



**Canadian Fuels**  
ASSOCIATION  
**canadienne des carburants**

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CODE OF PRACTICE  
FOR  
DEVELOPING AN  
EMISSION INVENTORY  
FOR REFINERIES AND TERMINALS

2022-2024

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## **1. INTRODUCTION**

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### **1.1. PURPOSE**

Understanding emissions from operations is an important element of member commitment to the Environment, Health and Safety Guiding Principles of the Canadian Fuels Association (Canadian Fuels).

This Code of Practice (Code) provides Canadian Fuels Association methods for developing the National Pollutant Release Inventory (NPRI) emission inventory for a Canadian refinery or terminal. The Code is structured to provide an inventory to satisfy the requirements of the NPRI.

Environment and Climate Change Canada (ECCC) requires an annual NPRI submission for sites that meet the reporting criteria (most Canadian Fuels members with refineries will meet this requirement). The Code can be used as a guidance document for developing non-NPRI emission inventories as well.

The Code is intended to improve consistency and inter-company comparability of the emission inventory data by reducing non-performance related variability of the estimated releases. The Code achieves this by assuring that relevant significant sources are considered, and that appropriate assumptions and methodologies are used in developing the emission inventory.

### **1.2. BACKGROUND**

An aid for compiling NPRI submissions from petroleum refineries was first prepared following a Canadian Petroleum Products Institute (CPPI - the Canadian Fuels Association (CFA) predecessor) member workshop on the subject in 1993. In 1995, a more substantive document entitled "Quality Assurance Guidelines for Preparing NPRI Submissions" was issued by CPPI. The Guidelines were developed to assist CPPI petroleum refiners to improve their NPRI data quality and consistency.

The Guidelines were updated in 1996 and re-named "Code of Practice for Developing a Refinery Emission Inventory". In 2002, the Guideline was re-named "The Code of Practice for Developing an Emission Inventory for Refineries and Terminals" – to reflect the addition of terminals to the NPRI Reporting Requirements for the 2002 reporting year. For reference purposes, Canadian Fuels keeps a list of acronyms at the Association head office.

The guidelines are reviewed and updated regularly to reflect additional reporting requirements, reporting experience, and revision of emission methodologies by leading environmental organizations including the U.S. Environmental Protection Agency (US EPA) and the American Petroleum Institute (API). A team of Association members participate in the revision process in an effort to be consistent with ECCC Gazette reporting requirements.

In May 2005, the Canadian Council of Ministers of the Environment (CCME) formally adopted a new approach to reduce emissions from the petroleum-refining sector. The National Framework for Petroleum Refinery Emission Reductions (NFPRER) is a unique

example of an industry-proposed initiative, in which all levels of government, industry, and non-governmental environmental and health organizations worked together. One of the elements of NFPRER is a Monitoring and Reporting (M&R) Strategy that provides guidance and tools for refineries to monitor and report emissions of air pollutants and toxics in a manner that allows jurisdictions to determine whether facility-wide emission limits (caps) are being achieved. The original NFPRER had a ten-year implementation period which would be written into provincial regulatory approvals. While this period has past, there are likely refineries that are still committed to the NFPRER. Practitioners should check with their Provincial requirements to ensure quality assurance and quality control along with appropriate records are kept, that demonstrate appropriate methods (or jurisdictional approved alternatives) were utilised in emission monitoring. These methods can be entered into the Single Window Information Manager (SWIM) per the NFPRER.

### **1.3. SCOPE**

The Code covers the major categories of emission sources: process, fugitives, tanks, loading/transfer, land farm, wastewater, incidents, combustion, underground injection (deep well disposal), and off-site transfers.

For each category, a methodology is described in the Requirement Section that provides a conservative estimate of the emission for that source. In the majority of the sections, an alternative methodology is described as well, that usually requires more data, but provides for a less conservative and more representative estimate of the emission. Assumptions/default values are provided where appropriate, as well as, what to include and exclude within the scope of the estimation. Emission factors have been included with appropriate reference(s).

The structure of the Code is intended to address reporting of Schedule 1, Part 1, Group A substances in Sections 3 to 11. These substances are governed by the original manufacture, process, or otherwise use (MPO) reporting threshold of 10 tonnes. Substances governed by Alternate Thresholds are addressed in Sections 12 to 15. Other reporting requirements are covered in Sections 16 and 17.

Methods or procedures for speciation are defined where appropriate in each section, with references to Appendix A, which provides a guide to identifying potentially reportable NPRI substances and their emission sources.

### **1.4. CODE OF PRACTICE REVISIONS/ENHANCEMENT**

This Emissions Code of Practice is administered and managed by the Canadian Fuels Environmental Emissions Working Group (EEWG). The Code is intended to be a living document with the objective of providing continually improving guidance to Canadian Fuels members on how to generate accurate and consistent emissions inventories.

Recommendations for enhancement are welcomed and should be brought to the attention of company EEWG representatives so that they can raise them for discussion at EEWG meetings. Enhancements (not all inclusive) include suggestions for clarification of existing methods, as well as, new emission methodologies and factors.

In the event that your company does not have an EEWG representative, improvement suggestions can be forwarded to the Canadian Fuels Association's Committee Support and Data Analysis Manager, who is also a member of the EEWG.

## **1.5. REFERENCES**

National Framework For Petroleum Refinery Emission Reductions (NFPRER), Canadian Council of Ministers of the Environment (CCME, 2005)

<https://ccme.ca/en/res/nfprerpn1338esecure.pdf>

## **2. ASSET BASE FOR EMISSION INVENTORIES**

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### **2.1. SCOPE**

This Code provides methods for Canadian Fuels member refiners to establish emission inventories. The inventory is representative of all refinery and terminal related facilities and activities.

The operating company of a refinery or terminal is responsible for reporting all NPRI releases from that facility including those associated with the processing of third-party product.

This Code is applicable to the 2022 to 2024 reporting years, referred to as the 2022RY, 2023RY, and 2024RY. Reporting to the NPRI for the previous year is required on or before June 1 of every year.

### **2.2. REQUIREMENTS**

#### **2.2.1. General**

Include emissions from all sources within the actual physical refinery or terminal limits. Emission estimates should take into account downtimes lasting one month or more on any unit or tankage. Guidance on estimating emissions from start-up and shutdown is provided in Section 8.

#### **2.2.2. Marine Loading**

Include emissions associated with bulk loading of product onto marine vessels at a dock or wharf if the product is supplied directly from the refinery or terminal storage tanks.

#### **2.2.3. Fuels Marketing/Distribution**

Exclude emissions from the operations that market/distribute refined product for final retail sale (prior to use). Emissions associated with the loading/unloading at refineries of tank cars/trucks/marine vessels are usually included from refineries. Emissions from terminals associated with refineries should be reported independent of the refinery. Data for the entire site (e.g. refinery + terminal) should be used to determine which substances must be reported.

Buildings, equipment, structures, and stationary items that are located on a single site or on contiguous or adjacent sites that are owned by or operated by the same person/corporation should also be included. Include emissions from terminals and storage facilities.

### **3. INTERPRETATION OF NPRI REPORTABLE SUBSTANCES**

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#### **3.1. SCOPE**

The requirements for reporting to NPRI are contained in the Canada Gazette Notice, Part I. This section provides guidance on reporting criteria as defined by ECCC and interpreted by the Canadian Fuels Environmental Emissions Working Group (EEWG). This revision of the Code of Practice is applicable starting with the NPRI 2022 reporting year, and NPRI submissions are due to the Minister of Environment and Climate Change on June 1 of every year.

#### **3.2. DEFINITIONS**

##### **Article**

This is a manufactured item that does not release an NPRI substance when it undergoes processing or other use or when there is a release it occurred during recycling with due care. Any item can lose its article status from one year to the next if it results in a release to the environment or a transfer of waste off-site for disposal. (An example would be mercury released from lamps and thermometers that are broken and transferred off-site for disposal, or a catalyst that remains in the reactor for a whole year). See Section 3.3.3 for Specific Interpretations.

There is no similar measure of due care applicable to the recycling of NPRI Part 1B substances. If there are releases during the processing or other use of an article containing a Part 1B substance, the amount released must be included in the threshold calculation.

##### **By-product**

A by-product is an NPRI substance which is incidentally manufactured, processed, or otherwise used at a facility at any concentration, AND is released to the environment or transferred off-site for disposal. A substance that is recycled or remains in the final product, is not considered a by-product.

The total weight of the NPRI substance in the by-product must be used in the calculation of the reporting threshold regardless of the concentration. Note that this does not include the entire weight of the substance manufactured, processed, or otherwise used at the facility, just the amount that is released as a by-product.

For instance, in a case where 5 tonnes of an NPRI substance is incidentally manufactured and 3 tonnes are released on-site (i.e. 2 tonnes still in the product or is destroyed in the process), the by-product weight to be included in the threshold calculation is 3 tonnes.

##### **Contiguous Facility**

A contiguous facility means all buildings, equipment, structures, and stationary items that are located on a single site or on contiguous or adjacent sites, that are owned or operated by the same person/corporation and that function as a single integrated site, including

wastewater collection systems that release treated or untreated wastewater into surface waters.

Consistent with the agreement of the first NPRI consultative group, and past NPRI reporting practices, Canadian Fuels companies can report emissions from a chemical facility, a terminal, or refinery separately, provided the substances are determined on a total site basis. This approach meets NPRI's definition of facility and the need for transparent reporting, while allowing companies the flexibility to reflect operations that are in different sectors and often under different management.

### **Refinery Operations**

Per the NPRI definition of a contiguous facility, a refinery is described as a facility that processes crude oil into refined petroleum products. This includes “all buildings, equipment, structures, and stationary items that are located on a single site or on contiguous or adjacent sites and that are owned or operated by the same person/corporation and that function as a single integrated site”. (See Section 3.2 for further information).

### **Terminal Operations**

Terminal operations include:

- (i) the use of storage tanks and associated equipment at a site used to store or transfer crude oil, artificial crude, or intermediates of fuel products into or out of a pipeline; or
- (ii) operating activities of a primary distribution installation normally equipped with floating roof tanks that receives gasoline by pipeline, railcar, marine vessel, or directly from a refinery.

Activities that take place on a refinery site under the NPRI definition and do not fall under the above definition of a terminal are included as part of the refinery definition.

### **Fossil Fuel**

For NPRI, a fossil fuel is a fuel that is in a solid or liquid state at standard temperature and pressure, such as coal, petroleum, or any solid or liquid fuel derived from such.

### **Manufacture**

The production, preparation, or compounding of an NPRI substance including by-products and impurities.

### **Process**

Process of an NPRI substance is the preparation after manufacture for distribution in commerce. Processing includes preparation of a NPRI substance with or without changes in physical state or chemical form and includes processing of the NPRI substance as a by product.



### **Other Use or Otherwise Used**

All other uses of a substance include use as a chemical processing aid, manufacturing aid, or some other ancillary use and includes the other use of by-products.

### **Tailings**

These are defined as waste material from ore or mined materials processing that remains after the extraction of marketable constituents such as metals, minerals or bitumen. Tailings may consist of ground rock material, sand, clay, process chemicals or residual metals, minerals or bitumen, petroleum coke, and sulphur.

### **Waste Rock**

This is the rock that is removed during mining to give access to the ore but is not further processed. Unconsolidated overburden, including soil, glacial deposits, sand and sediment, is not considered as waste rock.

### **Releases**

An on-site release is a discharge of an NPRI substance to the environment within the boundaries of the reporting facility. This includes releases to air, surface waters, land, and deep well underground injection.

Releases are subdivided as follows:

- *Air*: stacks and other point sources, storage tank and related handling releases, fugitive emissions, spills or other accidental releases, unpaved road dust or other non-point sources.
- *Surface Water*: discharges, spills, and leaks.
- *Land*: spills, leaks, and other land releases.
- *On-site Disposal*: landfill, land treatment, underground injection, tailings or waste rock management areas.
- *Off-site Disposal*: landfill, land treatment, underground injection, storage, tailings or waste rock management areas.
- *Off-site Treatment*: physical, chemical, or biological treatment; incineration or thermal treatment; or treatment in a municipal wastewater treatment plant.
- *Off-site Recycling*: energy recovery; recovery of solvents, organic substances (not solvents), metals and compounds, inorganic materials (not metals), acids or bases, catalysts, pollution abatement residues; as well as refining or re-use of used oil and others.

Further descriptions of air releases can be found at <https://www.canada.ca/en/environment-climate-change/services/national-pollutant-release-inventory/report/tools-calculating-emissions.html> and this text is reproduced below for information purposes.

- *Stack or point releases*: releases from stack or point sources including stacks, vents, ducts, pipes, flares, or other confined process streams. Releases to air from pollution-control equipment generally fall into this category.
- *Storage tank and related handling releases*: releases to air from storage or handling of materials. This includes related loading, unloading and cleaning, degassing, and maintenance operations.
- *Fugitive releases*: releases to air that do not occur through a confined stream. These releases include:
  - fugitive equipment leaks from valves, pump seals, flanges, compressors, sampling connections, open-ended lines, etc.;
  - evaporative losses from surface impoundments and spills;
  - releases from building ventilation systems; and
  - any other fugitive or non-point air emissions from land treatment, mine tailings, storage piles, space heating, cooling towers, solvent use, wastewater treatment, etc.
- *Spills or other accidental releases*: accidental releases to air including those occurring during loading, unloading and cleaning of tanks.
- *Unpaved Road dust*: total particulate matter, PM<sub>10</sub> and PM<sub>2.5</sub>, releases from road dust must be reported if vehicles travelled more than 10,000 vehicle-kilometres on unpaved roads at the facility.
- *Other non-point releases*: any other non-point air releases not captured in one of the above air-related release types. Detailed comments should be provided to the NPRI if reported under this category

In this Code, there are several additional terms used all of which are incorporated in the term releases. These terms include: (i) emissions - which fundamentally refer only to air releases (i.e. related to point or fugitive sources); (ii) liquid effluents (wastewater discharges to surface water); (iii) on-site waste disposal or treatment (e.g. underground injection); and (iv) abnormal discharges (i.e. spills).

### **Off-site Transfers for Disposal**

NPRI substances that are present in wastes which are sent off-site for final disposal or treatment prior to disposal. This includes waste that is:

- (i) Sent to Municipal Sewage Treatment Plants,
- (ii) Landfilled
- (iii) Incinerated, or
- (iv) Underground Injection.

### **Off-site Transfers for Recovery, Re-use or Recycling**

NPRI substances that are present in materials sent to an off-site location for re-processing, cleaning, reclamation, or integrated to create a new product. Examples include:

- (i) Reclaimed chemicals,
- (ii) Spent catalyst used for cement production,
- (iii) Hydrocarbons used to displace regular fossil fuels, and
- (iv) Recycled used lube oil.

## **3.3. RECOMMENDED REPORTING PRACTICE**

### **3.3.1. Due Diligence**

A facility is expected to demonstrate “due diligence” in collecting all relevant data it already possesses, along with any information that may be reasonably obtained as stipulated in the following excerpt from Subsection 46(1) of CEPA.

“The Minister may ... publish in the *Canada Gazette* and in any other manner that the Minister considers appropriate a notice requiring any person described in the notice to provide the Minister with any information that may be in the possession of that person or to which the person may reasonably be expected to have access ...”

From the NPRI Guide for Reporting 2022-2024 (ECCC, 2022), ECCC expects the following level of effort in the sourcing of relevant data:

“Information on releases, disposals, and transfers for recycling needs to be reported if the owner/operator possesses the information or may reasonably be expected to have access to the information. The Notice specifies that if emissions are already monitored or measured under provincial or federal legislation or a municipal bylaw, those measurements must be used to report to the NPRI.”

“If emissions are not monitored or measured under provincial or federal legislation or a municipal bylaw, reasonable efforts must still be undertaken to gather information on releases, disposals, and transfers of a substance. What is “reasonable” depends on individual circumstances but may include additional monitoring for NPRI substances.”

“In deciding whether additional efforts should be undertaken to generate new information for the purposes of NPRI reporting, the following factors, among others, should be considered:

- “the health and environmental risks posed by a substance, including whether the substance has been declared toxic under CEPA;
- the relative contribution of the industrial sector to releases, disposals, and transfers for recycling of a substance in Canada;
- the relative contribution of the facility to releases, disposals, and transfers for recycling of a substance in Canada; and

- the cost of additional monitoring.”

The above NPRI guidance is consistent with those stipulated in CEPA.

It is recommended that Canadian Fuels members use the methods outlined in this Code of Practice unless better and defensible methods are available to the facility, and when estimating CACs or benzene, that any provincial permit requirements are used. When specific facility data is not available, it is suggested to use petroleum industry emission factors (generally called American Petroleum Institute/Western States Petroleum Association or API/WSPA factors), since these factors are based on data from the industry and should be the most applicable to Canadian Fuels member facilities. When the petroleum industry does not have a factor, EPA emission factors, sources, or guidance documents should be utilised. In rare circumstances, other factors may be considered from other regulatory agencies.

As a reference, Appendix A lists the NPRI substances that Canadian Fuels refinery members commonly report. Facilities are encouraged to review this appendix to ensure that their NPRI reporting is as complete as possible.

### **3.3.2. Reportable Substances**

There are six categories of substances reportable to NPRI based on their reporting thresholds Part 1A, Part 1B, Part 2, Part 3, Part 4, Part 5.

#### **Schedule 1, Part 1 A Substances**

The bulk of the substances fall into Schedule 1, Part 1, Group A (Part 1A) Substances, which are governed by the 10-tonne mass and 1% (weight) concentration MPO reporting threshold.

When total releases of a Part 1A substance are less than one tonne, a facility may choose to report the release as a total without specifying the environmental media (air, water, or land). However, facilities are still encouraged to report the break down by media, if the information is available.

1. An NPRI substance is reportable if it has been manufactured, processed, or otherwise used (MPO), in quantities of 10 tonnes (10,000 kg) or more per year.
2. The calculation of the 10-tonne reporting threshold must include the quantity of the substance manufactured, processed or otherwise used (MPO) at the facility (An overview of a facility’s activities to be considered for quantifying Part 1A substances is shown in Figure 5 of the 2022-2024 NPRI guide.) where the NPRI substance is in concentrations greater than 1% by weight. It must also include the quantities of the NPRI substance considered as a by-product (which has no limitation on concentration).
3. Once it is determined that a particular NPRI substance meets the above reporting threshold, then all releases of that substance must be reported, regardless of concentration. Guidance is given for the calculation of fugitive emissions from very low concentration streams in Section 4.2.2.

4. Air, water, land, and underground injection releases need not be reported separately when the sum is less than 1 tonne. However, it may be useful for future benchmarking to separate these releases if the information is available.
5. Releases to land are to include underground and surface discharges. Land releases are to be separated by spills, leaks, or other releases to land that are not disposals. For land releases that are not disposals, the nature of the releases must be reported. For substances that are released to land, recovered, and then disposed of or transferred off-site for recycling, their quantities must be reported accordingly. Comments on the amount of substances recovered are also required.

The quantity of land releases represents the net amount released, i.e. the quantity released minus the quantity recovered in the reporting year, even when the net value is zero or negative (reported as zero).

### **Schedule 1 Part 1B Substances – Alternate Threshold Substances**

Schedule 1, Part 1, Group B (Part 1B) Substances possibly present at refineries are acrylonitrile, arsenic (and its compounds), Bisphenol A, cadmium (and its compounds), cobalt (and its compounds), hexavalent chromium (and its compounds), hydrazine (and its salts), isoprene, lead (and its compounds), mercury (and its compounds), nonylphenol and its ethoxylates, selenium (and its compounds), tetraethyl lead, and thallium (and its compounds).

1. The transfers and releases of Part 1B substances must be reported if they have been manufactured, processed, or otherwise used (MPO), incidentally manufactured, processed, or otherwise used (as by-product), and/or present in disposed tailings and waste rock at any concentration, in quantities totalling the per year thresholds listed Table 3-1. These substances are reported to the NPRI in kg.
2. The calculation of the reporting threshold must include all streams where the NPRI substance is present in any concentration.
3. Once it is determined that the substance meets the reporting threshold, then all releases must be reported, regardless of concentration. Guidance is given for the calculation of emissions in Section 13.
4. See Section 3.3.4 on determination of non-detection data for further requirements on reporting.
5. Facilities must report mercury and criteria air contaminant releases to air for each electricity generation unit if the unit has a capacity of 25 MW or more and if the unit distributes or sells to the grid 33% or more of its potential electrical output (during the current or previous years). For more detail regarding this reporting requirement, please refer to Section 13.2 within the Code.

**Table 3-1 List of Group B Substances possibly applicable to Canadian Fuels Members and Reporting Thresholds**

<b>Substance</b>	<b>CAS RN</b>	<b>2022-2024 Mass Threshold (kg)</b>	<b>2022-2024 Concentration Threshold (weight %)</b>
Acrylonitrile	107-13-1	1000	0.1
Arsenic (and its compounds)	NA-02	50	1
Bisphenol A	80-05-7	100	1
Cadmium (and its compounds)	NA-03	5	0.1
Cobalt (and its compounds)	NA-05	50	0.1
Hexavalent Chromium (and its compounds)	NA-19	50	0.1
Hydrazine (and its salts)	302-01-2	1000	1
Isoprene	78-79-5	100	1
Lead (and its compounds)	NA-08	50	0.1
Mercury (and its compounds)	NA-10	5	N/A
Nonylphenol and its ethoxylates	NA-20	1000	1
Selenium (and its compounds)	NA-12	100	0.000005
Tetraethyl lead	78-00-2	50	0.1
Thallium (and its compounds)	NA-37	100	1

**Schedule 1, Part 2 Substances – PAH’s**

Schedule 1, Part 2 refers to polycyclic aromatic hydrocarbons (PAHs). Starting with the 2018 reporting year, anthracene has been moved from Part 1A to Part 2.

1. Thirty-one PAHs are governed by an alternate threshold reporting structure. These PAHs are listed in Section 14 and are reported to the NPRI in kg. For these PAHs, the threshold calculations are based on quantities released, disposed of, and/or transferred off-site for recycling as a result of incidental manufacture rather than being manufactured, processed or otherwise used (except for the activity of wood preservation using creosote). The reporting threshold is 50 kg or more of the sum of all specified PAHs, which exclude the NPRI Part 1A reportable PAH naphthalene. Amounts of individual PAHs released on site, disposed of, and/or transferred off-site must also be reported if the respective quantity released is known and is equal to or greater than 5 kg.
2. The calculation of the 50 kg reporting threshold must include all PAHs considered together as a group.

3. Once it is determined that total PAHs meet the above reporting threshold of 50 kg, there are three ways to report PAHs depending on the information available. If the quantities of individual PAHs which are incidentally manufactured are available, then the individual PAHs that are released, disposed of, and/or transferred for recycling in quantities greater than or equal to 5 kg are to be reported. In cases where the quantities of individual PAHs are known for some processes and only unspciated PAHs are known for others, the amount of known individual PAHs, that are equal to 5 kg or more, as well as the unspciated PAHs, that exclude the individual PAH reported quantities, should both be reported. If the quantities of individual PAHs are not known, the quantity of total PAHs is to be reported under “PAHs, total unspciated” in ECCC’s online NPRI reporting system SWIM.
4. See Section 3.3.4 on determination of non-detection data for further requirements on reporting all other sources (includes incidentally MPO as a by-product, in tailings, and in waste rock that is not inert and that is disposed).

As mentioned above, although naphthalene (CAS RN 91-20-3) is a PAH, it is a Part 1 A substance and is therefore subject to Part 1A reporting requirements and **must not** be considered in the Part 2 PAH calculations.

### **Schedule 1, Part 3 Substances – Dioxins, Furans & Hexachlorobenzene**

Part 3 substances are polychlorinated dibenzo-p-dioxins (dioxins), polychlorinated dibenzofurans (furans) and hexachlorobenzene, and are required to be reported where specified activities take place regardless of quantities or concentrations. However, as indicated below these specified activities generally do not apply to the downstream petroleum industry, but each facility should verify that the activities do not apply to their specific operation.

1. 18 individual Dioxins/Furans are listed as Part 3 substances. For all listed dioxins/furans and HCBs, there are no thresholds based on quantities of the substances and no obligatory reporting for facilities.
2. The determination of whether NPRI reporting is required is based on the activities engaged in by the facility. Different activities, based on employee hours, are categorized as being required to report. These activities generally do not apply to the downstream petroleum industry, but each facility should verify that the activities do not apply to their specific operation. Although refineries are not specifically required to report dioxins and furans to NPRI, the Ontario Monitoring and Reporting Regulation (Reg. 127) does require refineries to report, if the release to air threshold of 0.1 g/year is met. No Ontario refineries were above this threshold as reported in 2018.
3. Dioxins/furans are reported in Toxic Equivalences (TEQ) of dioxins/furans. HCBs are reported in grams. Calculations are outlined in ECCC’s “Guide to Reporting the National Pollutant Release Inventory (NPRI) 2022-2024”.
4. Once it is determined that dioxins/furans or HCBs meet the above reporting criteria, then all releases and transfers of the substances must be reported. The actual information reported will depend on whether direct measurements (CEMS, PEM or

source testing) or other methods (mass balance, emission factors or engineering estimates) are used to measure on-site releases and off-site transfers.

5. Air, water, land, and underground injection releases must be reported separately, even when the sum is less than 1 tonne.

### **Schedule 1, Part 4 Substances - Criteria Air Contaminants**

Part 4 substances consist of criteria air contaminants (CACs), which include: carbon monoxide, sulphur dioxide, nitrogen oxides (expressed as nitrogen dioxide), volatile organic compounds (total), PM<sub>2.5</sub> (particulate matter with a diameter less than or equal to 2.5 micrometres), PM<sub>10</sub> (particulate matter with a diameter less than or equal to 10 micrometres), total particulate matter (filterable particulate matter, on a dry basis, and excludes condensable particulate matter).

1. Seven CACs are listed below along with their corresponding reporting thresholds in Table 3-2. For these CACs, the threshold calculations are based on quantities released to air rather than manufactured, processed or otherwise used.

**Table 3-2 Mass Reporting Thresholds for CAC Substances**

<b>CAC Substances</b>	<b>Mass Reporting Threshold</b>
Carbon monoxide	20 tonnes
Nitrogen oxides (expressed as NO <sub>2</sub> )	20 tonnes
PM <sub>2.5</sub>	300 kilograms
PM <sub>10</sub>	500 kilograms
Sulphur dioxide	20 tonnes
Total particulate matter	20 tonnes
Volatile organic compounds (total)	10 tonnes

2. Road dust from refinery dirt roads is an NPRI reporting requirement (See Section 15.6.2.4)
3. Nitrogen oxides should be expressed as nitrogen dioxide on a mass basis.
4. Guidance is given for the calculation of CACs emissions in Section 15.

