



NATIONAL COUNCIL FOR AIR AND STREAM IMPROVEMENT

**TOTAL REDUCED SULPHUR,
HYDROGEN SULPHIDE, CHLORINE,
CHLORINE DIOXIDE, CHLOROFORM
AND METHANOL AND THE
FOREST PRODUCTS INDUSTRY**

**TECHNICAL BULLETIN NO. 930
APRIL 2007**

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Acknowledgments

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National Council for Air and Stream Improvement, Inc. (NCASI). 2007. *Total reduced sulphur, hydrogen sulphide, chlorine, chlorine dioxide, chloroform and methanol and the forest products industry*. Technical Bulletin No. 930. Research Triangle Park, N.C.: National Council for Air and Stream Improvement, Inc.

PRESIDENT'S NOTE

A number of recent Canadian environment policy initiatives relevant to the forest products sector have focused on identifying, characterizing, and mitigating releases to air for a spectrum of substances considered to be of high priority for action. National-level discussions for reducing air emissions from Canada's pulp and paper and wood products industries have identified up to eight substances (or substance groups) as being most relevant for release reduction. Most of these substances are either currently, or will potentially be, declared "toxic" under the Canadian Environmental Protection Act (CEPA). They have also been cited within the national-level Pulp and Paper Air Quality Forum discussions as key substances, and many are related to recently developed Canada-wide standards. These eight substances include particulate matter (including total PM, PM₁₀, PM_{2.5}), volatile organic compounds (VOC), NO_x, SO₂, total reduced sulphur (TRS), ClO₂, dioxins and furans, and greenhouse gases. Within the VOC substance group, methanol (for pulp and paper), as well as formaldehyde, acetaldehyde, and acrolein (for wood products) have been specifically identified as being of interest for reducing releases to air.

The current report provides background information regarding substances that may be associated specifically with the forest products industry. These substances include total reduced sulphur (TRS) (with specific focus on hydrogen sulphide (H₂S), which is currently under review for potential listing as "toxic" under CEPA), certain chlorinated substances [including chlorine (Cl₂), chlorine dioxide (ClO₂), and chloroform (CHCl₃)], and methanol. The report provides the context necessary to evaluate forest products industry emissions relative to the overall sources of these emissions. While not intended as a comprehensive review of available information, the report attempts to present a concise summary of the most relevant information.

The report discusses how ClO₂ is intentionally manufactured and used by the industry for pulp bleaching, while the rest of the substances are only unintentionally formed during normal production of pulp or wood products. In all cases, the forest products industry emits a significant fraction of industrial releases of these substances. However, modern bleaching and emission control technologies have largely enabled facilities to limit these releases to below levels of relevance to environmental or health benchmarks.

Analytical methods for forest products industry emissions of virtually all of these substances are well documented and releases of each have been relatively well characterized. Ongoing characterization work by NCASI related to TRS emissions from effluent treatment, however, will augment the limited available knowledge related to these fugitive releases.

This report provides documentation that the forest products industry, while a significant industrial source of these compounds, has largely limited their release through application of modern bleaching and emission control technologies.

A handwritten signature in black ink, appearing to read "Ron Yeske". The signature is fluid and cursive, with the first name "Ron" and last name "Yeske" clearly distinguishable.

Ronald A. Yeske

April 2007

MOT DU PRÉSIDENT

Récemment, certaines démarches en matière de politiques environnementales canadiennes s'adressant au secteur des produits forestiers ont mis l'accent sur l'identification, la caractérisation et la mitigation des rejets dans l'air d'un éventail de substances considérées comme hautement prioritaires dans les plans d'actions. Sur le plan national, les discussions sur les réductions des émissions atmosphériques de l'industrie canadienne des pâtes et papiers et des produits du bois ont mené à l'identification de huit substances (ou groupes de substances) qui s'avèrent les plus pertinentes pour la réduction des rejets. La plupart de ces substances sont soit actuellement, ou seront potentiellement déclarées « toxiques » en vertu de la Loi canadienne sur la protection de l'environnement (LCPE). Elles ont également été citées dans le cadre des discussions nationales tenues lors du Forum des pâtes et papiers sur la qualité de l'air comme étant des substances clés et plusieurs d'entre elles sont associées aux normes nationales récemment développées. Ces huit substances sont les suivantes : matières particulaires (incluant les particules totales PM, les PM₁₀ et les PM_{2,5}), composés organiques volatils (COV), NO_x, SO₂, composés de soufre réduit totaux (SRT), ClO₂, dioxines et furannes et gaz à effet de serre. À l'intérieur du groupe des COV, le méthanol (pour les pâtes et papiers) de même que le formaldéhyde, l'acétaldéhyde et l'acroléine (pour les produits du bois) sont reconnus comme étant des composés d'intérêt pour la réduction des rejets dans l'air.

Ce rapport contient de l'information de référence sur les substances qui sont susceptibles d'être associées à l'industrie des produits forestiers. Il s'agit des composés de soufre réduit totaux (SRT) (principalement le sulfure d'hydrogène (H₂S) qui est actuellement sous révision pour se retrouver éventuellement sur la liste des substances « toxiques » en vertu de la LPCE), certaines substances chlorées (incluant le chlore (Cl₂), le dioxyde de chlore (ClO₂) et le chloroforme (CHCl₃)) et le méthanol. Le rapport présente également le contexte nécessaire pour évaluer les émissions de l'industrie des produits forestiers relativement à l'ensemble des sources d'émissions de ces substances. Ce rapport n'a pas comme objectif de réaliser une revue détaillée de l'information disponible, mais plutôt de présenter une synthèse concise de l'information la plus pertinente.

Dans ce rapport, le lecteur trouvera d'une part des informations portant sur la fabrication et l'utilisation intentionnelle du ClO₂ par l'industrie, pour le blanchiment de la pâte et d'autre part, des informations sur le reste des substances, qui sont uniquement fabriquées fortuitement lors de la production normale de pâte ou de produits du bois. Dans tous les cas, l'industrie des produits forestiers émet une fraction significative des rejets industriels de ces substances. Toutefois, les procédés modernes de blanchiment et les technologies de contrôle des émissions ont permis aux fabriques et aux usines de limiter ces rejets en deçà des niveaux significatifs pour l'environnement et la santé.

Les méthodes analytiques employées pour mesurer les émissions de la majorité de ces substances qui caractérisent l'industrie des produits forestiers demeurent correctement documentées et l'industrie a relativement bien caractérisé les rejets de chacune de ces substances. Toutefois, les travaux de

caractérisation que NCASI effectue régulièrement sur les émissions de SRT par les systèmes de traitement des effluents permettront d'améliorer la connaissance actuellement limitée de ce type d'émissions fugitives.

Ce rapport contient de l'information qui confirme la réussite de l'industrie des produits forestiers, une source d'émissions industrielles significative de ces composés, quant à limiter considérablement les rejets grâce à l'application de techniques de blanchiment modernes et de contrôle des émissions.



Ronald A. Yeske

Avril 2007

**TOTAL REDUCED SULPHUR, HYDROGEN SULPHIDE, CHLORINE,
CHLORINE DIOXIDE, CHLOROFORM AND METHANOL
AND THE FOREST PRODUCTS INDUSTRY**

TECHNICAL BULLETIN NO. 930
APRIL 2007

ABSTRACT

Total reduced sulphur (TRS), hydrogen sulphide, chlorine, chlorine dioxide, chloroform, and methanol are six candidate substances or substance groups under review for potential classification as “toxic” under the Canadian Environmental Protection Act (CEPA). In addition, TRS, H₂S, chlorine, chlorine dioxide, chloroform, and volatile organic compounds (VOCs, of which methanol is the most relevant for pulp and paper facilities) have been recently reviewed by the national Pulp and Paper Air Quality Forum for potential release reduction. This report is a summary of information related to these six substances (or substance groups) that should provide valuable context as Environment Canada undertakes its obligations under CEPA, as well as document what is known about their use and/or unintentional formation within the forest products industry. It updates and expands on earlier inventories of total sources of these compounds. The environmental fate and significance of the compounds are reviewed. Their toxicological characteristics are briefly reviewed and discussed in the context of the bases for their potential determination as “CEPA toxic.” Finally, analytical methods are summarized, and information on emission factors is reviewed or tabulated.

KEYWORDS

analytical methods, Canadian Environmental Protection Act, CEPA, chlorine, chlorine dioxide, chloroform, emission factors, fate, hydrogen sulphide, methanol, persistence, toxicology, TRS, VOC

RELATED NCASI PUBLICATIONS

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

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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.*

LES COMPOSÉS DE SOUFRE RÉDUIT TOTAUX, LE SULFURE D'HYDROGÈNE, LE CHLORE, LE DIOXYDE DE CHLORE, LE CHLOROFORME ET LE MÉTHANOL DANS L'INDUSTRIE DES PRODUITS FORESTIERS

BULLETIN TECHNIQUE N^o 930
AVRIL 2007

RÉSUMÉ

Les composés de soufre réduit totaux (SRT), le sulfure d'hydrogène, le chlore, le dioxyde de chlore, le chloroforme et le méthanol constituent six substances ou groupes de substances sous révision pour une classification potentielle sur la liste des substances « toxiques » en vertu de la Loi canadienne sur la protection de l'environnement (LCPE). De plus, les SRT, le H₂S, le chlore, le dioxyde de chlore, le chloroforme et les composés organiques volatils (COV, parmi lesquels le méthanol est le plus pertinent pour les fabriques de pâtes et papiers) ont récemment fait l'objet d'une révision par le Forum des pâtes et papiers sur la qualité de l'air, dans l'optique de la réduction potentielle des rejets. Ce rapport fait office de synthèse d'information sur ces six substances (ou groupes de substances) et il est susceptible de fournir un contexte intéressant puisqu'Environnement Canada remplit actuellement ses obligations en vertu de la LCPE. De plus, il documente la connaissance sur l'utilisation et/ou la fabrication fortuite de ces substances dans l'industrie des produits forestiers et il met à jour et complète les inventaires précédents des sources d'émissions totales de ces composés. Les auteurs ont revu le devenir environnemental et l'importance environnementale de ces composés, de même qu'ils ont brièvement revu et analysé leurs caractéristiques toxicologiques afin d'établir les bases pour leur classification potentielle sur la liste des substances « toxiques » de la LCPE. Enfin, le rapport fait la synthèse des méthodes analytiques et fait la revue ou présente sous forme de tableau les informations sur les facteurs d'émissions.

MOTS CLÉS

Méthodes analytiques, Loi canadienne sur la protection de l'environnement, LCPE, chlore, dioxyde de chlore, chloroforme, facteurs d'émission, devenir environnemental, sulfure d'hydrogène, méthanol, persistance, toxicologie, SRT, COV

AUTRES PUBLICATIONS DE NCASI DANS CE DOMAINE

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TOTAL REDUCED SULPHUR, HYDROGEN SULPHIDE, CHLORINE, CHLORINE DIOXIDE, CHLOROFORM AND METHANOL AND THE FOREST PRODUCTS INDUSTRY

1.0 INTRODUCTION

Current discussions with Environment Canada and Health Canada related to the development of a national-level approach for reducing air emissions from Canada's pulp and paper industry recently identified eight substances (or substance groups) as being most relevant for release reduction. In addition, most of these substances are either currently, or will potentially be, declared "toxic" under the Canadian Environmental Protection Act (CEPA). These eight substances are particulate matter (including total PM, PM₁₀, PM_{2.5}), total volatile organic compounds (VOC, as carbon), NO_x, SO₂, total reduced sulphur (TRS), ClO₂, dioxins and furans, and greenhouse gases. 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. In parallel, policy arising from the multi-stakeholder national-level Pulp and Paper Air Quality Forum may elect to require cross-industry emissions reductions independent of any designation as "CEPA toxic."

The current report addresses the background information needed by both Environment Canada and the forest products industry on what is known about the highly industry-relevant substances that include total reduced sulphur (TRS), hydrogen sulphide (H₂S), chlorine (Cl₂), chlorine dioxide (ClO₂), chloroform (CHCl₃), and methanol in the pulp, paper, and wood products industries, methanol representing the most prominent VOC emitted by the forest products industry (FPI). Other NCASI reports provide perspective on the remaining substances not covered in this document. This report 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' potential listings as "CEPA toxic." 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 in kraft pulp mills of the reduced sulphur compounds that comprise the substance group TRS, as well as the unintentional formation of methanol in various pulp mill and wood products facility processes, is summarized in Section 2. Also included in Section 2 are the causes for unintentional formation of small quantities of chlorine and chloroform during pulp bleaching and a discussion on the intentional manufacture and use of chlorine dioxide for pulp bleaching in the FPI. Section 2 also highlights the non-FPI sources of chlorine, chloroform, methanol, TRS, and H₂S released to the environment to put forest products industry emissions into perspective.

Section 3 reviews the environmental fate and significance of these 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 are critical to assessing the significance of these substances (or substance groups) and will be important to understand as Environment Canada and the industry move forward. Section 4 reviews analytical methods for sampling methanol, TRS/H₂S, Cl₂, ClO₂, and CHCl₃ in air and sampling methanol, CHCl₃, and TRS/H₂S in water and pulp mill residuals.

The literature and previous surveys/compilations of average emissions of these compounds relevant to both pulp mills and wood products facilities in the FPI are summarized in Section 5. NCASI has had a very active program documenting air emissions of methanol in support of the U.S. industry's MACT-related air regulation development work and in facilitating reporting for Canada's National Pollutant Release Inventory (NPRI) and the U.S. Toxics Release Inventory (TRI). TRS emissions are also routinely monitored and compiled by NCASI on behalf of the kraft pulping industry. Bleach plant emissions of Cl_2 and ClO_2 are monitored routinely by bleached pulp mills in the U.S., and frequently in Canada.

2.0 SOURCES AND FORMATION

2.1 Total Reduced Sulphur (TRS) and Hydrogen Sulphide (H_2S)

2.1.1 Formation in Kraft Pulping and Recovery Processes

The kraft process, which uses white liquor, a mixture of sodium hydroxide (NaOH) and sodium sulphide (Na_2S), to cook wood, continues to be the dominant chemical wood pulping process. Consequently, the generation of odorous sulphur compounds characteristic of this process is unavoidable, although intensive odour abatement programs have been implemented at kraft pulp mills during the past two decades. According to Environment Canada (EC), total reduced sulphur (TRS) refers to a group of compounds containing the sulphur atom in its reduced state (http://www.ec.gc.ca/pdb/npri/documents/WG2005/WG_substances/WG_sub2_e.cfm). EC states that TRS consists of hydrogen sulphide (H_2S), carbon disulphide (CS_2), carbonyl sulphide (COS), dimethyl sulphide ($\text{C}_2\text{H}_6\text{S}$), mercaptans (CH_4S), dimethyl disulphide ($\text{C}_2\text{H}_6\text{S}_2$), diethyl disulphide ($\text{C}_4\text{H}_{10}\text{S}_2$), thioesters, and alkyl sulphides. However, it has been determined that hydrogen sulphide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulphide ($(\text{CH}_3)_2\text{S}$) and dimethyl disulphide ($(\text{CH}_3)_2\text{S}_2$) constitute the four principal reduced sulphur compounds that make up the so-called "total reduced sulphur" (TRS) category associated with kraft pulping. Measurements of FPI releases for other reduced sulphur compounds have invariably shown them to be negligible in comparison to those for these four compounds.

Early studies on the effect of kraft pulping conditions upon the formation of reduced sulphur compounds shed some light on why the concentrations of these compounds in non-condensable gases (NCGs) vary considerably both with time and from one source to another. These studies (McKean et al. 1967; McKean, Hrutford, and Sarkanen 1968; Andersson 1970; Tsuchiya and Johanson 1972) suggest the following:

1. During kraft cooking, methyl mercaptan (MM) is produced first through the reaction of hydrogen sulphide ion (HS^-) with methoxyl groups (OCH_3). The mercaptide ions (CH_3S^-) then react with the methoxyl groups present in the pulping liquor and in the lignin structure to produce dimethyl sulphide (DMS). Dimethyl disulphide (DMDS) is not formed in the pulping process, but rather through the oxidation of MM when black liquor comes into contact with air.
2. Odour formation is proportional to the methoxyl content in the pulping system.
3. Hardwoods have more methoxyl groups than softwoods. Also, in hardwood cooking, a rapid initial demethylation of some labile methoxyl groups occurs. Consequently, if all other conditions remain the same, hardwood pulping produces more methyl mercaptan and dimethyl sulphide than softwood pulping.
4. Odour formation is also directly proportional to the sulphur concentration in the pulping liquor.

5. Approximately 2.3 to 2.5% of the sulphur charged to the digester (kg of sulphur/kg of wood chips) is converted to organic sulphides. Thus, reducing the net sulphur charge reduces the formation of MM and DMS.
6. Cooking at higher sulphidity increases the generation of MM and DMS.
7. Black liquor recycling to the digester increases the sulphidity of liquor and its methoxyl group content. This increases the formation of MM and DMS.
8. Higher alkali charge during cooking results in converting more of the mercaptan to dimethyl sulphide. Conversely, cooking at lower alkali charge reduces liquor pH and decreases the conversion of MM to DMS, thus increasing the amount of MM in the liquor and blow gases.
9. Cooking to a lower pH results in a higher fraction of MM in the digester relief and blow gases.
10. Increasing the duration of cooking results in higher generation of MM and DMS.
11. Cooking hardwoods at higher temperature results in higher generation of MM and DMS. Temperature has less of an effect on the formation of MM during softwood cooks. However, at high pulping temperatures, odorous compounds form at a reasonably high rate, and an increase in pulping time, such as a delay in batch digester blow, results in increased odour.

White liquor is occasionally used to scrub non-condensable gases (NCGs) in an attempt to reduce the NCG sulphur content before oxidation to SO₂ in an incineration device and also to return some of the sulphur to the cooking cycle. Among the four reduced sulphur compounds, DMS and DMDS are neutral, while H₂S and MM are mildly acidic. Thus, only H₂S and MM are scrubbed by the white liquor and returned to the digester. This contributes to higher sulphidity in the digester, which in turn is expected to increase the generation of MM and DMS. The use of this white liquor with depleted alkali content during cooking versus the use of fresh white liquor may result in lowered pH during the cook. This in turn could lead to a lower conversion of MM to DMS, thus increasing the levels of MM in blow and relief gases and in the weak liquor.

Some of the reduced sulphur compounds generated during pulping are released from the cooking liquor and end up in digester relief and blow gases. Insufficient cooling of kraft NCGs has often been identified as the cause of high levels of volatile organic compounds (VOCs) in the NCGs, especially the non-sulphur-containing VOCs such as terpenes and methanol. However, similar observations with reduced sulphur compounds have not been well documented. Of the four reduced sulphur compounds, H₂S and MM have relatively high vapour pressures. Thus, they would be expected to remain predominantly in the gaseous NCG phase, irrespective of how well the equipment designed to treat the reduced sulphur-laden gases were to operate. On the other hand, newer equipment designs for cooking wood, pulp washing and chemical recovery that allow for extremely low gas venting volumes might be expected to lead to higher concentrations but lower overall mass emissions of the four reduced sulphur compounds.

Odorous reduced sulphur compounds, inadvertently generated during kraft pulping, are present in non-condensable gases and condensates from digester blow and relief gases, digester flash steam, black liquor evaporation gases, turpentine recovery systems, and non-condensable gas handling and collection systems. Reduced sulphur compounds in condensates may be released to the atmosphere when the condensates are reused during brownstock washing or in the recausticizing area. Reduced sulphur compound emissions from wastewater treatment plants may occur if these condensates are seweraged without pre-treatment.

