E-02	lb/MSF 1/8	200,000 MSF/yr	4,800
Total Emitted – Stack/Point Releases				***10,546***

[a]   lb/ODT – lb per oven dry ton of wood; lb/MSF – lb per thousand square feet of veneer dried (based on a single surface); lb/MSF 1/8 – lb per thousand square feet of product dried adjusted to thickness of 1/8 inch

Solid wastes (e.g., log yard debris, sawdust, trim)

NCASI is not aware of any data characterising levels of acrolein in solid wastes from wood products facilities. Given the low octanol-water partition coefficient, there is no reason to believe that significant levels of acrolein will partition onto solids, and NCASI has no reason to believe acrolein is formed by microbial means.

6.0   CONCLUSIONS

Although knowledge of the exact mechanism of formation of formaldehyde, acetaldehyde, and acrolein is imperfect, it is known that these compounds are unintentionally produced as by-products of both the pulping and wood products industries. Of the three compounds, only formaldehyde is used as a component of formulations used in the processes. In the paper industry it is used in some wet strength additives, and in the panel board industry it is used in urea- or phenol-formaldehyde resins.

As part of the evaluations of its Priority Substance List (PSL) Assessment, Environment Canada partially inventoried emissions sources. It did not inventory some very important sources, including some non-road sources, forest fires, prescribed burning, wood stoves and fireplaces, other heating sources, and non-coal power generation. Using the USEPA 1996 National Toxics Inventory to estimate the relative importance of these sources, the Canadian source inventory could be from 60 to 85% low.

The 2001 NPRI data indicate that the forest products industries' releases of CEPA aldehydes account for a very high percentage of industrial releases (Table 6.1). However, when these releases are compared to all emissions sources, the forest products industries contribute only a small amount.

Table 6.1   Releases of CEPA Aldehydes

Compound	Wood Products % of Industrial Sources	Pulp and Paper % of Industrial Sources	Wood Products % of Total Emissions[a]	Pulp and Paper % of Total Emissions[a]
Acetaldehyde	32	59	3	6
Acrolein	98	0	2	0
Formaldehyde	82	5	4	0.2

[a] NCASI adjusted the Environment Canada source inventory to reflect non-inventoried sources as indicated by the 1996 USEPA NTI data. A correction was also made to account for more recent NPRI reporting by the wood and pulp and paper industries. These estimates are only useful for rough indications until a proper, complete inventory can be completed.

Based on reviews by a number of international organisations, all three aldehydes react and degrade quickly in air, water, or soil and are readily biodegradable in water, sediment, and soil. As a result, they have short half-lives in essentially all environmental compartments, generally estimated in terms of hours. The overall short half-lives preclude any long-term transport. All three compounds have very low octanol-water partition coefficients, and thus have little tendency to adsorb to soils or bioaccumulate.

The Environment Canada CEPA PSL Assessments concluded that these aldehydes are not expected to have harmful effects on the environment or its biological diversity. The Assessments also concluded that reducing exposure in the ambient environment was of only moderate priority, and that

options to reduce this exposure are not a high priority. The bulk of human exposures occur in the indoor environment, and it is these exposures that resulted in the listing of the aldehydes. The primary source of exposure is through inhalation.

Due to extensive MACT studies conducted in the U.S., air testing methods for measuring all the CEPA aldehydes in forest products industry air emissions have been developed and published. Some of these methods have also been validated by the protocol developed by USEPA. Although a number of analytical procedures have been published for these compounds, few, if any, have been validated for use in pulp and paper industry wastewaters. Limited NCASI data suggest that there is a significant potential for bias for formaldehyde measured by some procedures.

Formaldehyde and acetaldehyde are regulated exclusively as air pollutants in the U.S.; thus, there have been few measurements of their concentrations in mill effluents. Acrolein was given some attention during the data gathering portion of the Cluster Rule. Data published in the literature and limited NCASI data indicate that these compounds are efficiently reduced in biological treatment systems. Examination of the limited data available suggests that the levels discharged do not represent a threat to aquatic organisms. The CEPA aldehydes have short aquatic half-lives. All three CEPA PSL Assessment Reports took these and other factors into consideration and concluded that there were no threats to the aquatic environment.

The extensive MACT testing studies conducted by NCASI provide reliable CEPA aldehydes air emission factor estimates for essentially all sources within the forest products industry. The emission factors cover a wide enough range of process parameters that facilities can confidently estimate their emission rates.

Overall, the forest products industry contributes only a small part to the total emissions of the CEPA aldehydes. Given that the primary reason for listing the aldehydes as CEPA toxic was indoor air exposure, it is not likely that emissions from manufacturing processes are contributing significantly to the general population's exposure to these substances.

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APPENDIX A

CONVERSION FACTORS

The basic units of measurement used in the tables for wood products facilities are pound (lb), short ton (T), inch, feet (ft), British thermal unit (Btu), second (sec), hour (hr), litre (L), and gallon (gal). Table A1 is a list of relevant factors for converting these into SI units.

Table A1 Conversion Factors

Convert From	To	Multiply by	Divide by
Basic Units			
pound (lb)	kilogram (kg)		2.2
short ton (T)	metric tonne (t)		1.1
Btu	joule (J)	1055.04	
inch	ft		12
ft	m	0.3048	
ft^2	m^2	0.0929	
ft^3	m^3	0.0283	
gal	litre (L)	3.7854	
litre (L)	m^3		1000
Units in Report			
MSF ($1000\ ft^2$)	m^2	92.9	
MSF 1/8	m^3	0.295	
MSF 3/8	m^3	0.885	
MSF ½	m^3	1.180	
MSF ¾	m^3	1.770	
lb/MSF 1/8	kg/m^3		0.649
lb/MSF 3/8	kg/m^3		1.947
lb/MSF ½	kg/m^3		2.596
lb/MSF ¾	kg/m^3		3.894
$lb/10^6$ Btu	$kg/10^9$ J		2.321
lb/ODT	kg/odt		2.0
lb/yr	kg/y		2.2

ODT – oven dry short ton
odt – oven dry metric tonne
MSF – thousand square feet (based on a single surface)
MSF 1/8, 3/8, ½, ¾ – thousand square feet of panel dried at a thickness of 1/8, 3/8, ½, ¾ inch, respectively