### **Schedule 1, Part 5 Substances - Speciated Volatile Organic Compounds**

Part 5 substances are selected, speciated volatile organic compounds (VOCs), comprising of 62 VOCs in three groups (individual substances, isomer groups, and other groups and mixtures), with additional reporting requirements. A complete VOC listing is included in Appendix C.



Articles that are processed or otherwise used are not included in the one tonne threshold calculation, provided there is no NPRI substance release or off-site waste transfer.

It is important to note that Alternate Threshold reporting criteria are dependent on the substance under consideration and calculations differ depending on the substance.

1. Selected speciated VOC substances are also on the NPRI list of substances governed by an alternate threshold reporting structure. These VOC substances are listed in Table 3-3.
2. Any VOC species on the list in Table 3-3 will be reportable if the total quantity is  $\geq 1$  tonne per year. In addition, for each stack that is greater than 25 m, the speciated VOC must be reported if 0.25 tonnes or more is released from the stack. A breakout of VOC emissions are required for the stack as per the Part 5 list below. A detailed list of Part 5 VOCs, their CAS numbers, isomers, and synonyms is included in Appendix C Table C-1. In addition, VOCs must be broken out by stationary fuel combustion for energy purposes, combustion of fuels for non-energy purposes, flaring, use of fuels for non-energy products and all other sources.
3. Certain Part 5 substances may also be reportable under other NPRI substance categories. For example, benzene is reportable both as a Part 1A and a Part 5 substance depending on whether its respective Part 1A and Part 5 reporting thresholds are met. To assist members in determining the reporting required under the various substance categories, a couple of examples on benzene reporting have been included in Appendix D.

**Table 3-3 Selected VOC Substances for Speciation**

Substance Classes	Name of Substances	
Individual VOC substances	Acetylene	D-Limonene
	Benzene	Methanol
	1,3 Butadiene	Methyl ethyl ketone
	2-Butoxyethanol	Methylcyclopentane
	p-Dichlorobenzene	Methyl isobutyl ketone
	1,2-Dichloroethane	Myrcene
	Dimethylether	Beta-Phellandrene
	Ethanol	Alpha-Pinene
	Ethyl acetate	Beta-Pinene
	Ethylene	Propane
	Formaldehyde	n-Propyl alcohol
	Furfuryl alcohol	Propylene
	n-Hexane	Styrene
	Isopropyl alcohol	Tetrahydrofuran
		Toluene
	1,2,4-Trimethylbenzene	

Substance Classes	Name of Substances	
		Vinyl acetate
Isomer Groups	Butane Butene Butyl acetate Cycloheptane Cyclohexene Cyclooctane Decane Ethyltoluene Heptane	Hexane Hexene Nonane Octane Pentane Pentene Propyl acetate Propylene glycol methyl ether acetate (all isomers) Trimethylbenzene Xylene
Other Groups and Mixtures	Analytically unresolved hydrocarbons (C <sub>10</sub> to C <sub>16</sub> <sup>+</sup> ) Heavy aromatic solvent naphtha Hydrotreated heavy naphtha Hydrotreated light distillate Light aromatic solvent naphtha Mineral spirits Naphtha Other glycol ethers and acetates (and their isomers) Solvent naphtha light aliphatic Solvent naphtha medium aliphatic Stoddard solvent VM & P naphtha	

### 3.3.3. Specific Interpretations

1. Chemical purchases are included in the determination of reportable NPRI substances.
2. A fixed bed catalyst containing "NPRI substances" can be classified as an article, if it remains unmodified or there are no releases within the reporting year. Where a fixed bed catalyst is transferred off-site or is released it would lose its article status and must be included in the calculation of the 10-tonne MPO reporting threshold. Spent catalyst is not an article as it has been modified from its original form and should be included in the calculation of the reporting threshold.
3. Heating/cooling liquids such as Dowtherm or Ethylene Glycol can be classified as "Otherwise Used" substances. Recirculating fluid systems need to be included in the threshold calculation even if there are no emissions.

4. Asbestos insulation is also an “Otherwise Used” substance and is reportable if it is disposed of to landfill in quantities of 10 tonnes or more per year.
5. Nickel and vanadium (Part 1A Substances) found in heavy fuel oil are “by-products” when this fuel is burned at the refinery. These substances are released to the environment via the flue gas and must be reported regardless of concentration, provided the yearly release quantities are 10 tonnes or more per year.
6. When conducting analysis of speciated VOC profile data, caution should be taken to avoid “double counting” since a given profile may contain a mix of VOC species which are reportable individually under Parts 1, 2 and/or 5 of Schedule 1 of the Canada Gazette Notice, while some species are also reported collectively within Total VOCs (NA – M16) in Part 4. For example, quantities of benzene could be reported under both Part 1, Part 5, and in the Total VOCs reported under Part 4. Moreover, total VOCs reported under Part 4 may be different from the total of all individually reported VOC species for a number of reasons, such as differences in reporting requirements, reporting thresholds, the definition of Total VOC in Part 4 (which contains numerous VOCs beyond those listed in the other Parts), and/or estimation methodologies.

### **3.3.4. Interpretation of Non-Detection Data**

The interpretation of non-detection data is especially critical for the determination of threshold and release calculations for alternative threshold substances (alternative threshold metals, PAHs, dioxins/furans, and HCBs). ECCC has indicated that when some measurements are below the detection limit, a value of one-half the detection limit should be used. If all measurements are below the detection limit, the users may use half the detection limit if they believe that the substance is present. If the users believe the substance is not present, the concentration of the substance can be assumed to be zero.

When a direct discharge to surface waters is reported, the average annual concentration (ppm) of the NPRI substance in the effluent is also required to be reported. Additional clarification for release estimates made using the method detection limit (MDL) can refer to Figure 3 of the 2022-2024 NPRI guide.

#### ***Interpretation of Multiple Data Points and Non-detected Values***

Facilities should use reasonable judgement as to the presence and amount of an NPRI-listed substance based on the best readily available information. An indication that a reportable substance is below the method detection limit is not equivalent to stating that the substance is not present. If the substance is known to be present, a concentration equivalent to half the method detection limit should be used. Facilities should not estimate releases solely on monitoring devices, but should also rely on their knowledge of specific conditions at the plant.

The following scenarios illustrate these general principles:

Where one or more measurements over a year in a given process stream/waste are all below the method detection limit and the facility has no other reason to believe that substance is present, the facility should assume that the concentration of the substance is zero. In cases where a facility is not certain whether a reportable substance is present in the given process

or waste stream while all measurement values are below method detection limit, ECCC NPRI guidance is to assume zero since the presence of the substance is not proven.

Where some measurements over a year in a given process/waste stream for a specific substance are above the method detection limit and some measurements are below the method detection limit, the facility has good reason to assume that the substance is present. The facility should therefore use a concentration value of half the method detection limit for those measurements below the method detection limit to estimate releases/transfers. This methodology was used to estimate the average mercury content in crude oil from a number of Canadian Fuels Association refineries.

### **3.3.5. Use of Median versus Mean Value**

The mean value of a dataset can sometimes be skewed by a few outliers. In this case, the use of the median value of the dataset may be more appropriate. CONCAWE recommends that the median value be used when the mean value of the dataset is more than 10 times that of the median value.

### **3.3.6. Significant Digits**

ECCC's SWIM system allows reporting of emissions to the nearest tenth of a kilogram. Reporters should take into account the number of significant digits in their data when determining the number of significant digits in their reported emissions. Helpful guidance on how to determine the number of significant digits can be found at the following sources:

- <https://www.physics.uoguelph.ca/significant-digits-tutorial>
- [http://en.wikipedia.org/wiki/Significant\\_figures](http://en.wikipedia.org/wiki/Significant_figures)
- <https://www3.epa.gov/ttn/emc/faqs/rounding.pdf>

An example is provided below for member consideration:

- Use one decimal point for numbers reported in kilograms and tonnes (i.e. up to 0.1 kg for reporting substances in kg such as Part 2 PAHs, 0.1 tonne for Part 1A and Part 5 substances).
- If a substance is reportable due to threshold but emission is less than 0.1 kg or 0.1 tonne, report with first significant digit (e.g. Mercury emission of 0.0023 kg reported as 0.002 kg).
- Use the lowest significant digit for each release type for reporting all releases (e.g. if fugitive releases are 0.005 tonnes, stack releases should be reported to the third decimal place as well).

### **3.3.7. Revision of Historic Data**

Revision of historic data is not necessary if changes are the result of revised calculation or estimating techniques. It is recommended that historic data be revised when a new release source is identified (which also existed in the past) or estimation errors are identified. These revisions should be reported to ECCC when total releases and/or transfers for that

substance change, according to the following guidance provided in the Canada Gazette Part I Explanatory Note (December 29, 2012):

“It is important that ... any errors in submitted data be corrected in a timely manner, so that the information provided to the NPRI continues to be relevant and accurate. Therefore, persons who submitted reports for a previous year are strongly encouraged to update their information, through the online reporting system or by contacting ECCC directly, if the person becomes aware that the information submitted for any previous year was mistaken or inaccurate.”

Although ECCC does not prescribe a percentage threshold for historic data revision and re-submission, members are expected to exercise due diligence and professional judgement regarding the materiality of the change in the historic data prior to re-submission.

It must be noted that ECCC will only accept revisions for the latest year which was submitted and the two years prior to that. Once NPRI data is revised, it is recommended that notification be given to Canadian Fuels so that revisions can be incorporated in the Environmental Safety and Performance Report (ESPR).

### **3.4. REFERENCES**

1. “Notice with Respect to Substances in the National Pollutant Release Inventory for 2022, 2023, and 2024”, Canada Gazette Part I, February 12, 2022.  
<https://www.canada.ca/en/environment-climate-change/services/national-pollutant-release-inventory/report/legal-requirements-gazette-notices.html>
2. “Air Pollutant Emission Estimation Methods for E-PRTR Reporting by Refineries”, CONCAWE, July 2019. <https://www.concawe.eu/publication/air-pollutant-emission-estimation-methods-for-e-prtr-reporting-by-refineries/>
3. “Guide to Reporting to the National Pollutant Release Inventory: 2022-2024”, Environment and Climate Change Canada, 2022.  
<http://publications.gc.ca/pub?id=9.506026&sl=0>
4. E-mail from Environment and Climate Change Canada (Kedrouss, Fouzi to Zhang, Hong) on reporting of VOC emissions, November 6, 2019

## **4. PROCESS FUGITIVE EMISSIONS**

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### **4.1. SCOPE**

Fugitive emissions from all process units that handle hydrocarbons (and/or NPRI reportable substances) as related to the asset base defined in Section 2.2, are calculated for NPRI. The procedures outlined for estimating process fugitive emissions include both Volatile Organic Compounds (VOCs) and other specific substances.

For refineries reporting to the NPRI, VOC “means volatile organic compounds as defined in the *Reduction in the Release of Volatile Organic Compounds Regulation (Petroleum Sector)*, published in the *Canada Gazette*, Part II, Vol. 154, No. 23 (Ottawa, Tuesday, November 10, 2020)”.

For this section, “Volatile organic compound” or “VOC” means a compound that participates in the atmospheric photochemical reactions and that is not excluded under item 65 of Schedule 1 to the Canadian Environmental Protection Act (CEPA) 1999. The full list of substances excluded from the NPRI definition of VOC is shown in Appendix C Volatile Organic Compounds of this Code.

To conduct the NPRI emission inventory, the types of equipment components, leak rates and screening value correlation equations is the recommended methodology as outlined in the *Canada Gazette*, Part II, Vol. 154, No. 23 (Ottawa, Tuesday, November 10, 2020)”.

Unless field practices are to the contrary, all open-ended lines are assumed to be capped and sampling connections closed, purged/vented and not counted for the purposes of estimating fugitive emissions. Aqueous streams containing hydrocarbon (>10 weight%) should be included and emissions estimated for components in this service.

### **4.2. REQUIREMENTS**

#### **4.2.1. Component Counts**

All equipment components that are listed in a facility’s inventory must be counted and inspected for leaks three times per calendar year with the exception of equipment components that are normally operated at internal pressure that is at least 5kPa below ambient pressure or are located underground, or of which a minor assembly is composed; seal-less pumps, including canned motor pumps and diaphragm pumps; bellows seal valves; diaphragm valves; storage vessels; oil water separators. Difficult to inspect components can be inspected once per year. Pumps are visually inspected once per week.

The formal inventory of equipment components must be updated once in each calendar year, before the first inspection carried out in that year.

#### 4.2.2. Fugitive Emission Calculations

The Screening Value Correlation Equation method is used to calculate emissions, which is regarded as providing the most representative emission for process fugitive estimation. Note that the use of optimal gas imaging cameras versus US EPA Method 21 to measure VOCs could lead to different results when calculating screening value correlations.

1. For process units which are subject to strict fugitive emission control, for example, HF and CCl<sub>4</sub>, the emissions may be considered negligible and assumed to be zero.

e.g. For an aqueous stream containing 12% hydrocarbons, 1% Methyl ethyl ketone (MEK) of the total hydrocarbons results in:

$$\text{VOC kg/hr} = 0.00023 * 0.12 * 1000 = 0.0276$$

$$\text{MEK kg/hr} = 0.0276 * 0.01 = 0.000276$$

2. Mass balances for specific units can be used to estimate total emissions, including fugitive, especially where there are sources with emissions for which no estimation methodology exists.

Examples of this are Methyl ethyl ketone (MEK) and Methyl isobutyl ketone (MIBK), which are solvents often used in the production of base lube oils. Because of the type of equipment used in the lube oil production process, using conventional fugitive emission factors may not be adequate to estimate the fugitive air releases from these units. Since MEK and MIBK are purchased chemicals, an alternative method can be used for calculating air emissions. MEK and/or MIBK use can be calculated by summing the particular solvent purchased and subtracting inventory change. Not all of the solvent used is released to the air as some is entrained with the product. Each facility should determine a factor to account for losses to the product. If the facility specific factor is not available, assume 30 weight% of the solvent usage is lost to the product.

3. The hourly leak rate is the rate determined for the component type for either a Zero Leak Rate (less than three drops per minute) or a Pegged Leak Rate (greater than three drops per minute or if no inspection was carried out). It is based on the inspection carried out closest to that hour, whether carried out in the calendar year or the preceding or subsequent calendar year. If the number of hours between the hour identified and the preceding inspection is the same as the subsequent inspection, the hourly leak rate is based on the preceding inspection. If an inspection indicates a significant leak, the hourly leak rate is determined for every hour in the period starting with the hour of the inspection and ending with the hour the component was repaired.

Screening Value Correlations - The use of petroleum industry Leak Rate/Screening Value Correlations (*Canada Gazette*, Part II, Vol. 154, No. 23, Schedule 3 (Ottawa, Tuesday, November 10, 2020)”) are shown in Table 4-1.

**Table 4-1 Petroleum Industry Leak Rate/Screening Value Correlations for Refineries and Marketing Terminals**

Item	Type of Equipment Component	Hourly Default Zero Leak Rate (kg/hr per equipment component)	Hourly Pegged <sup>a</sup> Leak Rate (kg/hr per equipment component)	Hourly Correlation Equation Leak Rate (kg/hr per equipment component) <sup>b</sup>
<b>Hourly Leak Rates for Process Units Primarily Engaged in Activities Under NAICS Code 325 (Chemical Manufacturing)</b>				
1	Gas valve	6.60E-07	0.11	$1.87E-06 \times SV^{0.873}$
2	Light-liquid valve	4.90E-07	0.15	$6.41E-06 \times SV^{0.797}$
3	Heavy-liquid valve	4.90E-07	0.15	n/a
4	Compressor, pressure relief device, agitator, light-liquid pump	7.50E-06	0.62	$1.90E-05 \times SV^{0.824}$
5	Heavy-liquid pump	7.50E-06	0.62	n/a
6	Connector (other than a flange)	6.10E-07	0.22	$3.05E-06 \times SV^{0.885}$
7	Flange	3.10E-07	0.084	$4.61E-06 \times SV^{0.703}$
8	Open-ended pipe	2.00E-06	0.079	$2.20E-06 \times SV^{0.704}$
9	Gas minor assembly	1.65E-05	0.11	n/a
10	Light-liquid minor assembly	1.23E-05	0.15	n/a
11	Heavy-liquid minor assembly	1.23E-05	0.15	n/a
12	Any equipment component other than referred to in items 1 to 11	4.00E-06	0.11	$1.36E-05 \times SV^{0.589}$
<b>Hourly Leak Rates for All Other Process Units (Recommended for NAICS Code 324)</b>				
13	Gas valve	7.80E-06	0.14	$2.29E-06 \times SV^{0.746}$
14	Light-liquid valve	7.80E-06	0.14	$2.29E-06 \times SV^{0.746}$
15	Heavy-liquid valve	7.80E-06	0.14	n/a
16	Light-liquid pump	2.40E-05	0.16	$5.03E-05 \times SV^{0.610}$
17	Heavy-liquid pump	2.40E-05	0.16	n/a
18	Connector (other than a flange)	7.50E-06	0.03	$1.53E-06 \times SV^{0.735}$
19	Flange	3.10E-07	0.084	$4.61E-06 \times SV^{0.703}$
20	Open-ended pipe	2.00E-06	0.079	$2.20E-06 \times SV^{0.704}$
21	Minor assembly	1.95E-04	0.14	n/a
22	Any equipment component other than referred to in items 13 to 21	4.00E-06	0.11	$1.36E-05 \times SV^{0.589}$

<sup>a</sup> in respect of a reading on a portable monitoring instrument, means a reading indication that the concentration of VOCs is above the highest concentration of VOCs that the instrument is capable of measuring

<sup>b</sup> SV = Screening value = measured concentration of VOC expressed in ppmv.



### **4.2.3. Yearly Calculations**

The emission quantification methods require use of the “Mid-Point calculation methodology”. This methodology is approved by ECCC and is summarized below (excerpt from Appendix A of Guidance Document: Reduction in the Release of Volatile Organic Compounds Regulations (Petroleum Sector)):

**Step 1:** Convert the time and date of each LDAR activity into the hour of the calendar year.

**Step 2:** Calculate the midpoint hour between all activities.

**Step 3:** Apply the activity results (i.e., non-detect, SV or pegged) from the midpoint to the previous activity to the midpoint of the subsequent activity unless the activity identifies a significant leak. In the case that an activity identifies a significant leak, apply that activity result from that hour until the hour before repair.

**Step 4:** Calculate the duration of hours that the activity result applies to.

**Step 5:** Calculate the emission rate in kg/hr for the activity using Hourly Default Zero Leak Rate, Hourly Correlation Equation Leak Rate or Hourly Pegged Leak Rate, as applicable.

**Step 6:** Calculate the emissions in kilograms for each duration by multiplying the emission rate in kg/hr by the duration in hours

**Step 7:** Sum the emissions in kg for all hours in each calendar year

### **4.2.4. Speciation**

For process fugitive emissions where leakage arises from pressurized sources, the speciation (composition) of the emission is assumed to be the same as the stream under consideration. There is no liquid/vapour phase equilibrium with different liquid and vapour phase composition considered or calculated.

1. Components defined under the LDAR program are assigned a stream name and are speciated based on this stream name using site specific data or representative industry data.
2. Speciation of specific component profiles is available from US EPA SPECIATE. The profiles available are for compressor seals and relief valves. Use data representative of actual composition of streams where available. See Section 15.4 for more information on VOC Speciation.
3. If site representative data is not available, use industry average compositions as shown in EPA - 450/2-90-001a “Air Emissions Species Manual, January 1990.” However, this data is limited in scope.
4. Refer to Appendix A of this Code to review typical sources of NPRI emissions within refineries.
5. For non-hydrocarbon NPRI substances (i.e. H<sub>2</sub>S) where specific emission factors are not available, it is recommended to use standard VOC fugitive emission factors and speciate the substance as if it were a hydrocarbon.

### **4.3. REFERENCES**

1. Reduction in the Release of Volatile Organic Compounds Regulations (Petroleum Sector): SOR/2020-231; Canada Gazette, Part II, Volume 154, Number 23, November 10, 2020
2. “Air Emissions Species Manual”, EPA - 450/2 - 90 - 001a, January 1990.
3. Guidance Document: Reduction in the Release of Volatile Organic Compounds Regulations (Petroleum Sector), Oil and Gas Alternative Energy Division, ECCC, 2019

## **5. RELEASES FROM STORAGE TANKS**

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### **5.1. SCOPE**

Emissions from storage tanks, relative to the asset base defined in Section 2.2, are calculated as part of the inventory process.

Tank emissions are evaluated for tanks in crude, gasoline, avgas, jet fuel or distillate service or for any component tanks from which products are blended. Asphalt and Heavy Fuel Oil (HFO) tanks are included if a cutter stock is used. Tank emissions from non-routine events such as tank cleaning and floating-roof landings are discussed separately in Section 8 of this Code.

On April 6, 1998, Canadian Fuels issued a guideline with respect to the measurement and reduction of Volatile Organic Compounds (VOCs) from Above Ground Storage Tanks. This guideline recommended that Canadian Fuels refineries adopt the provisions of the June 1995 CCME “Environmental Guidelines for Controlling Emissions of Volatile Organic Compounds from Above Ground Storage Tanks” (with minor qualifications).

### **5.2. REQUIREMENTS**

#### **5.2.1. Emissions Methodology**

Storage tank emissions are calculated in accordance with the latest version of EPA AP-42 Chapter 7.1 (Organic Liquid Storage Tanks) - dated November 2019, available at <https://www.epa.gov/sites/production/files/2020-10/documents/ch07s01.pdf>, which were developed based on information provided in the API Manual of Petroleum Measurement Standards. The revisions to AP-42 Section 7.1 are extensive as a result of adding guidance on emission estimation methods for time period of less than one year and addressing additional scenarios that EPA considers as non-routine emission modes or special operating conditions such as cleaning and splashing. Below is a full list of the additions or revisions to AP-42 Section 7.1 as cited from the EPA website accessible via: <https://www.epa.gov/air-emissions-factors-and-quantification/final-revisions-ap-42-chapter-7-section-71-organic-liquid>.

- Landing a floating roof.
- Tank cleaning.
- Tanks containing unstable liquids, such as tanks which have air or other gases injected into the liquid (sparging), tanks storing liquids at or above their boiling point (boiling), or tanks storing liquids which contain gases that have the potential to flash out of solution (flashing).
- Variable vapour space tanks.
- Pressure tanks designed as closed systems without emissions to the atmosphere.
- Time periods shorter than one year.
- Internal floating roof tanks with closed vent systems.

- Case-specific liquid surface temperature determination.
- Adapting equations for heating cycles in fixed roof tanks.
- Applying Raoult’s Law to calculate the contribution of individual chemical species to the total emissions.
- Worked examples (AP-42 Section 7.1.5).
- Equations in AP-42 Section 7.1.6 that have been used historically to obtain approximate values have been replaced with more accurate equations.

With respect to the TANKS emissions estimation tool, although the TANKS 4.09d software is available at:

<https://www.epa.gov/air-emissions-factors-and-quantification/tanks-emissions-estimation-software-version-409d>

It had historically been the official and default tool for calculation of tank emissions, EPA has stopped updating and supporting its own software since October 5, 2006 due to known technical problems and difficulties incorporating and implementing AP-42 Section 7.1 equations correctly. Some of the most notable deficiencies documented by EPA that render TANKS 4.09d as an inadequate and outdated tool for calculating storage tank emissions include:

- Underestimation of monthly emissions resulting from incorrect use of annual average liquid bulk temperature in the monthly calculations.
- Inability to handle heated tanks that are not insulated or only partially insulated as TANKS 4.09d assumes that all heated tanks are well insulated and are heated to a uniform temperature such that there are no or negligible breathing losses.
- Lacking capacity to calculate non-routine emission scenarios (such as landing) and specialized tank operations (such as splashing).

Accordingly, EPA advised the use of equations and procedures specified in AP-42 Section 7.1 to estimate storage tank emissions instead of relying on TANKS 4.09d. There are many commercially available tanks emissions estimation programs that offer alternatives to TANKS 4.09d by following the latest AP-42 Section 7.1 version. Given that EPA has not yet officially endorsed, validated, nor provided recommendations on the selection and use of these commercial programs, facilities should consider seeking feedback, guidance or acceptance from EPA or the applicable regulators when deviating from the recommended direct use and application of equations and methodologies as set out in AP-42 Section 7.1.

In calculating the tank emissions, for a given facility, observed average temperatures from either the historical weather dataset or the Canadian Climate Normals dataset for the nearest and representative meteorological data can be used. This data can be obtained online via the ECCC historical data portal at:

[https://climate.weather.gc.ca/climate\\_normals/index\\_e.html](https://climate.weather.gc.ca/climate_normals/index_e.html)

### 5.2.2. Tank Throughput/Turnovers

1. If the actual number of tank turnovers/year is available, this data should be used. Otherwise, calculate tank turnovers per tank, per liquid (i.e. crude, intermediate or product) using the following formula:

$$\text{No. of Turnovers per Tank} = \frac{\text{Total Annual Throughput Volume}}{\text{Total Tank Working Capacity Volume}}$$

2. For push-pull tanks and tanks that are intermediate, assume turnover = 1/year, unless better data is available.

### 5.2.3. Speciation

Unlike fugitive process emissions that represent leaks from pressurized sources, storage of liquid streams is generally at atmospheric pressure. Therefore, the composition of the vapour phase will differ from the actual liquid stream (proportionally more of the higher volatility substances in the vapour phase).

1. Raoult's law - See AP-42 Section 7.1.4 Speciation Methodology for Cases and equations

<https://www.epa.gov/air-emissions-factors-and-quantification/final-revisions-ap-42-chapter-7-section-71-organic-liquid>

2. If composition of the specific material in the storage tank is not available, use data from EPA - 450/2-90-001a, "Air Emissions Species Manual", January 1990. The report: "Air Emissions from CPPI Terminals and Bulk Plants" can also be used as a source of information.
3. If no vapour phase data is available, the preferred method for determining emissions for H<sub>2</sub>S released during storage is to use tank vapour space analytical data. Another method is to apply a factor of 50x to the liquid phase concentration to attain the vapour phase concentration (Slack 1988). TANKS 4.09d and other commercial tools for calculating tank emissions in accordance to the AP-42 Section 7.1 may be better suited for estimating emissions of VOCs and should only be used as a secondary back up approach for H<sub>2</sub>S emissions.