The black liquor separated from pulp washing systems is concentrated in a series of evaporators and concentrators until the liquor will support combustion in a recovery furnace. The concentration and volatility of the reduced sulphur compounds in the liquor, together with the amount of vapour flashed, would be expected to govern the amount of reduced sulphur compounds released with the water vapour. Thus, the more volatile constituents (H_2S and MM) should predominate in evaporator NCGs, decreasing as the black liquor concentration increases. However, three factors complicate this simple picture: first, the ionization of H_2S and MM in alkaline solution; second, the reactions of odorous constituents, chiefly with oxygen and with each other; and third, departure from equilibrium because of slowness in the transport of one or more of the constituents between phases (Sarkanen et al. 1970).

The volatility of H_2S and MM is greater in hot than in cold systems, but this effect is dwarfed by the influence of pH (Sarkanen et al. 1970). As the liquor concentrates, so does the fraction of un-ionized H_2S and MM in the liquor. However, at pHs >10 , H_2S is essentially non-volatile, whereas MM decreases in volatility only moderately as pH is increased. Thus, during evaporation of the black liquor, the concentration of MM in evaporator NCGs might approach levels of H_2S in the beginning stages. On the other hand, for H_2S , the result of high ionization but low volatility at high pH tends to “spread out” its volatility, so that even in the last vacuum evaporator or the direct contact evaporator, appreciable vapour pressure exists, leading to large releases in the relief gases (Sarkanen et al. 1970). DMS and DMDS do not ionize, and their volatilities are uninfluenced by pH. Consequently, their loss is much greater early in the evaporation cycle than in the latter stages.

Besides the reduced sulphur compounds generated during kraft pulping and black liquor evaporation that end up in various kraft pulping and evaporator non-condensable gases (NCGs) and condensates, these compounds are also generated during kraft chemical recovery operations. These operations include black liquor combustion in recovery furnaces, black liquor oxidation, lime generation in lime kilns, smelt dissolution in dissolving tanks, and tall oil acidulation in tall oil reactors.

Reduced sulphur compound emissions from kraft recovery furnaces result from the fact that 20 to 30% of the sulphur in the black liquor volatilizes during liquor pyrolysis as reduced sulphur compounds, predominantly H_2S . Many of the reduced sulphur compounds released into the combustion gases oxidize to SO_2 (which is captured as saltcake), while trace amounts are emitted via the stack gases. TRS emissions from kraft recovery furnaces are affected by a number of process and operating variables such as flue gas O_2 content, combustion air-to-solids ratio, furnace rated capacity, liquor firing rate, air distribution and velocity, spray coarseness, furnace temperature, and liquor sulphidity (NCASI 2001). Iisa (1997) provides a good review on the source of sulphur gas emissions in kraft recovery furnaces and their control. Reduced sulphur compound emissions during black liquor oxidation result primarily from the stripping effect of the air used to oxidize the sulphides in the liquor.

Lime kiln TRS emissions are related to the presence of soluble sulphides in the lime mud sent to the kiln (NCASI 1975). Jarvenisu, Kivivasara and Saari (1998) discuss the formation mechanisms of H_2S , the main reduced sulphur compound in a lime kiln, and explore various ways to reduce TRS emissions from lime kilns. TRS emissions from smelt dissolving tanks are a combination of reduced sulphur compounds (mostly H_2S) released from the green liquor and reduced sulphur compounds stripped from the scrubbing and smelt dissolving liquids (such as weak wash and condensates) (Frederick, Danko, and Ayers 1996). TRS emissions resulting from tall oil acidulation are due to the presence of reduced sulphur compounds in tall oil soap that is acidulated, as well as the potential acidulation reactions that generate reduced sulphur compounds.

2.1.2 Comparison of Pulp and Paper Mill H_2S and TRS Emissions with Other Sources

The releases of both H_2S and TRS are reported in the province of Ontario. According to Environment Canada (http://www.ec.gc.ca/pdb/npri/consultations/TRS2005_e.cfm), hydrogen sulphide makes up

almost two-thirds of the anthropogenic TRS released in Ontario (see Table 2.1). Of the remaining 38% (that typically comprises methyl mercaptan, dimethyl sulphide, and dimethyl disulphide), 99% resulted from NAICS 3221 (Pulp, Paper and Paperboard Mills). Over 70% of all reported TRS releases in Ontario resulted from NAICS 3221. Other significant releases of TRS were from NAICS 3311: Iron and Steel Mills and Ferro-Alloy Manufacturing, which reported 23% of all TRS releases in Ontario (98% of which was H₂S).

Table 2.1 Facilities Reporting TRS to MOE and H₂S to the NPRI in Ontario for Year 2005

	NPRI - H ₂ S (tonnes)	MOE - TRS (tonnes) ^a	% H ₂ S of Total
Total released in Ontario	972.2	1560.8	62.29
Releases from pulp and paper	518.9	1099.3	47.20
Releases from refineries	24.1	25	96.40

NOTE: Only facilities reporting to both MOE and NPRI were considered. There were, however, significant releases reported to the NPRI but not to the MOE

^a expressed as H₂S

Western Canada may be affected differently than the province of Ontario. Environment Canada (http://www.ec.gc.ca/pdb/npri/consultations/TRS2005_e.cfm) states that “when looking at H₂S releases reported to the NPRI across the country, 51% are from pulp and paper mills and nearly 40% are related to various petroleum and gas related activities (extraction, products manufacturing, refineries, distribution, transport), with 35% reported from NAICS 2111: Oil and Gas Extraction” (see Table 2.2). Most of these releases were reported by facilities in Western Canada; there are no oil and gas extraction facilities in Ontario. In comparing the releases reported by petroleum-related facilities (mostly refineries: NAICS 3241) in Ontario, 97% of all TRS releases were H₂S, suggesting that most TRS releases from petroleum activities, including extraction, are hydrogen sulphide (http://www.ec.gc.ca/pdb/npri/consultations/TRS2005_e.cfm).

According to the reporting of NPRI releases of H₂S to the environment for the year 2004 (http://www.ec.gc.ca/pdb/querysite/query_e.cfm), 196 sources across Canada released on-site a total of 4,586 tonnes of H₂S. Of these, 38 were pulp and paper mills (NAICS 3221) that released about 1,811 tonnes or about 39.5%.

Table 2.2 National H₂S Releases as Reported to the NPRI for Year 2005

	H ₂ S (tonnes)	% of total H ₂ S	Number of Facilities	Average Release (tonnes)
Total H ₂ S reported	4871	100%	205	23.8
Releases from pulp and paper mills	2468.8	51%	41	60.2
Releases from oil and gas extraction	1714.7	35%	92	18.6
Releases from petroleum and coal products manufacturing	94.6	2%	21	4.5
Releases from iron and steel mills, and ferro-alloy manufacturing	478.3	10%	5	95.7

Anthropogenic sources of total reduced sulphur released into the Canadian environment account for approximately 74% of the total sulphur budget in the atmosphere, with natural sources contributing the remaining 26% (Bates et al. 1992). Sources of anthropogenic emissions of TRS include kraft pulp mills, natural gas wells, petroleum refineries, steel mills, coking operations, the manufacturing of certain abrasives, and some sewage treatment plants. Although the contribution of TRS compounds to the global sulphur budget is very minor, it can be significant on a regional basis (e.g., near a pulp and paper mill).

The two major natural sources of TRS are from terrestrial regions (mostly from decaying organic matter) and from the oceans. In terrestrial environments, TRS compounds are released from decaying organic matter, such as in marshes and wetlands. TRS compounds (primarily H₂S) are also emitted from sulphur springs, geothermal areas (volcanoes) and sour gas wells. In a study of the continental USA, it was found that 65% of the biogenic (natural) TRS emitted was H₂S (Aneja 1990). TRS releases in oceanic environments (~90% dimethyl sulphide) are produced mainly as the result of phytoplankton decomposition by microorganisms (Andrae 1990; Aneja 1990). This natural release of dimethyl sulphide is increasing in importance because it may affect climate changes.

Even without industrial emissions, natural sources of total reduced sulphur cause a measurable background ambient level. Components of TRS are even created in the human body when cells decompose. Typically, studies performed to measure background levels of TRS range from 0.14 - 1.4 ppb, although this may be higher near sulphur springs or areas of geothermic activity (WHO 1987). A 1995 study of the Canadian Shield found that levels of H₂S ranged from just 0.007 ppb to 0.094 ppb (Sharma 1997). Consequently, even without anthropogenic sources, TRS is always present in the Canadian environment.

Total reduced sulphur is monitored and subject to ambient air criteria in nearly every province in Canada. These standards range from 4.5 to 31 ppb for 1-hour concentrations and from 2.2 to 6 ppb for 24-hour concentrations (see Table 2.3). The average ambient air quality levels near pulp and paper mills are shown to be in the range of 5-10 ppb, while refinery sites usually had lower levels (<5 ppb). It was reported by Environment Canada (2005) that high concentration events (>60 ppb) did occur, but they were relatively rare. Some communities in British Columbia, however, regularly experienced quantities ranging from 40 to 60 ppb, including Castegar, Kamloops, Prince George, and Robson (Environment Canada 2005). The data also showed a decrease in ambient hydrogen sulphide levels beginning in 1990, displayed through a significant drop in facilities with levels >5 ppb, and a further decrease in high concentration events (Environment Canada 2005). The odour threshold for TRS

substances ranges from approximately 1 to 20 ppb, with adverse health effects only being observed at much higher levels (~5 ppm).

Table 2.3 Provincial Ambient Air Criteria for TRS

Provinces	Ambient Air Quality (ppb)	
	24 hour	1 hour
Newfoundland		22
Nova Scotia	6	30
New Brunswick	3.7	11
Quebec		4.5
Ontario		31
Manitoba	3.7	11
Saskatchewan	3.7	11
Alberta	3	10
British Columbia	2.2	5

2.2 Chlorine Dioxide (ClO₂)

2.2.1 Use in Pulp Bleaching

Chlorine dioxide is not manufactured during bleaching and non-bleaching operations in pulp mills. At the current time, ClO₂ is widely used as an oxidant for pulp bleaching. A number of oxidants such as chlorine gas, sodium hypochlorite, and chlorine dioxide have been traditionally used as bleaching agents for pulp bleaching. However, due to concerns about the generation of chlorinated organic compounds which can result in chlorinated organic emissions from bleaching system vents and chlorinated constituents in bleach plant effluents, use of chlorine and hypochlorite has been more or less discontinued and chlorine dioxide has become common as a replacement for all of the chlorine used to bleach chemical pulps. Solutions containing chlorine dioxide are unstable; therefore, chlorine dioxide used for pulp bleaching is produced on site in generators. There are six basic commercial processes used to generate chlorine dioxide for use in pulp bleaching. These are described in Table 2.4.

Fredette (1996) provides an excellent description of the use of ClO₂ for bleaching in pulp mills, including its properties, the process chemistry involving ClO₂, the ClO₂ generation systems (atmospheric and vacuum evaporator processes), the testing of ClO₂ solution, and safety hazards associated with the use of ClO₂.

Table 2.4 Chlorine Dioxide Generation Processes (modified from Stockburger 1993)

Process	Chemical Reactions	Reducing Agent	Effluent Produced
Mathieson	$2\text{NaClO}_3 + \text{SO}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{ClO}_2 + 2\text{NaHSO}_4$	SO_2	spent acid solution
Solvay	$2\text{NaClO}_3 + \text{CH}_3\text{OH} + \text{H}_2\text{SO}_4 \rightarrow 2\text{ClO}_2 + 2\text{H}_2\text{O} + \text{HCHO} + \text{NaHSO}_4$	CH_3OH	spent acid solution
R2	$\text{NaClO}_3 + \text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{ClO}_2 + 0.5\text{Cl}_2 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$	NaCl	spent acid solution and chlorine
R3 and SVP	$\text{NaClO}_3 + \text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{ClO}_2 + 0.5\text{Cl}_2 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$	NaCl	saltcake and chlorine
R6, Lurgi, Chemetics, Vulcan	a. $\text{NaCl} + 3\text{H}_2\text{O} \rightarrow \text{NaClO}_3 + 3\text{H}_2$ b. $\text{Cl}_2 + \text{H}_2 \rightarrow 2\text{HCl}$ c. $\text{NaClO}_3 + 2\text{HCl} \rightarrow \text{ClO}_2 + 0.5\text{Cl}_2 + \text{NaCl} + \text{H}_2\text{O}$	HCl	none
R8, SVP-MeOH, SVP-LITE	$9\text{NaClO}_3 + 2\text{CH}_3\text{OH} + 6\text{H}_2\text{SO}_4 \rightarrow 9\text{ClO}_2 + 3\text{Na}_3\text{H}(\text{SO}_4)_2 + 0.5\text{CO}_2 + 1.5\text{HCOOH} + 7\text{H}_2\text{O}$	CH_3OH	acid saltcake
R10 (R8 plus metathesis)	Metathesis reaction: $2\text{Na}_3\text{H}(\text{SO}_4)_2 \rightarrow 3\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$		neutral saltcake

2.2.2 Comparison with Other Sources

Chlorine dioxide is used predominantly for bleaching pulp. As such, it is not expected to be emitted in large enough quantities by any other industrial sector other than bleached chemical wood pulp mills. For example, in 2004 (http://www.ec.gc.ca/pdb/querysite/query_e.cfm), 43 sources across Canada released on site a total of 538.4 tonnes of ClO_2 . Of these, 36 were bleached pulp and paper mills (NAICS 3221) that released about 536.1 tonnes or about 99.6%. Natural sources of ClO_2 emissions are also expected to be negligible.

2.3 Chlorine (Cl_2)

2.3.1 Use and Generation in Pulp Mills

In pulp and paper mills, chlorine may be used for pulp bleaching, although as explained in Section 2.2.1, this practice is fast becoming obsolete by the replacement of Cl_2 with ClO_2 . Chlorine may also be used for effluent treatment, raw water treatment, and sanitary effluent treatment. Trace quantities of chlorine could also be coincidentally manufactured during ClO_2 generation and from the breakdown of ClO_2 in bleaching towers. Estimates of air emissions from coincidental manufacture of chlorine for various ClO_2 generation processes are given in Table 2.5 (NCASI File Information).

Table 2.5 Chlorine Emissions from ClO₂ Generators and ClO₂ Storage Tanks (NCASI File Information)

Process	Emissions, kg/kg ClO ₂
Mathieson*	0.0004
Mathieson, salted*	0.10
R2**	0.007
R3/SVP**	0.007
R3H**	0.003
R7*	0.003
R8*	0.0004
Solvay*	0.0004
Solvay, salted*	0.10

*no scrubber for removing Cl₂ from generator vent gases

**caustic scrubber installed

2.3.2 Comparison with Other Sources

Chlorine is used in and emitted from various industries. At the current time, Cl₂ emissions from pulp and paper mills in Canada (NAICS 3221) are expected to be rather small compared to emissions from all industries due to the near complete replacement of Cl₂ by ClO₂ for pulp bleaching. For example, in 2004 (http://www.ec.gc.ca/pdb/querysite/query_e.cfm), 211 sources across Canada released on-site a total of 610.2 tonnes of Cl₂. Of these, 24 were pulp and paper mills (NAICS 3221) that released about 155.8 tonnes or about 25.5%. Just as for ClO₂, natural sources of Cl₂ emissions are expected to be negligible.

2.4 Chloroform (CHCl₃)

2.4.1 Formation in Bleached and Unbleached Pulp Mills

Chloroform is formed as a by-product when pulp is bleached with hypochlorite. Trace amounts of CHCl₃ are also formed during pulp bleaching with Cl₂ or ClO₂. Estimates for virgin pulp bleach plant generation of CHCl₃, based on NCASI laboratory studies and field data, are presented in Tables 2.6 and 2.7 (NCASI 1988, 2003; FPAC 2003; NCASI File Information). Table 2.6 gives estimates of emissions from bleach plant vents and the release to bleach plant sewers for bleaching sequences that include the use of hypochlorite. Table 2.7 provides estimates for total CHCl₃ formed and released in the bleach plant for essentially hypochlorite-free bleaching sequences. Of the total amount of CHCl₃ formed in bleach plants an average of 52% (range 6 to 90%) is released through bleach plant vents, with the remaining 48% (range 6 to 94%) discharged with the bleach plant effluent to the waste treatment facility (NCASI 1988, 2003). Thus, estimates of total CHCl₃ generated in the bleach plant as obtained from Table 2.7 should be multiplied by 0.52 and 0.48 to obtain amounts in air emissions and releases to waste treatment facility, respectively.

Table 2.6 Estimates of Chloroform Formation in Bleach Plants With Hypochlorite Sequences

Bleaching Sequence Hypochlorite Use ^a	Chloroform, kg/adtbp ^b					
	Air Emissions from Vents		Discharge to Waste Treatment Facility		Total	
	Range	Average	Range	Average	Range	Average
0.1 to <0.5%	0.035 to 0.375	0.13	0.04 to 0.38	0.12	0.15 to 0.50	0.25
0.5 to 2%	0.06 to 0.55	0.26	0.07 to 0.57	0.24	0.25 to 0.75	0.50
>2%	0.12 to 1.10	0.39	0.135 to 1.14	0.36	0.5 to 1.5	0.75

^a Percent hypochlorite use includes the hypochlorite generated by scrubbing Cl₂ from ClO₂ generator gases and used in the E stage. It is expressed as (kg available chlorine used/kg air dry bleached pulp) x 100. If sodium hypochlorite usage rates are known, then the following conversion applies:

$$\frac{\text{kg available } Cl_2 \text{ used}}{\text{kg air dry bleached pulp}} = \frac{35.5}{74.5} \times \frac{\text{kg NaOCl used}}{\text{kg air dry bleached pulp}}$$

^b air dry tonne of bleached pulp

Table 2.7 Estimates of Chloroform Formation in Bleach Plants With ≤0.1% Hypochlorite Sequences

Pulp Species, Chlorination Stage Conditions*	Total Chloroform Released, kg/adtbp**
Hardwood, ≤70% Substitution	0.92 x Chlorine Factor - 0.03
Softwood, Chlorine Factor ≥0.15, Zero Chlorine Dioxide Substitution, or Simultaneous Addition of Chlorine and Chlorine Dioxide, or <40% of Total Available Chlorine Applied as Chlorine Dioxide is Added Before Chlorine. Total Substitution May or May Not be Higher than 40%.	2.03 x Chlorine Factor - 0.25
Softwood, Chlorine Factor <0.15, Zero Chlorine Dioxide Substitution, or Simultaneous Addition of Chlorine and Chlorine Dioxide, or <40% of Total Available Chlorine Applied as Chlorine Dioxide is Added Before Chlorine. Total Substitution Between Zero and 90%.	0.37 x Chlorine Factor
Softwood, ≥40% of Total Available Chlorine Applied as Chlorine Dioxide is Added Before Chlorine. Total Substitution ≥40% and ≤70%	(1.455 x Chlorine Factor) - 0.045
100% ClO ₂ Substitution, All Conditions	0.0025

$$\text{Chlorine Factor} = \frac{\text{Chlorine, Percent}}{\text{Kappa No.}}$$

$$\text{Chlorine, Percent} = \frac{\text{kg Chlorine}}{\text{kg OD Brownstock}} \times 100$$

** air dry tonne of bleached pulp

Table 2.8 contains NCASI test data (NCASI File Information, NCASI 1993) on the formation of CHCl_3 during hypochlorite bleaching of repulped and deinked pulps. Although the data in Table 2.8 would suggest compared to bleaching of virgin fibres less of CHCl_3 is produced during hypochlorite bleaching of recovered fibres, the virgin fiber generation data in Table 2.6 include nearly 0.15 kg/adtp formed in the chlorination stage of virgin fibre bleaching. Excluding the impact of the chlorination stage, the generation estimates for recovered fibres in Table 2.8 seem to be consistent with the generation estimates for virgin fibres in Table 2.6. Thus, in the absence of mill-specific information, one may estimate the amount of CHCl_3 generated in recovered fibre bleaching by using the estimates for virgin fibre bleaching in Table 2.6, after adjusting for a decrease of 0.15 kg/adtp in the absence of a chlorination stage in the recovered fibre bleaching sequence.