## 5.3. IMPROVEMENT OPTIONS

1. Calculate tank emissions monthly, quarterly, or seasonally using appropriate throughputs, product vapour pressures, and meteorological data.
2. Perform vapour space analyses on individual tanks to determine speciation. This approach can be used to estimate the emission of individual substances, such as Total Reduced Sulphur (TRS) species, from storage tanks.
3. While the US EPA AP-42 Section 7.1 is the default guideline for estimating storage tank emissions, the user should be aware that the emission factors and reference datasets are tailored to conditions relevant to US refineries and terminals. For example,

the properties of refined products stored, such as composition and Reid Vapour Pressure (RVP) values, as well as climatic factors are quite different than those found in Canada. EPA - 450/2-90-001a, “Air Emissions Species Manual”, January 1990

#### **5.4. REFERENCES**

1. Fixed Roof Tanks - API Bulletin 2518, Oct. 1991.
2. External Floating Roof Tanks - API Bulletin 2517 *Addendum*.
3. Internal Floating Roof Tanks - API Bulletin 2519, June 1983.
4. EPA TANKS 4.09d Program, latest version.  
<https://www3.epa.gov/ttnchie1/software/tanks/>
5. “Air Emissions Species Manual”, EPA - 450/2-90-001a, January 1990.  
<https://nepis.epa.gov/Exe/ZyPDF.cgi/00001VFS.PDF?Dockkey=00001VFS.PDF>
6. “Summary Report - Hydrogen Sulphide in Residual Fuel Oil and Storage Tank Vapour Space”, Slack, D. J., Am. Ind. Hyg. Assoc. 48(4):205-206, 1988.
7. “API Manual of Petroleum Measurement Standards (MPMS): Chapter 19 Evaporation Loss Measurement.”
8. Revisions to AP-42, Chapter 7, Section 7.1 – Organic Liquid Storage Tanks, US EPA: <https://www.epa.gov/air-emissions-factors-and-quantification/final-revisions-ap-42-chapter-7-section-71-organic-liquid>

## 6. RELEASES FROM LOADING OPERATIONS

### 6.1. SCOPE

Emissions from loading operations, relative to the asset base defined in Section 2.2, are calculated as part of the inventory process.

### 6.2. REQUIREMENTS

#### 6.2.1. VOC Losses

- VOC loading losses are estimated as the product of throughput multiplied by an emission factor. The emission factors are given in EPA AP-42 (fifth edition, January 1995), Chapter 5.2, “Transportation and Marketing of Petroleum Liquids”, as shown in Table 6-1 through Table 6-4 below. Vapours that are displaced from tanks receiving liquid product are returned to the tanks delivering the product.
- For Liquefied Petroleum Gas (LPG) rail cars, there are no widely accepted factors to estimate loading emissions. Most of the emissions are from a type of gauge rod, used on some rail cars that vent to atmosphere during loading (slip tube gauge). One Canadian Fuels member did a limited amount of testing and estimated emissions to be 0.07 kg VOC/m<sup>3</sup> of LPG loaded. This assumed that 50% of the rail cars loaded had the slip type of gauge. If no other data is available, this factor can be used.
- For other rail cars and tank trucks, use the following table:

**Table 6-1 Total Organic Compound Emission Factors for Petroleum Liquid Rail Tank Cars and Tank Trucks (mg TOC /litre transferred)**

Emission Source	Gasoline <sup>a</sup>	Crude Oil <sup>b</sup>	Jet Naphtha (JP-4)	Jet Kerosene	Distillate Oil No. 2	Residual Oil No. 6
<b>Loading Operations<sup>c</sup></b>						
<b>Splash Loading</b>						
Dedicated Normal Service	1430	580	430	5	4	0.03
Vapour Balance Service <sup>a</sup>	980	400	300	d	d	d
<b>Submerged Loading</b>						
Vapour Balance Service <sup>a</sup>	980	400	300	d	d	d
Dedicated Normal Service	590	240	180	1.9	1.7	0.01

Source: AP-42, 5<sup>th</sup> Edition, Table 5.2-5.

<sup>a</sup> Gasoline factors represent emissions of non-methane/non-ethane VOC, as well as, total organic emissions, since methane and ethane constitute a negligible weight fraction of the evaporative emissions from gasoline. The example gasoline has an RVP of 10 psia.

<sup>b</sup> Non-methane/non-ethane VOC emission factors for a typical crude oil are 15% lower than the total organic factors shown. The example crude oil has an RVP of 5 psia.

- <sup>c</sup> Loading emission factors are calculated using Equation 1 for a dispensed product temperature of 15°C.
- <sup>d</sup> Not normally used.

4. For marine loading: use the following tables:

**Table 6-2 Total Organic Emission Factors for Petroleum Marine Vessel Sources<sup>a</sup> (mg TOC /litre transferred)**

Emission Source	Gasoline <sup>b</sup>	Crude Oil <sup>c</sup>	Jet Naphtha (JP-4)	Jet Kerosene	Distillate Oil No. 2	Residual Oil No.6
<b>Loading Operations:</b>						
Ships/Ocean Barges	d	73	60	0.63	0.55	0.004
Barges	d	120	150	1.6	1.4	0.011
<b>Tanker Ballasting:</b>	100	e	f	f	f	f

Source: EPA AP-42, 5<sup>th</sup> Edition, Chapter 5.2, Table 5.2-6.

- <sup>a</sup> Emission factors are calculated for a dispensed product temperature of 15°C.
- <sup>b</sup> Factors shown for gasoline represent non-methane/non-ethane VOC emissions, as well as, total organic emissions. The example gasoline has an RVP of 10 psia.
- <sup>c</sup> Non-methane/non-ethane VOC emission factors for a typical crude oil are 15% lower than the total organic factors shown. The example crude oil has an RVP of 5 psia.
- <sup>d</sup> See Table 6-3 for these emission factors.
- <sup>e</sup> See Table 6-4 for these emission factors.
- <sup>f</sup> Unavailable.

**Table 6-3 Volatile Organic Compound Emission Factors for Gasoline Loading Operations at Marine Terminals<sup>a</sup> (mg VOC or TOC/litre transferred)**

Vessel Tank Condition	Previous Cargo	Ships/Ocean Barges <sup>b</sup>	Barges <sup>b</sup>
Uncleaned	Volatile <sup>c</sup>	315	465
Ballasted	Volatile	205	d
Cleaned	Volatile	180	e
Gas-freed	Volatile	85	e
Any Condition	Non volatile	85	e
Gas-freed	Any cargo	e	245
Typical <sup>f</sup>	Any cargo	215	410

Source: EPA AP-42, 5<sup>th</sup> Edition, Chapter 5.2, Table 5.2-2.

- <sup>a</sup> Factors represent emissions of non-methane/non-ethane VOC and total organic emissions, since methane and ethane have been found to constitute a negligible weight fraction of the evaporative emissions from gasoline.



- b Ocean barges (tank compartment depth about 40 feet) exhibit emission levels similar to tank ships. Shallow draft barges (compartment depth 10 to 12 feet) exhibit higher emission levels.
- c Volatile cargoes are those with a true vapour pressure greater than 1.5 psia.
- d Barges are not usually ballasted.
- e Unavailable.
- f Based on observation that 41% of tested ship compartments were uncleaned, 11% ballasted, 24% cleaned and 24% gas-freed. For barges, 76% were uncleaned.

**Table 6-4 Total Organic Emission Factors for Crude Oil Ballasting<sup>a</sup> (mg TOC/litre ballast water)**

Compartment Condition before Cargo Discharge	By Category	Typical <sup>b</sup>
Fully Loaded <sup>c</sup>	111	
Lightered or Previously		129
Short-loaded <sup>d</sup>	171	

Source: AP-42, 5<sup>th</sup> Edition, Chapter 5.2, Table 5.2-4.

- a Assumes crude oil temperature of 15°C and RVP of 5 psia. Non-methane/non-ethane VOC emission factors average about 85% of these total organic factors.
- b Based on observation that 70% of tested compartments had been fully loaded before ballasting. May not represent average vessel practices.
- c Assumed typical arrival ullage of 2 ft.
- d Assumed typical arrival ullage of 20 ft.

5. If data is not available on VOCs losses or capture from asphalt truck loading, data for Residual Oil No. 6 can be used as a substitute. The difference in properties is minimal.
6. Vapour Recovery: If vapour recovery is installed, the emissions are the product of emissions calculated as if there were no vapour recovery (see Section 6.2.1, Part 2) multiplied by 1 minus the efficiency factor (i.e.: 1 - eff./100).

The efficiency factor shall be representative of the actual performance of the recovery system. If such a factor is not available from field measurements or manufacturers’ data, the guidance from the US EPA Emission Estimation Protocol for Petroleum Refineries, as shown in Table 6-5, may be considered (US EPA, 2015). If members are considering adopting the efficiency factors provided in the EPA Protocol guidance, leak check information on their respective truck fleets, such as from EPA Method 27, annual and five-year tests or B620 inspections, should be gathered.

7. “VOC emissions from tanks including related loading, unloading and cleaning operations should be reported under Storage or Handling releases category. Any accidental releases to air should be reported under Spills category.” (Communication from Environment and Climate Change Canada)

**Table 6-5 Vapour Collection System Capture Efficiencies**

Loading Characteristics and Leak Check Frequency for Tankers	Capture Efficiencies
<ul style="list-style-type: none"> <li>• No leak check on tanker</li> </ul>	65%
<ul style="list-style-type: none"> <li>• No leak check on tanker</li> <li>• Maintain minimum positive pressure below +3 to +5 inches of water</li> </ul>	85%
<ul style="list-style-type: none"> <li>• Annual leak check on tanker per 40 CFR Part 60, Subpart XX (non-gasoline)</li> </ul>	95%
<ul style="list-style-type: none"> <li>• Semi-annual leak check on tanker per 40 CFR Part 60, Subpart XX (non-gasoline)</li> </ul>	97.5%
<ul style="list-style-type: none"> <li>• Annual leak check on tanker per 40 CFR Part 60, Subpart XX (gasoline)</li> </ul>	98.7%
<ul style="list-style-type: none"> <li>• Vacuum loading, maintaining vacuum less than – 1.5 inches of water</li> <li>• Hard-piped bolted, flanged connection from tanker to the vapor collection system</li> </ul>	100%
<ul style="list-style-type: none"> <li>• Pressure tank that is U.S. Department of Transportation certified</li> <li>• Hard-piped bolted, flanged connection from tanker to the vapor collection system</li> </ul>	100%

Source: US EPA, 2015 (original reference from TCEQ, 2000)

The previously recommended factor of 99.88% was determined in the Vapour Recovery Pilot Project for the Gasoline Distribution System in the Lower Fraser Valley Phase II (CPPI, 1993). While this efficiency factor is consistent with the VRU performance of 97% vapour reduction, as stipulated in Section 3.3 of the CCME Environmental Code of Practice for Vapour Recovery in Gasoline Distribution Networks for facilities operating in jurisdictions that do not have annual leak testing requirements, this value is dated and should be used with caution.

Direct measurement is deemed the most accurate approach in yielding site-specific efficiency for the VRU and is the recommended approach. Published literature has shown that VRUs are capable of recovery more than 95% of VOCs (IPIECA, 2013), which is also consistent with the performance value of 97% provided in the CCME Code of Practice. Hence, facilities may consider either adopting the 97% efficiency value in the CCME Code as the default or the EPA guidance shown in Table 6-5 when direct measurement data is not available.

### 6.2.2. Speciation

Use the same methodology to speciate VOC emissions from loading operations as discussed for storage tank VOC speciation in Section 5.2.3.

### 6.2.3. Improvement Options

1. For Rail Cars and Tank Trucks: If the actual physical properties of the petroleum liquid are known, use the following equation:

$$L_L = 124 * S * P * M / T \quad \text{Source: EPA AP-42, 5th Edition}$$

where:  $L_L$  = Loading loss, mg VOC/litre of liquid loaded

$M$  = Molecular weight of vapours, kg/kgmol

$P$  = True vapour pressure of liquid loaded, kPa (absolute)

$T$  = Temperature of bulk liquid loaded, °K (°C + 273.15)

$S$  = A saturation factor (see Table 6-6)

**Table 6-6 Saturation (S) Factors for Calculating Petroleum Liquid Loading Losses**

Cargo Carrier	Mode of Operation	S Factor
Tank Trucks and Rail Tank Cars	Splash loading of a clean cargo tank	1.45
	Splash loading: dedicated normal service	1.45
	Submerged loading: dedicated vapour balance service	1.00
	Splash loading: dedicated vapour balance service	1.00
	Submerged loading: dedicated normal service	0.60
	Submerged loading of a clean cargo tank	0.50
Marine Vessels	Submerged loading: ships	0.2
	Submerged loading: barges	0.5

Source: AP-42, 5th Edition, Chapter 5.2, Table 5.2-1.

2. The appropriate method of loading (e.g. splash, submerged) should be used to determine the correct saturation factor.
3. If reliable field measurements are available for the emissions of VOCs or other compounds from loading operations, these results should be used.

### 6.3. REFERENCES

1. Compilation of Air Pollutants Emission Factors - Volume I, 5th Edition, AP-42, US EPA: <https://www.epa.gov/air-emissions-factors-and-quantification/ap-42-Compilation-air-emissions-factors>
2. “Emission Estimation Protocol for Petroleum Refineries”, Version 3, prepared by RTI International for the US EPA, April 2015. <https://www.epa.gov/air-emissions-factors-and-quantification/emissions-estimation-protocol-petroleum-refineries>

3. “Air Permit Technical Guidance for Chemical Sources: Loading Operations”, June 2018, Texas Commission on Environmental Quality (TCEQ).  
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## **7. RELEASES FROM WASTEWATER SOURCES**

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### **7.1. PURPOSE**

Systems that are used in petroleum refineries for the collection and treatment of wastewater release NPRI substances to air, surface water, and solids, as well as, VOCs to air. These systems are referred to as fugitive sources in AP-42 and are often lumped together with conventional fugitive sources such as valves and flanges.

For the purposes of this Code of Practice, wastewater collection and treatment systems are considered separately from the conventional fugitive sources in order to deal specifically with the multi-media issues and simplify the assumptions related to these sources. However, air emissions from wastewater sources should be included along with other fugitive air emissions for reporting under the "Air Releases: fugitive" category within the NPRI software.

### **7.2. SCOPE**

Sources of VOC and NPRI releases to air from wastewater collection and treatment systems include:

Collection Units:

- a) Process drains and collectors
- b) Manholes & reaches
- c) Junction boxes
- d) Lift stations
- e) Trenches
- f) Sumps

Treatment Units:

- a) Equalization basins
- b) Gravity oil-water separators
- c) Air flotation systems
- d) Clarifiers
- e) Biological treatment basins
- f) Sludge digesters
- g) Settlement tanks
- h) Surface impound basins and ponds for storm water
- i) Cooling water towers

- j) Air/steam stripping
- k) Aeration ponds

Of the NPRI substances reported, used or produced by wastewater treatment facilities, there have been reporting requirement changes for Nonylphenol and Octylphenol and their Ethoxylates as well as Phosphorus (total).

Nonylphenol and its ethoxylates and derivatives (NP/NPEs), as a group, have been included in the NPRI Part 1 Group A list of substances since the 2003 reporting year, if applicable threshold requirements are met. This group consists of 29 substances and the MPO reporting threshold for the entire group of compounds is 10 tonnes. Previously, thirteen individual NPs and NPEs were included in the NPRI Part 1 substance list, each with an MPO threshold of 10 tonnes. With the intent of obtaining better data coverage for this group of substances, ECCC included Nonylphenol and its ethoxylates and derivatives as a single group in the 2003 NPRI Part 1, Group A substance list. In addition, ECCC also included the group of Octylphenol and its ethoxylates (OP/OPEs) on the same list since OP/OPEs may be used as replacements for NP/NPEs. OP/OPEs are considered more toxic and may be associated with higher estrogenic effects.

Industry sources of these groups of substances include manufacturers, as well as, effluents from users, such as textile and pulp and paper mills, and municipal wastewater treatment facilities.

In addition to Phosphorus (yellow or white), Phosphorus (total) has been added to the NPRI Part 1 Group A list of substances and reporting is required, starting with the 2003 reporting year, if applicable thresholds are met. The MPO reporting threshold for Phosphorus (total) is 10 tonnes, expressed on a mass basis as Phosphate ( $\text{PO}_4^-$ ) equivalent which is the form that is normally measured and reported.

At the time of delisting Phosphoric Acid in 2001, ECCC was committed to consider the addition of Phosphates or Phosphorus to the NPRI list of substances in order to capture releases in the appropriate form. Phosphorus is a nutrient and its release can potentially impact the aquatic environment. Industry sectors affected by the addition of this substance for 2003 reporting include municipal sewage treatment plants which account for 80% of total point source releases, pulp and paper mills, detergent manufacturers, fertilizer manufacturers, and the food products sector. In refineries, Phosphorus (total) may potentially be present in wastewater treatment streams.

Naphthenic Acid Fraction Compounds (NAFC CAS #: NA-47) are on the NPRI Part 1A list. Naphthenic acids are found in hydrocarbon deposits (petroleum, oil sands tailings, crude oil). Depending on the make up of the crude (Conventional light crude oils generally contain low concentrations of NAFCs, while heavier crudes and oil sands bitumen contain significant levels), if present at a refinery in significant enough amounts, it would be released through effluent discharge. Corrosion of equipment could be an indicator of the presence of NAFCs. A method for determining total NAFC concentration was developed by Jivraj et al. in 1995 and Holowenko et al. in 2002 and they have become widely used in the oil sands industry for routine monitoring of NAFC. Methods include acidification, liquid-liquid extraction, and Fourier-Transform Infrared Spectroscopy (FT-IR) and/or Gas Chromatograph Mass Spectroscopy (GCMS).

There are no published emission factors or methodologies currently available to specifically estimate releases of the additional NPRI substances described above from refining operations. Given that refineries have not reported any individual substance from this group of compounds in the past, it is likely that these are not present in refinery process streams. However, to show due diligence, refiners should review their available data to determine if any of this group of compounds are present in its process and wastewater streams and if so to determine whether the aggregate total meets the MPO threshold for NPRI reporting.

### **7.3. DEFINITIONS**

#### **Process Drains and Collectors**

Equipment in use that includes *drains*, *junction boxes*, and gas-trap *manholes* in oily-water service. Some facilities may have *trenches* that direct wastewater to *sumps* instead of drains. Excluded are equipment in clean water (minimal potential for contact with oil) or stormwater service.

#### **Lift Stations**

A lift station (headwork) is for the transport of collected wastewater to the treatment system by providing sufficient head pressure. Various equipment may be used to transport raw wastewater, screen out debris, measure flow rates, and collect samples.

#### **Equalization Basins**

Equalization basins may be covered, stirred, or aerated. These basins, upstream of settling units such as clarifiers and treatment systems, are designed to provide surge capacity, as well as, to minimize fluctuations in wastewater flow and organic content to downstream units and processes.

#### **Gravity Oil-Water Separators and Treatment/Diversion Ponds**

Separators or ponds that routinely handle oily-water streams and depend on the difference in gravity for separation. These ‘separators’ always have a layer of oil floating on the water that is removed by skimming or decanting. Included are: API separators, corrugated plate interceptors (CPI), and oily-water treatment ponds. Separators can be uncovered or covered.

#### **Air Flotation Systems**

Systems or equipment in use that routinely handle oily-water streams and typically follow a gravity oil-water separator. These systems use air or gas in the wastewater to assist in the removal of free and emulsified oil and other impurities. Typical units in refineries include Dissolved Air Flotation systems (DAFs) and Induced Air Flotation systems (IAFs). These can be uncovered or covered. Note that IAFs are often equipped with an unsealed roof.

### **Clarifiers**

Clarifiers, typically equipped with surface skimmers, are used to remove oils, grease, scum, and solids present in the wastewater.

### **Biological Treatment Basins**

Microorganisms are used in these treatment basins, in conjunction with aeration, to facilitate the biodegradation of organic compounds in the wastewater.

### **Sludge Digesters**

Organic sludge from various wastewater treatment processes can be treated in digesters operating under aerobic or anaerobic conditions. In aerobic digestion, the sludge is aerated by means of air diffusers or surface aeration equipment. In the anaerobic digestion process, organic sludge is converted under anaerobic conditions to by-products including methane and hydrogen sulphide. If the anaerobic digester gas is used in on-site combustion equipment, NPRI reportable CACs may be released.

### **Surface Impound Basins and Ponds**

Basins and ponds that handle clean (minimal potential for contact with oil) water or storm water and should not have a separate oil layer floating on water. No estimate of emissions is recommended for these sources in this section. For oily water ponds, emission factors for API separators can be used.

### **Cooling Water Towers**

Equipment in use to transfer waste heat from cooling water to the atmosphere. Sound management practices should prevent oil from entering these systems.

### **Wastewater Effluent**

Process water stream that is treated through the site wastewater treatment system. The treatment system typically includes primary and secondary treatment units for: gravity separation, biological oxidation, and other units such as: clarification, sand filtration, etc. Untreated storm water is excluded.

### **Air and Steam Stripping Systems**

Prior to secondary and tertiary wastewater treatment, some facilities may use air or steam to strip out the volatile organic constituents, such as free and emulsified oil and other impurities. Air releases from these systems may contain NPRI reportable organics if these exhausts are not treated.

## **7.4. REQUIREMENTS - METHODOLOGIES**

In the March 2019 NPRI Guidance Document for the Wastewater Sector, it listed the following methodologies that may be used for the estimation of releases to various receiving environmental media from wastewater collection and treatment systems.



- Continuous emission monitoring;
- Predictive emission monitoring;
- Source testing;
- Mass balance;
- Published emission factors;
- Site-specific emission factors, and
- Engineering estimates.

The applicability of the above methods for estimating releases of NPRI substances to each receiving medium is discussed further in the sections that follow. NPRI has also provided pollutant removal efficiencies for various treatment systems, which are reproduced in Table 7-1 if site-specific data is lacking.

**Table 7-1 Pollutant-Removal Efficiencies of Wastewater Treatment Processes for Certain NPRI Substances\***

Treatment Process	Ammonia Nitrogen	Inorganic Nitrogen	Sulphides	VOCs	Heavy Metals
Coagulation, Flocculation, Sedimentation	N/A	N/A	N/A	N/A	60-99%
Primary sedimentation	N/A	N/A	N/A	N/A	0-60%
Sedimentation following Biological Treatment	N/A	N/A	N/A	N/A	60-99%
Sedimentation following Biological Treatment with Chemical Addition to Influent	N/A	N/A	N/A	N/A	60-99%
Conventional Aerobic Treatment	0-20%	0-20%	90-99%	60-99%	N/A
Biological Denitrification	60-99%	60-99%	90-99%	60-99%	N/A
Low-loading Trickling Filter	60-99%	0-20%	90-99%	60-99%	N/A
High-loading Trickling Filter	0-20%	0-20%	60-99%	60-99%	N/A
Anaerobic Treatment	0-20%	0-20%	N/A	60-99%	N/A
Disinfection	20-90%	N/A	60-99%	N/A	N/A
Air Stripping	60-99%	N/A	60-99%	60-99%	N/A
Carbon Adsorption	20-90%	0-20%	60-99%	N/A	60-99%

\* Taken from Table 2-3 of 2019 NPRI Reporting Guidance for the Wastewater Sector.  
N/A – not applicable.

## 7.5. REQUIREMENTS - RELEASES TO AIR

Air emissions occur through diffusive transfer of a compound at the liquid surface when its concentration in the liquid phase is higher than that in the ambient air, and convection transfer when volatilized gaseous substances from the surface are removed by air flows over the liquid surface.

For air releases, the applicability of emission estimation methods, outlined in Section 7.4, varies depending on the NPRI substance of interest. Table 7-2 shows the requirements for each applicable method for a given NPRI substance class.

**Table 7-2 Applicability of Estimation Methods for Substances Released to Air\***

Substance Class	Monitoring	Mass Balance	Emission Factor	Engineering Estimation	
				Removal Efficiency	Mass Transfer
Metals	N/A	√	N/A	N/A	N/A
Volatile Organics	√	√	√	N/A	√
Volatile Inorganics	√	√	√	N/A	√
Non-volatile Substances	N/A	√	N/A	N/A	N/A
Special Substances (e.g. Mercury)	√	√	√	√	√

\* Taken from Table 2-2 of NPRI 2019 Guidance for the Wastewater Sector.

√ = applicable and data potentially available or attainable.

N/A = not applicable.

For the purposes of this section, it is recommended that VOC and other NPRI emissions to air be estimated for process drains and collectors, gravity oil-water separators and treatment or diversion ponds and air flotation systems only. Surface impound basins/ponds for storm water and cooling water towers should be considered as minor sources provided that there is no free oil (i.e. sound operating and maintenance practices are in place). If free oil is present in the impounding basins/ponds, these should be treated as oil-water separators.

### 7.5.1. Component Counts: Drains

1. An assessment of the process drains, and junction boxes should be made to determine if they vent directly to atmosphere or are controlled (water seal). All unsealed drains and junction boxes are sources of VOC emissions and an estimate of emissions should be made. Any equipment that is sealed with water should not be a source of emissions and these can be excluded.

The assessment can be done by process unit or area, since the equipment configuration is likely uniform within an area.

2. Actual drain/junction box count should be used if this is available.

3. A refinery can estimate its drain count by using industry average numbers based on the pump count in the particular process area or unit: 2.6 drains per pump.

### 7.5.2. VOC Emission Factors

1. If actual envelope measurements of VOC emissions are not available, the principle reference for VOC emission factors is EPA-450/3-85-001a, February 1985, “VOC Emissions from Petroleum Refinery Wastewater Systems - Background Information for Proposed Standards”.

**Table 7-3 Air Emission Factors for Wastewater Treatment Systems  
(Reference: EPA-450/3-85-001a)**

	Emission Factors			Comments
	Uncontrolled	Controlled	Units	
Drains & Junction Boxes	0.032	0.000	kg/hr-drain	100% control with water seal
Oil-Water Separators	0.11100	0.00330	kg/m <sup>3</sup> -wastewater	97% net control with tight cover
DAF/IAF	0.00400	0.00012	kg/m <sup>3</sup> -wastewater	97% net control with tight cover
Impound Basins & Ponds	negligible	negligible		Sound operating & maintenance practices
Cooling Water Towers	negligible*	negligible*		Sound operating & maintenance practices

\* If historical company data and/or source specific monitoring data is not available, refer to Section 7.9.

2. The AP-42 emission factor for oil-water separators is not recommended and should not be used (See Section 7.9.2).

### 7.5.3. VOC Speciation

Where actual VOC speciation data is not available, the composition of the facility feedstock (e.g. crude oil) should be used.

## 7.6. REQUIREMENTS - RELEASES TO SURFACE WATER

For releases to surface water, the applicability of emission estimation methods, outlined in Section 7.4 and summarized in Table 7-4, varies depending on the class of NPRI substances.

**Table 7-4 Applicability of Estimation Methods for NPRI Substances Released in Effluent\***

Substance Class	Monitoring	Mass Balance	Emission Factor	Engineering Estimation	
				Removal Efficiency	Mass Transfer
Metals	√	√	nd	√	N/A
Volatile Organics	√	√	nd	√	N/A
Volatile Inorganics	√	√	nd	nd	N/A
Non-volatile Substances	√	√	nd	nd	N/A
Special Substances (e.g. Mercury)	√	√	nd	nd	N/A

\* Taken from Table 2-2 of NPRI 2019 Guidance for the Wastewater Sector.

√ = applicable and data potentially available or attainable.

N/A = not applicable.

nd = no data.

In addition, the wastewater effluent stream is a source of NPRI releases to surface water. This stream is typically process water treated through the site wastewater treatment system. Any releases to surface water should be based on water samples/lab results and mass balances.

1. Wastewater effluent streams contain reportable NPRI substances including: Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX), ammonia, nitrates, phenol, and metals. When assessing NPRI releases in wastewater effluent streams, the by-product rule in NPRI must be considered (see Section 3.2).
2. NPRI reporting should be based on actual wastewater effluent quality testing, required for federal/provincial regulatory compliance. Actual wastewater flow rates should also be used in the calculation of total quantities of substances released or discharged.
3. Where phenolics are tested in wastewater streams (and not phenol, an NPRI substance), assume that 100% of the phenolics are phenol for NPRI reporting purposes, unless refinery specific testing shows otherwise.
4. NPRI releases in storm water can be ignored for NPRI reporting as these should contain insignificant amounts of reportable substances.

The NPRI requirement to report the concentration of substances released to surface waters is required to provide contextual information for water releases. When a direct discharge to surface waters is reported, the average annual concentration (ppm) of the NPRI substance in the effluent must also be reported. Where the method detection limit (MDL) is used to provide estimates, the MDL needs to be provided. If more than one MDL applies, provide details in comments.

## 7.7. REQUIREMENTS - RELEASES IN SLUDGE, RAW SOLIDS AND BIOSOLIDS

Table 7-5 summarizes the applicability of various estimation methods for estimating reportable substances in sludge and solids that may be transferred off-site. As shown in this table, monitoring data and/or the mass balance method can be used to estimate substances present in off-site waste transfers.

**Table 7-5 Applicability of Estimation Methods for NPRI Substances Released in Waste Stream (Sludge/Raw Solids/Biosolids)\***

Substance Class	Monitoring	Mass Balance	Emission Factor	Engineering Estimation	
				Removal Efficiency	Mass Transfer
Metals	√	√	nd	√	N/A
Volatile Organics	√	√	nd	√	N/A
Volatile Inorganics	√	√	nd	nd	N/A
Non-volatile Substances	√	√	nd	nd	N/A
Special Substances (e.g. Mercury)	√	√	nd	nd	N/A

\* Taken from Table 2-2 of NPRI 2019 Guidance for the Wastewater Sector.

√ = applicable and data potentially available or attainable.

N/A = not applicable.

nd = no data.

## 7.8. IMPROVEMENT OPTIONS

### 7.8.1. Emission Measurements (VOCs)

Where measurements are available, the estimate of VOC air emissions from wastewater collection and treatment should be based on these results. If available, such testing can also include VOC speciation data and may apply to covered or uncovered wastewater systems. Site specific data, including analysis of refinery wastewater streams, could be used if available.

### 7.8.2. Waste Water Treatment Pond Software (WWTP)

Downloadable WWTP software, for example WATER 9 is available at no cost, for determining emissions. Commercial software products are also available; however, results should be checked to ensure emissions are representative of the facility and compatible with US EPA methods since in some software models underestimation could occur.

The NPRI Toolbox provides the following listing of WWTP emission estimating software that may be considered for use in NPRI reporting (ECCC, 2003).

- WATER9 – US EPA (<https://www.epa.gov/chief/water9-version-30>)
- TOXCHEM –Hydromantis (<http://www.hydromantis.com/TOXCHEM.html>)
- SEAM (Secondary Emission Assessment Model) – incorporated as subcomponent of TOXCHEM model (Tata et al, 2003)
- BASTE (Bay Area Sewage Toxics Emissions) – developed by CH2M Hill
- PAVE (Programs to Assess Volatile Emissions) – developed by the Chemical Manufacturers Association
- CORAL+ – predecessor to SEAM
- FATE (Fate and Treatability Estimator) – developed by ABB Environmental Inc. for the US EPA

Of the software listed above, WATER9 and TOXCHEM are the two models that are readily available. The WATER9 model can be downloaded directly from US EPA while TOXCHEM is commercially available. From the 2009 survey of Canadian Fuels members, the majority of refineries did not use WWTP software for emissions estimation. Of the facilities that have utilized software, WATER 9 and TOXCHEM were employed. In several facilities, proprietary or actual measurement data were used to quantify emissions for some of the wastewater emission sources.

In addition to the above computer models, US EPA has developed a simplified Excel-based spreadsheet tool to assist refineries to estimate their air emissions from wastewater collection and treatment systems, including weirs, junction boxes, oil-water separators, dissolved air flotation units, equalization tanks, and biological treatment units (US EPA, 2010). The methodology is based on those in Chapter 4.3 of the US EPA AP-42 manual and includes relevant updates found in recent literature.

## **7.9. EXPLANATORY NOTES**

### **7.9.1. Drains**

AP-42 clearly shows drains as a source of fugitive VOCs and refers to EPA-453/R93-026 (now EPA-453/R95-017) for drain emission factors. However, in these documents, drains are nowhere to be found in the tables of fugitive emission factors. Reference is therefore made to a previous version of AP-42 (Fourth Edition, September 1985), and more importantly, to EPA-450/3-85-001a. Both of these references include the refinery average emission factor for drains as noted in Section 7.5.2, Part 1 above.

### **7.9.2. Oil-Water Separators**

AP-42 has an oil-water separator VOC emission factor (0.6 kg/kL of wastewater) that is significantly higher than that noted in EPA-450/3-85-001a. This factor is about 5.4 times

the emission factor recommended in this section. The AP-42 emission factor is not recommended for use in estimating emissions from oil-water separators.

Detailed explanations are given in EPA-450/3-85-001a as to why the AP-42 factor should not be used. AP-42 is based on a very old study done in Los Angeles in 1958. More recent studies confirm operational improvements since then, which result in less wastewater, less oil entrained to wastewater, and hence less VOC releases/emissions.

As the following Table 7-6 shows, a few envelope tests done on uncovered oil-water separators within some Canadian Fuels refineries in the 1990s confirm the recommendation given in this section. The emission factor, as recommended, adequately includes VOCs from free-oil and soluble-oil components.

**Table 7-6 - Oil Water Separator Emission Factors**

Emission Factor Source	Emission Factor; kg/m <sup>3</sup> Wastewater (uncovered)	Comments
AP-42	0.6	Not Recommended
EPA-450/3-85-001a	0.111	Recommended
Plant A	0.096	Average of 2 tests
Plant B	0.0010	Based on one test

### **7.9.3. Air Flotation**

AP-42 does not have an emission factor for a DAF/IAF. The factor noted in EPA-450/3-85-001a and provided in Section 7.5.2, Part 1 should be used.

### **7.9.4. Surface Impound Basins and Ponds**

There is no mention of impound basins and ponds as being important sources of VOCs in either AP-42 or EPA-450/3-85-001a. No emission factors are provided. SCAQMD (South Coast Air Quality Management District) has emission factors based on pond surface area. However, if good operating and maintenance practices are used in Canadian Fuels refineries to prevent oil from entering these water systems (through spills or leaks), it is assumed that these systems are negligible sources of VOCs.

### **7.9.5. Cooling Water Towers**

VOC emissions may result from heat exchanger oil leaks that enter the cooling water system. These are punctual events that are rapidly identified by the cooling water operator and corrected because it is a safety issue. Therefore, the quantity of VOCs from this source is expected to be minor (as is supported by historical monitoring data).

From the NPRI Guidance on estimating VOC emissions from cooling towers (2013), two methodologies are provided, namely the measurement method and the emission factor approach. The measurement method is based on mass balance and is the recommended method by NPRI. If VOC concentrations in the cooling tower inlet and outlet streams are known, emissions can be estimated by the difference in inlet and outlet VOC mass quantities. The following equation is provided in the NPRI Toolbox:

$$\text{VOC[t]} = (C_{\text{VOC,In}} - C_{\text{VOC,Out}}) [\text{ppmw}] \times D_{\text{water}} [\text{t/m}^3] \times \text{Water Flow Rate} [\text{m}^3/\text{hr}] \times H [\text{hr}]$$

Where:

$C_{\text{VOC,In}}$  = Concentration of VOC in the cooling water prior to entering the cooling tower

$C_{\text{VOC,Out}}$  = Concentration of VOC in the cooling water after leaving the cooling tower

$D_{\text{water}}$  = Density of water at 1 kg/L or  $10^6$  g/m<sup>3</sup> or 1 t/m<sup>3</sup>

H = Number of hours of operation of the cooling tower since the last measurement

For a refining facility in which scheduled measurement events are performed through the year, the quantity of VOC estimated for each monitoring event should be summed to determine the total VOC released in the given year.

The VOC sampling procedures from the Texas Commission on Environmental Quality (TCEQ) are recommended by ECCC. While this sampling method is preferred, reporters are offered the flexibility to choose other suitable methods for VOC measurements, provided these alternative methods are deemed comprehensive, defensible, and applicable by ECCC.

If a company has no means to ensure low emissions and/or no available source specific monitoring data, VOC emissions can be calculated using the uncontrolled VOC emission factors provided in Table 7-7. Based on this method, uncontrolled annual VOC emissions can be calculated according to the following equation provided by NPRI.

$$\text{VOC[t/y]} = \text{EF}_{\text{Unc}} [\text{kg}/10^6 \text{ L}] \times \text{Water Flow Rate} [\text{m}^3/\text{hr}] \times H [\text{hrs}] \times 10^{-3} [\text{t/kg}]$$

Where:

$\text{EF}_{\text{Unc}}$  = Uncontrolled VOC emission factor for cooling tower and is equal to 0.7 kg per million litres of cooling water

H = Number of hours of operation of the cooling tower during the year

Considering the good operating and maintenance practices in place at Canadian Fuels refineries to prevent and promptly repair oil leaks, the amount of VOC released is expected to be low. Based on the NPRI guidance, if a refinery monitors for hydrocarbons in its cooling water or if it can ensure that the heat exchanger water pressure is at least 35 kPa above the VOC pressure, the controlled VOC emission factor given in Table 7-7 can be applied when company specific data is not available.



**Table 7-7 Emission Factors for Petroleum Refinery Cooling Towers**  
(Source: AP-42, Chapter 5.1, Table 5.1-2)

	Emission Factors		Control Description
	kg/10 <sup>6</sup> L Cooling Water	lb/10 <sup>6</sup> gal Cooling Water*	
Uncontrolled Emissions	0.7	6	
Controlled Emissions	0.08	0.7	<ul style="list-style-type: none"> <li>➤ Minimization of oil leaks into cooling water system;</li> <li>➤ Cooling water monitoring for oil.</li> </ul>

\* If cooling water rate is unknown, assume it to be 40 times the refinery crude feed rate to the atmospheric distillation column.

For NPRI reporting purposes, ECCC requires that the reported VOCs be classified as “fugitive releases” to air since the source of VOC in the cooling tower is believed to originate from equipment leaks. For the measurement method, the use of code “C” (mass balance method) is required because the VOC released to the atmosphere is not directly measured.

## 7.10. REFERENCES

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## **8. NON-ROUTINE RELEASES**

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### **8.1. PURPOSE**

Non-routine occurrences at refineries that cause releases to the environment can result in emissions of NPRI substances to all media and VOCs to air.

This section outlines a practical approach to quantify these non-routine releases to the environment, which considers their relative contribution to overall emissions and their impact on each of the media. Further, this approach is consistent with other regulatory release reporting requirements.

### **8.2. DEFINITIONS**

#### **Non-routine Release**

A release to the environment that includes spills, leaks, and airborne discharges of hydrocarbons (liquid or vapour) or of any other product (or substance) used in refining. For flaring emissions, discussions are provided in Sections 9, 12, 14 and 15 of this Code.

Emissions arising from periodic storage tank cleaning and floating roof landing events are also considered non-routine releases. Quantification of evaporative releases from these events is included in this section. For floating roof tanks, landing scenarios include the presence of a full liquid heel (stock liquid remaining across the entire bottom of the tank), a partial heel (pools of free-standing stock liquid covering only parts of the tank bottom), and the absence of stock liquid when the tank is drained dry. Emissions from routine storage tank working and breathing evaporative losses are discussed in Section 5 of this Code.

### **8.3. REQUIREMENTS - SPILLS**

#### **8.3.1. Release Volume**

1. The release volume is calculated on the basis of the actual non-routine release (spills, leaks, discharges) using the best estimate of the volume released.
2. Throughput-based emission factors should not be used to estimate release volume.
3. All non-routine releases that exceed a minimum threshold volume should be included. Recommended minimum volumes recognize the potential contribution to overall emissions of VOCs and other NPRI substances and are provided below (see also explanatory notes in Section 8.8):
  - a) Spills and Leaks to Surface Water: include all non-routine releases greater than 10 litres to surface/receiving water bodies.
  - b) Spills and Leaks to Land: include all non-routine releases greater than 200 litres.
  - c) Airborne Discharges: include all non-routine releases greater than 100 litres.

4. In addition to those noted in Part 3 above, include all other non-routine releases that are reported to the regulatory authorities and that have the potential for an adverse effect.

This release volume is called gross release volume, before evaporation or recovery.

### **8.3.2. Product Recovery**

1. The net release volume is estimated by subtracting the actual recovered volume from the gross release volume (see Section 8.3.1, Part 4).
2. For all airborne discharges and for cases where the actual recovered volume is not available, assume no recovery.

### **8.3.3. Allocation to Air**

1. For airborne discharges, assume that 100% of the release is to air or follow the procedure set out in Section 8.6.1.
2. For spills and leaks, if the receiving media is water or an impervious pad, the bulk of the non-recovered product is exposed to air. In this case, the VOC losses to air are estimated by multiplying the net release volume (from Section 8.3.2, Part 1) by an evaporation factor. For gasolines and lighter products, assume 100% of product evaporates to air. For jet fuels and heavier products, assume no product evaporates to air.
3. For spills and leaks, if the receiving media is a non-impervious (porous) surface, assume all the non-recovered product has seeped into the soil and that there are no losses to air.

### **8.3.4. Allocation to Water and Land**

1. For airborne discharges, assume no release to water or land.
2. Similar to Section 8.3.3, Part 2 above, when a release is to water or an impervious surface, the amount of released product that goes to either water or land is the difference between the net release volume and the amount allocated to air.
3. For spills and leaks to a non-impervious surface, assume all the non-recovered product (net release volume from Section 8.3.2, Part 1 above) has seeped into the soil (land).

### **8.3.5. Speciation**

For spills and leaks, speciate based on the stream material released to all media. If specific speciation data is not available, use the appropriate estimation procedure recommended in Section 4.2.4.

## **8.4. REQUIREMENTS – STORAGE TANK FLOATING ROOF LANDINGS**

Section 5 of this Code provides the methodology for the estimation of standing and refilling (working) emissions from a storage tank when the floating roof is floating on the liquid. As the stock liquid is being withdrawn to a level close to the bottom of the tank, the floating roof will eventually land on legs or supports. This causes the vacuum breaker vent on the floating roof to open, allowing vapour from under the landed roof to flow into the space above the landed roof and subsequently to the atmosphere. Landing events result in additional emissions from the evaporation of residual stock liquid in the tank beneath the landed roof during the period when the tank stands idle prior to refilling and the time when the tank is refilled sufficiently to refloat the roof.

An API publication (API, 2004) has provided detailed methodologies for estimating standing idle and subsequent re-filling emissions for floating-roof landing events. The API model also establishes upper and/or lower bounds for some parameters, such as vapour space saturation factors, to reflect method uncertainties. Emissions from other activities, such as tank cleaning, that may take place when the empty tank remains idle also need to be quantified separately and are in addition to emissions from landing events.

However, it should be noted that in November 2019 the EPA published revisions to AP-42 Section 7.1 (Organic Liquid Storage Tanks), which added guidance on estimating emissions from tank cleanings, as well as, expanded on the emission estimation methodologies for tank landing events. The new version of AP-42 Section 7.1 should be used as the default reference for calculating tank emissions. Please refer to Section 5 of this Code for more details with regards to the AP-42 Section 7.1.

### **8.4.1. Standing Idle Emissions**

#### **8.4.1.1. Emissions Methodology**

1. The API method approximates standing idle vapour loss from internal floating roof tanks (IFRT), with a full or partial liquid heel, as breathing loss. This loss is assumed to occur daily for as long as the roof remains idle as expelled vapour is replaced by evaporated vapour from the liquid heel.
2. Vapour loss from idling external floating roof tanks (EFRT), with a full or partial liquid heel, is estimated based on wind-driven loss and is similar to that of rim-seal loss. This loss is also assumed to occur daily for as long as the roof remains idle.
3. For floating roof tanks that drain dry, vapour loss during idling is estimated as heavy clingage loss and, unlike the above 2 scenarios, this type of loss is considered a one-time event.

#### **8.4.1.2. Stock Liquid Properties**

The API methodology applies to petroleum liquids. Input data for stock liquid properties, including true vapour pressure, vapour molecular weight, and liquid density, allows for the inclusion of various refined products and crudes. Properties of selected petroleum stocks, as provided in the API report and shown in Table 8-1, may be considered if refinery specific data is not available.

**Table 8-1 Properties of Selected Petroleum Stocks**

Petroleum Stock	Parameters									
	Liquid Density	Molecular Weight	A	B	True Vapour Pressure (psia) at Selected Temperatures					
	Lb/gal	Lb/lb-mole	-	-	40 F	50 F	60 F	70 F	80 F	90 F
Motor Gasoline (RVP 13)	5.6	62	11.644	5043.6	4.7	5.7	6.9	8.3	9.9	11.7
Motor Gasoline (RVP 10)	5.6	66	11.724	5237.3	3.4	4.2	5.2	6.2	7.4	8.8
Motor Gasoline (RVP 7)	5.6	68	11.833	5500.6	2.3	2.9	3.5	4.3	5.2	6.2
Jet Naphtha (JP-4)	6.4	80	11.368	5784.3	0.8	1.0	1.3	1.6	1.9	2.4
Jet Kerosene (Jet A)	7.0	130	12.390	8933	0.004	0.006	0.008	0.011	0.015	0.021
Distillate Fuel Oil No.2	7.1	130	12.101	8907	0.003	0.005	0.007	0.009	0.012	0.016

Table taken from API, 2004; Antoine’s equation constants A & B are cited from API MPMS 19.2 and other parameters are from EPA AP-42. For associated equations, see “Evaporative Loss from Storage Tank Floating Roof Landings”, Final Report, Prepared for the American Petroleum Institute, November 15, 2004.

#### **8.4.1.3. Landing Episodes**

1. For a given landing event, the daily evaporative loss estimate provided by the API method should be multiplied by the actual number of days in which the tank remains idle. Similarly, idling emissions from all landing episodes that occur in a given year are to be summed to arrive at an annual estimate.
2. The API model is not designed to account for partial days when the floating roof sits idle for less than a day. The model can still be used in these cases, but the resulting evaporation vapour loss estimates will be conservative.
3. As mentioned previously, idling vapour loss for floating roof tanks that are drained dry is considered a one-time event during which all the liquid clinging to the wetted surfaces is evaporated and is regardless of the number of days the tank remains idle for a given landing event.

#### **8.4.1.4. Liquid Heel**

1. For tanks with a liquid heel, the total emissions generated during the idling period should not exceed the amount of liquid in the tank.
2. After being emptied, a tank containing pools of free-standing liquid on the bottom or at the sump is considered to be one with partial liquid heel.
3. A tank is classified as a drain-dry tank only if all free-standing liquid is removed.

### **8.4.2. Filling Emissions**

#### **8.4.2.1. Emissions Methodology**

1. The vapour loss during tank filling is made up of vapour left under the landed roof at the end of the idling period, or the “arrival” component, and vapour evaporated from the incoming liquid, or “generated” component. Although the arrival vapour component is created during tank idling, these emissions have been included as part of the tank filling releases in the API methodology.
2. The API method approximates filling loss from internal floating roof tanks (IFRT), with a full or partial liquid heel, as those from submerged-fill loading (see Section 5).
3. Vapour loss from the filling of an external floating roof tank (EFRT), with a full or partial liquid heel, is estimated based on similar tank loading methodology with due consideration being given to the partial evacuation of the arrival vapour component by wind. This is accomplished by establishing upper and lower limits for the vapour saturation factor.
4. For floating-roof tanks that drain dry, only the generated vapour component is included in the API methodology since the arrival component has been accounted for during tank idling.



#### **8.4.2.2. Stock Liquid Properties**

If the floating roof tank is refilled with a different stock, the stock vapour properties for the arrival and generated components of the filling loss estimate should be differentiated.

#### **8.4.2.3. Saturation Factors**

1. Filling loss is estimated as the product of the vapour space beneath the landed roof and the vapour concentration. The latter parameter is highly dependent on the vapour saturation level. For IFRTs, the API methodology assumes a saturation factor of 60%, 50%, and 15% for full liquid heel, partial liquid heel, and drain dry scenarios, respectively.
2. For external floating roof tanks (EFRT), API sets the upper bound of the saturation factor to that of submerged fill loading with no wind action and the lower bound to that for loading of a degassed vessel.

#### **8.4.3. Speciation**

Use the same methodology to speciate VOC emissions from landing events as discussed for storage tank VOC speciation in Section 5.2.3.

### **8.5. REQUIREMENTS – STORAGE TANK CLEANING**

Emissions from the tank cleaning process may occur during the following events:

- Tank idling,
- Vapour space purge,
- Sludge removal,
- Tank refilling.

An API report (API, 2007) has provided detailed calculation methods for each of the above events. The API methods have been incorporated into the recent update to EPA AP-42 Chapter 7.1, “Organic Liquid Storage Tanks” as discussed in Section 5.2. Total vapour loss from tank cleaning represents the sum of emissions during tank idling periods, vapour space purging, and tank refilling.

For normal pump out, API has assumed no emissions as an inflow of outside air into the tank is expected. As for a cleaned tank in which volatile materials are removed, API also assumes no emissions during any idling period.

However, it should be noted that the November 2019 release of AP-42 Chapter 7.1 added guidance on estimating emissions from tank cleanings, as well as, expanded on the emission estimation methodologies for tank landing events. The new version of AP-42 Section 7.1 should be used as the default reference for calculating tank emissions. Please refer to Section 5 of this Code for more details with regards to the AP-42 Section 7.1.

### **8.5.1. Standing Idle Emissions**

A tank may remain idle between cleaning steps. During this period with no forced ventilation, vapours are generated from volatile materials remaining in the tank bottom and will be subsequently released into the atmosphere due to diurnal temperature changes and also wind action in the case of an external floating roof tank.

1. The methodologies for estimating tank idling emissions from floating-roof tanks with full liquid heel, partial liquid heel, or those that are drained dry are the same as those given in Section 8.4.1 above.
2. For fixed-roof tanks, idling emissions can be estimated as standing (breathing) losses and the methodology is provided in another API document (API, 2002). If the idling period has already been included in determining the number of days during which the tank was in service (for the purpose of calculating annual breathing losses), it should not be included in tank cleaning emissions.

### **8.5.2. Vapour Space Purge Emissions**

Vapour remaining in the tank is flushed out by means of fans or blowers (forced ventilation) prior to any sludge removal operation. The API methodology approximates vapour space purging emissions as one working loss (filling) cycle of the vapour space.

1. For fixed-roof tanks, the volume of purged vapour space is the entire volume under the tank roof, as opposed to the maximum level to which the tank can be filled (as defined in the API working loss equation). The saturation factor, based on API methodology, has an upper-bound of 0.5 and a lower-bound of 0.25 (API, 2005).
2. For floating-roof tanks, the purged vapour space represents the volume under the floating roof. Since vapour space purging operation does not involve incoming new stock liquid, emissions consist only of the “arrival” and not the “generated” component of the API tank refilling methodology.

### **8.5.3. Sludge Removal Emissions**

Following vapour space purging, some volatile materials may remain in the tank, resulting in additional vapour releases from forced ventilation during sludge removal operation. In the API report, three methods for estimating sludge removal emissions were compared, namely the vapour concentration method, the sludge volume method, and the air driven loss method. API concluded that the vapour concentration method is the preferred method since it is the only method in which key calculation parameters can be validated by field measurements. This method is based on the average vapour concentration in the vapour space (as percent of the stock’s lower explosive limit, or LEL), the ventilation rate and the sludge removal time period.

1. Vapour concentration is the percent concentration as measured by an LEL monitor. If the vapour concentration level is below the detection limit of the instrument, a conservative approach is to use the detection limit as the vapour concentration.

2. Table 8-2 shows reported LEL values for selected petroleum stocks should site specific values not be readily available.

**Table 8-2 LEL Values for Selected Petroleum Refining Stocks**

<b>Stock</b>	<b>LEL (vol% in air)</b>
Dodecane (C12)	0.6
Kerosene	0.7
Decane (C10)	0.8
Octane (C8)	1.0
Hexane (C6)	1.1
Benzene	1.2
Gasoline	1.4
Butane (C4)	1.9
Ethanol	3.3
Methane (C1)	5.0

Data taken from API, 2005.

3. Sludge removal emissions should not exceed the total quantity of sludge, assumed conservatively to comprise of stock liquid only.

#### **8.5.4. Refilling Emissions**

When the clean tank is refilled, vapour is generated by the incoming liquid stock and is subsequently expelled from the tank as the liquid level rises. The API method is based on the estimation methodology for working (filling) losses.

1. In the case of a floating-roof tank, vapour from under the landed roof is being displaced and released until the roof is re-floated. The methodology for estimating emissions from the refilling of the clean floating-roof tank is the same as that for the filling of a drained dry tank, as outlined in Section 8.4.2 above. This means only the “generated” vapour component from the incoming stock is included in refilling emission estimates as volatile materials are no longer present following tank cleaning.
2. If more than a day is required for refilling before the landed roof is re-floated, breathing losses over the refilling period should also be accounted for.
3. For fixed-roof tanks, refilling emissions can be estimated as working (filling) losses and the methodology is provided in a related API document (API, 2002).