Table 2.8 Formation of Chloroform in Recycled Pulp Bleaching

Mill	Secondary Fibre Sources	Bleach Sequence	Weight Percent Hypo Used**	Chloroform Discharged, kg/adtp		
				Vents	Sewers	Total
A (2)	Repulped	H	1.10	0.04	0.31	0.35
B (2)	Deinked	H	0.56	<0.01	0.29	0.29
C (2)	Repulped	H	0.95	0.27	0.12	0.39
D (2)	Repulped	CH	1.92	1.02	0.64	1.66
E (3)	Deinked	H	0.25	0.04	0.02	0.06
F (3)	Deinked	HY*	0.30	<0.01	0.15	0.15

*Y - hydrosulphite bleaching stage

** - weight percent hypo as defined in Table 2.6

2.4.2 Formation in Bleached and Unbleached Pulp Mills

Chloroform is also produced in trace quantities during the chlorination of water. According to the United States Environmental Protection Agency, 0.41 kg of chloroform/ 10^6 m^3 of water are formed and emitted during the chlorination of "once-through" cooling water systems (USEPA 1984). Additionally, 3.06 kg/ 10^3 m^3 and 0.041 kg/ 10^3 m^3 of chloroform are formed and emitted during the chlorination of "recirculating" cooling water systems and drinking water, respectively.

2.4.3 Comparison with Other Sources

Like chlorine dioxide, chloroform is not expected to be emitted in large enough quantities by any other industrial sector other than bleached chemical wood pulp mills. For example, in 2004, (http://www.ec.gc.ca/pdb/querysite/query_e.cfm), 13 sources across Canada released on site (emitted) a total of 49.9 tonnes of CHCl_3 . Of these, 5 were pulp and paper mills (NAICS 3221) that released about 49.2 tonnes or about 98.6%. It should be noted that although only 5 mills filed a report in 2004 for CHCl_3 in all of Canada under the NPRI, several other pulp and paper mills with bleach plants do generate and emit CHCl_3 . However, they do not file a report under the NPRI since the amount of generation is far less than the 10-tonne reporting threshold. Natural sources of CHCl_3 emissions are expected to be negligible.

2.5 Methanol (MeOH)

Methanol (MeOH) is a volatile organic compound unintentionally generated in various pulp mill and wood products operations, primarily in chemical pulping and recovery. It is among the list of volatile organic substances designated by EPA as 'air toxics' or hazardous air pollutants (HAPs). It is also used as a surrogate for all HAPs by EPA and subject to control in U.S. mills under the MACT provisions (40 CFR Part 63) of the Cluster Rule (USEPA 1998). Its release is not nationally regulated in Canada. Due to its abundance relative to other organic HAPs, methanol is an acceptable and widely used surrogate for demonstrating compliance with the MACT provisions, which apply to a series of organic HAPs. In the U.S., many kraft mills are complying with the MACT kraft condensate standards by collecting and treating at least 5.55 kg MeOH per tonne of oven-dried (OD) bleached pulp and/or 3.6 kg MeOH per tonne of OD unbleached pulp. These standards apply uniformly to all kraft mills irrespective of raw materials and process conditions. Some mills, especially kraft linerboard mills, have found that collection of these amounts is difficult. It is known that because of differences in wood chemistry, softwoods generate less methanol per ton of wood than hardwoods.

2.5.1 Formation in Pulp and Paper Mills

Experimental data support the theory that methanol is generated during alkaline cooking of wood by the alkaline hydrolysis of 4-O-methylglucuronic acid residues in xylan hemicellulose to form hexenuronic acid groups and methanol, and via the demethylation of lignin (Zhu, Chai, and Dhasmana 1999; Kirkman et al. 2001). Based on lab cooks of southern U.S. softwoods, Zhu et al. (2000) estimated that about 40% of the methanol formed was due to the former reaction, and about 35% to the latter. The remaining 25% was attributed to methanol present in the uncooked wood. Methanol formation was shown by these researchers to depend on the extent of cooking. Bleachable grade pulps produced more methanol than high-kappa pulps, though the relationship was not linear. Formation was slow during the initial phase of cooking, increased rapidly as the temperature reached 170°C, and slowed again as the kappa dropped below about 80, after about 90 minutes total cooking time. Effects of other variables, including anthraquinone dosage and liquor sulphidity, suggest that total methanol generation increases in proportion to the cooking time as well as the active alkali (OH) concentration. Methanol in the uncooked wood is likely formed due to fermentation of wood sugars, which would depend upon conditions such as chip pile temperatures and rotation times.

2.5.1.1 Wood Species Influence

With respect to wood species, differences in methanol generation will depend on the number of 4-O-methylglucuronic acid groups in hemicellulose, and the number of methoxyl groups in lignin. 4-O-methylglucuronic acid groups are components of xylan hemicellulose, so the amount of xylan should be a key variable in methanol generation potential. In general, hardwoods contain two to three times more xylan than softwoods. However, the ratio of 4-O-methylglucuronic acid groups per unit of xylose residues is on the order of two times greater in softwoods than in hardwoods, so that the total amount of 4-O-methylglucuronic acid groups may not be very different between hardwood and softwoods. Table 2.9 shows some xylan and lignin content data from various literature sources.

Xylan content values for softwoods range from 7 to 14% on wood, whereas xylan in hardwoods ranges from 15 to 35%. Eucalyptus (*E. grandis*) has the lowest reported value for the hardwoods, a level similar to that of the softwoods, and would thus be expected to generate the least amount of methanol from xylan degradation.

The lignin content of the wood will also help determine the amount of methanol generated during the cook. Softwoods contain more lignin than hardwoods, as shown in Table 2.9. However, this is offset by the fact that hardwood lignin contains more methoxyl groups than softwood lignin. Hardwood lignin contains both coniferyl alcohol (50 to 75%), with one methoxyl group, and sinapyl alcohol (25-

50%), with two methoxyl groups, whereas softwood lignin contains only coniferyl alcohol. Among the hardwoods listed in Table 2.9, one would expect that *E. grandis* would generate the most methanol due to lignin demethylation.

Table 2.9 Xylan and Lignin Content of Various Wood Species

Wood Species	Xylan, % on wood	Lignin, % on wood	Ref.
Softwoods	8 to 11	26 to 31	a
Scots pine, <i>Pinus sylvestris</i>	8	27	b
Balsam fir, <i>Abies balsamea</i>	9	29	c
White spruce, <i>Picea glauca</i>	13	27	c
Eastern white pine, <i>Pinus strobus</i>	9	29	c
Eastern hemlock, <i>Tsuga canadensis</i>	7	33	c
Northern white-cedar, <i>Thuja occidentalis</i>	14	31	c
Hardwoods	20 to 30	20 to 26	a
Birch, <i>Betula verrucosa</i>	30	20	b
Red maple, <i>Acer rubrum</i>	25	24	c
Paper birch, <i>Betula papyrifera</i>	35	19	c
American beech, <i>Fagus grandifolia</i>	26	22	c
Quaking aspen, <i>Populus tremuloides</i>	24	21	c
American elm, <i>Ulmus americana</i>	19	24	c
Eucalyptus, <i>E. grandis</i>	15.3	26.2	d

^a Dence and Reeve 1996

^b Malcolm et al. 1989

^c Saka 1991

^d Durán and Fardim 2001

2.5.1.2 Methanol Generation Rates

A few studies have been conducted to quantify methanol generation during alkaline pulping. Zhu, Chai, and Dhasmana (1999) reported methanol concentrations from kraft cooks of birch and southern pine to kappa 15 and 31, respectively. The birch cook generated about 30% more methanol than the pine. Data from Zhu et al. (2000) show that for bleachable grades, softwood pulping generated from 7.3 to 9.3 kg methanol/ODT (oven dry tonne) pulp, and hardwood pulping generated from 9.6 to 15.0 kg methanol/ODT pulp. Data for each species studied are shown in Table 2.10. Average methanol generation rates, calculated from the data provided, are also shown. Based on these average values, the hardwoods generated about 43% more methanol than the softwoods.

Table 2.10 Methanol Generation in Softwood and Hardwood Species
(data from Zhu et al. 2000)

Wood Species	Bleachable Grade		Linerboard Grade	
	Methanol, kg/ODT pulp	Kappa No.	Methanol, kg/ODT pulp	Kappa No.
Douglas fir	8.3	31.4	5.6	63.4
White spruce	9.1	30.5	7.2	56.6
Western hemlock	7.3	30.1	6.0	76.1
Southern pine	9.3	28.2	7.3	70.5
SOFTWOOD AVG.	8.5		6.5	
Aspen	9.6	10.7		
Bass	13.1	13.5		
Birch	11	14.1		
Maple	11.3	13.4		
Oak	12.8	17.4		
Sweet gum	15.0	15.2		
HARDWOOD AVG.	12.1			

ODT – oven dry tonne

2.5.1.3 Summary

In pulp and paper mills, methanol is generated during alkaline pulping of wood via alkaline hydrolysis of 4-O methylglucuronic acid groups on xylan hemicellulose, and by demethylation of lignin. In general, hardwoods contain more xylan than softwoods, but hardwood xylan contains fewer 4-O methylglucuronic acid groups than softwood xylan. Softwoods contain more lignin than hardwoods, but hardwood lignin contains more methoxyl groups than softwood lignin. The net result of these differences in wood chemical composition between hardwoods and softwoods is that hardwoods in general produce on the order of 30-45% more methanol than do softwoods. For a given wood species, the length of the cook has a large impact on total methanol generation. Linerboard grade pulping (~70 kappa) produced about 75% of the methanol produced during bleachable grade softwood pulping (~30 kappa) in a lab study.

Methanol may also be present in the wood due to microbiological fermentation of wood sugars, and this could be a significant source. It is possible that methanol so formed would reduce the amount subsequently produced in the digester due to xylan degradation. Lab studies also suggest that methanol may be generated during black liquor evaporation via lignin demethylation (Zhu et al. 1999).

It is important to note that irrespective of the amount of methanol generation during kraft pulping, the amount of methanol emitted from a particular kraft pulp mill unit operation is mostly independent of this fact. For example, the extent to which methanol is emitted from brownstock washers immediately after the pulp is removed from the digesters depends mainly on the quality of the condensates (relative to methanol content) used in the last stage shower. The bulk of the methanol generated during kraft pulping and evaporation is expected to end up in the “foul” or “dirty” condensates resulting from these operations. Thus, the differences in methanol generation among various wood types are expected to influence the amount of methanol contained in the condensates generated during pulping and liquor evaporation, which in turn would affect the amount of methanol stripped from

condensates (for mills with strippers) or the amount sent for treatment in the wastewater treatment system.

2.5.2 Formation in Wood Products Operations

In wood products operations, wood is heated for the purpose of removing water. When the wood is heated, some of the so-called extractive compounds present in the wood, such as the methanol present in uncooked wood alluded to in the previous section of this report, will also be released. These organic compounds that are in gaseous form at the elevated temperature of the wood are comprised largely of lower molecular weight volatiles (methanol being one of them), and higher molecular weight resin and fatty acids. The type and amounts of compounds released will depend on several factors related to the drying process, including the temperature of wood and the length of time at this temperature, the surface area of the wood material relative to its mass, and amount of water removed from the material. Releases are also a function of wood species, location in the tree from which the wood material originated (heartwood versus sapwood), season during which the wood was harvested, and length of time between harvest and drying.

Other factors being equal, releases of organic compounds including methanol will normally increase with

- higher dryer temperatures
- longer residence times in the dryer
- larger surface area to mass ratios
- greater amounts of water removal
- decreasing time between wood harvest and drying.

Methanol is thus coincidentally manufactured as a by-product in wood products manufacturing operations, the primary sources being wood dryers, panel presses, and lumber kilns. Small amounts of methanol may also be manufactured in wood-fired boilers, pressurized refiners and digesters, exhaust gases from sanders, chippers, saws, and other wood handling and finishing sources. However, their contribution to the total methanol manufactured in a mill is generally relatively small.

Releases of individual organic compounds such as methanol vary significantly between softwoods and hardwoods for wood processing or mechanical pulping, while they are essentially similar for chemical pulping. Even for the same wood species, releases of organic compounds can depend upon the location within the tree where the wood originated. For example, drying of veneer made from sapwood (less mature outer portion of bole) will usually result in greater releases than the drying of veneer from heartwood. Releases may also be affected by the presence of knots that contain resinous material. In some species like loblolly pine, the resin content is dependent on sap flow, which in turn fluctuates with season and climatic conditions.

2.5.3 Comparison with Other Sources

In Canada, methanol is predominantly released on site (mostly emitted) by the paper and allied products and wood industry sectors. For example, in 2004 (http://www.ec.gc.ca/pdb/querysite/query_e.cfm), a total of 556 sources released on site 20,823 tonnes of methanol of which 149 sources belonging to the paper and allied products industry released 14,367 tonnes (69.0%) and 76 sources belonging to the wood industry released 3,153 tonnes (15.1%). Besides these forest products industry sectors, 149 sources in the chemical and chemical processing industry released about 1,342 tonnes of methanol (6.4%) and 85 sources in the crude petroleum and natural gas industry released about 858 tonnes (4.1%).

3.0 ENVIRONMENTAL FATE AND SIGNIFICANCE

3.1 Total Reduced Sulphur (TRS)

3.1.1 *Environmental Fate and Persistence*

Since hydrogen sulphide exists as a gas at atmospheric pressure, it is likely to partition into the air after environmental releases (ATSDR 2006). In the atmosphere, H₂S is oxidized by molecular oxygen and hydroxyl radicals, forming the sulfhydryl radical and ultimately sulphur dioxide or sulphate compounds (WHO 2003). The atmospheric residence time of H₂S is typically less than one day, but has been reported to be as long as 42 days in the winter (WHO 2003).

Methyl mercaptan exists as a gas at atmospheric pressure and is likely to partition into the air after environmental releases (ATSDR 1992). Methyl mercaptan in the atmosphere will be degraded in reactions with photochemically produced hydroxyl (daytime) or nitrate (night time) radicals (HSDB 2005a). The half-life is estimated to be less than 12 hours (HSDB 2005a).

Dimethyl disulphide is expected to exist in the environment primarily in the atmosphere (HSDB 2005b). In the atmosphere, dimethyl disulphide will be degraded primarily through reaction with photochemically produced hydroxyl radicals with a half-life of about 4 hours (HSDB 2005b). Direct photolysis (daytime) and reaction with nitrate radicals (night time) play a minor role in degradation as well (HSDB 2005b).

Dimethyl sulphide exists as a gas at atmospheric pressure and is expected to exist solely as a vapour in the ambient atmosphere (HSDB 2005c). During the day, dimethyl sulphide will be degraded in the atmosphere by reaction with hydroxyl radicals and atomic oxygen with an estimated half-life of 2.2 days (HSDB 2005c). At night, reaction with nitrate radicals predominates (HSDB 2005c).

In water, hydrogen sulphide is a weak acid (ATSDR 2006). At a pH of 7, the ratio of dissolved H₂S to the bisulphide ion (HS⁻) is about 1:1. If the pH exceeds 11, a second dissociation occurs, yielding the sulphide ion (S⁻). In surface waters, H₂S is readily oxidized by molecular oxygen (ATSDR 2006).

Although most methyl mercaptan released to the environment partitions into the air, a small amount may dissolve in water. There is no information about the fate of methyl mercaptan in water, although it is likely that it will photooxidize and oxidize in water (ATSDR 1992). Similarly, volatilization and photodegradation are expected to be the major fate process for dimethyl disulphide in water (HSDB 2005b). For dimethyl sulphide, volatilization is expected to be the major fate process in water, with sensitized photolysis and microbial degradation playing minor roles (HSDB 2005c).

None of the four major TRS compounds are likely to persist in the environment.

3.1.2 *Toxicology*

3.1.2.1 **Potential for Harmful Effects on Human Health**

The health effects of the four major TRS gases have been reviewed by NCASI (NCASI 1995). The effects of hydrogen sulphide on humans have been the subject of study for several hundred years. Halle, in his 1785 publication describing the ills of Parisian sewer workers, accurately identified what are still the two most commonly reported effects of occupational exposure to H₂S: eye irritation and asphyxiation (NRC 1978). Concentrations of around 500 ppm and higher can cause respiratory arrest, unconsciousness, and collapse. Prolonged exposures to concentrations greater than about 250 ppm or brief exposures to higher concentrations can lead to the development of pulmonary oedema, which may be life threatening. Exposure to concentrations above about 5 ppm in the workplace causes eye irritation, known in the past as “gas eye” by sewer workers and “spinner's eye” by workers in the viscose-rayon industry.

Studies conducted on experimental animals reveal effects similar to those reported in humans. However, there have also been several studies in which H₂S has been demonstrated to cause nasal lesions in rodents. There is some controversy on this subject, since there is a considerable body of literature describing the differences in human and rodent nasal anatomy and physiology, leading some scientists to question the relevance of rodent nasal lesions to human risk assessment.

There is much less information available on the health effects of the other three TRS gases. The effects of methyl mercaptan on humans appear to be similar to those of hydrogen sulphide, although somewhat higher concentrations may be required to elicit the same effects. Based on a limited number of animal studies, dimethyl disulphide appears to be on the same order of toxicity as methyl mercaptan and its effects on humans may be similar. Dimethyl sulphide appears to be considerably less toxic than the other TRS gases. Based on very limited study, it appears that exposure to very high concentrations (several thousands of ppm) of dimethyl sulphide may produce effects similar to those reported with other TRS gases.

The very low odour threshold and unpleasant odour of reduced sulphur gases raises certain health concerns that are unique to such compounds. These are described in detail in NCASI Technical Bulletin No. 691 (NCASI 1995). In short, some individuals have reported a variety of health symptoms following exposure to very low, but above odour threshold, levels of reduced sulphur gases. These symptoms, such as headache and fatigue, are difficult to study because they are difficult to measure or assess in an objective, quantitative fashion. There is also uncertainty over whether such symptoms should be attributed to direct physiological effects of exposure to reduced sulphur gases or to indirect responses to the perception of unpleasant odours, which would not be specific to reduced sulphur gases. Various regulatory agencies have taken different approaches to this issue, with some deciding to base regulation strictly on more traditional toxicological endpoints such as rodent nasal lesions and others basing regulations on more nebulous endpoints such as the percentage of the population annoyed by the odour.

3.1.2.2 Harmful Effects on the Environment or Its Biological Activity

A review of the effects of TRS compounds on vegetation revealed that there is virtually no information available for methyl mercaptan, dimethyl disulphide, or dimethyl sulphide (CEPA/FPAC 1998). The same review reported that vegetation is relatively insensitive to short-term exposure to hydrogen sulphide, but that long-term exposure to concentrations greater than 0.28 ppm can inhibit growth and cause visible injury. Hydrogen sulphide has been shown to have harmful effects on vegetation, although this information comes almost exclusively from laboratory studies. Following a gas well blowout in Alberta, where measured H₂S concentrations ranged from 5 to 10 ppm for several hours and peaks were probably higher, alfalfa and hay yields were reportedly reduced by one-half to two-thirds (USEPA 1993). In one study, citrus trees in poorly drained soils in Florida suffered root injury after 5 days of exposure to 2.8 mg/L sulphide in soil water (USEPA 1993).

There is no information available on the effects of methyl mercaptan, dimethyl disulphide, or dimethyl sulphide in air on wildlife (CEPA/FPAC 1998). There are a few studies describing the effects of H₂S on wildlife. Ambient levels of H₂S do not appear to have any adverse effects on wildlife, but high concentrations due to accidental releases have resulted in mortality in birds and wild animals (USEPA 1993). For example, following the release of high concentrations of H₂S and other compounds from a British Columbia pulp mill during a process upset, 200 to 500 songbirds were killed (CEPA/FPAC 1998). Ambient air levels of up to about 4 ppm in an area of geothermal activity in New Zealand have no apparent effect on birds, with the local wildlife reserve supporting abundant populations of both seasonal and non-migratory bird species (USEPA 1993).