## **8.6. START-UP AND SHUTDOWN**

Generally, emissions estimation methods used to quantify substances released, transferred, and disposed characterize the emissions during normal operating conditions. According to the US EPA’s Emission Estimation Protocol for Petroleum Refineries (US EPA, 2015), during start-up and shutdown, the process operations are not normal and emission characteristics of the processes may be significantly different than those during normal operations. It suggests that when the emission estimation methodology relies on normal operating conditions (e.g., most site-specific and default emission factors), it is important to specifically estimate the emissions during start-up and shutdown and include these emissions in the facility’s annual emission totals (US EPA, 2015).

For the purpose of this guideline, US EPA’s Emissions Estimation Protocol for Petroleum Refineries Section 11 is used as reference. Since the operations of each refinery are site-specific, it is beyond the scope of this document to provide methods of estimation emissions during all start-up and shutdown events. However, according to the US EPA Protocol, the primary refinery emission event during start-up or shutdown is expected to be vessel depressurization and purging (or degassing). The following sections provide guidance on how to account for emissions from these events.

Effective as of 2018 NPRI reporting year, facilities must report the following additional information on shutdown periods:

1. Will the shutdown period occur at or around the same time in future years?
2. Was the shutdown a partial or complete shutdown?

ECCC defines a shutdown period as “... a temporary facility closure”. When all normal operations at a facility cease, this can be considered to be a “complete” shutdown. For example, if a manufacturing facility stops manufacturing for two weeks during the summer, this is a complete shutdown. Some activities, such as maintenance, may still occur at the facility, but the regular activities are suspended, affecting typical releases or transfers from the facility. Only complete shutdown periods of seven days or longer are required to be reported to the NPRI. Shorter complete shutdown periods can be voluntarily reported if the information can help with interpreting facility releases and transfers.

Partial shutdowns can also be voluntarily reported, especially where they result in a noticeable change in reported quantities for a certain time period. A partial shutdown occurs when only some of the activities at the facility are suspended, for example, if one of several manufacturing lines or one of several boilers or electricity generating units is shut down temporarily for maintenance. This information is useful for data interpretation since it can also affect typical releases or transfers from a facility during the partial shutdown. For partial shutdowns, facilities can provide details in the shutdown period comment field provided in the online reporting system. The shutdown period fields in the reporting software should only be used to indicate when a facility is temporarily closed. A Facility Closure report should be submitted to indicate a permanent facility closure.

### 8.6.1. Gaseous Process Vessel Depressurization and Purging

For gaseous processes, emissions from process vessel depressurization can be estimated using the ideal gas law equation shown below, shown in imperial and metric units, and with the addition of a void fraction term to account for packing material, distillation trays, and other inert material which occupy the gaseous space. However, if the solid material in the vessel, such as petroleum coke or activated carbon, adsorbs some of the constituents in the gas space, the calculated emissions may be underestimated. For process gases that do not follow the ideal gas law, compressibility factors need to be considered.

$$E_i = \left\{ \frac{(P_V + 14.7)}{14.7} \times \frac{528^\circ R}{T_V} \times (V_V \times f_{void}) \times \frac{MW_i}{MVC} \times MF_i \right\}$$

Where:

- $E_i$  = Emissions of pollutant “i” during depressurization event (lbs/event).
- $P_V$  = Gauge pressure of the vessel when depressurization gases are first routed to the atmosphere (pounds per square inch gauge, psig).
- 14.7 = Assumed atmospheric pressure (pounds per square inch, psi).
- $T_V$  = Absolute temperature of the vessel when depressurization gases are first routed to the atmosphere (degrees Rankin, °R).
- 528 = “Standard” temperature used in the calculation (°R).
- $V_V$  = Volume of the vessel (cubic feet, ft<sup>3</sup>).
- $f_{void}$  = Volumetric void fraction of vessel. Use 1 unless packing material or trays are present in the vessel.
- $MW_i$  = Molecular weight of pollutant “i” (lb/lb-mole).
- MVC = Molar volume conversion factor (385.3 scf/ lb-mole).
- $MF_i$  = Volume fraction of pollutant “i” in vessel gas (scf pollutant i/scf of gas).

$$E_i = P_v \times (V_v \times f_{void}) \times VF_i \times MW_i / R / T_v$$

Where:

- $E_i$  = Emissions of pollutant “i” during depressurization event (kg/event).
- $P_v$  = Absolute pressure of the vessel when depressurization gases are first routed to the atmosphere (kPa).
- $V_v$  = Volume of the vessel (m<sup>3</sup>).
- $f_{void}$  = Volumetric void fraction of vessel. Use 1 unless packing material or trays are present in the vessel.

- $VF_i$  = Volume fraction of pollutant “i” in vessel gas ( $m^3$  of pollutant “i”/ $m^3$  of gas).
- $MW_i$  = Molecular weight of pollutant “i” (kg/kmol).
- $R$  = Ideal gas constant (8.3145 kJ/kmol/°K).
- $T_v$  = Absolute temperature of the vessel when depressurization gases are first routed to the atmosphere (degrees Kelvin, °K).

Gases from vessel depressurization and purging events are typically linked to the refinery fuel gas system, flare, or similar control device. Combustion of these gases should be accounted for and the preceding equation can be used to calculate the quantity of purged gases that are being directed to these refinery systems. In cases where the combined flow rate and composition or heating value of the system input fuel/flare gas are measured, special calculations are not required because episodic releases to these fuel/flare systems, such as those from depressurization and purging events, should have been adequately accounted for.

### **8.6.2. Liquid Process Vessel Depressurization and Purging**

For the depressurization and purging of vessels that contain liquids, emissions may be purged to a flare or other control device while some fraction may be purged directly to the atmosphere. Emissions from these events can be estimated by assuming that the entire liquid “heel” that remains in the vessel before purging is eventually volatilized. This approach assumes that the mass of the liquid remaining in the vessel will dominate over the quantity of contaminants present in the headspace. However, when very volatile substances such as butane in gasoline are involved, the initial gaseous emissions for the most volatile components may need to be considered and quantified (using the equation provided in preceding section) in addition to the liquid heel. Individual substances in the purged gas may be speciated based on knowledge of the process stream.

## **8.7. IMPROVEMENT OPTIONS**

### **8.7.1. Spills**

Partitioning of spill releases to the various receiving environmental media can be refined. The assumption that all unrecovered spilled substances will eventually be released to air can be very conservative. There are currently two methods available to enable the estimation of evaporative losses to air from spills, with the balance being released to other receiving media.

ECCC (1985) has published a method to quantify the evaporation rate for chemicals that form a liquid pool when spilled on a ground water surface. This approach was superseded by another method, published by Environment Australia (1999), which partitions spill releases to air and land and incorporates actual wind conditions which is an important factor. The Australian method is shown below.

For evaporative loss to air  $E_i = 1.2 \cdot 10^{-10} (M(P_i^0)/T)u^{0.78} x^{0.89} y$

Where:

- $E_i$  = evaporation rate of substance i (g/s)
- $M$  = molecular weight of substance i (g/gmol)
- $P_i^0$  = vapour pressure of substance i at spill temperature T
- $T$  = temperature (K)
- $u$  = wind speed over spill surface (cm/s)
- $x$  = downwind dimension (cm)
- $y$  = crosswind dimension (cm)

For the balance of a spill to land  $ER_{land,i} = Qtty_{spill} - (t \cdot E_i)$

Where:

- $ER_{land,i}$  = release to land of substance i
- $Qtty_{spill}$  = quantity of substance i in the liquid spilled
- $t$  = time period between when liquid was initially spilled and eventual cleanup
- $E_i$  = evaporation rate of substance i (g/s)

The Ontario MECP (2005) gives a similar equation,  $Q = 8.5 \cdot 10^{-10} \cdot (M(P_i^0)/T)u^{0.78} \cdot A$  where Q is in (kg/s),  $P_i^0$  is in Pascal's, and A is the area of the pool in square metres.

If relevant chemical and meteorological data are available for each spill event, the use of above estimation methods will provide a more realistic estimate of releases to each receiving medium.

### **8.7.2. Floating Roof Tank Landing Emissions**

The API model input parameters for landing events consist of stock liquid and vapour properties and meteorological data. Improvement options include the following.

1. Use site specific daily temperature data for each landing episode, particularly actual temperature measurements below the landed roof, if available.
2. Stock properties, based on sampling, should be incorporated when available.

### **8.7.3. Storage Tank Cleaning Emissions**

Site specific information pertaining to stock properties, meteorology, and activities that are carried out during each tank cleaning event should be used whenever available.

## **8.8. EXPLANATORY NOTES**

The following sections outline recommended reporting thresholds for spills. However, federal/provincial spill reporting requirements should always take precedence over the following minimum threshold volumes.

### **8.8.1. Spills to Water**

A minimum threshold volume of 10 litres is recommended. In petroleum refineries, most streams rarely contain NPRI substances in quantities that exceed 10 %. At this concentration, a 10 L spill will result in a reportable substance amount of 1 kg, which is the smallest reportable number in NPRI for Schedule 1, Part 1 substances. Most 10 L spills will result in less than 1 kg of NPRI substances. However, this threshold suitably captures the resolution necessary given the heightened sensitivity to preventing releases to surface water.

### **8.8.2. Spills to Land**

A minimum threshold volume of 100 litres is recommended for spills from storage facilities or process works and 30 litres for spills during transport. This is based on, and consistent with, the guidelines for flammable liquids release reporting issued by the provinces of BC and Ontario. The reporting requirements under Part 8 of the Transportation of Dangerous Goods Regulation, under the Transportation of Dangerous Goods Act (TDGA Canada) were revised last in December 2017 and now require reporting of an accidental release from containment of Class 3, Packing Group III of 30 L or more and Class 3, Packaging Group I or II any quantity. Since most streams in petroleum refineries do fall under Class 3 (flammable liquids) of TDGA, the 100 L threshold is considered appropriate for NPRI reporting purposes unless the release occurred during transport by road, rail, or marine vehicles.

### **8.8.3. Airborne Discharges**

A minimum threshold volume of 100 litres is recommended. Typically, airborne discharges in petroleum refineries occur because of non-routine releases of compressed gases, including such NPRI substances as ethylene, propylene, and ammonia. Reference is made to the guidelines for release reporting issued by the province of Alberta which state that any quantity that could pose a danger to public safety or any sustained release of 10 minutes or more. Consistent with this are the reporting requirements under the Transportation of Dangerous Goods Act (Canada). These streams in petroleum refineries generally fall under Class 2.1 (compressed gas, flammable) of TDGA.

### **8.8.4. Regulatory Reports with Adverse Effect**

Non-routine releases that cause an adverse effect are generally reportable to the local regulatory authorities. These releases should be included in the estimate of NPRI releases even when the volume is less than the minimum reporting threshold



recommended in this Code. This approach is intended to capture in NPRI all non-routine releases that have caused, or may have caused, an adverse effect. For example, an airborne discharge of ammonia in an amount less than 100 litres, but reported to the regulatory authorities because it had an adverse effect, should be included in the report of NPRI releases. Similarly, a benzene spill to water in an amount less than 10 litres should also be included since it is reportable to regulatory authorities due to the potential for an adverse effect.

## **8.9. REFERENCES**

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7. “Enviro TIPS (Technical Information for Problem Spills) Introduction Manual”, ECCC, August 1985.
8. “Emission Estimation Technique Manual for Petroleum Refining”, Environment Australia, February 1999. <https://www.dceew.gov.au/sites/default/files/documents/petroleum.pdf>
9. “Procedure for Preparing an ESDM Report”, Ontario Ministry of Environment, Conservation, and Parks, March 2018. <https://www.ontario.ca/document/guideline-10-procedure-preparing-emission-summary-and-dispersion-modelling-esdm-report>
10. “Emission Estimation Protocol for Petroleum Refineries”, Version 3, US EPA, April 2015. <https://www.epa.gov/air-emissions-factors-and-quantification/emissions-estimation-protocol-petroleum-refineries>
11. Classification and Exemption of Spills and Reporting of Discharges, Ontario Regulation 675/98, consolidated to October 31, 2011 <https://www.ontario.ca/laws/regulation/980675>

12. Spill Reporting Regulation, BC Reg 221/2017  
[http://www.bclaws.ca/civix/document/id/complete/statreg/187\\_2017](http://www.bclaws.ca/civix/document/id/complete/statreg/187_2017)
13. Revisions to AP-42, Chapter 7, Section 7.1 – Organic Liquid Storage Tanks,  
US EPA: <https://www.epa.gov/air-emissions-factors-and-quantification/final-revisions-ap-42-chapter-7-section-71-organic-liquid>

## **9. RELEASES FROM COMBUSTION SOURCES AND HYDROGEN PLANTS**

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### **9.1. PURPOSE**

In addition to conventional pollutants (NO<sub>x</sub>, SO<sub>x</sub>, CO, and particulates), refinery combustion sources release VOCs and other NPRI substances. Typically, these pollutants are released from these sources in concentrations less than 1 weight%. Therefore, the “by-product” rule in NPRI might apply, where total releases exceed the reporting threshold (e.g. 10 tonnes). CAC emissions from combustion sources are covered in Section 15.

### **9.2. SCOPE**

Sources may include the following:

- a) Heaters & Boilers,
- b) Catalytic Cracking Unit (CCU) Regenerators,
- c) Catalytic Reforming Unit Regenerators,
- d) Steam Methane Reformers (SMR) or Hydrogen Units, and/or
- e) Flares.

### **9.3. REQUIREMENTS**

#### **9.3.1. Metals in Stack Gases**

1. Consistent with the by-product rule in NPRI, only nickel, vanadium, and metals reported at an alternate threshold (i.e. mercury and its compounds, cadmium and its compounds, cobalt and its compounds, arsenic and its compounds, lead and its compounds, selenium and its compounds, thallium and its compounds, tetraethyl lead, and hexavalent chromium compounds) are likely to exceed the reporting threshold. Unless the site has data to the contrary, all other metals can be assumed insignificant for the purposes of developing emission inventories or determining NPRI reporting requirements. AP-42 emission factors generally have low quality ratings and as an alternate the emission factors presented in the Canadian Energy Partnership for Environmental Innovation (CEPEI) Natural Gas Emissions Calculator (ORTECH 2022) should be used to replace the API/WSPA (1998) emission factors. The Natural Gas Emissions Calculator is updated annually to address the NPRI reporting requirements of air contaminants related to natural gas use. As of publication, the latest version of the calculator is 2022 (for the 2021 Reporting year). Members should check for the latest version in future years.
2. If stack source testing is not available, nickel and vanadium releases due to liquid fuel burning should be based on the known amount of liquid fuel and an estimate or measurement of the nickel and vanadium contents of the fuel. An estimate can

be made based on the crude processed (and crude assays) and the composition of the liquid fuel. It is assumed that all metals are lost to the air through the stack.

3. If stack source testing is not available, nickel and mercury releases from the catalytic cracking unit (CCU) regenerator can be estimated based on an industry wide study by ExxonMobil Research and Engineering Company (ExxonMobil Study). The average detected emission factor for nickel is 1.73 grams per 1000 kilograms of coke burned (1.73E-03 lbs/1,000 lbs of coke burned) and for mercury is 0.0524 grams per 1000 kilograms of coke burned (5.24E-05 lbs/1000 lbs of coke burned). Vanadium release can be estimated based on the known catalyst losses to air and the average vanadium content of the CCU catalyst (based on routine catalyst activity testing).
4. If stack source testing is not available, nickel and vanadium releases from CCU regenerators with CO boilers can be estimated based on the known amount of coke burned and an estimate or measurement of the nickel and vanadium contents of the coke. An estimate can be made based on the crude processed and the composition of the CCU feed. An estimate should be made on the amount of metals lost to air through the stack and the amount in the slag sent off-site for disposal.

### **9.3.2. Formaldehyde in Stack Gases**

Based on company data, Canadian Fuels refineries are not near the reporting threshold for formaldehyde in stack gases and formaldehyde is not reportable.

### **9.3.3. Other Substances in Stack Gases**

Specific requirements for VOCs and benzene, are provided in Section 15.4. Requirements for other substances are described below.

1. VOCs from combustion sources (e.g. heaters, boilers,) should be included in the overall VOC estimate (using AP-42 emission factors), refer to Section 15.4. Speciation of these VOCs is based on fuel type and is determined by assuming the VOC has the same composition as the fuel. An alternative is the use of substance-specific emission factors from AP-42.
2. For CCU regeneration sources, emissions of other substances can be estimated based on the ExxonMobil Study which is based on API inventory submission to EPA and additional test data. The Study includes median and average speciation data for selected substances. Only those compounds with emission factors greater than 0.1 grams per 1000 kilograms of coke burned have been listed in Table 9-1; other substances can be found in the original document.

For hydrogen cyanide, the US EPA has developed and published, in its AP-42 manual (2015), an emission factor of 0.43 g/kg coke burned (or 430 g/1000 kg coke burned) for fluid catalytic cracking units equipped with controls including scrubbers and electrostatic precipitators. Based on input from the membership, this generic AP-42 factor does not fully account for all FCC processing configurations and operating modes such as partial burn versus full burn versus COB boiler bypass

and others. Hence, caution is recommended when determining the most appropriate emission factor that reflects site-specific operations.

**Table 9-1 Emission Factors of Other Substances for CCU Regeneration Sources**

<b>Chemical</b>	<b>Median Emission Factor</b> (gram emissions per 1000kg of coke burned)
Acetaldehyde	0.907
Ammonia <sup>a</sup>	239
Bromomethane	0.137
Cyanide	3.23
Hydrogen Cyanide	1.5 (430 <sup>b</sup> )
Formaldehyde	1.98
bis (2-ethylexyl) Phthalate	0.186
m, p Xylenes	0.151

<sup>a</sup> Ammonia emissions are for complete combustion of coke. See Section 9.3.4 for partial burns and emission control devices (i.e. CO boilers).

<sup>b</sup> Factor in bracket is from EPA AP-42 Chapter 5.1 Table 5.1-2 for FCCUs equipped with emission controls (See Section 0 for explanatory note)

- 3 The preferred estimation method for determining VOCs emissions from flares is provided in Section 15.4 to use US EPA AP-42 emission factors (AP-42 Chapter 13.5, Table 13.5-2) which are based on firing capacity (BTU, lower (net) heating value of the vent gas). In the 2015 update to AP-42, a flaring VOC emission factor of 0.57 lb/10<sup>6</sup> BTU was published by the US EPA. Previously, only a THC emission factor of 0.14 lb/10<sup>6</sup> BTU was available for use in flaring emission estimations. In 2018 the VOC factor was updated by EPA to 0.66 lb/10<sup>6</sup> BTU. The VOC emission factor was based on an average destruction efficiency of 98.9% and should be used for flaring VOC emission estimate. Sample calculations for estimating emissions from flares are provided in Appendix D.
4. For catalytic reforming units (CRU), EPA has published an emission factor of 0.0007 kg/ 10<sup>3</sup>L feed for total hydrocarbons. This factor was based on CRUs which are equipped with either chlorosorb or scrubber controls and was developed by EPA following a review of refinery data collected during its 2011 Refinery Information Collection Request (ICR). However, based on membership input, this new EPA factor does not consider the impact of process configuration and the dataset used is too small to provide representative emission factors. Hence, discretion is needed when choosing a factor which is the most representative of facility operations.

### **9.3.4. Ammonia from CCU Partial Burns**

Ammonia is released during the CCU regeneration process. The amount of ammonia released depends upon its severity. When catalytic cracking units operate in a "partial-burn" mode without a CO boiler, the emissions can be estimated using 0.155 kg of ammonia per thousand litres of fresh feed (EPA AP-42, Table 5.1.1). If the CO boiler is operating with CCU or the CCUs operate on "full burn", emissions of ammonia are considered negligible (CONCAWE 2019).

### **9.3.5. Methanol and NOx from Hydrogen Synthesis Plants**

Hydrogen synthesis plants (steam methane reformers) have been identified as potential sources of methanol emissions to the atmosphere. Hydrogen synthesis plants that have a low temperature shift (LTS) reactor/methanator configuration can generate methanol that is subsequently emitted in CO<sub>2</sub> desorber and de-aerator vents. High moisture content in these streams makes direct measurement extremely difficult. Alternative methods of estimating emissions have been developed in the U.S., but are not straightforward or standardized (no reference for method can be given). Methanol emissions will vary because of the size of the unit, catalyst type, catalyst age, unit configuration, and operating conditions. Note that hydrogen plants that have only a high temperature shift (HTS) reactor and no LTS reactor or methanator do not produce reportable quantities of methanol.

For hydrogen plants with an LTS, methanol emissions can be estimated through a combination of sampling the liquid effluent streams for methanol and doing either detailed engineering flash calculations or a material balance. An alternative to measurement of the methanol in the liquid effluent streams is to use catalyst manufacturer's kinetic models to predict methanol made and then do the flash calculations. Either method usually requires data that will require additional sampling/work by the refineries.

The EPA published a new emission factor in 2015 for uncontrolled emissions of NOx from hydrogen plants. The new factor of 0.081 lb/MMBtu in Table 5.1-2 of AP-42 is based on information gathered by EPA during the 2011 Refinery Information Collection Request (ICR). However, based on input from Canadian Fuels members, the majority of existing hydrogen plant reformer furnaces have NOx control technologies installed and therefore this uncontrolled NOx emission factor would not be applicable.

## **9.4. EXPLANATORY NOTES**

### **9.4.1. Metals in Stack Gases**

API/WSPA (1998) and latest AP-42 provides emission factors for NPRI metals related to liquid fuel burning. With the exception of nickel, vanadium, and metals reported at an alternate threshold (mercury and its compounds, cadmium and its compounds, cobalt and its compounds, arsenic and its compounds, lead and its compounds, selenium and

its compounds, thallium and its compounds, tetraethyl lead, and hexavalent chromium compounds), these metals remain non-reportable for most refineries.

The CEPEI Natural Gas Emissions Calculator (ORTECH, 2022) emission factors are derived on the premise that inorganic compounds found in stack gas should originate from the fuel itself. Revised factors are based on recent gas analysis of Canadian pipeline natural gas. Factors for NPRI reportable metals are shown in Table 9-2 and are applicable to natural gas-fired boilers, heaters, and turbines, and heaters.

**Table 9-2 Metals Emission Factors for Natural Gas Combustion**

<b>Metal Species</b>	<b>Emission Factors (lb/MMBtu)</b>	<b>CONCAWE Emission Factors (lb/MMBtu)*</b>
Antimony and its compounds	1.84E - 12	N/A
Arsenic and its compounds	1.65E - 11	8.19E-13
Cadmium and its compounds	7.96E - 12	5.09E-12
Chromium and its compounds	1.90E - 11	1.56E-11
Cobalt and its compounds	1.84E - 12	N/A
Copper and its compounds	1.15E - 10	7.65E-12
Lead and its compounds	9.24E - 11	3.75E-12
Manganese and its compounds	2.69E - 11	N/A
Mercury and its compounds	3.06E - 13	8.65E-13
Nickel and its compounds	3.31E - 11	1.71E-11
Nickel and its compounds (Residual Fuel Oil)	N/A	1.80E-11
Selenium and its compounds	4.28E - 12	3.63E-12
Silver and its compounds	1.10E - 12	N/A
Thallium and its compounds	1.22E - 12	N/A
Vanadium (except when in an alloy) and its compounds	2.45E - 12	N/A
Zinc and its compounds	1.71E - 09	3.95E-11

\* Converted from CONCAWE report using 1 g/GJ \*0.00000002326 = lb/MMBtu; All emission factors are for Refinery Fuel Gas unless otherwise stated; All heating values are net calorific values (NCVs) and all emission factors require the use of the corresponding fuel NCV..

In June 2016, CONCAWE published a report entitled “Emission Factors for Metals from Combustion of Refinery Fuel Gas and Residual Fuel Oil”. This report contains updated emission factors for a variety of metals from the combustion of refinery fuel

gas and residual fuel oil in boilers and heaters (CONCAWE, 2016). However, these European factors have not been adopted by the US EPA for North American refineries nor have they been fully evaluated pertaining to Canadian refining operations. Hence, members should assess the appropriateness of these factors carefully prior to adopting them for their respective refining operations. In the absence of any site-specific information, the CONCAWE emission factors are currently the best available data.

#### **9.4.2. Catalytic Cracking Units**

The ExxonMobil Study document, “Emission of Trace Compounds from Catalytic Cracking Regenerators,” is based on 1995 field test data on emissions from CCUs submitted by API members, data obtained by EPA submissions, as well as, additional unreported test data. The document includes results from over 1000 observations for hazardous air pollutants (HAPs). If the emission factors are to be used, then based on member company data, Canadian Fuels recommends using the median emission factors contained in the document.

In 2015, the US EPA published a new hydrogen cyanide emission factor for fluid catalytic cracking units (FCCU), with or without CO boiler, which are equipped with control devices including scrubbers and electrostatic precipitators. This new factor, shown in Table 9-1, is based on EPA’s review of refinery data gathered during the 2011 Refinery Information Collection Request (ICR). However, as stated in Section 9.3.3, this generic AP-42 factor does not fully account for all FCC processing configurations and operating modes such as partial burn versus full burn versus COB boiler bypass and others. Hence, discretion is required when determining the most appropriate emission factor that reflects site-specific operations.



## **9.5. REFERENCES**

1. “EPA AP-42, Fifth Edition: Compilation of Air Pollutant Emission Factors, Volume 1: Stationary Point and Area Sources” US EPA, January 1995.
2. “EPA AP-42, Fifth Edition: Emission Factors Section 13.5 - Industrial Flares”. US EPA, February 2018.
3. “Air Toxics Emission Factors for Combustion Sources Using Petroleum-Based Fuels. Volume 1 Development of Emission Factors Using API/WSPA Approach”. API Pub. #348, August 1998.
4. “Emission of Trace Compounds from Catalytic Cracking Regenerators”. Bertrand, Rene R and Jeffrey H. Siegell, ExxonMobil Research and Engineering Company, Virginia, US, 2002.
5. “Guide for Emissions Calculator –Airborne Contaminant Emissions from Natural Gas Combustion”, Prepared by ORTECH Environmental for Canadian Energy Partnership for Environmental Innovation (CEPEI), March 10, 2022.
6. “EPA AP-42, Fifth Edition: Emission Factors Section 5.1 – Petroleum Refining”. US EPA, April 2015.
7. “Emission Estimation Protocol for Petroleum Refineries” Version 2.1.1, Final ICR Version – Corrected, prepared by RTI International for the US EPA, March 2011.
8. “Air Pollutant Emission Estimation Methods for E-PRTR Reporting by Refineries”, CONCAWE, July 2019. <https://www.concawe.eu/publication/air-pollutant-emission-estimation-methods-for-e-prtr-reporting-by-refineries/>
9. “Emission Factors for Metals from Combustion of Refinery Fuel Gas and Residual Fuel Oil”, CONCAWE, Report no 9/16, June 2016, [https://www.concawe.eu/wp-content/uploads/2017/01/concawe-rpt\\_16-9.pdf](https://www.concawe.eu/wp-content/uploads/2017/01/concawe-rpt_16-9.pdf)

## **10. RELEASES TO UNDERGROUND INJECTION**

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### **10.1. DEFINITION**

#### **Underground Injection**

Disposal of wastewater and other contaminated waters (e.g. sour water) into isolated geological formations uniquely suited to accept them, generally to great depths. Also referred to as Deep Well Injection or Disposal Well, this practice is limited to Alberta refineries and is controlled by regulations.

### **10.2. SCOPE**

All untreated wastewater streams that are disposed of through underground injection, thus avoiding the need to treat them and discharge the treated effluent to surface water.

### **10.3. REQUIREMENTS**

1. Sour water, oily water, and other contaminated waters that are disposed through underground injection contain reportable NPRI substances, including ethylene glycol, BTEX, ammonia, and H<sub>2</sub>S. When assessing NPRI releases in wastewater effluent streams, the by-product rule in NPRI must be considered (see Section 3.2).
2. NPRI reporting should be based on actual wastewater quality testing or typical results obtained through non-routine testing. Actual wastewater flow rates should be used in the calculation of total quantities of substances released or disposed of.
3. Estimates should be made of the ethylene glycol, BTEX, and ammonia releases to underground injection. Typical refinery specific data representative of wastewater quality should be used for estimating purposes.
4. Estimates should be made of the H<sub>2</sub>S releases to underground injection. These are dependent on the water pH and should be calculated in accordance with Section 12.

## 11. OFF-SITE TRANSFERS FOR DISPOSAL OR RECYCLING

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### 11.1. DEFINITIONS

#### **3Rs (Recovery, Re-use, Recycle)**

Any material sent off-site where NPRI substances are recovered, re-used, or recycled. “Recycling refers to activities that keep a material or a component of the material from becoming a waste destined for final disposal.” (Guide for Reporting to the National Pollutant Release Inventory (NPRI) 2022-2024).

#### **Waste**

Any material sent off-site where NPRI substances are ultimately disposed of through: landfill, treatment (stabilization), incineration, etc.

### 11.2. SCOPE

All materials sent off-site for disposal (including treatment prior to disposal) or recycling, which contain NPRI substances, are considered in determining NPRI off-site transfers.

### 11.3. REQUIREMENTS

1. Include all materials that are sent off-site for disposal, recovery, re-use, or recycling and that are known to contain reportable NPRI substances. When assessing the threshold calculation of NPRI substances in wastes, the by-product rule in NPRI must be considered (see Section 3.2). However, note that some processes intend to recycle a catalyst or solvent and therefore, the regeneration of that product is NOT considered to be a recycling activity since the product would not have been destined for final waste disposal in any event.
2. Type and quantity of transferred material should be based on actual shipments (e.g. bills of lading, manifests, invoices).
3. Speciation of the material transferred off-site is based on actual site data that is representative of the material. Alternatively, if no such data is available, then typical composition can be derived from industry reports.

#### 11.3.1. Spent Sulphuric Acid

Petroleum refineries belonging to the Canadian Fuels Association consider sulphuric acid used in a refining alkylation process and its on-going regeneration an essential and integral part of the alkylation process design and operation. The shipment of sulphuric acid for processing to restore the acid strength from ~90% to ~99.5% and return to the refinery for continued use is not intended to divert this material from a final disposal option but is an integral part of the alkylation process design. Therefore, before 2006, the sulphuric acid was not reported previously as a material sent off site for recycling.

This position was reviewed with François Lavallée and colleagues in the ECCC NPRI offices in mid-2007 in light of changes in federal export and import legislation of wastes and hazardous recyclable materials. After review, ECCC concluded that this transfer should indeed be reported as material sent off site for recycling.

#### **11.4. REFERENCES**

1. “Analytical Data Summary Refinery Waste Characterization Study”, API report prepared by Rocky Mountain Analytical Lab of Arvada, Colorado, July 1995.
2. “Fate of Polynuclear Aromatic Hydrocarbons in Refinery Waste Applied to Soil”, PACE Report No. 88-1.
3. “The Significance of Trace Substances in Petroleum Industry Sludges Disposed of on Land. A Literature Survey”, PACE Report No. 83-2.
4. “Guide for Reporting to the National Pollutant Release Inventory 2022-2024”, Environment and Climate Change Canada, 2022.  
<http://publications.gc.ca/pub?id=9.506026&sl=0>

## **12. HYDROGEN SULPHIDE (H<sub>2</sub>S)**

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### **12.1. H<sub>2</sub>S SCOPE**

Hydrogen sulphide was added to the NPRI substance list as of the 1999 reporting year (June 1, 2000 submission). Most Canadian Fuels refineries manufacture and/or process greater than 10 tonnes/year of H<sub>2</sub>S and therefore, have reported H<sub>2</sub>S emissions (Appendix A, Table A - 3). H<sub>2</sub>S releases exist for most of the following emission sources:

- a) Process Fugitives.
- b) Storage Emissions (including emissions from liquid sulphur storage pits).
- c) Loading Emissions (related to liquid sulphur loading).
- d) Wastewater Treatment (API Separator).
- e) Stacks/Combustion.
- f) Flares/Vents.
- g) Deep Well Injection.

Since the 2007 reporting year, total reduced sulphur (TRS), expressed as hydrogen sulphide is reportable to NPRI and includes the following substances with their respective CAS numbers:

- |                        |           |
|------------------------|-----------|
| 1. Hydrogen sulphide   | 7783-06-4 |
| 2. Carbon disulphide   | 75-15-0   |
| 3. Carbonyl sulphide   | 463-58-1  |
| 4. Dimethyl sulphide   | 75-18-3   |
| 5. Dimethyl disulphide | 624-92-0  |
| 6. Methyl mercaptan    | 74-93-1   |

A survey of member refineries was conducted in 2009 to determine the methodologies used by Canadian Fuels refinery members to quantify their releases of any of the new TRS substances. For H<sub>2</sub>S emissions reporting, the survey results indicated that members use the methods included in the Canadian Fuels Code of Practice when facility specific data is not available.

The approach outlined in this section is intended for normal refinery operations and non-routine releases may require different emissions estimation approaches.

### **12.2. REQUIREMENTS**

No standard methodologies with well-developed emission factors exist for H<sub>2</sub>S emission estimation based on a review of currently available literature. Therefore, emissions estimates should be based on actual facility fugitive emissions measurements/monitoring. If not available, it is recommended that H<sub>2</sub>S emissions be

estimated using the standard methodologies identified within this Code of Practice as follows:

**Process Fugitives from Sour Hydrocarbon Streams** – utilize Section 4 applying H<sub>2</sub>S speciation to the generic VOC emissions estimated. For sour water streams, heavy liquid VOC emission factors should be used along with H<sub>2</sub>S speciation.

**Process Fugitives from Amine Systems** – utilize Section 4 applying H<sub>2</sub>S speciation to the generic VOC emissions estimated. Use heavy liquid emission factors for both rich and lean amine streams. Because of the strict Occupational Health & Safety (OH&S) requirements related to high concentration acid gas (sulphur plant feed) streams, it is assumed that H<sub>2</sub>S emissions from these acid gas streams are negligible.

**Process Fugitives from Sulphur Plants** – due to the OH&S concerns and use of on-line H<sub>2</sub>S monitors, process fugitives from sulphur plants are assumed to be negligible.

**Storage Tank Emissions from Hydrocarbon Storage** – refer to Section 5.2.3 (point 3) methodology with appropriate speciation for hydrocarbon storage tanks.

**Emissions from Sulphur Product Storage** – most facilities employ sulphur pit sweeping with tail gas incineration of the sweep gas. Under these conditions, H<sub>2</sub>S emissions can be considered negligible. Very large sulphur producing facilities may utilize the more rigorous sulphur product degassing option, whereby air is bubbled through the product to extract dissolved H<sub>2</sub>S. This is usually followed by off-gas incineration with assumed negligible final H<sub>2</sub>S emissions. In the absence of such degassing facilities, an estimate of emissions can be generated by establishing the equilibrium ratio of H<sub>2</sub>S to sulphur in the enclosed sulphur pit.

**Loading Operations of Hydrocarbon Streams** – refinery products generally do not contain significant amounts of hydrogen sulphide. Utilize Section 6 for hydrocarbon product loading.

**Loading Operations of Sulphur Product** – in the event that a facility engages in the more rigorous process of sulphur degassing (rather than sweeping), H<sub>2</sub>S emissions from sulphur loading operations can be assumed to be negligible. Where sweeping only is employed, it is recommended to use a factor of 0.15 kg H<sub>2</sub>S/tonne of sulphur based on measurements taken with respect to a degassing engineering design project. Unless site-specific data is available, it is recommended that this factor be used to approximate loading emissions.

**Storage and Loading of Asphalt** – asphalt inherently has little H<sub>2</sub>S as it has been mostly stripped out and the vapour pressure is typically quite low. Formation of H<sub>2</sub>S could occur from the decomposition of other sulphur compounds due to high temperatures near heating coils. This will depend on whether sulphur specific compounds are present in significant concentrations and what their contributions are. Temperatures of heating and residence time of the asphalt are also factors affecting emissions. Therefore, unless site specific information indicates the contrary, H<sub>2</sub>S emissions from these sources may be ignored because they are typically very small.

**Wastewater Releases** – in some cases, inlet to wastewater treatment facilities (API separator) are monitored and can be used to approximate H<sub>2</sub>S emissions (if any). Barring availability of such monitoring data, emissions are assumed negligible.

**Stacks/Combustion** – unless site specific data is available, assume 100% destruction of H<sub>2</sub>S to sOx in all controlled combustion activities. This includes the sulphur plant tail gas incinerator. To date, no estimation methodologies have been established to estimate this emission.

**Flares/Vents** – assume 98% of sulphur is combusted to SO<sub>2</sub> and 2% remains uncombusted as H<sub>2</sub>S. The use of a 98% flare combustion efficiency is consistent with the Canadian industry average. Sample calculations for estimating emissions from flares are given in Appendix D.

**Deep Well Injection** – when H<sub>2</sub>S is dissolved in water, as in deep well injection, a series of chemical reactions take place. This includes the dissociation of the molecular H<sub>2</sub>S to form the bisulphide ion (HS<sup>-</sup>). Only the molecular form (H<sub>2</sub>S) is reportable to the NPRI. The relative amounts of the two species of sulphide (H<sub>2</sub>S and HS<sup>-</sup>) are very dependent on the pH of the water in which the sulphide is dissolved. A nomograph is available which shows the relationship between the ion levels based on water pH (see Reference 2).

For a general guideline of the percentage of sulphide that would be in the form of H<sub>2</sub>S, Table 12-1 has been derived from the nomograph referenced above.

**Table 12-1 Effect of pH on H<sub>2</sub>S Dissolved in Water**

<b>PH</b>	<b>% of Dissolved Sulphide in H<sub>2</sub>S Form</b>
5.0	100
6.4	80
7.0	50
7.6	20
9.0	0

(Source: Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, p. 478, 16<sup>th</sup> Ed., 2005)

### **12.3. REFERENCES**

1. Shell Canada Products estimate from measurements of 0.3 kg H<sub>2</sub>S / tonne of sulphur during the loading, transport, and unloading of sulphur product. Assume 50% loss during loading (remaining loss assumed to occur during transport and unloading).
2. “Standard Methods for the Examination of Water and Wastewater, American Public Health Association”, American Water Works Association, Water Pollution Control Federation, 16<sup>th</sup> Ed., 2005.
3. “Emission Estimation Protocol for Petroleum Refineries”, Version 3, prepared by RTI International for the US EPA, April 2015. <https://www.epa.gov/air-emissions-factors-and-quantification/emissions-estimation-protocol-petroleum-refineries>



## **13. ALTERNATE NPRI REPORTING THRESHOLDS METALS (Hg, Cd, Cr<sup>6+</sup>, As, Pb, TEL, Se, Co, Tl)**

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### **13.1. SCOPE**

This section provides guidance on reporting for selected substances that do not fall under the 10 tonne MPO reporting threshold and are part of Schedule 1, Part 1, Group B. As of the 2018 reporting year, these substances include:

- Mercury (Hg) and its compounds,
- Cadmium (Cd) and its compounds,
- Arsenic (As) and its compounds,
- Lead (Pb) and its compounds,
- Hexavalent chromium (Cr<sup>6+</sup>) compounds,
- Tetraethyl lead (TEL),
- Selenium (Se) and its compounds,
- Thallium (Tl) and its compounds, and
- Cobalt (Co) and its compounds.

For all substances in this category, releases to each medium (air, land, water, and underground injection) must be reported separately, even when the sum of releases is less than 1 tonne.

### **13.2. MERCURY (Hg)**

Releases or transfers of mercury and its compounds are reported in kg. The threshold reporting criteria is 5 kg or more of total mercury and its compounds per year from the categories of manufactured, processed, or otherwise used; the incidental manufactured, processed, or otherwise used as a by-product; the quantity in tailings; and the quantity in waste rock disposed of during the calendar year.

There is no concentration exemption for the mercury threshold calculation.

Appendix 8 of ECCC's Supplementary Guide for Alternate Threshold Reporting contains a list of products and materials expected to contain mercury. For the downstream petroleum industry, potential products and materials of interest include:

- Purchased sulphuric acid,
- Batteries, fluorescent lamps,
- Residual, distillate, and crude oil.

Mercury sources such as batteries and lamps will retain article status (and therefore, do not need to be considered for NPRI reporting threshold calculations) unless the item is damaged or broken, thus releasing the mercury.

For most refineries, the source of mercury and its compounds that could trigger the reporting threshold will be in the crude oil feed. Estimates of mercury concentrations in crude oil have historically had a wide range of variability. A national default value was recommended which did not account for regional variation. To resolve this issue and develop more accurate Canadian regional estimates, ECCC in partnership with Canadian Fuels surveyed a wide variety of crude oils processed in Canadian refineries. The study analyzed over 100 crude oil types representing 88% of total crude oil types processed in Canada in 2002. In the absence of any site-specific information, the recommended Canadian average mercury content in crude oil based on the results of the study is  $2.6 \pm 0.5$  ppb (or ng/g oil). For synthetic crude oils, the Canadian average value is  $2.2 \pm 0.4$  ppb. At a concentration of 2.6 ppb, approximately 41,000 bbl/d of crude inlet would trigger NPRI reporting of mercury (based on crude with 0.855 specific gravity).

Effective for the 2018 reporting year, facilities must report mercury and criteria air contaminant releases to air for each electricity generation unit that meets the following two criteria:

1. The unit has a capacity of 25 MW or more, and
2. The unit distributes or sells to the grid 33% or more of its potential electrical output (during the current or previous years).

An electricity generation unit means physically connected equipment that operates together to produce electricity for sale or distribution to the grid by means of thermal energy, is stationary when used, and is not in or on a machine that is self-propelled. Potential electrical output means the quantity of electricity that would be generated by a unit in a calendar year if the unit were to operate at capacity, at all times, during that calendar year. The 33% threshold must be assessed on an annual basis. If a unit meets the 33% threshold in a calendar year, but does not meet it in the subsequent year, reporting at the unit level for that unit is still required. Facilities that meet the threshold requirements for unit-level reporting must also provide details about the unit, including:

- unit gross generating capacity
- commissioning year
- technology or fuel type
- whether the unit includes emissions from duct firing or other secondary combustion sources
- air pollutant controls installed and operating on the unit

In 1998, API/WSPA published a report entitled: "Air Toxics Emission Factors for Combustion Sources using Petroleum-Based Fuels". This report contained emission factors for a number of metals including mercury. However, the results developed at the time were based on only one to two data sources and had a low data quality rating (i.e. 'below average' to 'poor') according to US EPA. Since then, the European organization CONCAWE has performed further research, having sampled and collected additional measurement data from over thirty refinery sources. See Sections 9.3.1 and 9.4.1.

### **13.2.1 Combustion Sources**

Emission factors for mercury from combustion emissions can be found in the API/WSPA report entitled: "Air Toxics Emission Factors for Combustion Sources using Petroleum-Based Fuels" August 1998 p. ES-6. Mercury from CCUs can be estimated from the ExxonMobil study (see Section 9.3.1).

### **13.2.2 Direct Measurement**

Direct measurement of mercury content in waste streams such as water effluent, spills, or within land farm/landfill sludges should be used and applied as in previous sections of the Code. ECCC's guidance on interpretation of non-detect data (see Section 3.3.4) should be followed when calculating mercury releases and transfers.

### **13.2.3 Off-site Transfers**

Mercury contained in fluorescent lights, batteries, and thermometers, etc. will lose its article status if the item is damaged or broken, as may be the case when disposed to a landfill. Appendix 8 of ECCC's Supplementary Guide for Alternate Threshold Reporting lists typical mercury contents for these items or more site-specific data can be used.

## **13.3. CADMIUM (Cd)**

Releases or transfers of cadmium and its compounds are reported in kg. The threshold reporting criteria is 5 or more kg of cadmium and its compounds per year based on the total release from the categories of manufacture, process, or otherwise used, the incidental manufactured, processed or otherwise used as a by-product, as well as the quantities in tailings and waste rock disposed of during the calendar year.

A 0.1% concentration by weight exemption applies to cadmium under the manufactured, processed or otherwise used category. There is no concentration exemption for cadmium in the other categories.

Pure cadmium and the equivalent weight of cadmium contained in alloy or mixture should be included in the calculation of the mass reporting threshold.

For most refineries, the source of cadmium is fossil fuels used in boilers, process heaters, etc. Cadmium is found as a trace contaminant in fossil fuels such as natural gas, coal, oil, and waste. During combustion of fuels, due to the volatility of cadmium, it is partitioned from the ash and gas exhaust stream. The most current and updated emission factors for cadmium and other metals released from natural gas combustion have been published and are provided in Table 9-2. Individual refineries should check total combustion plus other sources to determine threshold reporting.

The recycling of batteries and waste water effluent can also be sources of cadmium. ECCC's guidance on interpretation of non-detect data (see Section 3.3.4) should be followed when calculating these by-product releases and transfers (detection limit discussion).

### **13.4. SELENIUM (Se)**

Releases or transfers of selenium and its compounds are reported in kg. The threshold reporting criteria is 100 or more kg of selenium and its compounds per year according to Part 1 of the December 24, 2011, Canada Gazette notice. The mass reporting threshold represents the total selenium and its compounds from the categories of manufactured, processed, or otherwise used, the incidental manufactured, processed, or otherwise used as by-product, as well as, those present in tailings and waste rock disposed of during a calendar year. The calculation of the 100 kg reporting threshold must include all streams where the NPRI substance is present in 0.000005% or more concentration by weight under the MPO category. The quantity of selenium as a by-product in tailings and waste rock is to be included in the mass reporting threshold calculation regardless of concentration.

For most refineries, the main source of selenium is from the combustion of fossil fuels used in boilers, process heaters, etc. Selenium is present as a trace contaminant in fossil fuels such as natural gas, coal, oil, and waste. During combustion of fuels, due to the volatility of selenium, it is partitioned from the ash and gas exhaust stream. For refineries, stationary combustion, Catalytic Cracking Unit, and Fluid Coking Unit are the three main process sources to be considered for selenium emission estimation.

The most current and updated emission factors for selenium and other metals released from natural gas combustion have been published and are provided in Table 9-2 (ORTECH, 2022). In addition to the three major process sources, individual refineries should check total combustion plus other sources, such as coke calcining, refinery start-up/shutdown or malfunctions, to determine if their facilities meet the reporting threshold.

### **13.5. THALLIUM (Tl)**

Releases or transfers of thallium and its compounds are reported in kg. The reporting threshold is 100 or more kg of thallium and its compounds per year according to Part 1 of the July 12, 2014 Canada Gazette notice. The mass reporting threshold represents the total thallium and its compounds from the categories of manufactured, processed, or otherwise used, the incidental manufactured, processed, or otherwise used as by-product, as well as, those present in tailings and waste rock disposed of during a calendar year. The calculation of the 100 kg reporting threshold must include all streams where the NPRI substance is present in 1% or more concentration by weight under the MPO category. The quantity of thallium as a by-product, in tailings and waste rock is to be included in the mass reporting threshold calculation regardless of concentration.

Thallium is typically released as a by-product from major industrial emitters, including coal burning power plants, metal smelters, metal mines, cement manufacturers using coal as fuel, lime manufacturing, steel coke production, and waste treatment and disposal. While petroleum refineries are not key thallium emitters, it is recommended that members should check their respective process sources, such as coke calcining and

refinery fuel gas fired heaters where emissions factors are available (US EPA, 2015), to determine if their facilities meet the reporting threshold.

### **13.6. LEAD, ARSENIC AND OTHERS (Pb, As, Co, Cr<sup>6+</sup>, TEL)**

Lead, arsenic, cobalt, hexavalent chromium compounds, and tetraethyl lead are all Group B substances of Schedule 1, Part 1. Releases or transfers of these Group B substances are reported in kg. The threshold reporting criteria for each substance, whether it is manufactured, processed, or otherwise used, incidentally manufactured, processed, or otherwise used as a by-product, present in tailings and waste rock, is 50 kg or more per year. There is no concentration exemption for these substances except for the MPO category, which has a 0.1% concentration by weight criteria. The reporting criteria for lead and its compounds do not include the amounts contained in stainless steel, brass, or bronze alloys.

Trace metals may be found from direct measurement, if applicable, of refinery waste streams such as water effluent, spills, or within land farm/landfill sludges. ECC's guidance on interpretation of non-detect data (see Section 3.3.4) should be followed when calculating these by-product releases and transfers.

The most current emission factors for NPRI reportable metals from natural gas combustion have been provided in Table 9-2.

## **13.7. References**

1. “Supplementary Guide for Reporting to the National Pollutant Release Inventory – Alternate Thresholds – 2000”, ECCCC, September 22, 2000.  
<http://publications.gc.ca/collections/Collection/En40-495-1-2000-3E.pdf>
2. “Sampling in Crude Oil”, CFA Study by Levelton Engineering, June 2000.
3. “Air Toxics Emission Factors for Combustion Sources Using Petroleum-Based Fuels, Volume 1 Development of Emission Factors Using the API/WSPA Approach”. API publication # 348, August 1998.
4. “Mercury in Crude Oil Refined in Canada”, ECCCC, October 2007.  
<https://www.canadianfuels.ca/wp-content/uploads/2009/10/Mercury-in-Crude-Oil-Refined-in-Canada-11Oct07.pdf>
5. “Guide for Reporting to the National Pollutant Release Inventory 2022-2024”, Environment and Climate Change Canada, 2022.  
<http://publications.gc.ca/pub?id=9.506026&sl=0>
6. “Emission Factors for Metals from Combustion of Refinery Fuel Gas and Residual Fuel Oil”, CONCAWE, Report no 9/16, June 2016. [https://www.concawe.eu/wp-content/uploads/2017/01/concawe-rpt\\_16-9.pdf](https://www.concawe.eu/wp-content/uploads/2017/01/concawe-rpt_16-9.pdf)
7. “Emission Estimation Protocol for Petroleum Refineries”, Version 3, Prepared by RTI International for the US EPA, April 2015.
8. “Guide for Emissions Calculator – Airborne Contaminant Emissions from Natural Gas Combustion”, Prepared by ORTECH Environmental for Canadian Energy Partnership for Environmental Innovation (CEPEI), March 10, 2022.

## 14. POLYCYCLIC AROMATIC HYDROCARBONS (PAHS)

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### 14.1. SCOPE

The scope of this section focuses on releases of PAHs from refineries. PAHs occur naturally in crude oil but are also formed in high temperature catalytic cracking and hydrocracking reactions and could be released as fugitive emissions from refinery streams associated with these reactions. Another formation mechanism for PAHs is through incomplete combustion resulting in emissions from refinery boilers, process heaters, and flares. Sources of polycyclic organic matter (POM) emissions from petroleum refinery processes are process heaters, and catalytic cracking units, and fugitive emissions (including wastewater emissions).

In addition to PAHs from refinery sources, Canadian Fuels has conducted a sampling program to determine PAHs in refinery waste streams. Findings of this program are included in this section.

### 14.2. DEFINITIONS AND BACKGROUND

#### POM

The term polycyclic organic matter (POM) defines a broad class of compounds which generally includes all organic structures having two or more fused aromatic rings. PAHs are one of eight major categories of compounds that have been identified by the US EPA to constitute the class known as POM.

#### PAH

Polycyclic aromatic hydrocarbons (PAH or PCA) are also known as polycyclic aromatic compounds (PAC) and polynuclear aromatic hydrocarbons (PNA). For the purposes of this section of the Code, the PAH substances are limited to those identified in Part 2 of the Canada Gazette Notices for the NPRI. In Part 2 of the Canada Gazette Notice for 2022-2024, dated February 12, 2022, 31 PAH substances were identified. The 2022-2024 substances with their CAS numbers are:

- |    |                      |          |
|----|----------------------|----------|
| 1. | Acenaphthene         | 83-32-9  |
| 2. | Acenaphthylene       | 208-96-8 |
| 3. | Anthracene           | 120-12-7 |
| 4. | Benzo(a)anthracene   | 56-55-3  |
| 5. | Benzo(a)pyrene       | 50-32-8  |
| 6. | Benzo(b)fluoranthene | 205-99-2 |
| 7. | Benzo(e)pyrene       | 192-97-2 |
| 8. | Benzo(g,h,i)perylene | 191-24-2 |
| 9. | Benzo(j)fluoranthene | 205-82-3 |

10.	Benzo(k)fluoranthene	207-08-9
11.	Chrysene*	218-01-9
12.	Dibenzo(a,h)acridine	226-36-8
13.	Dibenzo(a,h)anthracene	53-70-3
14.	Dibenzo(a,j)acridine	224-42-0
15.	Dibenzo(a,e)fluoranthene	5385-75-1
16.	Dibenzo(a,e)pyrene	192-65-4
17.	Dibenzo(a,h)pyrene	189-64-0
18.	Dibenzo(a,i)pyrene	189-55-9
19.	Dibenzo(a,l)pyrene	191-30-0
20.	7H-Dibenzo(c,g)carbazole	194-59-2
21.	7,12-Dimethylbenz(a)anthracene	57-97-6
22.	Fluoranthene	206-44-0
23.	Fluorene	86-73-7
24.	Indeno(1,2,3-c,d)pyrene	193-39-5
25.	3-Methylcholanthrene	56-49-5
26.	5-Methylchrysene	3697-24-3
27.	1-Nitropyrene	5522-43-0
28.	Perylene	198-55-0
29.	Phenanthrene	85-01-8
30.	Pyrene	129-00-0
31.	Quinoline	91-22-5

One PAH substance is on the NPRI Part 1A list of substances with a standard reporting threshold of 10 tonnes manufacture, processed or otherwise used:

32.	Naphthalene	91-20-3
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\*: Chrysene was previously named as benzo(a)phenanthrene

### **Reporting Threshold**

All releases and transfers of the specified PAHs (excluding Naphthalene) must be reported individually (if individual PAH data is available) when more than 50 kg of the PAHs in total are released or transferred. Amounts of individual PAHs released on site, disposed of, and/or transferred off-site must also be reported if the quantity released is equal to or greater than 5 kilograms.