Only hydrogen sulphide and methyl mercaptan have been evaluated for aquatic toxicity. Hydrogen sulphide is considered to be highly toxic to a number of aquatic organisms. The LC₅₀ values in

various species of fish range from about 7 to 780 ppb, with fry being generally more sensitive (USEPA 1993). For methyl mercaptan, the minimum lethal concentrations for various species of fish in one study were in the range of 0.9 to 1 ppm (HSDB 2005a). Another study reported methyl mercaptan LC₅₀ values for salmonids of 0.55-0.9 ppm.

3.2 Chlorine Dioxide (ClO₂)

3.2.1 Environmental Fate and Persistence

Chlorine dioxide gas is unstable. In the presence of sunlight, it undergoes rapid photodecomposition, with a reported lifetime of 13-37 seconds (NCASI 1999). In the dark, thermodecomposition and reaction with hydroxyl radicals are primarily responsible for ClO₂ degradation, with an estimated lifetime of 43 hours, or until the sun comes up (NCASI 1999).

In water, ClO₂ does not hydrolyse to any appreciable extent and is stable in dilute solutions if kept cool, well sealed, and in the dark (ATSDR 2004). In the absence of oxidizable substances and in the presence of hydroxyl ions, it will gradually decompose to form chlorite and chlorate ions (ATSDR 2004). In the presence of oxidizable substrates, ClO₂ is rapidly transformed to chlorite, which is also an oxidizing agent and is subsequently transformed to chloride (ATSDR 2004). In an aqueous solution of ClO₂, a number of different ionic species, including chlorite and chlorate, exist in equilibrium (ATSDR 2004). Chlorine dioxide in aqueous solutions also readily degrades in the presence of sunlight (ATSDR 2004).

3.2.2 Toxicology

3.2.2.1 Potential for Harmful Effects on Human Health

The ATSDR Toxicological Profile for Chlorine Dioxide and Chlorite provides a comprehensive review of the toxicology of chlorine dioxide (ATSDR 2004). There are some studies of the toxicity of ClO₂ aqueous solutions to humans and experimental animals. Most studies, though, have focused on the toxicity of chlorite solutions, since chlorite is the predominant chemical form present in drinking water treated with ClO₂. Consumption of low levels of chlorine dioxide or chlorite (<0.15 mg/kg/day) does not appear to have any adverse effects on humans or experimental animals.

In animal studies, neurodevelopment is generally considered to be the endpoint most sensitive to oral exposures to ClO₂ or chlorite. For both ClO₂ and chlorite, the no-observed-adverse-effect-level (NOAEL) for this endpoint is a maternal exposure of 3 mg/kg/day. Aqueous ClO₂ at doses of 40-80 mg/kg can be lethal to rodents; the LD₅₀ is calculated to be about 90 mg/kg.

Inhalation exposure to ClO₂ is primarily an occupational concern, since the general public is unlikely to encounter circumstances under which they would be exposed to ClO₂ gas. Upper respiratory tract injury is the most commonly reported adverse effect of occupational exposure to ClO₂, but since such effects are typically associated with accidental releases, exposure concentrations are generally not known.

In animal studies, inhalation of ClO₂ damages the respiratory tract, resulting in effects such as pulmonary oedema, respiratory infection, nasal discharge, and inflammation. The lowest-observed-adverse-effect-levels (LOAELs) for respiratory endpoints in rats and rabbits following exposures of varying durations range from 1 to 10 ppm.

3.2.2.2 Harmful Effects on the Environment or Its Biological Activity

There are few published reports of the ecotoxicity of ClO₂. In a marine study, the effects of aqueous ClO₂ on germination of spores of giant kelp, development of purple sea urchin embryos, and survival of kelp bass eggs were examined. The no-observed-effect-concentration (NOEC) for bass and sea

urchin was 25 mg/L while the NOEC for giant kelp spore germination was 2.5 mg/L (HSDB 2005d). In an acute lethality study using freshwater fish, the 96-hr LC₅₀ values for fathead minnows were 0.02 and 0.17 mg/L for juveniles and adults, respectively, and 0.15 mg/L for juvenile bluegill sunfish (HSDB 2005d).

In the early 1980s, there were reports of toxicity to the marine plant bladderwrack from chlorate in effluents of a Swedish pulp and paper mill using ClO₂ in the bleaching process. It was subsequently shown that many species of brown algae were especially sensitive to chlorate at concentrations above 10-20 µg/L (WHO 2002).

As part of a study on effluent from an Alberta mill, the effects of chlorate on five species of insect were determined by exposing stoneflies, mayflies (two different species), Hemiptera (true bugs), and beetles to 0.5, 5.0, and 50.0 mg/L chlorate for 10 days. The survival of the test organisms was not different from that of the controls. The 48-hr LC₅₀ value for Daphnia was also determined to be about 3,000 mg/L (Doddall et al. 1997).

3.3 Chlorine (Cl₂)

3.3.1 Environmental Fate and Persistence

Chlorine (Cl₂) exists in the environment as a gas. During daylight hours, chlorine in the atmosphere undergoes rapid photodissociation with reported lifetimes ranging from 8.3 to 83.3 minutes (NCASI 1999). Chlorine in air is also degraded through reaction with hydroxyl radicals (NCASI 1999). This reaction is much slower than photolytic degradation, with reported lifetimes ranging from 2.9 to 5 hours, but during night time hours this may be the dominant reaction (NCASI 1999).

Chlorine reacts readily with water to form solvated chlorine, Cl₂ (aqueous), which disproportionates rapidly (in the order of milliseconds) to hypochlorous acid and hydrochloric acid (USEPA 1999a). Under typical environmental conditions, the resultant hydrochloric acid is completely dissociated to yield chloride anions and hydronium ions (USEPA 1999a). Hypochlorous acid is a strong oxidant and will react with inorganic and organic matter in the water. Depending on the pH, some of the hypochlorous acid will dissociate to yield hypochlorite anions. The mechanisms and rates of decomposition of hypochlorous acid and hypochlorite anions are dependent on a number of factors including pH, chemical concentration, sunlight, and temperature (USEPA 1999a). The half-life in natural freshwater systems has been estimated as 1.3 to 5 hours (USEPA 1999a).

3.3.2 Toxicology

3.3.2.1 Potential for Harmful Effects on Human Health

Chlorine is an irritant and corrosive gas. The acute effects of exposure to chlorine gas range from sensory irritation at concentrations around 1 ppm to difficulty breathing, anxiety, vomiting, cyanosis and pulmonary oedema at concentrations of 30-40 ppm (USEPA 1999a). Concentrations above about 400 ppm are lethal after exposures of 30 minutes and concentrations above 1000 ppm are lethal within a few minutes (HSDB 2006a). There is some evidence that asthmatics may have a greater sensitivity to chlorine (USEPA 1999a). Following chronic (2-year) inhalation exposures to rats and mice, there was no evidence of any carcinogenic potential; however, nasal lesions were associated with exposures even to relatively low (0.4 ppm) concentrations (USEPA 1999a).

3.3.2.2 Harmful Effects on the Environment or Its Biological Activity

Elemental chlorine (Cl₂) does not exist as such in water. Aquatic toxicity studies have been conducted, however, using substances that yield hypochlorous acid and hypochlorite anions in

solution. On the basis of those studies, EPA classifies chlorine as very highly toxic to highly toxic to fish and aquatic invertebrates, with LC₅₀ values ranging from 0.02–1.4 ppm (USEPA 1999a).

3.4 Chloroform (CHCl₃)

3.4.1 *Environmental Fate and Persistence*

Chloroform is degraded in the atmosphere through hydroxyl radical reactions with reported lifetimes ranging from 26 to 548 days, with a median value of 207 days (USEPA 1999a). Chloroform will be removed from the atmosphere by precipitation (NCASI 1999).

In soil, chloroform is expected to have a very short residence time due to rapid volatilization (HSDB 2006b). Similarly, chloroform released to water is expected to dissipate primarily through volatilization to the atmosphere (HSDB 2006b). Biodegradation does not appear to be a significant route of chloroform dissipation from soil or water (HSDB 2006b).

3.4.2 *Toxicology*

3.4.2.1 Potential for Harmful Effects on Human Health

Chloroform was once used as a general anaesthetic because of its central nervous system effects. Levels of 3,000 to 30,000 ppm induce anaesthesia (ATSDR 1997). In workplace environments, inhalation exposures above about 900 ppm caused dizziness, vertigo, headache, and slight intoxication (ATSDR 1997). Nausea and vomiting were frequently observed side effects of chloroform anaesthesia and have also been reported by workers exposed to 14-400 ppm chloroform in workplace atmospheres over a period of 1-6 months (ATSDR 1997). Chloroform-induced hepatotoxicity is one of the major toxic effects observed in both humans and animals after inhalation exposure (ATSDR 1997). The ATSDR Intermediate Minimal Risk Level (MRL) for chloroform is based on an occupational study in which workers exposed to 14-400 ppm chloroform over a period of 1-6 months developed toxic hepatitis (ATSDR 1997). While there are few reports of kidney damage among humans exposed via inhalation to chloroform, the kidney is one of the primary targets of inhaled chloroform in laboratory animals (ATSDR 1997). There are no studies of the carcinogenicity of chloroform following inhalation exposure (ATSDR 1997).

There have been numerous studies of the toxicity of chloroform following oral exposures due to concerns about the effects of exposure to chlorination by-products in drinking water. The liver and kidneys appear to be the primary target organs following oral exposures, although neurological effects have also been reported in some studies (ATSDR 1997). There is a lack of good dose-response data for humans following oral exposures to chloroform. For laboratory animals, reported no-observed-adverse-effect-levels (NOAEL) for hepatic effects of chloroform administered in drinking water range from 34 to 145 mg/kg/day. Chloroform has also been administered to laboratory animals in other vehicles, such as corn oil or toothpaste. The results of these studies may not provide useful dose-response data because there is evidence that administration in oil potentiates the hepatic effects of chloroform.

Chloroform has been classified as possibly carcinogenic to humans by the International Agency for Research on Cancer (IARC). EPA has concluded that chloroform is likely to be carcinogenic to humans by all routes of exposure under high-exposure conditions that lead to cytotoxicity and regenerative hyperplasia in susceptible tissues, but that chloroform is not likely to be carcinogenic to humans by any route of exposure under exposure conditions that do not cause cytotoxicity and cell regeneration (USEPA 2001a).

3.4.2.2 Potential for Harmful Effects on the Environment or Its Biological Activity

Reported 48-hr LC₅₀ values for *Daphnia magna* range from 29 to 79 ppm (WHO 1994). The 96-hr LC₅₀ values reported for various species of freshwater fish range from 18 to 191 ppm (WHO 1994). The LC₅₀ values for various species and life stages of amphibians range from 0.3 to 35 ppm (WHO 1994). In a comprehensive review, the World Health Organization (WHO) concluded that levels of chloroform in surface water are generally low and would not be expected to present a hazard to aquatic organisms (WHO 1994).

3.5 Methanol (MeOH)

3.5.1 Environmental Fate and Persistence

In the atmosphere, methanol degrades in reaction with photochemically produced hydroxyl radicals with reported lifetimes in the atmosphere ranging from 4.3 to 42.9 days (NCASI 1999). Methanol can also be removed from the air by rainfall. A significant proportion of methanol released to water or soil is likely to volatilize; what remains will biodegrade rapidly (HSDB 2005e).

3.5.2 Toxicology

3.5.2.1 Potential for Harmful Effects on Human Health

The acute toxicity of methanol varies widely with species due to differences in the ability to metabolize formate, the last intermediate in the metabolic pathway for methanol (WHO 1997). Primates are much more susceptible to methanol toxicity. That said, methanol is still not highly toxic, even to primates. Reported LD₅₀ values for monkeys, for example, range from 2,000 to 7,000 mg/kg (WHO 1997). According to Starr and Festa (2003), the most sensitive endpoint of toxicity in laboratory animals is developmental effects. In mice, birth defects were observed following gestational exposures to methanol vapour at concentrations above 5,000 ppm. In non-human primates (*Macaca fascicularis*), there were no methanol-related effects on offspring birth weight or newborn health status following gestational exposure to up to 1,800 ppm of methanol vapour (Burbacher et al. 2004).

In humans, acute oral and inhalation exposures to high concentrations of methanol have resulted in central nervous system depression, blindness, coma, and death (WHO 1997). According to a WHO review, for humans, the minimum lethal dose in the absence of medical treatment ranges from 0.3 to 1 gm methanol/kg body weight (WHO 1997). Chronic exposures to methanol vapour in the range of 365-3080 ppm have resulted in headache, dizziness, nausea, and blurred vision (WHO 1997).

3.5.2.2 Potential for Harmful Effects on the Environment or Its Biological Activity

The toxicity of methanol to aquatic organisms quite low. In fish, reported LC₅₀ values range from 10,880 to 29,700 ppm (WHO 1997). In studies with a variety of aquatic invertebrates, reported LC₅₀ values ranged from 1,580 to 35,884 ppm (WHO 1997).

4.0 ANALYTICAL METHODS

4.1 Total Reduced Sulphur (TRS)/Hydrogen Sulphide (H₂S)

A number of reduced sulphur compounds are generated during kraft pulping and chemical recovery operations. Since these compounds have very low odour thresholds, the emissions of reduced sulphur compounds from kraft mill sources are regulated as TRS. For regulatory purposes, when the TRS emission standard from a source is in parts per million (ppm), it is measured as the sum of the concentrations of hydrogen sulphide, methyl mercaptan, dimethyl sulphide, and 2 x dimethyl disulphide. For sources where TRS emission limits are set as a mass emission standard, the TRS concentration is multiplied by the molecular weight of hydrogen sulphide.

This section describes some of the well established and approved methods for measuring and/or monitoring hydrogen sulphide and TRS compounds.

4.1.1 Air Monitoring

The most widely used method for measuring the concentrations of various reduced sulphur compounds in stack gases is EPA Method 16 (USEPA 2000a), which, with some modifications, has also been published as Environment Canada Method EPS 1/RM/6 (Environment Canada 1992) and has been adopted by several provinces, including Alberta (Alberta Stack Sampling Code 1996a), British Columbia, and Ontario. Both versions utilize a gas chromatograph equipped with a flame photometric detector (FPD) for sample analysis. The U.S. version, however, is based on direct analysis of the stack samples. The Environment Canada version specifies sample collection in a Teflon or Tedlar bag or a glass container followed by GC analysis. An appropriate column is used in the gas chromatograph for separating the reduced sulphur compounds prior to their quantification via the FPD. The detection limit for this method is 1-2 ppb (v/v) for individual compounds. In those instances where only the total reduced sulphur compound concentration is desired, the source gases are oxidized to SO₂. This is subsequently measured either by using wet chemistry, according to EPA Method 16A (USEPA 2000b), or on a gas chromatograph equipped with a flame photometric detector, according to EPA Method 16B (USEPA 2000c). Several provinces (British Columbia, Quebec) have also adopted Methods 16A and 16B (USEPA 2000b, 2000c).

Ambient measurements of speciated reduced sulphur compounds are generally measured on a gas chromatograph equipped with a cryogenic trapping concentrator and a pulsed flame photometric detector (Wardencki 1998; Baltussen et al. 1999; Ochiai et al. 2001; Inomata et al. 1999; Kim, Ju, and Joo 2005). NCASI has developed and used a method for measuring low parts per billion levels of reduced sulphur compounds in the ambient air (Crawford 2006). The method utilizes specially passivated/coated canisters for sample collection. Moisture is removed from the ambient air by passing it through a Nafion dryer prior to entering the canister.

In addition to the chromatographic methods for total reduced sulphur compounds, a number of other methods are available for specifically measuring H₂S. Among the wet chemistry-based methods for H₂S determination are colorimetric (NIOSH 1977, 1979; Van Den Berge, Devreese, and Vanhoorne 1985), iodometric (USEPA 1978), and potentiometric methods (Ehman 1976). Continuous monitoring methods for ambient H₂S include methods which utilize lead-acetate impregnated tape (USEPA 1978), mercuric chloride impregnated tape (USEPA 1978), silver membrane filters (USEPA 1978), and gold film sensors (Arizona Instrument LLC, Tempe, AZ). These methods are listed in the analytical methods section of the ATSDR draft report on hydrogen sulphide (ATSDR 2006). Many of these methods exhibit positive interference from other reduced sulphur compounds likely to be present in ambient environments affected by kraft mill sources. Consequently, caution has to be exercised in using these methods for measuring/monitoring ambient H₂S levels around kraft mills.

For measuring H₂S in air, British Columbia and Ontario have adopted EPA Method 11 (USEPA 2000d). Method 11 is based on capturing H₂S in cadmium sulphate solution followed by iodometric analysis.

4.1.2 Aqueous

A variety of methods have been used for measuring speciated reduced sulphur compounds in aqueous samples. These techniques include solvent extraction, headspace analysis, purge and trap, and direct injection. Some of these methods are described below.

In 1976, a method was published based on extraction of reduced sulphur compounds with solvents and analysis on a gas chromatograph equipped with a flame photometric detector (Prakash and Murray 1976). It was reported that the method could determine a minimum of 10 ppm by weight of hydrogen sulphide, methyl mercaptan, dimethyl sulphide, and dimethyl disulphide. Vitenberg et al. (1977) published a method for analysis of speciated reduced sulphur compounds based on a combination of headspace analysis and microcoulometry. Reduced sulphur compounds at concentration levels of 0.01 to 1 ppm were analyzed with this method. Tsuji, Nakano, and Okuno (1990) used headspace analysis with a flame photometric detector to achieve lower detection limits. Leck and Bågander (1988) used a method based on purging the aqueous solution with nitrogen, followed by cryogenic trapping of the sulphur gases and analysis using a gas chromatograph equipped with a flame photometric detector. The reported detection limits for H₂S, CH₃SH, DMS, and DMDS were 1, 0.6, 0.2, and 0.4 mg/L, respectively, in 200 mL samples. NCASI modified this method to eliminate the need for cryogenic trapping (NCASI 1994). Paprican further modified this method to make it easier to implement (O'Connor and Genest 1997). The current NCASI method includes a sample preservation step followed by direct injection into a gas chromatograph equipped with a pulsed flame photometric detector (NCASI 2002a). The reported detection limits for hydrogen sulphide are 32 µg S/L and for CH₃SH, DMS, and DMDS 20 µg S/L. No specific test methods for measuring the TRS content of aqueous solutions have been adopted by Environment Canada. Alberta, however, refers to the book of Standard Methods for such analysis (APHA 1998a).

As opposed to the methods for determining the speciated reduced sulphur content of aqueous samples, all of which utilize a gas chromatograph, a number of methods are available for determining the hydrogen sulphide content of aqueous samples. These methods are similar to the colorimetric, spectrometric, iodometric, colorimetric, and gravimetric methods discussed earlier for determining ambient H₂S levels. British Columbia has adopted methods for sulphide analysis of water which include a) a sulphide ion selective electrode or iodometric titration method, b) Standard Method 4500-S2 (APHA 1998b), and c) EPA Method 376.1 (USEPA 1979).

4.2 Chlorine/Chlorine Dioxide (Cl₂/ClO₂)

The following is a brief description of the currently available methods for Cl₂/ClO₂ analysis.

4.2.1 Air Monitoring

For measuring Cl₂/ClO₂ emissions from bleach plants, NCASI has published a method based on capture of chlorine dioxide and chlorine in an impinger containing potassium iodide. The capture solution is titrated with sodium thiosulphate at neutral and acid pHs to determine the chlorine dioxide and chlorine contents of the sampled gas stream (NCASI 1997a). EPA has promulgated this method as modified Method 26A (USEPA 2000e). The modifications are described in section 40 CFR 63.457 of the pulp and paper MACT standards (USEPA 2001b). This method has been adopted by British Columbia for measuring Cl₂. Ontario has adopted EPA Method 26/26A for chlorine measurement. However, this method is subject to interference from ClO₂. The Cl₂ and ClO₂ test method adopted by Alberta (Alberta Stack Sampling Code 1996b) is similar to the NCASI method (1997a).

NCASI Technical Bulletin No. 409 (NCASI 1983b) describes a method for measuring workplace concentrations of chlorine and chlorine dioxide. This method was later modified and published in Special Report No. 04-05 (NCASI 2004b). The new version of the method is suitable for demonstrating compliance with the current ClO_2 workplace permissible exposure level of 0.1 ppm. A number of detector tubes, passive card monitors, passive bubblers, and fixed area monitors are also available for monitoring workplace ClO_2 levels. NCASI has published several reports describing the results of such evaluation (NCASI 1999, 2004).

OSHA Method ID-202 for workplace chlorine dioxide is based on the capture of ClO_2 in a buffered potassium iodide solution followed by chlorite analysis of the capture solution through ion chromatography (OSHA 1991).

4.2.2 Aqueous

A number of spectrophotometric methods have also been proposed for determining the ClO_2 content of water and wastewater samples. These methods utilize indicators such as N, N-diethyl-p-phenylenediamine, chlorophenol red, methylene blue, and Lissamine Green B (APHA 1998c, 1998d; USEPA 2005). Amperometric and ion chromatography-based methods are also available. These methods have, however, not been validated for pulp and paper or bleach plant effluents. Neither Environment Canada nor any of the provinces has promulgated methods for measuring Cl_2 and/or ClO_2 in aqueous samples. Alberta, however, recommends using the methods included in Standard Methods (APHA 1998a) for such analyses.

4.3 Chloroform (CHCl_3)

Chloroform is produced as a result of the reaction of hypochlorite or chlorine with lignin present in pulp. The following is a brief review of the methods available for measuring chloroform in pulp or paper mill air emissions.

4.3.1 Air Monitoring

The most widely used method for source gas chloroform testing is based on chloroform capture on Tenax TA followed by extraction with hexane and analysis on a gas chromatograph (GC) with electron capture detection. NCASI carried out extensive evaluation of this method and reported in Technical Bulletin No. 531 that a) the method yielded ca. 90% recovery, b) the precision of the method was ca. 15% relative standard deviation, and c) it was desirable to use a KI impinger ahead of the Tenax tube in bleach plant sources containing significant levels of Cl_2 and/or ClO_2 (NCASI 1987).

Other solid adsorbent methods for chloroform analysis, which have not been specifically evaluated for bleach plant sources, include EPA, NIOSH, and OSHA. Chai and Pawliszyn (1995) have published a solid phase microextraction technique for chloroform analysis in air. EPA Method TO-14A (USEPA 1999b) is capable of determining chloroform in the ambient air.

NCASI also evaluated an infrared detector-based method for bleach plant stack gas chloroform monitoring. The results, reported in Technical Bulletin No. 531, showed that in field tests, the instrument exhibited an inconsistent positive bias as compared to the solid sorbent method (NCASI 1987).

Neither Environment Canada nor any of the provinces has adopted a specific method for analysis of chloroform in air. However, several provinces, including Alberta, British Columbia, and Quebec, have adopted EPA Method 18 (USEPA 2000f). This method, applicable to a large number of volatile organic compounds, is based on capture of the source gas in a Tedlar bag followed by GC analysis using an appropriate column for separation and a suitable detector for quantitation. EPA Method 0030

(USEPA 1986), which is based on collection of the samples on solid sorbents followed by thermal desorption and analysis on a gas chromatograph, has been adopted by Alberta, British Columbia, and Quebec.

4.3.2 Aqueous

Early NCASI studies directed at measuring chloroform in bleach pulp mill effluents utilized a purge and trap technique similar to that contained in EPA Report 670/4-74-009, 1974. In this technique a small effluent sample was purged with air and trapped on Tenax. The Tenax trap was placed in the injection port of a gas chromatograph and purged with nitrogen. Chloroform was measured using a microcoulometric, mass selective or electron capture detector (NCASI 1977, 1983a). Later NCASI studies utilized hexane extraction followed by analysis on an electron capture detector (NCASI 1988, 1990, 1991a). In addition to these, others have also published chloroform analysis methods based on the purge and trap technique (USEPA 1991a, 1991b, 1991c, 1992; APHA 1992; Ho 1989; Lopez-Avila, Heath, and Hu 1987), solid-phase microextraction (Chai et al. 1993; King, Readman, and Zhou 2003), and solvent extraction (Daft 1988; USEPA 1990; Kroneld 1986).

A number of provinces, including Alberta, British Columbia, Ontario, and Quebec, have specified methods based on purge and trap followed by GC/MS analysis. Quebec has listed this method as MA. 400-COV 1.1 (Centre d'Expertise en Analyse Environnementale du Québec 2002). Alberta has specified EPA Method 8240 with EPA Method 5030. These methods are included in the SW-846 manual (USEPA 1986).

4.4 Methanol (MeOH)

4.4.1 Air Monitoring

A number of methods are available for measuring methanol emissions from forest products industry sources. In its Methods Manual, NCASI has published Methods CI/SG/PULP-94.02, CI/SG/PULP-94.03, CI/WP-98.01, IM/CAN/WP-99.02, and ISS-FP-A105.01 for measuring methanol emissions from pulp and paper mill and wood products industry sources. With some variations related to the capture and analysis of other analytes, all of these methods are based on capture of methanol in deionized organic-free chilled water followed by direct injection analysis of the capture solution on a gas chromatograph equipped with a flame ionization detector. In addition to these, EPA has adopted Methods 308 and 320 for source methanol emission testing (40 CFR 63, Appendix A). EPA Method 308 is a modification of NCASI Method CI/SG/PULP-94.03. EPA Method 320 is an extractive method, and it utilizes the principle of Fourier transform infrared (FTIR) spectroscopy to identify and quantify vapour phase organic and inorganic compounds in stack gases. In this method, the source gases are drawn from the stack and passed through a heated filter to remove the particulate matter. The filtered gases are transported via a heated line to an optical cell which has a source of infrared light. The absorption spectra of the sample are collected and compared to a known library to identify and quantify the compounds in the vapour phase. Although this method has been adopted by EPA, experience with the use of this method on forest products industry sources is extremely limited.

For ambient sampling and analysis of volatile organic compounds, the most widely used method is EPA Method TO-14A (USEPA 1999b). In this method, ambient air samples are collected in specially treated canisters and analyzed on a gas chromatograph equipped with a mass spectrometer. NCASI has successfully used a modification of this method for methanol analysis (NCASI 1997b) for non-chemical pulp mill sources, including ambient air. FTIR spectroscopy has also been used for measuring ambient concentrations of methanol.

Environment Canada has not adopted any specific method for measuring methanol in air. Alberta, British Columbia, and Quebec have, however, listed EPA Method 18 (USEPA 2000f) and EPA Method 0030 (USEPA 1986), which were described earlier.

4.4.2 Aqueous

NCASI has validated Method DI/MEOH-04.02 for determining the methanol content of process liquids and effluents from pulp and paper mills. In this method, the samples are collected and analyzed through direct injection into a gas chromatograph equipped with a capillary column. The GC column is temperature-programmed to separate the methanol from other compounds. The methanol is detected with a flame ionization detector. EPA has promulgated Method 305 for analysis of organics in water. This method is based on stripping the analyte from the sample followed by its capture and analysis. There are, however, significant problems with this method when it is used to analyze for highly polar compounds such as methanol.

Environment Canada has not specified a method of methanol analysis in aqueous solution. Alberta has not listed any specific method but has specified that facilities share a suitable Standard Methods (APHA 1998) method. Ontario and Quebec have listed EPA methods based either on purge and trap or direct injection on GC/FID. As discussed earlier, purge and trap is not well suited to methanol analysis of aqueous samples.

5.0 EMISSION FACTORS

5.1 Total Reduced Sulphur (TRS)

5.1.1 Air Emissions from Kraft Pulp Mill Operations

Tables 5.1 and 5.2 provide representative emissions of TRS and H₂S from various kraft pulp and paper mill operations, respectively. It should be noted that in a typical kraft pulp mill the sources with the highest levels of TRS and H₂S, namely the uncontrolled non-condensable gases from the pulping, evaporation and stripping operations, are invariably incinerated such that minimal controlled emissions of TRS and H₂S result. Also, the rest of the unit operations are run in a manner so as to minimize the emissions of TRS and H₂S, this often being the predominant objective. Emissions estimated from area sources in the wastewater treatment area of a kraft pulp mill are covered in Section 5.1.2.

Table 5.1 TRS Emissions (as Sulphur) from Kraft Pulp and Paper Mill Vents

Vent Description	Units	No. of Sources	Detects	Range	Median	Mean
Black Liquor Oxidation Tank	kg/t BLS	10	10	3.0E-03 to 1.5E-01	1.0E-02	3.5E-02
Bleach Plant	kg/ADTBP	26	16	ND to 5.5E-02	ND[3.8E-03]	8.0E-03
Brownstock Washers						
<i>Vacuum Drum Type</i>	kg/ADTUBP	31	31	2.6E-03 to 6.0E-01	5.0E-02	1.0E-01
<i>All Other^a</i>	kg/ADTUBP	15	15	2.4E-05 to 3.2E-01	1.8E-02	4.9E-02
Deckers	kg/ADTUBP	11	10	4.6E-03 to 7.0E-02	1.8E-02	2.6E-02
Deknotters	kg/ODTUBP	5	4	6.5E-05 to 1.9E-01	7.0E-04	4.0E-02
Lime Kilns	kg/t CaO	23	22	3.7E-03 to 1.1E-01	3.0E-02	4.1E-02
NGC Thermal Oxidizer	kg/ADTUBP	8	3	ND to 1.6E-03	4.8E-04	6.0E-04
Oxygen Delignification	kg/ADTUBP	4	4	2.3E-03 to 5.0E-02	3.0E-03	1.5E-02
Recovery Furnaces, DCE	kg/t BLS	18	18	2.8E-02 to 1.7E-01	4.6E-02	7.0E-02
Recovery Furnaces, NDCE	kg/t BLS	13	5	ND to 8.5E-02	9.0E-03	2.1E-02
Slaker/Cauticizer Combination	kg/t CaO	3	3	2.6E-04 to 1.1E-03	6.0E-03	6.0E-03
Smelt Dissolving Tank	kg/t BLS	22	22	5.5E-04 to 2.0E-01	6.0E-03	1.9E-02
Tall Oil Reactor	kg/t TO	7	7	0.0015 to 0.475	0.0165	0.0852
<i>Miscellaneous Kraft Vents</i>						
Weak Black Liquor Storage Tank	kg/hr per tank	6	6	0.008 to 6.15	0.049	1.56
Strong Black Liquor Storage Tank	kg/hr per tank	6	6	1.8E-05 to 0.625	0.082	0.196
Unbleached Pulp Storage Tank	kg/hr per tank	9	9	5.9E-04 to 1.357	0.190	0.328
Batch Digester Fill Exhaust	kg/t chips	4	4	3.5E-04 to 6.0E-03	1.0E-03	2.0E-03
Continuous Digester Chip Bin Exhaust ^b	kg/t chips	4	4	3.2E-03 to 7.5E-02	2.8E-02	2.8E-02
Continuous Digester Chip Bin Exhaust ^c	kg/t chips	1	1	--	1.4E-04	2.8E-04
Saltcake Mix Tanks	kg/t BLS	3	3	2.8E-05 to 3.2E-03	5.0E-05	1.1E-03
White Liquor Storage Tank	kg/hr per tank	5	3	4.5E-05 to 0.254	9.1E-05	0.086
Uncontrolled Kraft NCGs ^d						
<i>Pulping and Evaporator NCGs</i>	kg/ADTUBP	13	13	0.047 to 6.50	0.54	1.24
<i>Stripper Off-Gases Only</i>	kg/ADTUBP	4	4	0.58 to 2.28	1.57	1.65
Other Kraft Pulp Mill Sources						
<i>Wood & Combination Boilers^e</i>	kg/10 ⁹ J	13	4	ND to 0.023	0.0015	0.0038

NOTES: ^a Other washers - diffusion, pressure, belt and baffle; ^b using "live" or process steam; ^c using fresh steam; ^d these NCGs are typically incinerated; ^e at kraft pulp mills only; ND - non-detect; ND[x] - not detected at x; ADT & ODT - air dry & oven dry metric tonne; BP & UBP - bleached & unbleached pulp; BLS - black liquor solids; TO - tall oil

Table 5.2 H₂S Emissions from Kraft Pulp and Paper Mill Vents

Vent Description	Units	No. of Sources	Detects	Range	Median	Mean
Black Liquor Oxidation Tank	kg/t BLS	4	4	1.0E-04 to 2.3E-02	2.0E-03	4.0E-03
Brownstock Washers						
<i>Vacuum Drum Type</i>						
<i>All Other^a</i>						
Deckers	kg/ADTUBP	13	6	ND to 2.1E-02	5.5E-04 ⁽²⁾	1.8E-04 ⁽¹⁾
Deknotters	kg/ADTUBP	8	5	ND to 3.0E-03	1.5E-05	ND
Lime Kilns	kg/ODTUBP	1	0	--	ND	ND
NCG Thermal Oxidizer	kg/t CaO	1	0	--	ND	ND
Oxygen Delignification System Vents	kg/ADTUBP	9	7	ND to 1.1E-01	2.5E-02	3.4E-02 ⁽¹⁾
Recovery Furnaces, DCE	kg/ADTUBP	2	0	--	ND[7.9E-05]	ND[7.9E-05]
Recovery Furnaces, NDCE	kg/t BLS	1	1	--	1.4E-03	1.4E-03
Smelt Dissolving Tank	kg/t BLS	8	8	1.0E-02 to 1.3E-01	3.0E-02	4.1E-02
Tall Oil Reactor	kg/t BLS	5	4	ND to 6.5E-02	1.7E-03	8.0E-03
<i>Miscellaneous Kraft Vents</i>	kg/t TO	9	7	ND to 2.4E-02	3.0E-03	4.9E-03 ⁽¹⁾
Weak Black Liquor Storage Tank	kg/hr per tank	3	3	5.0E-04 to 3.1E-01	1.4E-02	5.5E-02
Strong Black Liquor Storage Tank	kg/hr per tank	4	3	ND to 1.7E-02	8.6E-03	8.6E-03
White Liquor Storage Tank	kg/hr per tank	3	3	1.4E-04 to 8.6E-02	2.2E-02	2.9E-02
Unbleached Pulp Storage Tank	kg/hr per tank	1	1	--	4.1E-03	4.1E-03
Batch Digester Fill Exhaust	kg/hr per tank	2	0	--	ND[4.5E-04]	ND[4.5E-04]
<i>Uncontrolled Kraft NCGs</i>	kg/t chips	1	0	--	ND	ND
<i>Pulping and Evaporator NCGs^b</i>						
<i>Stripper Off-Gases Only</i>	kg/ADTUBP	8	8	5.0E-05 to 1.47	1.9E-01	2.9E-01
<i>Chipp Bin Vent Gases</i>	kg/ADTUBP	4	4	0.105 to 8.9E-01	4.6E-01	4.8E-01
<i>Turpentine Decanter Gases</i>	kg/ADTUBP	1	0	--	ND[2.9E-06]	ND[2.9E-06]
<i>Concentrator Seal Tank & Hot Well</i>	kg/ADTUBP	1	1	--	1.3E-04	1.3E-04
		1	1	--	4.4E-02	4.4E-02

NOTES: ^a Other washers - diffusion, pressure, belt and baffle; ^b using "live" or process steam; ^c using fresh steam; ^d these NCGs are typically incinerated; ^e at kraft pulp mills only; ND - non-detect; ND[x] - not detected at x; ADT & ODT - air dry & oven dry metric tonne; BP & UBP - bleached & unbleached pulp; BLS - black liquor solids; TO - tall oil

5.1.2 Air Emissions and Water Releases from Wastewater Treatment Plant Operations

At the current time, NCASI is conducting a multi-year field testing program to characterize reduced sulphur compound air emissions from kraft pulp mill wastewater treatment plant (WWTP) area sources, although this study is mostly restricted to mills located in the southeastern U.S. An earlier NCASI report (NCASI 2002b) summarized TRS air emission data measured from several WWTP operations at kraft pulp mills including a) a primary clarifier at a Canadian mill, b) a wastewater treatment plant (WWTP) without secondary treatment at a U.S. mill, c) a spill lagoon and a 1-day ASB at a Canadian mill (1-day ASB tested with and without the spill lagoon pump on), and d) 5-day ASBs at two Canadian mills. These data summarized are reproduced in Table 5.3. TRS air emissions (as S) from the two 5-day (residence time) Canadian kraft mill ASBs ranged from 0.07 to 0.095 kg/ADTP.

Table 5.3 TRS Air Emissions From Kraft Pulp Mill Waste Treatment Systems

Source of Data	Source of Emission	TRS as H ₂ S		Metric TPPD ^a	TRS as S	
		Range (g/s)	Avg. (g/s)		Avg., kg/MT	Avg., lb/T
O'Connor & Ledoux, 2001	Primary Clarifier	--	0.055	620	0.0073	0.0145
NCASI 2000 ^b (1991 testing)	Primary Clarifier	--	2.86	472	0.494	0.987
Esplin, 1989	Mill A Spill Lagoon	2.4 to 8.1	4.9	685	0.58	1.16
Esplin, 1989	Mill A – 1-Day ASB ^c	0.56 to 1.2	0.85	685	0.101	0.201
Esplin, 1989	Mill A 1-Day ASB ^d	0.12	0.12	685	0.014	0.028
Esplin, 1989	Mill A&B 5-Day ASB	1.2 to 1.4	1.3	1475	0.072	0.143
Esplin, 1989	Mill C Two 5-Day ASBs	1.4 to 2.0	1.67	1450	0.094	0.188

^a TPPD – tonnes of pulp per day; ^b at the time of testing, this mill was sending foul condensates to the WWTP; ^c pump-up from spill lagoon; ^d spill lagoon pumps off

Due to the highly aerobic conditions and high biomass concentration in activated sludge reactors, TRS emissions from these treatment systems are expected to be very small. The reactors in oxygen activated sludge systems have highly oxidizing conditions, high biomass concentration, and extremely low flow rates. Consequently, TRS emissions from these systems are expected to be negligible.

5.2 Chlorine Dioxide (ClO₂)

5.2.1 Emissions from Bleach Plants at Pulp and Paper Mills

Chlorine dioxide emissions from pulp bleaching can occur at locations where pulp, pulp slurries, or bleaching filtrates are exposed to air. Typical emission points include bleaching tower vents, bleach plant washer vents, and filtrate tank vents. Uncontrolled bleach plant emissions of chlorine dioxide range from 0.015 to 12.75 kg/ADTP (NCASI 1991b). Chlorine dioxide generators can also be a source of chlorine dioxide emissions. Uncontrolled emissions from chlorine dioxide generators range from 0.1 to 3.06 kg ClO₂/tonne ClO₂ generated (NCASI 1991b). Chlorine dioxide emissions from bleach plant sources are commonly controlled using scrubbers. Typically, these scrubbers are of the packed tower type and use one of several scrubbing mediums. Scrubbing mediums include chilled water, caustic, extraction stage filtrate, sodium bisulphite, weak wash from the kraft recovery causticizing system, hydrosulphite, and white liquor. The effectiveness of these scrubbers is dependent on their design and choice of scrubbing medium. Achieving greater than 99% efficiency for both chlorine and chlorine dioxide is not uncommon. Controlling the addition of scrubbing chemicals is sometimes achieved by monitoring the pH, oxidation reduction potential, or sulphide content of the recirculated scrubbing medium (NCASI 1991b).