In cases where the quantities of individual PAHs are known for some processes and only total PAHs are known for others, the amount of known individual PAHs, that are



equal to 5 kg or more, as well as, total PAHs, excluding the individual PAH reported quantities, should both be reported. If the quantities of individual PAHs are not known, the amount of total PAHs is to be reported under “PAHs, total unspciated”.

### **14.3. ESTIMATION METHODOLOGIES**

#### **14.3.1. General**

PAHs are hydrocarbons and therefore, the methodologies and guidelines outlined in other sections of this Code for estimating hydrocarbon emissions can be applied for process equipment (e.g. process fugitives), storage tanks, loading, land farm operations, wastewater sources, incidents and underground injection. Average concentrations (see Reference 1) for the PAHs listed above by refinery stream are summarized in Table 14-1. These average stream concentrations can be used for emissions estimates when specific refinery PAH information is not available. The following sections indicate some guidance on how to use these stream concentrations plus specific considerations for PAH release and transfer estimations.

#### **14.3.2. Estimation Methodologies Fugitive Emissions**

Most fugitive emissions of PAHs are estimated using the emission factors for heavy liquids (Table 4-1) to determine total hydrocarbon releases and then applying speciation for the appropriate refinery streams (Table 14-1) to estimate releases of individual substances. For the lighter streams (e.g. gasoline) containing measurable PAHs, light liquid emission factors should be used (Table 4-1).

Emissions from wastewater treatment plants are included in the calculation of fugitive emissions of PAHs. The requirements described in Section 7.4 of the Code should be followed using the PAH speciation of crude oil (Table 14-2) when refinery specific data is not available.

Fugitive PAH emissions are also present in refinery waste streams and should be accounted for in estimating emissions from a facility. Sources of waste stream PAHs are listed below. Preferably, PAHs from waste streams should be estimated using refinery specific data. Due to different levels of concentrations between facilities, site specific PAH emissions data may or may not be available. If refinery specific data is not available, the requirements in Section 7.4 should be followed using the speciation of the following common waste streams in refineries (Table 14-2):

- Biox sludge,
- API separator sludge,
- IAF/DAF sludge,
- Slop oil tank sludge/emulsion,
- Crude tank sludge,
- Holding/diversion (oily) pond,

- Heat exchanger cleaning solids,
- Spent treating clay,
- Phenolic spent caustic,
- Desalter sludge,
- Sulphidic spent caustic, and
- Cat frac bottoms.

### **14.3.3. Storage and Handling Emissions**

Generally, tank emissions are estimated using the methods outlined in Section 5.2 in the Code where the composition of the vapour phase in the tanks (U.S. EPA Section 7.1/Raoult's Law) and not the liquid is used in the emissions estimation. Since PAHs typically have relatively low vapour pressures at atmospheric temperatures, emission estimates tend to be minimal from these sources, but individual refineries may want to check emissions using refinery tankage specifications.

Loading operations emissions are estimated using the methods in Section 6.2 using emission factors from Table 6-1 and Table 6-2. Emission factors tend to decrease significantly for the heavier liquids (jet kerosene, distillates, etc.) resulting in small amounts of emissions. Individual refineries may want to check the significance of these emissions.

### **14.3.4. Catalytic Cracking Units**

Two references are suitable. The EPA L&E factors (Table 4.5-1, Page 4-286, EPA-454/R-98-014) may be used. In general, the factors listed differentiate between different control types. Factors are listed for both fluid CCUs (FCCU) and moving-bed cracking units and are rated as D/E. Alternatively, the ExxonMobil Study document, "Emission of Trace Compounds from Catalytic Cracking Regenerators," based on 1995 field test data can be used. It uses emissions data from CCUs submitted by API members and provides a more comprehensive list of substances, although different control measures are not always accounted for, and averages are applied in certain circumstances. Both documents should be examined before selecting the appropriate emission factors to use.

Note: On control devices in the Reference 5 report, there appears to be an error on the first page in Table 4.5-1 where the lower emission factors for the repeated 5 PAHs (B(a)P to B(e)P) are for CO boiler controlled FCCUs. However, the text states that "Another way to reduce POM emissions from the catalyst regenerators is to achieve more complete combustion of CO to CO<sub>2</sub>. Processes such as the Universal Oil Products (UOP) hot regeneration and Amaco Ultracat have been developed to aid in the achievement of lower overall POM emissions" - no emission factors are provided for these types of units.

Site specific emission sampling and analysis will provide more representative results.

### **14.3.5. Combustion Sources**

PAHs are both combusted and generated as by-products in refinery boilers, process heaters, process equipment, and flares. According to the US EPA (US EPA, 1998), the general tendency for the combustion of various fuels to form PAH compounds increases from distillate oil, to residual oil, to waste oil, to wood, to coal. Other combustion characteristics, such as equipment operation and maintenance, also affect PAH emissions. Concentrations of PAHs have been shown to decrease rapidly with increasing temperature.

The extremely low concentration of trace combustion products makes both sampling and analysis difficult and costly. This has resulted in limited availability of data and in a wide variation in the reported concentrations of individual species. A study sponsored by API/WSPA has found that:

- PAH emission factors for liquid fired sources are higher than for gas fired sources;
- Factors for natural gas and refinery fuel gas firing are similar; and
- NOx emission controls had little impact on the emission factors

The API/WSPA report (1998) lists emission factors for most of the PAHs required for NPRI reporting. The Crude/Pipeline Oil Fired, Fuel Oil No. 6 Fired, and Gas Fired external combustion emission factors that are listed have EPA ratings of C/D, D and A respectively. In the EPA Emission Estimation Protocol for Petroleum Refineries (US EPA, 2015), there is a list of consolidated and comprehensive combustion emission factors, including those from the API/WSPA study and current factors from the AP-42 manual (US EPA, 2011), that members can refer to.

### **14.3.6. Direct Measurements**

Releases to land treatment, surface impoundment, incidents, water effluent, and off-site transfers can all be estimated using a material balance approach, whereby the total weight of a given waste is multiplied by concentration data from analysis of the waste when available. ECCC's guidance on interpretation of non-detect data (see Section 3.3.4) should be followed when calculating PAH releases and transfers.

## **14.4. IMPROVEMENT OPTIONS**

1. Site specific information, including analysis of refinery and waste streams.

## **14.5. REFERENCES**

1. "Speciation and Quantification of PAH Compounds in Refinery Streams and Products", report prepared for the Canadian Petroleum Products Institute by C. E. McGarvey, PhD., Imperial Oil Products and Chemicals Division, Sarnia Research Centre, March 2001.
2. "Guideline for Emission Calculation, Record Keeping and Reporting for Airborne Contaminant Discharge". Ontario Ministry of the Environment, Conservation, and Parks, MECP Publication No. 4099e03, revised December 2007.
3. "Fate of Polynuclear Aromatic Hydrocarbons in Refinery Waste Applied to Soil". PACE Report No. 88-1, May 1988.
4. "Air Toxics Emission Factors for Combustion Sources Using Petroleum-Based Fuels, Development of Emission Factors Using API/WSPA Approach", API Document # 348, August 1, 1998.
5. "Locating and Estimating Air Emissions from Sources of Polycyclic Organic Matter", July 1998, US EPA 454/R-98-014, <https://www3.epa.gov/ttnchie1/le/pompta.pdf>
6. "Emission of Trace Compounds from Catalytic Cracking Regenerators", Bertrand, Rene R and Jeffrey H. Siegell, ExxonMobil Research and Engineering Company, Virginia, US, 2002.
7. "Speciation and Quantification of PAH Compounds in Refinery Waste Streams", report prepared for the Canadian Petroleum Products Institute by Levelton Consultants Ltd., November 2009.
8. "Emission Estimation Protocol for Petroleum Refineries", Version 3, prepared by RTI International for the US EPA, April 2015. <https://www.epa.gov/air-emissions-factors-and-quantification/emissions-estimation-protocol-petroleum-refineries>
9. "Guide for Reporting to the National Pollutant Release Inventory 2022-2024", Environment and Climate Change Canada, 2022. <http://publications.gc.ca/pub?id=9.506026&sl=0>

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**Table 14-1 Average Concentrations of PAHs in Refinery Streams (from 2001 CPPI Study)**

Substance Name	Average Stream Composition (mg/kg)																				
	Crude	Gas	Diesel	HFO	CC Bttm	Lube Dist	Asphalt	AGO	VGO	LCO	HCO	HC Dist	HC GO	HC Bttm	Cat Feed	ATB	TC Res	HP VD	LP VD	Jet	Arom
Acenaphthene	14.8	7.3	77.1	162.3	70.5	0.0	0.0	35.7	14.9	1245.3	217.4	4.6	0.0	0.0	59.8	10.2	0.0	0.0	0.0	29.3	20.9
Acenaphthylene	2.5	0.0	1.9	0.0	3.6	0.0	0.0	2.1	1.6	13.1	2.2	0.0	0.0	0.0	3.4	0.0	0.0	0.0	0.0	0.0	2.6
Anthracene	2.8	9.2	6.0	72.8	122.3	0.0	0.0	11.3	22.5	508.1	740.0	0.0	1.2	0.0	44.7	0.0	3.4	0.0	0.0	5.0	15.1
Benzo(a)anthracene	6.4	5.3	2.5	144.9	1098.7	46.3	0.0	7.9	8.3	11.3	344.0	0.0	0.0	0.0	33.5	11.0	0.0	2.6	65.0	0.0	14.4
Benzo(a)pyrene	2.4	2.4	0.0	127.6	729.3	0.0	0.0	2.3	3.6	1.6	61.4	0.0	0.0	1.5	20.3	7.9	0.0	0.0	0.0	0.0	4.4
Benzo(b+j)fluoranthene	6.1	4.1	0.0	67.4	430.7	36.0	0.0	6.6	12.9	3.5	49.0	0.0	0.0	0.0	27.2	14.7	0.0	6.8	34.3	0.0	10.6
Benzo(e)pyrene	6.5	2.7	2.5	83.8	435.3	37.3	0.0	7.3	12.3	2.0	38.6	0.0	0.0	17.3	23.0	16.0	0.0	10.2	17.3	3.9	14.9
Benzo(ghi)perylene	3.6	3.1	9.3	70.0	232.5	0.0	0.0	8.8	4.1	0.0	12.5	0.0	69.0	177.0	5.7	6.7	0.0	19.0	0.0	4.3	106.2
Benzo(k)fluoranthene	2.3	4.1	0.0	11.1	79.8	2.2	0.0	3.3	2.7	0.0	5.8	0.0	0.0	2.7	4.8	4.9	0.0	0.0	7.3	0.0	4.0
Chrysene	25.7	3.0	4.3	256.9	2022.7	216.7	8.2	28.9	66.5	13.5	680.0	0.0	4.4	0.0	102.0	52.0	37.0	9.9	273.3	6.8	31.4
Dibenzo(a,j)acridine	0.0	0.0	0.0	12.7	60.8	0.0	0.0	3.4	0.0	0.0	0.0	0.0	3.9	5.5	0.0	0.0	0.0	0.0	0.0	0.0	5.7
Dibenzo(a,h)anthracene	0.0	0.0	0.0	0.0	102.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.0
Dibenzo(a,i)pyrene	0.0	0.0	2.6	9.4	122.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.2	0.0	0.0	0.0	0.0	0.0	0.0	4.6
Fluoranthene	5.7	3.0	10.2	34.1	118.3	3.2	0.0	15.9	12.5	88.1	390.0	8.0	1.3	6.9	18.5	9.9	0.0	0.0	7.1	0.0	15.3
Fluorene	73.5	13.5	241.5	272.4	143.9	0.0	2.9	131.6	133.3	1960.0	546.0	3.6	0.0	0.0	99.7	97.0	3.9	0.0	2.0	19.5	25.0
Indeno(1,2,3-cd)pyrene	2.4	3.6	3.0	0.0	60.4	0.0	0.0	3.9	0.0	0.0	0.0	0.0	12.6	17.6	0.0	0.0	0.0	0.0	0.0	0.0	12.9
Naphthalene	368.4	4150.0	756.5	630.7	279.1	0.0	2.1	228.0	292.1	4713.3	880.0	44.4	0.0	7.5	267.7	166.7	6.2	1.4	0.4	796.7	6901.9
Perylene	1.6	2.2	1.4	31.4	147.6	1.6	0.0	2.1	2.9	0.0	15.9	0.0	0.0	3.9	7.6	4.3	0.0	0.0	2.9	1.7	3.0
Phenanthrene	139.8	18.8	356.9	707.9	948.7	6.4	6.3	316.5	461.3	4268.7	5140.0	6.5	18.0	2.7	281.7	246.7	17.5	1.9	43.0	17.5	41.2
Pyrene	42.7	4.1	73.3	308.6	1074.7	20.0	3.5	152.2	51.2	361.8	2260.0	39.4	8.5	85.2	121.3	24.7	37.0	0.0	24.3	13.9	121.3
7H-Dibenzo(c,g)carbazole	0.0	0.0	0.0	0.0	52.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

See Section 14.2 for associated substance CAS numbers.

**LEGEND** – Crude - Crude Oil; Gas -Gasoline; HFO - Heavy Fuel Oil ; CC Bttm - Cat Cracker Bottoms; Lube Dist. – Lube Distillate; Asphalt - Asphalt (oxidized vs. straight run paving grade); AGO - Atmospheric Gas Oil; VGO - Vacuum Gas Oil; LCO - Light Cycle Oil (cat cracker distillate); HCO - Heavy Cycle Oil (cat cracker gas oil); HC Dist. - Hydrocracker Distillate; HCGO - Hydrocracker Gas Oil (covers cracked lube basestock); HC Bttm - Hydrocracker Bottoms; Cat Feed - Cat Cracker Feed; ATB - Atmospheric Bottoms; TC Res - Thermal Cracker Residue (visbreaker); HPVD – Heavy Paraffin Vacuum Distillate; LPVD – Light Paraffin Vacuum Distillate; Jet – Jet Fuel; Arom - Aromatic Extract Streams (heavy distillate extract, pole oil).

Note - Solvent extracted (straight run) lube base stock results were all below detection limits.

**Table 14-2 Average Concentrations of PAHs in Waste Streams (from 2007 CPPI Study)**

Substance Name	Average Waste Stream Composition (mg/kg) *										
	Biox	API Sep	IAF/DAF	Slop Oil	Crude	H/D OP	HX	Spent	Phen	Sulph	Cat Frac
1-Methylnaphthalene	ND	ND	ND	ND	ND	ND	ND	ND	ND	160000.0	ND
2-Methylnaphthalene	ND	ND	ND	ND	ND	ND	ND	ND	ND	320000.0	ND
3-Methylcholanthrene	7.6	119.0	69.8	7.4	ND	1.3	ND	1892.0	9119.9	ND	165.4
5-Methylchrysene	8.2	ND	8.6	8.5	ND	12.5	ND	ND	ND	ND	883.5
7H-Dibenzo(c,g) Carbazole	ND	3.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acenaphthene	11.1	89.2	195.6	119.1	15.3	125.1	10.7	7.7	990.5	2300.0	105.4
Acenaphthylene	2.9	23.6	49.8	151.9	3.9	44.8	1.5	5.6	149.9	ND	17.8
Anthracene	30.1	21.8	123.2	85.6	ND	11.9	3.6	ND	ND	ND	163.5
Benzo (a) anthracene	2.4	27.7	9.9	16.5	5.3	13.9	2.3	ND	ND	ND	866.5
Benzo (a) pyrene	0.6	21.3	3.8	6.6	ND	7.6	0.7	ND	37.5	20.0	649.2
Benzo(b+j)fluoranthene	0.9	10.7	6.9	5.3	ND	5.8	ND	ND	ND	ND	370.4
Benzo(e)pyrene	1.4	17.9	7.9	5.0	ND	7.3	2.1	ND	ND	ND	612.4
Benzo (g,h,i) perylene	1.6	10.6	11.7	3.3	ND	1.8	3.1	ND	ND	ND	241.7
Benzo (k) fluoranthene	ND	2.5	ND	2.3	ND	2.2	ND	ND	ND	ND	44.0
Chrysene	5.2	30.0	11.4	14.0	4.9	16.0	1.0	ND	ND	ND	978.7
Dibenzo(a,e)pyrene	ND	3.8	ND	ND	ND	3.7	ND	ND	ND	ND	41.7
Dibenzo(a,h)anthracene	ND	2.5	ND	ND	ND	1.5	ND	ND	ND	ND	120.3
Dibenzo(a,h)pyrene	ND	1.0	ND	ND	ND	1.6	ND	ND	ND	ND	56.6
Dibenzo(a,i)pyrene	ND	1.4	ND	ND	ND	7.5	ND	ND	ND	ND	ND
Dibenzo(a,j) acridine	ND	ND	ND	ND	ND	3.6	ND	ND	ND	ND	34.4
Fluoranthene	4.1	29.4	17.3	44.8	3.7	39.6	0.9	ND	138.3	220.0	313.5
Fluorene	17.6	100.7	164.8	165.2	28.8	40.5	31.6	9.2	1046.6	2800.0	123.8
Indeno(1,2,3-c,d)pyrene	ND	2.9	ND	2.2	ND	1.5	ND	ND	ND	ND	111.9

## Canadian Fuels Association Codes of Practice – Refineries and Terminals

Substance Name	Average Waste Stream Composition (mg/kg) *										
	Biox	API Sep	IAF/DAF	Slop Oil	Crude	H/D OP	HX	Spent	Phen	Sulph	Cat Frac
Naphthalene	80.7	367.0	1342.8	714.6	105.3	538.6	4.4	872.4	84792.5	240000.0	286.7
Perylene	0.8	5.4	6.5	2.4	ND	2.0	ND	ND	ND	ND	103.0
Phenanthrene	44.2	504.8	330.9	340.0	73.2	199.3	16.1	6.2	2364.9	6900.0	1132.5
Pyrene	15.0	87.5	30.5	92.7	10.5	115.4	5.1	ND	464.9	1200.0	1574.2

\* Concentration is based on mass of total sample (oil/water/solids); ND = Not detected

See Section 14.2 for associated substance CAS numbers.

**LEGEND** – Biox - Biox sludge; API Sep - API Separator sludge; IAF/DAF - IAF/DAF sludge; Slop Oil - Slop oil tank sludge/emulsion; Crude - Crude tank sludge; H/D OP - Holding/diversion (oily) pond; HX - Heat exchanger cleaning solids; Spent - Spent treating clay; Phen - Phenolic spent caustic; Sulph - Sulphidic spent caustic; Cat Frac - Cat. Frac. bottoms.

Note – Desalter sludge stream results were all below detection limits.

## 15. CRITERIA AIR CONTAMINANTS (CAC)

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### 15.1. CAC REQUIREMENTS

#### 15.1.1. Facility and Stack Height Criteria

NPRI is requiring the reporting of CACs released into the air, subdivided into stack and other point sources, storage tank and related handling releases, fugitive emissions, spills or other accidental releases, unpaved road dust or other non-point releases. Stacks include point sources, vents, ducts, pipes, or other confined process streams that release to air.

If the thresholds in Table 15-1 are met, then for each stack  $\geq 25$  metres above grade and the average annual stack temperature is either above 50°C or not measured, CAC and speciated VOCs must be reported.

**Table 15-1 Facility-wide and stack-specific release threshold for CACs and speciated VOCs**

CAC Substances (Part 4)	Facility-wide Release Threshold (tonnes)	Stack Release Threshold (tonnes)
Carbon Monoxide	20	10
Nitrogen oxides (expressed as NO <sub>2</sub> )	20	10
Sulphur Dioxide	20	25
Total Particulate Matter	20	25
PM <sub>10</sub>	0.5	0.5
PM <sub>2.5</sub>	0.3	0.25
Volatile Organic Compounds (total)	10	5
Speciated VOCs (Part 5)	1*	0.25*

\* The 1 tonne facility wide threshold and 0.25 tonne stack threshold applies to each of the speciated VOCs individually, as opposed to the total of speciated VOCs.

If reporting criteria are met, the facility must report for each stack or flare:

- Quantity of substance released for each of the following categories:
  - Stationary fuel combustion for energy purposes
  - Combustion of fuel for non-energy purposes
  - Flaring
  - Use of fuels for non-energy purposes
  - Releases from all other sources not included in the above categories.



- Stack height above grade; Effective stack height for flares
- Inner physical diameter of stack; Effective stack diameter for flares
- Average exit velocity (can use permit data if available), and
- Average exit temperature (can use permit data if available).

When a quantity is reported for a stack under any of the first four categories above, the fuel type(s) for that release must also be reported, categorized as follows:

Solid fossil fuels – includes coal, petroleum coke, coke (from metallurgical coal, coke breeze)

Liquid fossil fuels – refined petroleum products – includes heavy fuel oil (HFO), Light fuel oil (LFO), kerosene, diesel fuel, gasoline, naphtha

Gaseous fossil fuels – includes natural gas, an odourless mix of hydrocarbons predominantly made up of methane.

Natural Gas Liquids – includes propane, butane, ethane, other natural gas liquids

Industrial production by-products used as fuel – includes coke oven gas, blast furnace gas, basic oxygen furnace gas, spent pulping liquor, refinery still gas, hydrogen, chemical plant fuel gases

Biomass/biofuels – includes wood and wood biproducts/residues, agricultural waste, peat, biochar, charcoal, ethanol, biodiesel, glycerol, bio-oil/pyrolysis oil, biogas, syngas, biobutanol, other wastes

Waste materials – includes tires, plastics, municipal solid waste, used oil and lubricants, sewage sludge, asphalt shingles, refuse derived fuel, other wastes

Other fuels – any other substances or materials used as fuel that does not fall under any of the categories above.

Facilities must report the geographical coordinates (latitude and longitude) of a stack in decimal degrees to at least five decimal places. Provincial identification numbers of each stack must also be provided, where applicable. As well, facilities must report CAC releases to air for each electricity generation unit that meet the following two criteria:

1. The unit has a capacity of 25 MW or more and
2. The unit distributes or sells to the grid 33% or more of its potential electrical output (during the current or previous years).

An electricity generation unit means physically connected equipment that operates together to produce electricity for sale or distribution to the grid by means of thermal energy and is stationary when used and is not in or on a machine that is self-propelled. Potential electrical output means the quantity of electricity that would be generated by a unit in a calendar year if the unit were to operate at capacity at all times during that

calendar year. The 33% threshold must be assessed on an annual basis. If a unit meets the 33% threshold in a calendar year, but does not meet it in the subsequent year, reporting at the unit level for that unit is still required. Facilities that meet the threshold requirements for unit-level reporting must also provide details about the unit, including:

- unit gross generating capacity
- commissioning year
- technology or fuel type
- whether the unit includes emissions from duct firing or other secondary combustion sources
- air pollutant controls installed and operating on the unit

### **15.1.2. Exemptions**

Reporting is not required for a CAC if **all** of the following criteria are met:

- the only release to air occurs from stationary, external combustion equipment;
- the cumulative nameplate capacity of that equipment is **less than** 10 million BTU/hour; **and**
- the only type of fuel combusted in that equipment is commercial grade natural gas, liquefied petroleum gas, Number 1 or 2 fuel oil, or any combination thereof.

Individual stack reporting is not required for a CAC for:

- stacks and vents from storage tanks that emit releases at or near ambient temperature. Releases from these tanks still need to be reported at the facility level.
- stacks with an exit temperature less than 50°C as long as the exit temperature was determined through measurement.

## **15.2. SULPHUR DIOXIDE**

This section will assist refineries in quantifying their emissions of sulphur oxides. For the purpose of reporting, only SO<sub>2</sub> emission are required by NPRI and not SO<sub>x</sub>. The quantities of sulphite or sulphur trioxide (SO<sub>3</sub>) and sulphates (SO<sub>4</sub>) should not be included when reporting to NPRI.

When emission factors are used for estimation purposes, it is possible that only SO<sub>x</sub> factors are available for some processes. In these cases, the SO<sub>x</sub> factor can be used to give a conservative SO<sub>2</sub> estimate since only a small percentage of the sulphur will be emitted as other sulphur oxides. However, an equivalent H<sub>2</sub>SO<sub>4</sub> emission should be subtracted from the total sulphur oxides estimates to obtain emissions of SO<sub>2</sub>. H<sub>2</sub>SO<sub>4</sub> and COS are not CACs but are included in this section for completeness.

### **15.2.1. Requirements**

Emissions from all aspects of refinery operation should be included:

- combustion of fuel oil in heaters/boilers,
- combustion of coke,
- flare emissions,
- sulphur plant incinerator emissions, and
- Catalytic Cracking Units (CCU) emissions.

#### **15.2.1.1. Combustion Emissions**

For heater and boiler combustion related SO<sub>2</sub> emissions, assume all of the sulphur in the fuel is emitted as SO<sub>2</sub>. Estimate the average amount of sulphur contained in the fuel and multiply by the tonnes of fuel burned. Convert tonnes of sulphur into SO<sub>2</sub> by multiplying by 2 (from molecular weight ratios). If both heavy fuel oil and refinery fuel gas is used as fuel, most of the SO<sub>2</sub> emissions will come from the heavy fuel oil. Sweet refinery fuel gas typically has a sulphur content ranging between 10 – 30 ppm. When using the emission factor method, emissions may be adjusted to specific higher heating values (HHV) by multiplying the given emission factor by the ratio of the specified heating value to the average heating value.

For coke burning, use an estimate of sulphur content in the coke, as determined by the refinery based on a calculation using the sulphur content of the feed.

#### **15.2.1.2. Flare Emissions**

For flares, it can be assumed that normally the gas flared is sweet (no sulphur) or alternatively assume a nominal amount of sulphur if that is more representative of your facility. Some empirical testing has shown sulphur levels in flare gas of 0.2 – 0.5%. The sulphur content is especially important to consider if a flare gas recovery system is not in place because flared volumes are higher.

For flaring during upsets or shutdowns/start-ups, use operational records that track these events to determine source and likely sulphur content and volume of flared gas. Use this to estimate sulphur content of gas burned. Sample calculations for estimating emissions from flares are provided in Appendix D.