5.3 Chlorine (Cl₂)

5.3.1 Emissions from Bleached and Unbleached Pulp and Paper Mills

Uncontrolled emissions of Cl₂ from a bleach plant that uses Cl₂ (relatively rare) are reported to range from 0.01 to 5.2 kg/t pulp, averaging 0.35 kg/t pulp (NCASI File Information). Higher Cl₂ emissions correspond to higher vat residual Cl₂ concentrations. Table 5.4 provides the average Cl₂ removal efficiencies of various scrubbing fluids used in bleach plant scrubbers (NCASI File Information).

Table 5.4 Scrubber Efficiencies (NCASI 1991b)

Scrubbing Fluid	Scrubber Efficiency, %	
	Average	Range
E Filtrate	72	32 to 99
Caustic	85	83 to >99
Sodium Bisulphite	92	83 to >99
Weak Wash	99	>80 to >99
White Liquor	99	>89 to >99
Chilled Water & Caustic	90	
Chilled Water	81	63 to 96

Current bleaching practices will result in lower Cl_2 levels and correspondingly lower uncontrolled Cl_2 emissions. Median and mean controlled emissions of Cl_2 for 12 kraft mill bleach plants were estimated at 0.012 kg/adtp and 0.07 kg/adtp, respectively (NCASI 1995). Either these median/mean emissions or the product of the average uncontrolled emissions (0.35 kg/t pulp) and specific scrubber efficiency (given in Table 5.4), may be used to represent the controlled bleach plant emissions of Cl_2 .

5.4 Chloroform (CHCl_3)

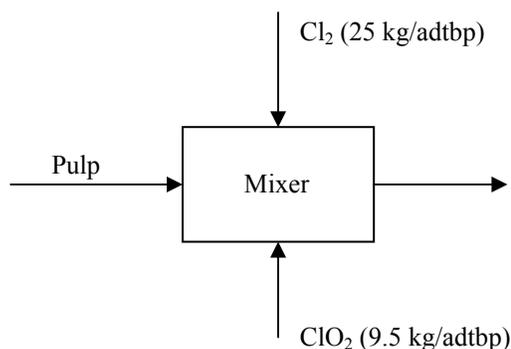
5.4.1 Pulp and Paper Mills

5.4.1.1 Releases to Air

Estimates of minor source chloroform air emissions from coincidental manufacture for various operations of relevance to the pulp and paper industry are given in Table 5.5 (NCASI 2003). In addition to these minor point sources, chloroform may also be emitted from a pulp mill's bleach plant and from its on-site wastewater treatment plant (WWTP). Table 5.6 provides estimates of partitioning of CHCl_3 in the WWTP, either an aerated stabilization basin (ASB) or an activated sludge treatment (AST) system (NOCEPM 2.1). Air emissions of this substance from the on-site WWTP may be obtained by combining the mass of the substance in the untreated effluent (product of effluent flow rate and untreated concentration, if available) with the percent substance volatilized given in Table 5.6. The amount in the untreated effluent will depend on the type of bleaching sequence practiced at the mill. CHCl_3 levels in bleach plant vents and in untreated bleach plant effluents were shown in Tables 2.6 and 2.7 for mills using hypochlorite and mills using almost no hypo (<0.1%).

Example Calculation: A virgin kraft mill bleaching 1000 adtp/d, 365 d/yr, uses a bleaching sequence with $\leq 0.1\%$ hypochlorite and as described below - the mill operates an aerated stabilization basin.

Simultaneous addition of 25 kg Cl_2 and 9.5 kg ClO_2 per adtp to softwood pulp, Kappa No. 28



For the above bleach plant, percent chlorine application

$$= \frac{25}{1000} \times 100 = 2.5\%$$

Table 5.5 Emissions of Chloroform from Pulp and Paper Mill Vents (NCASI 2003; FPAC 2003)

Vent Description	Units	No. of Sources	Detects	Range	NDs > 50%		NDs ≤ 50%	
					NOR-PLOT ⁽²⁾ or SDIn Avg. ⁽³⁾	Mean	Median	Mean
Kraft Mill Sources								
Black Liquor Oxidation Tank	kg/t BLS	10	3	ND to 2.0E-05	4.8E-08 ⁽²⁾			
Brownstock Washers								
<i>Vacuum Drum Type</i>	kg/ADTUBP	29	14	ND to 0.0225	6.4E-06 ⁽²⁾			
<i>All Other^a</i>	kg/ADTUBP	8	2	ND to 1.3E-04	1.0E-07 ⁽³⁾			
Deckers	kg/ADTUBP	8	2	ND to 0.01	4.5E-06 ⁽³⁾			
Deknotters	kg/ODTUBP	5	2	ND to 1.1E-06	2.0E-07 ⁽³⁾			
Prewasher Screen Systems	kg/ODTUBP	2	0	--				2.50E-05
Lime Kilns	kg/t CaO	34	4	ND to 1.1E-04	5.0E-06 ⁽²⁾			2.50E-05
NCG Thermal Oxidizer	kg/ADTUBP	6	1	ND to 5.0E-08	8.4E-10 ⁽³⁾			
Oxygen Delignification	kg/ADTUBP	9	5	ND to 4.5E-04				2.2E-04
Paper Machines & Pulp Dryers								
<i>Linerboard, Unbleached</i>	kg/ADTFP	2	0	--				3.00E-03
<i>Bleached Paper & Pulp</i>	kg/ADTFP	7	3	ND to 2.9E-04	1.8E-06 ⁽²⁾			
Recovery Furnaces, DCE	kg/t BLS	20	4	ND to 4.0E-03	4.8E-09 ⁽²⁾			
Recovery Furnaces, NDCE	kg/t BLS	24	2	ND to 9.0E-04	3.8E-07 ⁽³⁾			
Slaker/Causticizer Combination	kg/t CaO	2	0					7.3E-05
Slakers only	kg/t CaO	3	0					3.5E-07
Causticizers only	kg/t CaO	3	1	ND to 3.8E-08	7.3E-09 ⁽³⁾			
Smelt Dissolving Tank	kg/t BLS	32	4	ND to 1.1E-04	4.8E-08 ⁽²⁾			
Tall Oil Reactor	kg/t TO	7	3	ND to 4.0E-02	3.8E-06 ⁽²⁾			

All non-detect values are shown italicized at 1/2 the detection limit

(Continued on next page. See notes at end of table.)

Table 5.5 Continued

Vent Description	Units	No. of Sources	Detects	Range	NDs > 50%		NDs ≤ 50%	
					NOR-PLOT ⁽²⁾	or SDln Avg. ⁽³⁾	Median	Mean
ND = ½ Detection Limit								
<i>Miscellaneous Kraft Vents</i>								
Weak Black Liquor Storage Tank	kg/hr per tank	7	1	ND to 5.0E-07	1.8E-08 ⁽³⁾	6.4E-05	1.6E-03 ⁽¹⁾	
Strong Black Liquor Storage Tank	kg/hr per tank	9	5	ND to 0.065		5.0E-03	1.5E-02	
Unbleached Pulp Storage Tank	kg/hr per tank	5	3	ND to 4.3E-02				
Batch Digester Fill Exhaust	kg/t chips	4	1	ND to 1.6E-03	1.4E-04 ⁽³⁾			
Kamyr Chip Bins	kg/t dry chips	3	1	ND to 4.1E-07	7.5E-08 ⁽³⁾			
Saltcake Mix Tanks	kg/t BLS	3	0			1.7E-07	1.7E-07	
UNOX System Vent	kg/ADTUBP	1	0	--		9.5E-05	9.5E-05	
Lime Mud Precoat Filter	kg/t CaO	5	2	ND to 9.5E-06	8.2E-07 ⁽³⁾			
Precoat Filter Vac Pump Exhaust	kg/t CaO	3	1	ND to 5.5E-05	1.1E-05 ⁽³⁾			
Dregs Filter Hood Exhaust	kg/t CaO	2	0			4.8E-06	4.8E-06	
Green Liquor Clarifier	kg/t CaO	1	0	--		1.4E-05	1.4E-05	
Green Liquor Surge Tank	kg/t CaO	1	1	--		1.0E-06	1.0E-06	
White Liq/Wk Wash Press Filter	kg/t CaO	1	0	--		1.50E-04	1.50E-04	
White Liq Press Filter Tank	kg/t CaO	1	0	--		1.50E-04	1.50E-04	
Uncontrolled Kraft NCGs								
<i>Pulping and Evaporator NCGs^b</i>	kg/ADTUBP	3	2	ND to 1.9E-02		5.5E-03	8.0E-03	
<i>Pulping and Evaporator NCGs^c</i>	kg/ADTUBP	2	0	--		1.70E-05	1.70E-05	
<i>Stripper Off-Gases Only</i>	kg/ADTUBP	2	2	5.5E-04 to 1.1E-03		8.0E-04	8.0E-04	
Sulphite Pulp Mill Sources								
Recovery Furnaces	kg/t RLS	2	2	4.5E-05 to 9.59E-05		7.1E-05	7.1E-05	
All Pulping & Recovery Sources	kg/ODTP	4	3	ND to 0.015		1.2E-03	4.4E-03	
Bleach Plant	kg/ODTP	2	2	1.7E-03 to 0.008		4.7E-03	4.7E-03	

All non-detect values are shown italicized at ½ the detection limit

(Continued on next page. See notes at end of table.)

Table 5.5 Continued

Vent Description	Units	No. of Sources	Detects	Range	NDs > 50%		
					NOR-PLOT ⁽²⁾ or SDIn Avg. ⁽³⁾	Median Mean	
					ND = 1/2 Detection Limit		
Other Pulp Mill Sources							
ClO ₂ Generator Scrubber	kg/t ClO ₂	4	2	ND to 4.5E-03	5.2E-04	1.4E-03	
Semi-chem, Corrugated, Paper Machine	kg/ADTFP	1	0	--	1.6E-02	1.6E-02	
Cooling Tower - Kraft Mill	kg/ADTP	1	1	--	3.0E-03	3.0E-03	
Cooling Tower - TMP Mill	kg/ADTP	3	2	ND to 1.9E-04	5.4E-05	9.0E-05	
Bark Pile - Flux	mg/s/m ²	1	0	--	8.2E-06	8.2E-06	
Chip Pile - Flux	mg/s/m ²	3	1	ND to 1.1E-05	5.5E-06	6.4E-06	
Bark Cyclone	kg/t dry bark	1	0	--	1.4E-06	1.4E-06	
Chip Cyclone	kg/t dry chips	5	2	ND to 6.6E-03			
Boilers (emissions after PM control device)							
Wood residue	kg/10 ³ J	6	4	ND to 2.0E-05		1.3E-05	
Coal ^d	kg/t coal					3.0E-05	
Paper Machines With Mostly Non-Chemical Furnishes							
100% Secondary Fibre Furnish	kg/ADTFP	7	5	ND to 7.5E-03		1.8E-03 ⁽¹⁾	
Virgin Mechanical & Chem. Pulp Furnish	kg/ADTFP	11	6	ND to 0.024		8.6E-04 ⁽¹⁾	
Non-Integrated Mill Machine	kg/ADTFP	1	1	--		2.5E-04	
Secondary Fibre & Other ^e Furnish	kg/ADTFP	1	0	--	3.3E-03	3.3E-03	
OCC & Recycled Paperboard Stock Prep.	kg/ODTP	2	1	--	2.8E-05	2.8E-05	
Deinking (with Bleaching) Operations	kg/ADTP	6	4	ND to 0.07	4.5E-03	1.4E-02 ⁽¹⁾	
Mechanical Pulping Sources							
Stone Groundwood	kg/ODTP	5	2	ND to 3.9E-03	3.2E-04 ⁽³⁾		
Pressurized Groundwood	kg/ODTP	1	1	--		5.5E-06	
1.6E-05	kg/ODTP	7	7	2.3E-06 to 7.5E-04		6.0E-05	
	kg/ADTFP	1	0	--		3.30E-03	
1.3E-03							
4.1E-04							
2.5E-04							

All non-detect values are shown italicized at 1/2 the detection limit

NOTES: ^a Other washers - diffusion, pressure, belt and baffle; ^b batch digesters; ^c continuous digesters; ^d Reference No. 9; ^e Other - includes virgin chemical, groundwood and thermomechanical pulp; ND - non-detect; ADT & ODT - air dry & oven dry metric tonne; FP - finished product; BP & UBP - bleached & unbleached pulp; BLS & RLS - black & red liquor solids; TO - tall oil
⁽¹⁾ Trimmed Mean for data sets with 15 to 50% non-detects; ⁽²⁾ NOR-PLOT Average; ⁽³⁾ SDIn Average; The "Trimmed Mean," "NOR-PLOT Average," and "SDIn Average" are statistically derived sample averages discussed in Appendix A. The NOR-PLOT and SDIn averages are applicable to all data sets with greater than 50% non-detects.

Table 5.6 Partitioning of Chloroform in On-Site Wastewater Treatment System (NOCEPM 2.1)

	Aerated Stabilization Basin (ASB) ^{a, b}			Activated Sludge Treatment (AST) ^a
	One Basin	Two Basin	Three Basin	
Percent Volatilized	88.7	91.8	93.8	82.7
Percent Biodegraded	7.4	5.9	5.8	14.3
Percent in Effluent	3.9	2.3	0.3	3.0
Percent Overall Removal	96.1	97.7	99.6	97.0

^aTypical predictions applying NOCEPM.

^bThe one-basin model treats the WWTP as one well stirred tank. The two-basin model treats three-quarters of the WWTP as well stirred (with all the aeration HP) and the last quarter as a quiescent section (zero HP). The three-basin model treats the first 35% of the WWTP to be stirred with 50% of total HP, the next 40% to be stirred with the remaining 50% of total HP, and the last 25% to be quiescent. The two-basin and three-basin models are perhaps better representations of actual WWTP operation.

$$\text{Chlorine factor} = \frac{2.5}{28} = 0.089$$

ClO₂ substitution, calculated as Cl₂ equivalent (ClO₂ has 2.63 times the oxidizing power of chlorine on a kg per kg basis)

$$= \frac{9.5 \times 2.63}{(9.5 \times 2.63 + 25)} \times 100 = 50\%$$

Chlorine factor is <0.15 and all of the ClO₂ is applied simultaneously with Cl₂. Equation 3 of Table 2.7 would apply.

Total CHCl₃ formed and released from bleach plant

$$= 0.37 \times 0.089 = 0.033 \text{ kg/adtp}$$

Air emissions of CHCl₃ from bleach plant (using an average of 52% emission from bleach plant vents – Section 2.4.1)

$$= 0.52 \times 0.033 = 0.017 \text{ kg/adtp}$$

Annual emissions of CHCl₃ from bleach plant vents

$$= 1000 \text{ adtp/d} \times 365 \text{ d/yr} \times 0.017 \text{ kg/adtp} = 6,270 \text{ kg/yr} = 6.2 \text{ t/yr}$$

CHCl₃ released to the waste treatment system (remaining 48%)

$$= 0.48 \times 0.033 = 0.0158 \text{ kg/adtp}$$

CHCl₃ volatilized from the waste treatment system (from Table 5.6 using two-basin model)

$$= 0.0158 \times 0.918 = 0.015 \text{ kg/adtp}$$

Annual fugitive emissions of CHCl₃ from the treatment basin
 $= 1000 \text{ adtbp/d} \times 365 \text{ d/yr} \times 0.015 \text{ kg/adtbp} = 5,308 \text{ kg/yr} = 5.3 \text{ t/yr}$

5.4.1.2 Releases to Water

This can be obtained from the mill's final effluent flow rate and the concentration of CHCl₃ in the final effluent.

Sample Calculation:

For the mill described in Section 5.4.1.1, CHCl₃ released to the WWTP = 0.0158 kg/adtbp

Annual releases of CHCl₃ to the WWTP

$= 1000 \text{ adtbp/d} \times 365 \text{ d/yr} \times 0.0158 \text{ kg/adtbp} = 5,767 \text{ kg/yr}$

Using NOCEPM (two-basin model for ASB) estimates from Table 5.6, CHCl₃ discharge in final effluent

$= 5,767 \text{ kg/yr} \times 0.023 = 133 \text{ kg/yr} = 0.13 \text{ t/yr}$

5.4.1.3 Releases to Land

Discharges to land on site could occur either through primary and/or secondary sludges. The primary and secondary sludges may be pumped to a surface impoundment, such as a holding pond or lagoon, or dewatered and sent to either an on-site landfill or combustion device. Published reports and data available to NCASI show that the chloroform content of bleached kraft mill sludges ranges from 0 to 63.5 ppm on a dry basis, with a mean of 1.1 ppm (Warzyn 1980; NCASI 1984; NCASI File Information). These data can be used to estimate chloroform losses with primary and secondary sludges.

Sample Calculation:

A kraft mill produces 1100 adtubp/d which is then bleached to produce 1000 adtbp/d. It sends to a screw press 50 t/d of primary sludge solids at 5% consistency and 25 t/d of secondary sludge solids at 4% consistency. The dewatered sludges containing 40% solids are then sent to the on-site landfill.

For this mill, the chloroform in sludges sent to the landfill

$= ((50 + 25) \text{ tonnes sludge solids/d})(1000 \text{ kg/t})(365 \text{ d/yr})(1.1 \times 10^{-6} \text{ kg CHCl}_3/\text{kg sludge solids})$

$= 30.1 \text{ kg/yr} = 0.03 \text{ t/yr}$

5.5 Methanol (MeOH)

5.5.1 *Pulp and Paper Mills*

5.5.1.1 Air Emissions from Pulp Mill Operations

Table 5.7 provides representative emissions of methanol from various pulp and paper mill sources, including kraft and sulphite mills, non-chemical mills, and boilers. As for TRS and H₂S, the highest methanol concentrations are typically present in uncontrolled NCGs, which are invariably incinerated, resulting in negligible methanol emissions. The remaining unit operations are typically run in a manner so as to minimize methanol emissions; for example, methanol emissions typically result from stripping of methanol-containing mill water, and efforts are generally made to use mill water or condensate containing the least amount of methanol. The emission factors in Table 5.7 can be used to obtain the total amount of stack or point emissions of methanol from a facility.

5.5.1.2 Air Emissions from Wastewater Treatment Plant Operations

Table 5.8 provides typical concentrations of methanol in several untreated pulp mill effluents. Small amounts of methanol may also be emitted from primary clarifiers and the secondary wastewater treatment plant (WWTP) in a pulp mill due to volatilization. These emissions may be obtained by combining the mass of the substance in the untreated effluent (product of effluent flow rate and untreated effluent concentration given in Table 5.8) with the percent substance estimated to be volatilized in the clarifier or secondary WWTP.

NCASI has carried out flux chamber measurements of methanol emissions from three primary clarifiers treating kraft mill effluents. Fugitive emissions of methanol ranged from 0.13 to 0.17% of the inlet loads and averaged 0.15% during this study.

Partitioning of Methanol in Aerated Stabilization Basins (ASBs) – Performance Data from Hard Piping Mills

In the U.S., kraft mills employing the “hard piping” option to route condensates to aerated stabilization basins (ASBs) have, as part of initial and quarterly compliance demonstrations, generated site-specific data on the fate of methanol during biological treatment. Site-specific data on influent loading, effluent loading, and “in-basin” methanol concentrations have been used to quantify the biodegradation efficiency (F_{bio}) and emissions of methanol from these ASBs. Site-specific data obtained by NCASI from 15 hard piping mills indicate a range of 92% to 96% for methanol biodegradation efficiencies. Emissions due to volatilization/stripping from the ASBs ranged from 3% to 7% of inlet loads. Methanol concentrations in treated effluent were uniformly below method detection limits (ND [0.5 mg/L]) at these sources. In the absence of site-specific data, the above information could be used as a benchmark to estimate the partitioning of methanol in ASBs.

Facilities choosing to generate site-specific model predictions of methanol partitioning in their ASB have the option of building the model with site-specific treatment system characteristics (surface area, depth, aeration HP, suspended solids, etc.). In lieu of the default biorate constant available in WATER9 (EPA’s WWTP model) or NOCEPM (NCASI WWTP model), mills could use the mid-range value of 1.0 lit/g bio-hr (0.024 lit/mg bio-day) for generating the model predictions.

Table 5.7 Methanol Emissions from Pulp and Paper Mill Vents

Vent Description	Units	No. of		Range	Median	Mean
		Sources	Detects		ND = ½ Detection Limit	Detection Limit
Kraft Mill Sources						
Black Liquor Oxidation Tank	kg/t BLS	18	18	0.018 to 1.05	1.3E-01	2.2E-01
Bleach Plant	kg/ADTBP	56	56	ND to 0.30	6.0E-02	7.4E-02
Brownstock Washers						
<i>Vacuum Drum Type</i>	kg/ADTUBP	38	38	4.4E-02 to 1.25	2.9E-01	4.0E-01
<i>All Other^a</i>	kg/ADTUBP	10	10	4.1E-04 to 0.125	5.0E-02	5.5E-02
Deckers	kg/ADTUBP	7	7	0.007 to 0.10	1.5E-02	2.8E-02
Deknotters	kg/ODTUBP	8	8	2.2E-03 to 0.023	1.3E-02	1.3E-02
Prewasher Screen Systems	kg/ODTUBP	2	2	6.0E-03 to 2.2E-01	1.2E-01	1.2E-01
Lime Kilns	kg/t CaO	38	25	ND to 0.525	6.4E-03	1.8E-02 ⁽¹⁾
NCG Thermal Oxidizer	kg/ADTUBP	7	5	ND to 5.5E-03	2.8E-03	2.6E-03 ⁽¹⁾
Oxygen Delignification	kg/ADTUBP	13	13	0.08 to 0.96	3.6E-01	4.3E-01
Paper Machines & Pulp Dryers						
<i>Linerboard, Unbleached</i>	kg/ADTFP	2	2	4.6E-01 to 7.5E-01	6.0E-01	6.0E-01
<i>Bleached Paper & Pulp</i>	kg/ADTFP	7	6	ND to 0.05	1.6E-02	1.8E-02
Recovery Furnaces, DCE	kg/t BLS	26	26	ND to 0.675	7.7E-02	1.3E-01
Recovery Furnaces, NDCE	kg/t BLS	26	15	ND to 0.115	9.2E-03	1.3E-02 ⁽¹⁾
Slaker/Causticizer Combination	kg/t CaO	2	2	4.6E-03 to 0.12	6.2E-02	6.2E-02
Slakers only	kg/t CaO	3	2	ND to 1.80	2.7E-02	6.1E-01
Causticizers only	kg/t CaO	3	3	1.8E-05 to 0.13	2.8E-04	4.3E-02
Smelt Dissolving Tank	kg/t BLS	40	26	ND to 4.3E-01	5.5E-03	1.4E-02 ⁽¹⁾
Tall Oil Reactor	kg/t TO	8	8	6.0E-03 to 3.3E-01	4.7E-02	7.0E-02
Miscellaneous Kraft Vents						
Weak Black Liquor Storage Tank	kg/hr per tank	12	11	ND to 0.59	3.3E-02	1.2E-01
Strong Black Liquor Storage Tank	kg/hr per tank	9	9	0.042 to 0.68	5.9E-02	1.7E-01
Unbleached Pulp Storage Tank	kg/hr per tank	5	5	2.2E-02 to 3.7E-01	1.2E-01	2.1E-01
Batch Digester Fill Exhaust	kg/t chips	4	4	7.0E-04 to 7.0E-03	2.4E-03	3.1E-03
Kamyr Chip Bins	kg/t dry chips	3	3	0.06 to 0.10	9.2E-02	8.3E-02
Saltcake Mix Tanks	kg/t BLS	5	5	2.9E-05 to 3.3E-03	4.9E-04	1.2E-03
UNOX System Vent	kg/ADTUBP	1	0	--	6.0E-07	6.0E-07
Lime Mud Precoat Filter	kg/t CaO	5	4	ND to 0.6	6.0E-03	1.3E-01
Precoat Filter Vac Pump Exhaust	kg/t CaO	3	3	2.6E-04 to 0.042	1.8E-02	2.0E-02
Dregs Filter Hood Exhaust	kg/t CaO	2	1	ND to 0.0095	4.9E-03	4.9E-03
Green Liquor Clarifier	kg/t CaO	1	1	--	6.5E-02	6.5E-02
Green Liquor Surge Tank	kg/t CaO	1	1	--	5.5E-04	5.5E-04
White Liq/Wk Wash Press Filter	kg/t CaO	1	0	--	1.7E-02	1.7E-02
White Liq Press Filter Tank	kg/t CaO	1	1	--	7.5E-03	7.5E-03
Uncontrolled Kraft NCGs						
Pulping and Evaporator NCGs ^b	kg/ADTUBP	8	7	ND to 5.5E-01	1.4E-01	1.8E-01
Pulping and Evaporator NCGs ^c	kg/ADTUBP	5	5	3.1E-03 to 5.5E-02	2.2E-02	2.4E-02
Stripper NCGs Only	kg/ADTUBP	10	10	3.17 to 9.84	5.2E+00	5.2E+00
Sulphite Pulp Mill Sources						
Recovery Furnaces	kg/t RLS	6	6	0.009 to 3.15	3.3E-01	7.9E-01
All Pulping & Recovery Sources	kg/ODTP	4	4	0.12 to 1.3	6.5E-01	6.8E-01
Bleach Plant	kg/ODTP	2	2	0.026 to 0.31	1.7E-01	1.7E-01

All non-detect values are shown italicized at ½ the detection limit

(Continued on next page. See notes at end of table.)

Table 5.7 Continued

Vent Description	Units	No. of Sources	Detects	Range	Median ND = ½ Detection Limit	Mean
Other Pulp Mill Sources						
ClO ₂ Generator Scrubber	kg/t ClO ₂	4	3	ND to 7.5E-03	2.0E-03	2.9E-03
Semi-chem, Corrugated, Paper m/c	kg/ADTFP	1	1	--	1.5E-01	1.5E-01
Cooling Tower - Kraft Mill	kg/ADTP	1	1		4.1E-01	4.1E-01
Cooling Tower - TMP Mill	kg/ADTP	3	2	ND to 4.6E-03	4.3E-03	3.8E-03
Bark Pile – Flux	mg/s/m ²	1	1		2.3E-03	2.3E-03
Chip Pile – Flux	mg/s/m ²	3	2		1.1E-03	2.1E-03
Bark Cyclone	kg/t dry bark	1	0		<i>3.1E-05</i>	<i>3.1E-05</i>
Chip Cyclone	kg/t dry chips	5	2	ND to 0.37	3.7E-04 ⁽²⁾	
Boilers (emissions after APCD)						
<i>Wood residue</i>	kg/10 ⁹ J	4	3	ND to 6.5E-04	3.7E-04	3.6E-04
Paper Machines With Mostly Non-Chemical Furnishes						
<i>100% Secondary Fiber Furnish</i>	kg/ADTFP	7	7	8.0E-05 to 1.6E-01	3.6E-02	5.0E-02
<i>Virgin Mech. & Chem. Pulp Furnish</i>	kg/ADTFP	11	7	ND to 0.75	1.6E-02	1.5E-02 ⁽¹⁾
<i>Non-Integrated Mill Machine</i>	kg/ADTFP	1	1	--	1.7E-02	1.7E-02
<i>Secondary Fiber & Other^d Furnish</i>	kg/ADTFP	1	1	--	1.4E-02	1.4E-02
OCC & Recycled Paperboard Stock Prep.	kg/ODTP	2	2	8.5E-04 to 2.0E-03	1.4E-03	1.4E-03
Deinking (with Bleaching) Operations	kg/ADTP	6	6	9.5E-04 to 0.06	2.9E-03	1.7E-02
Mechanical Pulping Sources						
<i>Stone Groundwood</i>	kg/ODTP	5	4	ND to 0.39	2.0E-02	9.2E-02
<i>Pressurized Groundwood</i>	kg/ODTP	1	1	--	4.6E-02	4.6E-02
<i>Thermomechanical Pulping</i>	kg/ODTP	9	9	0.015 to 0.70	6.4E-02	1.4E-01
Solvent Coater Operations	kg/ADTFP	1	1	--	6.0E-03	6.0E-03

All non-detect values are shown italicized at ½ the detection limit

NOTES: ^a Other washers - diffusion, pressure, belt and baffle; ^b batch digesters; ^c continuous digesters; ^d Other - includes virgin chemical, groundwood and thermomechanical pulp; ND – non-detect; ADT & ODT - air dry & oven dry metric tonne; FP - finished product; BP & UBP – bleached & unbleached pulp; BLS & RLS – black & red liquor solids; TO – tall oil; APCD – air pollution control device; ⁽¹⁾ Trimmed Mean for data sets with 15 to 50% non-detects; ⁽²⁾ SDIn Average; The “Trimmed Mean” and “SDIn Average” are statistically derived sample averages

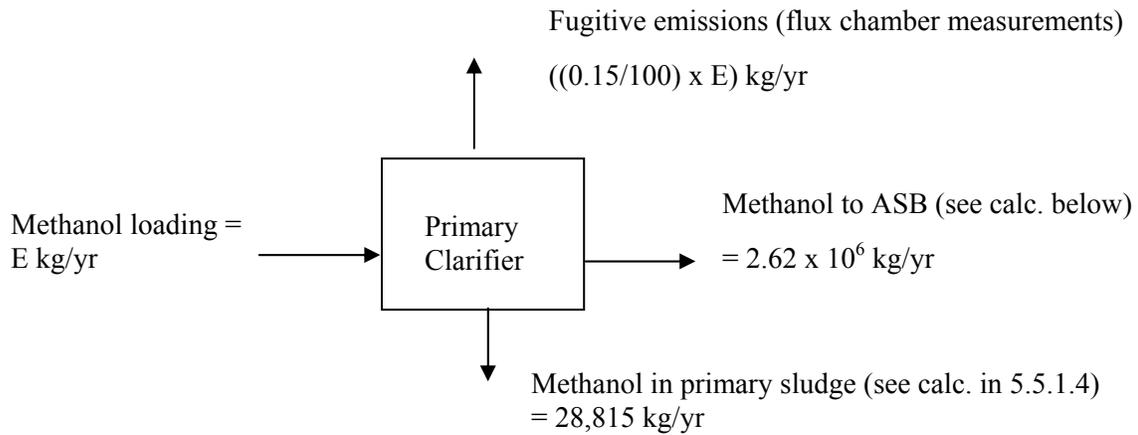
Table 5.8 Concentrations of Methanol in Untreated WWTP Effluents

Type of Pulping	Mills Sampled	Units	Untreated Effluent	
			Range	Average
Bleached Kraft	10	ppmw	55 to 135	83.1
Unbleached Kraft	3	ppmw	22 to 108	77.8
Bleached Sulphite	2	ppmw	15 to 79	47.4
Semi-Chemical	1	ppmw		27.1
Deinked Tissue	1	ppmw		2.7
Deinked Newsprint	1	ppmw		7.8
Wastepaper, Board	1	ppmw		1.0
Wastepaper, Corrugated	1	ppmw		5.3
Groundwood, Newsprint	1	ppmw		0.7

Example Calculation:

A bleached kraft mill operates all 365 d/yr and discharges about 1.0 m³/s of effluent to a primary clarifier followed by an aerated stabilization basin (ASB). It sends to a screw press 50 t/d of primary sludge solids at 5% consistency and 25 t/d of secondary sludge solids at 4% consistency. The dewatered sludges containing 40% solids are then sent to the on-site landfill.

This mill will have fugitive emissions of methanol from the primary clarifier (0.15% of clarifier influent load) and from the ASB (assume an average of 5% of ASB influent load for this example). Also, a portion of methanol in the influent to the clarifier is removed along with pore water in primary sludge (see Section 5.5.1.4). The remainder of the methanol enters the ASB. The distribution of methanol in the primary clarifier can be represented by the figure below.



Methanol in ASB influent (assuming methanol concentration in influent to ASB from Table 5.8)

$$= (1.0 \text{ m}^3/\text{sec}) \times (86,400 \text{ sec/d}) \times (1000 \text{ kg/m}^3) \times (365 \text{ d/yr}) \times (83.1 \times 10^{-6} \text{ kg/kg effl})$$

$$= 2,620,642 \text{ kg/yr}$$

Amount of methanol removed with pore water in primary sludge (see Section 5.5.1.3) = 28,815 kg/yr

The fugitive emissions from the primary clarifier can be calculated by carrying out a material balance for methanol around the primary clarifier (see above figure)

$$E = (0.15/100)E + 28,815 + 2,620,642$$

where E = methanol loading into primary clarifier (kg/yr)

solving for the above equation, E = 2.65 x 10⁶ kg/yr

Therefore, fugitive emissions from the primary clarifier = (0.15/100) x 2.65 x 10⁶

$$= 3,980 \text{ kg/yr}$$

Methanol volatilized from ASB (assuming 5% of influent load)

$$= (0.05)(2,620,642) = 131,032 \text{ kg/yr}$$

Total fugitive air emissions from treatment facility = 3,980 + 131,032 = 135,012 kg/yr

Partitioning of Methanol in Activated Sludge Treatment (AST) Systems

A bench-scale biotreatability study of methanol in pulp and paper mill effluents was carried out by NCASI and the results published in NCASI Technical Bulletin No. 724 (NCASI 1996). The biorate constant for methanol was calculated to be 0.2 lit/mg-bio day (8.33 lit/g-bio hr) during this study. This biorate constant has been used in NOCEPM and WATER9 to predict the partitioning of methanol in an example AST. NOCEPM and WATER9 model predictions of methanol partitioning in the AST indicate that ~ 99.7% of inlet methanol is biodegraded, <0.1% is emitted, and 0.2% remains in the final treated effluent. Table 5.9 provides estimates of partitioning of methanol in an activated sludge treatment (AST) system.

Table 5.9 Partitioning of Methanol in On-Site ASTs

	Activated Sludge Treatment (AST) ^a
Percent Volatilized	<0.1
Percent Biodegraded	99.7
Percent in Effluent	0.2
Percent Overall Removal	99.7

^a Typical predictions applying NOCEPM (NCASI WWTP model)

5.5.1.3 Releases to Water

Direct discharges of methanol can be obtained from the mill's final effluent flow rate and the concentration of methanol in the final effluent. As mentioned above in Section 5.5.1.2, methanol concentrations in treated effluents from 15 hard-piping kraft pulp mills were routinely below method detection limits of 0.5 mg/L.

Example Calculation:

For the mill described in Section 5.5.1.2, methanol discharged in the WTS final effluent (using one-half the detection limit)

$$= 1.0 \text{ m}^3/\text{sec} \times 86,400 \text{ sec/d} \times 1000 \text{ kg/m}^3 \times 365 \text{ d/yr} \times (0.5/2 \times 10^{-6} \text{ kg substance/kg effluent})$$

$$= 7,884 \text{ kg/yr}$$

5.5.1.4 Releases to Land

Discharges to land on site could occur either through primary and/or secondary WWTP residuals (sludges). The primary and secondary sludges may be pumped to a surface impoundment, such as a holding pond or lagoon, or dewatered and sent to either an on-site landfill or combustion device. Assuming all the methanol present in the sludge is due to the amount dissolved in the water contained in the sludge, the amount of the substance released to the environment with sludges can be estimated.

Example Calculation:

For the mill described in Section 5.5.1.2, methanol in primary sludges sent to the screw press

$$= 83.1 \times 10^{-6} \frac{\text{kg}}{\text{kg effluent}} \times \frac{95 \text{ kg effluent}}{5 \text{ kg sludge solids}} \times (50 \text{ t/d} \times 1000 \text{ kg/t} \times 365 \text{ d/yr}) \frac{\text{kg sludge solids}}{\text{yr}}$$

$$= 28,815 \text{ kg/yr}$$

Methanol in secondary sludges sent to the screw press

$$= 0.50/2 \times 10^{-6} \frac{\text{kg}}{\text{kg effluent}} \times \frac{96 \text{ kg effluent}}{4 \text{ kg sludge solids}} \times (25 \text{ t/d} \times 1000 \text{ kg/t} \times 365 \text{ d/yr}) \frac{\text{kg sludge solids}}{\text{yr}}$$

$$= 54.8 \text{ kg/yr}$$

Total methanol in sludges sent to the screw press

$$= (28,815 + 54.8) = 28,869.8 \text{ kg/yr}$$

Ratio of water in dewatered sludges to water in sludges before dewatering

$$= \frac{(50 + 25) \times (1000 \text{ kg solids/d}) \times (0.6 \text{ kg water}) / (0.4 \text{ kg solids})}{[(50 \times 1000 \times 95/5) + (25 \times 1000 \times 96/4)] \text{ kg water/d}} = 0.073$$

Since all the methanol is assumed to be in the water phase, the amount of methanol in dewatered sludges sent to the landfill

$$= 0.073 \times 28,869.8 \text{ kg/yr} = 2,107.5 \text{ kg/yr}$$

5.5.2 Wood Products Facilities

5.5.2.1 Release to Air from Wood Dryers

Methanol is coincidentally manufactured as a byproduct during the drying of wood. Temperature, wood species, and other variables affect methanol emissions. Given the limited amount and type of data presently available, the most practical approach for mills with little or no methanol emissions data may be to use uncontrolled emission averages from similar operations. Table 5.10 provides methanol emission averages for various types of dryers using different raw materials.

With the exception of blow-line-blend dryers, the uncontrolled methanol emissions given in Table 5.10 can be considered to represent the amount of methanol coincidentally manufactured in the dryer. Blow-line-blend dryers and other dryers in which methanol-containing resins are added prior to drying will coincidentally manufacture some methanol and also volatilize some methanol from the resin as it heats up and cures. The uncontrolled emission averages provided in Table 5.10 for blow-line-blend MDF and hardboard dryers include both coincidentally manufactured methanol and methanol volatilized from the resin. It would be difficult to accurately determine how much of the methanol in the dryer exhaust originates from the resin and how much is generated by the drying process.

If the dryer exhaust is routed to a wet scrubber or wet electrostatic precipitator, some of the methanol may be transferred from the gas stream to the scrubbing liquid. Test data from several mills show the amounts transferred are highly variable and depend on several site-specific parameters, including gas/liquid temperatures, liquid flow rates, and liquid make-up rates. Unless mill-specific test data are available, it may be best to assume on average, the net removal of this substance in wet control devices is zero.

5.5.2.2 Release to Air from Panel Presses

Like blow-line-blend dryers, uncontrolled methanol emissions from wood panel presses include both coincidentally manufactured methanol and methanol volatilized from resins. Table 5.11 provides uncontrolled methanol emission averages for various types of panel plant presses.

5.5.2.3 Release to Air from Boilers/Thermal Oil Heaters/Conical Burners

Emissions data for four wood-fired boilers at pulp and paper mills are shown in Table 5.7. Methanol emissions from burners that vent 100% of their exhaust to direct fired dryers should not be calculated separately, as those emissions are accounted for in the dryer emissions shown in Table 5.10.

Methanol emission sampling data are unavailable for beehive, silo, and conical burners. The gases leaving these combustion units generally do not have well defined and confined flow characteristics, making them very difficult to sample. Consequently, very little emission data of any kind are available for these units.

5.5.2.4 Release to Air from Lumber Kilns

Full-scale lumber kilns are difficult and expensive to test. As a result, small-scale kilns are sometimes used to estimate emissions from full-scale kilns. Using assistance from NCASI on how to sample small-scale kilns accurately, Forintek Canada Corporation has undertaken a program to measure individual and aggregated VOCs from such kilns (Forintek Canada Corporation 2005). A draft report has been issued presenting emission results from the drying of five batches (5 kiln cycles) of lodgepole pine. The data in this report were “quality assured” by NCASI personnel.

The results of the five charges are 0.072, 0.079, 0.077, 0.079, and 0.066 pounds of methanol per thousand board feet of lumber dried (lb/MBF). These values average 0.075 lb/MBF and have a standard deviation of 0.005 (average = 0.034 kg/MBF). Using the average lodgepole pine value, a mill processing 100 million board feet per year of lumber through dry kilns would emit approximately 3.4 tonnes per year of methanol.

The methanol values for Canadian lodgepole pine are included in Table 5.12 along with methanol data from tests conducted in the United States at both small-scale and full-scale lumber kilns. Note that the small-scale kiln data for Canadian lodgepole pine are provided separately from the lodgepole pine data obtained at the Oregon State small-scale kiln.

5.5.2.5 Release to Air from Miscellaneous Sources

Miscellaneous sources are defined here as all sources at wood products facilities other than wood dryers, panel presses, combustion units, and lumber kilns. Few sources in this category have been tested for methanol and, in cases in which tests were conducted, the data sets are generally small. Methanol data for miscellaneous sources are provided in Table 5.13. These data should be used with caution and only in the absence of site-specific data.

Table 5.11 Methanol Emissions from Panel Plant Presses

Product	Press Type	Resin Type	Wood Species	Mills/Units /Runs	Ratio of NDs	Range	Median	Mean	Units
MDF	Continuous	UF	Pine	1/1/3	0/3 nd	3.0E-01 to 3.4E-01	3.1E-01	3.1E-01	lb/MSF 3/4
MDF	Batch	UF	WSW, HW	3/3/15	0/15 nd	5.9E-02 to 1.3E+00	5.2E-01	6.6E-01	lb/MSF 3/4
PB	Batch	UF	WSW, Pine, Mix	5/5/28	0/28 nd	1.3E-01 to 1.0E+00	5.8E-01	5.2E-01	lb/MSF 3/4
OSB	Batch	PF+PF/MDI	HW, Pine	5/6/18	0/18 nd	1.0E-01 to 5.3E-01	3.2E-01	3.2E-01	lb/MSF 3/8
HB-WW	Batch	PF	HW, Pine	2/2/12	3/12 nd	ND to 4.9E-01	2.1E-01	2.1E-01	lb/MSF 1/8
HB-WD	Batch	Linseed Oil	Pine	1/1/3	0/3 nd	8.4E-02 to 1.0E-01	9.3E-02	9.3E-02	lb/MSF 1/8
HB-DD	Batch	PF	HW	1/1/6	0/6 nd	1.4E-01 to 3.2E-01	2.3E-01	2.3E-01	lb/MSF 1/8
HW-PLY	Batch	UF	HW, WSW	3/4/12	2/12 nd	ND to 8.6E-02	2.4E-02	3.2E-02	lb/MSF 3/8
SP-PLY	Batch	PF	Pine	5/6/16	0/16 nd	2.7E-02 to 4.1E-01	7.9E-02	1.3E-01	lb/MSF 3/8
WSW-PLY	Batch	PF	WSW	2/2/5	0/5 nd	3.1E-02 to 6.1E-02	4.5E-02	4.5E-02	lb/MSF 3/8
LVL	Bat+Cont.	PF	Pine	2/3/9	0/9 nd	2.4E+00 to 3.6E+00	3.2E+00	3.1E+00	lb/MCF

Product: MDF – medium density fiberboard; OSB – oriented strandboard; PB – particleboard; HB-WW – wet/wet hardboard; HB-WD – wet/dry hardboard; HB-DD – dry/dry hardboard; SP-PLY – pine plywood; WSW-PLY – western softwood plywood; HW-PLY – hardwood plywood (some “hardwood” plywood contains a softwood core); SW-PLY – softwood plywood; LVL – laminated veneer lumber

Press Type: Bat+Cont. – includes both batch and continuous presses

Resin Type: UF – urea-formaldehyde; PF – phenol-formaldehyde; MDI – methylene diphenyl diisocyanate

Wood Species: WSW – western softwood or WSW mix with <50% HW; HW – hardwood or HW mix >80% HW; Mix – wood furnish comprised of ≥ 50% HW and > 20% softwood; Pine – southern pine or other pine or pine mix with < 50% HW

Ratio of Non-Detects: Example: 1/6 nd indicates that one of six runs was non-detect (below detection limits)

Units: lb/MSF 1/8, 3/8, and 3/4 = lb of methanol per thousand square feet of panel pressed adjusted to thicknesses of 1/8, 3/8, and 3/4 inch, respectively; lb/MCF - lb of methanol per thousand cubic feet

Notes: ND – non-detect or below detection limits

Table 5.12 Methanol Emissions from Lumber Kilns

Lumber Kiln Type	Wood Species	Location	No. of Tests	Range	NDs ≤ 50%		Units
					Median ND = ½ Detection Limit	Mean	
Direct Wood Fired	Southern Pine (nos)	US	2	0.15 to 0.17		0.16	lb/MBF
Steam Heated	Southern Pine (nos)	US	5	0.15 to 0.28		0.24	lb/MBF
Small-Scale	Ponderosa Pine	US	2	5.0E-02 to 8.0E-02		6.5E-02	lb/MBF
Small-Scale	White Fir	US	2	9.6E-02 to 1.5E-01		1.2E-01	lb/MBF
Small-Scale	Lodgepole Pine	US	3	5.6E-02 to 6.3E-02	6.2E-02	6.0E-02	lb/MBF
Small-Scale	Douglas Fir	US	4	1.8E-02 to 2.6E-02	2.4E-02	2.3E-02	lb/MBF
Small-Scale	Black Spruce	Canada	5	0.10 to 0.13	0.12	0.12	lb/MBF
Small-Scale	Lodgepole Pine	Canada	5	6.6E-2 to 7.9E-2	7.5E-2	7.5E-2	lb/MBF
Small-Scale	White Spruce	Canada	3	8.9E-02 to 1.8E-01	1.4E-01	1.4E-01	lb/MBF

NOTES: nos – not otherwise specified; lb/MBF – pounds per thousand board feet; ND – non-detect or below detection limits

Table 5.13 Methanol Emissions from Miscellaneous Sources

Product	Source Description	Mills/Units/ Ratio of		Range	Median	Mean	Units
		Runs	NDs				
MDF	Blender-NBLB	1/1/3	0/3 nd	4.5E-01 to	4.8E-01	4.8E-01	lb/ODT
MDF	Board Cooler	2/3/9	3/9 nd	ND to	2.5E-02	4.2E-02	lb/MSF 3/4
MDF	Former-BLB	2/2/6	0/6 nd	5.0E-03 to	1.7E-02	1.7E-02	lb/ODT
MDF	Former-NBLB	1/1/3	0/3 nd	3.8E-01 to	4.1E-01	4.1E-01	lb/ODT
MDF	Metering Bin-BLB	1/1/3	0/3 nd	1.0E-02 to	1.0E-02	1.0E-02	lb/ODT
MDF	Sander	3/3/12	6/12 nd	ND to	4.0E-03	5.1E-03	lb/MSF
MDF	Saw	1/1/3	0/3 nd	4.5E-02 to	2.5E-01	2.5E-01	lb/ODT ⁽⁴⁾
PB	Blender	1/1/3	0/3 nd	1.8E-02 to	2.3E-02	2.3E-02	lb/ODT
PB	Board Cooler	4/4/15	0/15 nd	7.0E-03 to	4.9E-02	5.4E-02	lb/MSF 3/4
PB	Former	4/4/13	0/13 nd	3.0E-02 to	5.3E-02	8.1E-02	lb/ODT
PB	Refiner	6/6/19	4/19 nd	ND to	1.1E-02	1.5E-02	lb/ODT
PB	Sander	1/1/2	0/2 nd	1.3E-02 to	1.3E-02	1.3E-02	lb/MSF
PB	Saw	1/1/3	0/3 nd	1.7E-01 to	1.9E-01	1.9E-01	lb/ODT ⁽⁴⁾
OSB	Blender	1/1/3	0/3 nd	4.7E-02 to	6.3E-02	6.3E-02	lb/MSF 3/8
OSB	Fuel Bin	1/2/6	2/6 nd	ND to	1.1E-03	1.1E-03	lb/MSF 3/8
HB	Tempering Oven	1/1/6	2/6 nd	ND to	7.8E-03	7.8E-03	lb/MSF 1/8
HB	Chipper	1/1/2	1/2 nd	ND to	1.0E-03	1.0E-03	lb/ODT
HB-WD	Fiber Washer	1/1/3	0/3 nd	8.7E-02 to	1.3E-01	1.3E-01	lb/ODT
HB	Humidification Kiln	1/1/3	3/3 nd		ND[7.1E-03]	ND[7.1E-03]	lb/MSF 1/8
HB	Refiner, Pressurized	1/1/3	0/3 nd	2.4E-01 to	3.5E-01	3.5E-01	lb/ODT
HB-WW	Vacuum Former	1/1/9	0/9 nd	2.0E-02 to	5.4E-02	5.4E-02	lb/ODT
FB	Refiner, Atmospheric	1/1/3	0/3 nd	6.6E-03 to	8.4E-03	8.4E-03	lb/ODT
FB	Vacuum Former	1/1/3	0/3 nd	1.0E-03 to	1.1E-03	1.1E-03	lb/MSF 1/2

(Continued on next page. See notes at end of table.)

Table 5.13 Continued

Product	Source Description	Mills/Units/ Runs	Ratio of NDs	Range	Median	Mean	Units
WSW-PLY	Log Vat	1/1/3	0/3 nd	6.0E-03 to 8.3E-03	7.3E-03	7.3E-03	lb/MSF 3/8
MIX-PLY	Fuel Bin	2/3/9	3/9 nd	ND to 1.5E-02	7.8E-03	6.5E-03	lb/MSF 3/8
SP-PLY	Sander	1/1/3	0/3 nd	8.2E-03 to 1.6E-02	1.2E-02	1.2E-02	lb/MSF 3/8
SP-PLY	Saw	1/1/3	0/3 nd	3.4E-03 to 1.7E-02	1.2E-02	1.2E-02	lb/MSF 3/8

Product: MDF – medium density fiberboard; OSB – oriented strandboard; PB – particleboard; HB – hardboard; HB-WD – wet/dry hardboard;

SP-PLY – pine plywood; WSW-PLY – western softwood plywood; MIX-PLY – mixed hardwood and softwood plywood

Source Description: NBLB – non-blow line blend; BLB – blow line blend

Ratio of Non-Detects: Example: 1/6 nd indicates that one of six runs was non-detect (below detection limits)

Units: lb/MSF = lb per thousand square feet of surface; lb/MSF 1/8, 3/8, and 3/4 = lb of methanol per thousand square feet of panel pressed adjusted to thicknesses of 1/8, 3/8, and 3/4 inch, respectively; lb/ODT = lb per oven dry ton of wood; lb/ODT⁽⁴⁾ = lb per oven dry ton of sawdust generated

NOTES: ND – non-detect or below detection limits

5.5.2.6 Release to Water from Wood Products Plants

Untreated effluent concentrations of methanol in wood products facilities with WWTPs, if available, can be multiplied by the appropriate estimate for percentage in effluent shown in Section 5.5.1.2 for kraft pulp mill ASBs (~0.3% of influent load), to obtain the treated effluent concentration. Direct discharges can be obtained from the mill's final effluent flow rate and the concentration of substance in the final effluent.

6.0 CONCLUSIONS

In 2004, NCASI published a report that dealt with the CEPA toxics formaldehyde, acetaldehyde, and acrolein (NCASI 2004a). Unlike for these aldehydes, the mechanisms of formation for hydrogen sulphide and other reduced sulphur compounds (TRS), chloroform, and methanol are better understood and these have been reviewed and summarized in the current report. H₂S and TRS result from the kraft process which uses sodium sulphide to cook the wood; methanol results from various cooking, recovery, bleaching, and papermaking processes associated with pulp mills and from drying and pressing operations in wood products mills; and chloroform is principally generated when bleaching pulp with either chlorine or sodium hypochlorite, both processes being virtually extinct at the current time. Chlorine dioxide is intentionally manufactured at bleached pulp mills and is the predominant bleaching chemical used at the current time. Chlorine is not manufactured and only rarely used in pulp mills at the current time. Small amounts of chlorine could be generated by the breakdown of ClO₂ in bleach plants.

The 2004 NPRI data indicated that 38 pulp and paper mills released 1,811 tonnes or 39.5% of total emissions of H₂S to the environment. From data on facilities in Ontario that reported releases of H₂S to the NPRI and of TRS to the MOE, nearly 65% of the TRS released was estimated to be released as H₂S. The 2004 NPRI data indicated that 36 bleached pulp and paper mills released 536 tonnes or about 99.6% of total emissions of ClO₂ to the environment. Similarly, the 2004 NPRI data indicated that 24 pulp and paper mills released 156 tonnes or about 25.5% of total emissions of Cl₂ to the environment, and 5 pulp and paper mills released 49.2 tonnes or about 98.6% of total emissions of CHCl₃ to the environment. For methanol, the 2004 NPRI data indicated that 149 pulp and paper and allied mills released 14,367 tonnes or 69.0% of total emissions to the environment, while 76 sources in the wood products industry released 3,153 tonnes or 15.1% of total emissions to the environment.

TRS, H₂S, and methanol emissions are minimized by incinerating the non-condensable gas streams in a pulp mill in various combustion devices and/or by operating process units such that these emissions are minimized. Emissions of chloroform, mainly from bleaching, are minimized by avoiding the use of sodium hypochlorite or chlorine in bleaching. Emissions of ClO₂ are minimized by the use of efficient ClO₂-removing scrubbers. Chlorine emissions have been almost eradicated from bleached pulp mills, either by substitution or by scrubbing.

The reduced sulphur gases hydrogen sulphide, methyl mercaptan, dimethyl sulphide, and dimethyl disulphide exist as gases at atmospheric pressure and are likely to partition into the air after environmental releases in other media. The half-lives are relatively short, typically in the range of a few hours to a few days, and none of these compounds persist in the environment. The health effects associated with exposure to hydrogen sulphide are well studied, and although there is less information available on methyl mercaptan, dimethyl sulphide, and dimethyl disulphide, the principal effects appear to be similar, although associated with different exposure concentrations. As exposure concentrations increase from the 1-5 ppm level up to the 100-1000 ppm level, reported symptoms typically begin with eye irritation, then irritation of the respiratory tract, and eventually, at high concentrations, respiratory arrest, unconsciousness, and death. The reduced sulphur gases have low odour thresholds and unpleasant odours, characteristics that raise unique issues for regulatory

agencies and emission sources. There is uncertainty associated with the degree to which adverse health effects might be associated with exposure to, or with the perception of, unpleasant odours and there is no universal agreement on how this issue should be dealt with.

In the environment, chlorine dioxide has a very brief half-life in the presence of light or oxidizable substances. When water is treated with chlorine dioxide, ClO_2 is rapidly transformed to chlorite and subsequently to chloride. Inhalation exposure to ClO_2 is unlikely to occur except in occupational settings following accidental releases, where the health effects are expected to involve respiratory tract injury. Consumption of low levels of chlorite (<0.15 mg/kg/day) in drinking water do not appear to have any adverse health effects.

Chlorine typically exists in the environment as a gas with a relatively short lifetime of minutes during daylight and hours in the dark. In water, chlorine dissociates almost immediately to form hypochlorous and hydrochloric acid, which in turn react rapidly with oxidizable substances in the water or further dissociate to form chloride anions. The half-life of hypochlorous acid and hypochlorite anion in natural waters is estimated to be less than 5 hours. In the gaseous form, chlorine is an irritant and corrosive, causing sensory irritation in the 1 ppm range, respiratory tract injury at levels of 30-40 ppm, and death following exposures in the range of hundreds to 1000 ppm. Asthmatics may be more sensitive to chlorine gas than the general public.

Chloroform exists in the environment primarily as a gas. Reported atmospheric lifetimes range from 26-548 days. Relatively high chloroform exposures are associated with liver damage, and in animal studies, chloroform has been associated with the development of hepatic cancer. However, based on mechanistic studies, EPA has concluded that chloroform is not likely to be carcinogenic to humans unless exposures are high enough to cause cytotoxicity and regenerative hyperplasia in susceptible tissues. The Environment Canada Priority Substances List Assessment Report for chloroform concluded that chloroform should not be considered toxic as defined in Section 64 of CEPA 1999.

In the atmosphere, methanol degrades primarily through reaction with hydroxyl radicals, with reported lifetimes ranging from about 4 to 43 days. Most of the methanol released to water or soil will volatilize and what remains will biodegrade rapidly. The acute toxicity of methanol is dependent on species ability to metabolize formate, an intermediate in the methanol metabolic pathway. However, even for the most susceptible species, methanol is not highly toxic.

EPA Method 16 is the most widely used method for measuring the concentrations of various reduced sulphur compounds in stack gases. As opposed to the methods for determining the speciated reduced sulphur content of aqueous samples, all of which utilize a gas chromatograph, a number of methods are available for determining the hydrogen sulphide content of aqueous samples. For measurement of Cl_2/ClO_2 emissions, NCASI has published a method based on capture of chlorine dioxide and chlorine in an impinger containing potassium iodide. A number of spectrophotometric methods have also been proposed for determining the ClO_2 content of water and wastewater samples. The most widely used method for source gas chloroform testing is based on chloroform capture on Tenax TA followed by extraction with hexane and analysis on a gas chromatograph with electron capture detection. Several methods are available for measurement of CHCl_3 , including an NCASI method using hexane extraction followed by analysis on an electron capture detector. NCASI has published several methods for measuring methanol emissions from pulp and paper mill and wood products industry sources. All of these methods are based on capture of methanol in deionized organic-free chilled water followed by direct injection analysis of the capture solution on a gas chromatograph equipped with a flame ionization detector. In addition, NCASI has validated Method DI/MEOH-04.02 for determining the methanol content of process liquids and effluents from pulp and paper mills, where the samples are collected and analyzed through direct injection into a gas chromatograph equipped with a capillary column.

The extensive MACT testing studies conducted by NCASI provide reliable methanol and chloroform air emission factor estimates for essentially all sources within the forest products industry. Similarly, reliable TRS and H₂S measurement data have been obtained and compiled by NCASI from kraft pulp mills over the past several decades. Emission data for Cl₂ and ClO₂ from bleach plants are highly mill-specific, depending on the level of usage and bleach plant scrubber operations.

Unlike for the CEPA aldehydes covered in an earlier NCASI report (NCASI 2004a), the forest products industry in Canada contributes a sizable percentage to the total emissions of TRS and H₂S (50 to 70%), chlorine dioxide (>99%), chloroform (99%), and methanol (84%), and a significant percentage to the total emissions of chlorine (26%).

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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). The following is a list of relevant factors for converting these into SI units.

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 Handbook			
MSF (1000 ft ²)	m ²	92.9	
MSF 1/8	m ³	0.295	
MSF 3/8	m ³	0.885	
MSF 1/2	m ³	1.180	
MSF 3/4	m ³	1.770	
lb/MSF 1/8	kg/m ³		0.649
lb/MSF 3/8	kg/m ³		1.947
lb/MSF 1/2	kg/m ³		2.596
lb/MSF 3/4	kg/m ³		3.894
lb/10 ⁶ Btu	kg/10 ⁹ J		2.321
lb/ODT	kg/odt		2.0
Lb/yr	kg/yr		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, 1/2 and 3/4 = thousand square feet of panel dried at thickness of 1/8, 3/8, 1/2 and 3/4 inch, respectively