#### **15.2.1.3. Sulphur Plant Incinerator Emissions**

Emissions of SO<sub>2</sub> from sulphur plants are usually from the incinerator stack. In most jurisdictions, sulphur recovery efficiency is reported and SO<sub>2</sub> emissions are calculated as part of the operating approval. Use the regulatory approved method of calculating SO<sub>2</sub> emissions. Typically, this involves calculating incinerator stack losses based on the amount of sulphur produced and the sulphur plant recovery. Assume all sulphur that is not recovered is emitted through the incinerator stack. New emission factors for

other pollutants have been published by the US EPA in 2015 and these are shown in Sections 15.3 (NO<sub>x</sub>), 15.4 (VOC) and 15.5 (CO). However, membership feedback indicated that the impacts of variations in unit configuration have not been considered during the development of these EPA factors, especially with respect to the various tail gas treatment technologies in use in the industry which varies depending upon the type of amine used, the desired chemical reactions, the catalyst, and tail gas thermal oxidation/incineration design. Hence, caution is recommended in determining the appropriateness of available emission factors prior to use.

#### **15.2.1.4. Catalytic Cracker Unit (CCU) Emissions**

Some refinery CCUs may be equipped with continuous emission monitoring systems (CEMS) that measure pollutant concentrations, such as SO<sub>2</sub>, in the exhaust gas. This method is deemed the most accurate and the concentration data obtained should be used in emissions estimation when available. In the absence of CEMS data, use sulphur content in the coke, as determined by the refinery based on a calculation using the sulphur content of the feed. Alternatively, the US EPA has compiled emission factors for the Petroleum Industry (AP-42 Table 5.1-1) for SO<sub>x</sub> emissions (expressed as SO<sub>2</sub>). The preferred approach is to use site specific emission or sulphur content measurements where available.

### **15.2.2. H<sub>2</sub>SO<sub>4</sub>**

Studies by API indicate that sulphuric acid mist can be formed in stack gases under the right conditions. Since H<sub>2</sub>SO<sub>4</sub> is a NPRI reportable substance, it must be reported if it is formed.

The NPRI requirement is to report H<sub>2</sub>SO<sub>4</sub> from all sources. For combustion sources, only H<sub>2</sub>SO<sub>4</sub> formed in the stack is reportable. Any H<sub>2</sub>SO<sub>4</sub> formed after leaving the stack is not reportable.

In the past, most refineries have assumed that all of the sulphur in the fuel is converted to SO<sub>2</sub>. However, a small portion of the sulphur is further oxidized to SO<sub>3</sub>. Under the right conditions (temperature and moisture), some amount of the SO<sub>3</sub> is subsequently converted to H<sub>2</sub>SO<sub>4</sub> in the stack.

Currently, there is no commonly agreed to methodology available from EPA or API to estimate H<sub>2</sub>SO<sub>4</sub> releases from refineries. Table 15-2 summarizes the key information gathered from US sources and presents a suggested Canadian Fuels approach for NPRI reporting. It is likely that changes will be made in future years as this issue develops further. As with all other suggested methodologies in the Codes, if a company or refinery has better data (e.g. stack sampling) it would take precedence over this methodology.

The main sources of SO<sub>2</sub> from the refinery need to be individually assessed to determine the quantity of H<sub>2</sub>SO<sub>4</sub> formed. The main SO<sub>2</sub> sources from refineries are: fuel gas burning, fuel oil burning, FCCU, coker, sulphur plant incinerator, and flaring. Section 15.2.2.1 outlines the recommended general approach, together with sample

calculations. Further details for each of the H<sub>2</sub>SO<sub>4</sub> sources are provided in the subsequent sections.

**15.2.2.1. General Methodology**

For general screening for combustion sources, determine if the temperature of the source is above or below the dew point temperature. If the stack gas temperature is above the dew point temperature, the formation of H<sub>2</sub>SO<sub>4</sub> in the stack is unlikely. If the stack gas temperature is at or below the dew point, the following methodologies may be considered.

The steps for estimating H<sub>2</sub>SO<sub>4</sub> emissions are as follows:

1. Calculate total amount (mass) of sulphur in the fuel burned.
2. Calculate the portion of the sulphur converted to SO<sub>3</sub> (percentage of the total sulphur) using Table 15-2.
3. Calculate the amount of sulphur converted from SO<sub>3</sub> to H<sub>2</sub>SO<sub>4</sub>. Use Figure 1 or Figure 2 if stack temperature is available, otherwise use Table 15-2.
4. Calculate the tonnes of H<sub>2</sub>SO<sub>4</sub> by multiplying the sulphur from step 3 by ratio of the molecular weights.
5. Calculate the tonnes of SO<sub>x</sub> emitted as SO<sub>2</sub> by multiplying the total sulphur less step 3 sulphur, times the ratio of the molecular weights.

**Table 15-2 Recommended Factors for Use in H<sub>2</sub>SO<sub>4</sub> Calculations<sup>a</sup>**

Combustion Source/Fuel	Conversion of SO <sub>2</sub> to SO <sub>3</sub> (weight%)		Stack Water Content		Default Conversion to H <sub>2</sub> SO <sub>4</sub> if Stack Temp not Available
	Range Used in US Papers	Recommended Value for use	Range (vol%)	Typical (vol%)	
Refinery Fuel Gas	1-5%	5%	14-18	16	90%
Refinery Fuel Oil	2-3%	2%	9-12	11	90%
FCCU/Coker	1-3%	1%	14-18	17	90%
SRU TG Inc	2-5%	2%	20-25	22	90%
Flare – Acid Gas	1-2%	2%	10-25	17	0% <sup>b</sup>
Flares – Normal	1-5%	5%	10-25	17	0% <sup>b</sup>

<sup>a</sup> Based on an assessment of available data, primarily Shell Canada Products and ExxonMobil data from US presented at the API TRI workshop, April 15/16, 2003.

<sup>b</sup> Can be assumed that no NPRI reportable H<sub>2</sub>SO<sub>4</sub> is formed from flare operation (flame temp. too high).

### Sample calculation steps for estimating H<sub>2</sub>SO<sub>4</sub> emissions

#### Example 1 – Calculation for Fuel Oil (Stack Temp Unknown)

Sulphur MW = 32

SO<sub>2</sub> MW = 64

SO<sub>3</sub> MW = 80

H<sub>2</sub>SO<sub>4</sub> MW = 98

Assume fuel oil with 2.5 weight% sulphur

Yearly consumption of 100,000 tonnes

Sulphur in fuel oil burned = 100,000 \* .025 = 2,500 tonnes

Amount of sulphur converted to SO<sub>3</sub> = 2,500 x .02 = 50 tonnes

Amount of sulphur converted to H<sub>2</sub>SO<sub>4</sub> = 50 x 0.9 = 45 tonnes

(using default conversion of 90%; 45 tonnes of sulphur emitted as H<sub>2</sub>SO<sub>4</sub>)

Tonnes of H<sub>2</sub>SO<sub>4</sub> emitted = 45 x 98/32 = 138 tonnes

#### Example 2 – Calculation for Fuel Oil (Stack temperature of 600 F)

Same as example 1 except stack temperature is known

As in example 1 amount of sulphur in fuel converted to SO<sub>3</sub> = 50 tonnes

Using Figure 1, and water content of 11 vol%, the conversion to H<sub>2</sub>SO<sub>4</sub> ~ 76%

Amount of sulphur converted to H<sub>2</sub>SO<sub>4</sub> = 50 x .76 = 38 tonnes

(38 tonnes of sulphur emitted as H<sub>2</sub>SO<sub>4</sub>)

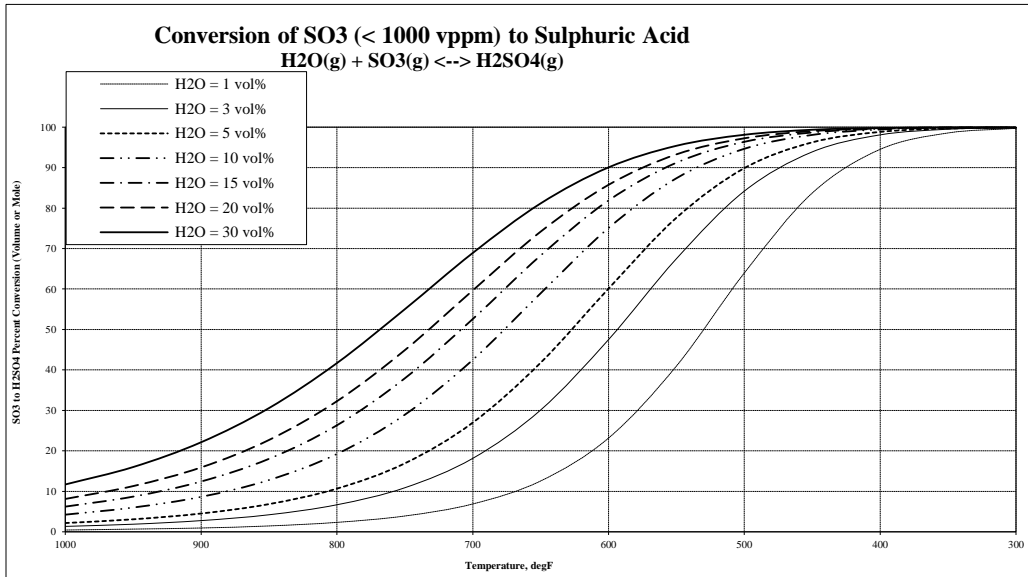
Tonnes of H<sub>2</sub>SO<sub>4</sub> emitted = 38 x 98/32 = 116 tonnes

#### Example 3 – Estimation of the Conversion of SO<sub>3</sub> to H<sub>2</sub>SO<sub>4</sub> for a Given Stack Temperature and Moisture content

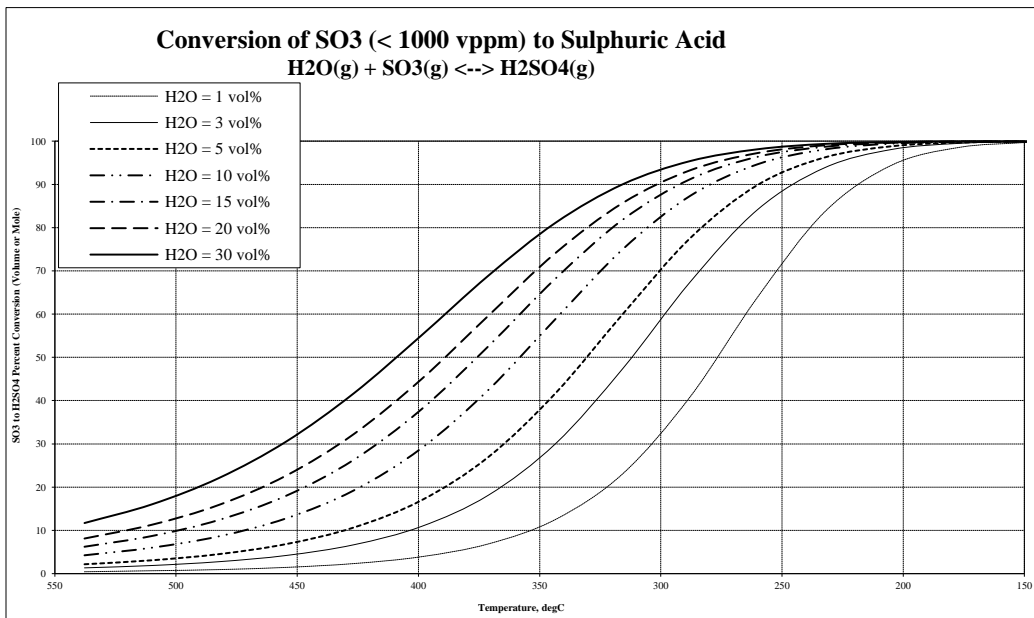
Figure 1 and Figure 2 can be used to estimate SO<sub>3</sub> to H<sub>2</sub>SO<sub>4</sub> conversion for a given stack temperature and moisture content.

These figures are taken from an ExxonMobil paper “Estimating Sulfuric Acid Emissions from Boilers and Fired Heaters”, by R. D. Springer, I. D. Crane, J. H. Siegell, ExxonMobil Research and Engineering Company, 3225 Gallows Road, Fairfax, Virginia 22037, 703-846-3641.

**Figure 1 - Conversion of SO<sub>3</sub> to H<sub>2</sub>SO<sub>4</sub> (°F)**



**Figure 2 - Conversion of SO<sub>3</sub> to H<sub>2</sub>SO<sub>4</sub> (°C)**



**15.2.2.2. Fuel Oil Combustion**

The amount of sulphur converted to SO<sub>3</sub> in the combustion of fuel oil varies and seems to depend on the amount of sulphur in the fuel. With the limited data available, a value of 2.0 weight% of the sulphur in the fuel oil converted to SO<sub>3</sub> is recommended in Table 15-2.

Data from ExxonMobil, as shown in Figure 1 and Figure 2 in Example 3 of the sample calculations, can be used to determine the conversion of SO<sub>3</sub> to H<sub>2</sub>SO<sub>4</sub> using stack temperature and moisture. If stack moisture data is not readily available, the default values given in Table 15-2 can be used. If the stack temperature is unknown, use 90% conversion to H<sub>2</sub>SO<sub>4</sub>.

**15.2.2.3. Fuel Gas Combustion**

The available data shows considerable variation in the amount of sulphur in fuel gas that is converted to SO<sub>3</sub>. The recommended conversion to SO<sub>3</sub> is 5.0 weight%.

Figure 1 or Figure 2 can be used to determine the amount of conversion of SO<sub>3</sub> to H<sub>2</sub>SO<sub>4</sub>. The stack water content data shown in Table 15-2 can be used if no other information is available. If stack temperature is unknown, use 90% conversion to H<sub>2</sub>SO<sub>4</sub>.

**15.2.2.4. Sulphur Plant**

The recommendation is to use 2% conversion to SO<sub>3</sub>. However, in many cases, the stack top temperature for a sulphur plant incinerator is >538°C, resulting in no conversion of SO<sub>3</sub> to H<sub>2</sub>SO<sub>4</sub>.

**15.2.2.5. Catalytic Cracking Units (CCU's)/Coker**

There is no EPA guidance for FCCU or Cokers; however, Imperial Oil Limited and Shell US have done some testing of FCCU stacks with typical results varying from 0-8 weight%.

Figure 1 or Figure 2 can be used to determine the amount of conversion of SO<sub>3</sub> to H<sub>2</sub>SO<sub>4</sub>. The stack water content data shown in Table 15-2 can be used if no other information is available. If stack temperature is unknown, use 90% conversion to H<sub>2</sub>SO<sub>4</sub>.

**15.2.2.6. Flaring – Acid Gas and Normal**

Table 15-2 recommends using 2 weight% conversion to SO<sub>3</sub> while flaring acid gas and 5 weight% during normal flaring. However, the Canadian Fuels recommendation is to report nil H<sub>2</sub>SO<sub>4</sub> from flaring of any kind because the flame temperature is higher than the condensation point of H<sub>2</sub>SO<sub>4</sub>. Any condensing of H<sub>2</sub>SO<sub>4</sub> would occur in the atmosphere and therefore not be reportable to NPRI.



### 15.2.3. Improvement Options

An improvement option for H<sub>2</sub>SO<sub>4</sub> would be to conduct actual stack tests (a combination of CFR Method 8-Determination of Sulphuric Acid Mist and SO<sub>2</sub> emissions from Stationary sources and CFR Method 5b-Determination of Non-Sulfuric Acid Particulate Matter Emissions from Stationary Sources) to attain appropriate percentages of SO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and SO<sub>2</sub>.

### 15.2.4. Carbonyl Sulphide

#### 15.2.4.1. Background

Carbonyl sulphide (COS) is an NPRI Part 1 Group A substance, and reporting is required if the applicable 10 tonne MPO threshold is met.

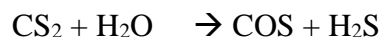
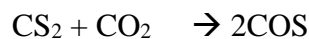
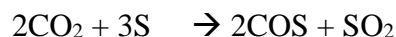
This substance is predominantly a by-product (See Appendix A - 2 By-product emissions) and is potentially present in emissions from refinery sulphur plant operations, FCCU, and combustion sources. In the US, refineries have been reporting COS releases, primarily to air, to the Toxics Release Inventory (TRI) for some time. ECCC considered the reported COS quantities significant, which prompted the addition of this substance to the NPRI list.

The following sections outline available methodologies for estimating COS releases should site specific data not be available.

#### 15.2.4.2. Estimation Methodologies

##### *Sulphur Plant*

COS can be formed by a number of processes in the Claus reaction furnace and is usually destroyed before becoming emissions from a stack. Possible formation reactions are shown below.



Although U.S. refineries have been reporting COS releases to TRI for some time, the methodologies used to determine such releases are not readily available in public literature. In a presentation by Shell Global Solutions, potential COS releases from a 100 LTPD sulphur recovery plant were estimated and the resulting emission factors are

shown in Table 15-3. Stack sampling data, if available, should be used instead of the preliminary factors shown.

**Table 15-3 Preliminary COS Emission Factors from a 100 LTPD Sulphur Recovery Plant**

Process Units	COS Emission Factors (lb/ton S produced)
SRU	28.8
TGTU	1.44
Incinerator	0.0036*

\* Based on average release.

***Fluidized Catalytic Cracking Unit***

As reported by Shell US, COS concentrations in the range of 50 to 500 ppmv are common in gasification and partial combustion applications such as FCCU, fluid cokers, and gasifiers. A single emission factor was found in the California Air Toxics Emission Factors Database (CATEF) and is shown in Table 15-4.

**Table 15-4 COS Emission Factors for Fluid Catalytic Cracking Unit (SCC 30600201)**

Material Type	Control Device	Emission Factors (lb/MBar)		
		Maximum	Mean	Median
Refinery Gas/Oils	Electrostatic Precipitator / CO Boiler	0.168	0.168	0.168

MBar = 10<sup>3</sup> barrels.

***Other Combustion Sources***

In other combustion processes, COS can potentially form if the fuel contains sulphur compounds. Table 15-5 shows the range of COS emission factors found in the CATEF Database for process heaters.

**Table 15-5 COS Emission Factors for Process Heaters (SCC 30600106)**

Material Type	Control Device	Other Description	Emission Factors (lb/MMcf)		
			Maximum	Mean	Median
Refinery Gas	NO <sub>x</sub> Scrubber (NH <sub>3</sub> injection) / Selective Catalytic Reduction /None	EA<100%	0.974	0.947	0.956
	Selective Catalytic Reduction /None	EA>100%	2.43	2.16	2.25

EA = excess air over stoichiometric.

#### **15.2.4.3. Improvement Options**

1. Site specific measurement data, including analysis of refinery and waste streams, should be used if available.
2. Canadian Fuels members can consult with their U.S. colleagues to determine the appropriate estimation methodologies for their respective refining operations.

### **15.3. NITROGEN OXIDES**

This section will assist refineries in quantifying their emissions of nitrogen oxides. For the purpose of this inventory, all nitrogen oxides (NO<sub>x</sub>) are reported as NO<sub>2</sub>. However, various forms of nitrogen oxides (NO<sub>x</sub>) are produced during combustion. The majority of the NO<sub>x</sub> is in the form of NO but NO<sub>2</sub>, NO<sub>3</sub> and N<sub>2</sub>O are also present. In calculating NO<sub>x</sub> releases, both NO and NO<sub>2</sub>, expressed on a NO<sub>2</sub> equivalent basis, are to be included while N<sub>2</sub>O, a greenhouse gas, should be excluded for NPRI reporting.

Typically, NO<sub>x</sub> are formed from:

- a) the nitrogen in the combustion air (thermal NO<sub>x</sub>),
- b) the nitrogen found in the fuel being burned (fuel NO<sub>x</sub>).

The formation of NO<sub>x</sub> is dependent on many combustion conditions such as:

- fuel type,
- amount of excess air,
- fuel and combustion air inlet temperature,
- burner design,
- combustion chamber design, and
- gas residence time in the combustion zone.

Although the amount of nitrogen in the combustion air is usually much higher than that contained in the fuel, the nitrogen in the fuel is highly reactive and therefore, contributes more to the formation of NO<sub>x</sub>.

#### **15.3.1. Requirements**

As NO<sub>x</sub> formation is dependent on combustion conditions, the amount formed in different equipment and combustion processes will also vary. The US EPA has developed a range of emission factors (AP-42, Volume I, 5<sup>th</sup> Edition, 1998 and updates) that can be used within the oil and gas sector. Table 15-6 lists the AP-42 reference tables for common refinery equipment and processes.

The sulphur plant can be ignored as a source of NO<sub>x</sub> emissions, as ammonia is converted completely to nitrogen in the process.

**Table 15-6 NO<sub>x</sub> Emission Factor Reference Tables<sup>a,b</sup>**

<b>Equipment/Process Type</b>	<b>EPA AP-42 Table Reference</b>
Fuel Oil Combustion	Table 1.3-1
Natural Gas / Flue Gas Combustion	Table 1.4-1
Catalytic Cracking Units	Table 5.1-1
Refinery Flares	Table 13.5-1
Gas Turbines, Reciprocating Engines, Industrial Engines	Tables in Section 3.1 to 3.4
Claus Sulphur Recovery <sup>c</sup>	Table 8.13-2

<sup>a</sup> The AP-42 emission factors for nitrogen oxides are as NO<sub>2</sub>.

<sup>b</sup> Emission factors, except for sulphur recovery, are based on an average natural gas higher heating value of 1,020 Btu/scf. These may be converted to other natural gas heating values by multiplying the given emission factor by the ratio of the specified heating value to this average heating value.

<sup>c</sup> Emission factors are based on the quantity of sulphur produced and are applicable to sulphur recovery process equipped with combustion type controls such as thermal oxidizers. [Please refer to Section 15.2.1.3 regarding the applicability of new emission factors provided in AP-42 Table 8.13-2 (2015 version).]

Ensure that the correct emission factor is used for the size of the heater or boiler and type of burner. In addition, NO<sub>x</sub> emission measurements should be used where available, if they are representative of typical operating conditions.

### **15.3.2. Improvement Options**

Site specific emission factors or measurement data should be used when available. Alternatively, a detailed method for estimating NO<sub>x</sub> emissions, published by ExxonMobil and incorporated by CONCAWE in its Petroleum Refining Estimating Guide, can be used. For flares, data from the vendor is preferred over the use of generic emission factor if site specific information is not readily available.

## **15.4. VOLATILE ORGANIC COMPOUNDS (VOCS)**

### **15.4.1. Background**

This section provides methods to estimate emissions of VOCs that contribute to the formation of ground level ozone. The definition of VOC, as used by the US EPA, NPRI, and ON MECP varies somewhat. For the purpose of the Code of Practice, the NPRI definition is used. When reporting under Ontario Regulation 127, members should ensure that they are using the Ontario definition.

For the NPRI, VOC “means volatile organic compounds as defined in the *Proposed Order Adding Toxic Substances to Schedule 1 to the Canadian Environmental Protection Act, 1999*, published in the *Canada Gazette*, Part I, Vol. 136, No. 30 (Ottawa, Saturday, July 27, 2002)”. Specifically, “Volatile organic compound” or “VOC” means volatile organic compounds that participate in atmospheric photochemical reactions but excludes a list of specific substances or classes of substances on the basis of their negligible photochemical reactivity. The 2022-2024 list of substances excluded from the NPRI definition of VOC is shown in Appendix C of this Code. For NPRI threshold determination and reporting, ECCC also uses the physical chemistry definition of a VOC, which defines it as any compound that contains carbon and at least one other element and has a vapour pressure of greater than or equal to 2 mmHg (Seaman, 2004). Substances with vapour pressures greater than 2 mmHg, such as COS and CS<sub>2</sub>, are deemed to be VOCs by ECCC in this physical chemistry definition.

VOCs have the potential to contribute to the formation of ground level ozone or be hydrocarbons with low photo-reactivity. Through work on new sector codes, the CCME continues to identify additional substances that have negligible photo-reactivity such as acetone (depending on the type of application) and methylchloroform.

The sum of three types of organic compounds (volatile, semi-volatile, and condensable) has been referred to as total organic compounds (TOCs). All three forms are included as a first step in estimating emissions compiled for the NPRI. Since emissions of non-VOCs can make up a large part of hydrocarbon emissions from some sources, it is important that non-VOCs be excluded (from TOCs) when reporting VOCs if that detail is known.

VOC emissions include all organic compounds that contribute to the formation of ground level ozone.

ECCC requires VOCs to be speciated based on a specified list (Part 5). Any species on the list will be reportable if the species *minimum quantities* (1 tonne per year) are met. A speciated VOC must be reported for an individual stack if 0.25 tonnes or more is released from the stack.

### **15.4.2. Scope**

VOCs emission sources include the following (with references to sections in this code):

1. Process fugitive emissions (4 Process Fugitive Emissions)
2. Tanks (5 Releases from Storage Tanks)
3. Loading (6 Releases from loading operations)
4. Water effluent (7 Releases from Wastewater Sources)
5. Spills (8 Non-Routine Releases)
6. Combustion (15.4.3.2 VOCs from Combustion Sources)

The prominent sources of VOCs from petroleum refineries are process fugitive emissions, tanks, and loading.

The emissions estimated by the factors referenced above provide the simplest basis of comparisons or benchmarking. For simplicity, they may be called VOCs, although they may include some non-VOC emissions (e.g. methane) or non-hydrocarbon emissions (e.g. hydrogen, nitrogen). Total VOC emissions are determined by summing those emissions. Any non-hydrocarbon emissions or non-VOC emissions should be excluded if they are known. Often it is not clear whether an emission is VOC or TOC (e.g. heavy liquid emissions). Using TOCs to represent VOCs is a conservative emissions estimation approach.

Speciation of VOCs should be conducted once total emission estimates of individual VOCs that are reportable to NPRI and the total VOCs have been estimated.

### **15.4.3. Requirements**

#### **15.4.3.1. Total VOCs**

Emissions of TOCs are made prior to speciating total emissions into specific substances. Refer to the separate sections of this Code for the estimation methodologies. This will ensure consistent approaches to estimating the total emissions of organic compounds, both for specific NPRI / reportable substances and VOCs.

Exclude non-hydrocarbon emissions to air such as catalysts, metals in coke, and CO.

Exclude organic compounds that are negligible contributors to ground level ozone (e.g. methane and ethane) where information is available.

Factors estimating process fugitive (Section 4) and loading (Section 6) emissions generally exclude methane.

Assume methane and ethane emissions from tankage are negligible.

***NOTE: Revisions to API emission factors indicate that combustion is a source of TOCs.***

Unless specific information is available, assume that ethane emissions are negligible and don't need to be specifically excluded when estimating VOCs.

#### **15.4.3.2. VOCs from Combustion Sources**

VOCs from combustion sources (e.g. heaters, boilers,) should be included in the overall VOC estimate (using AP-42 emission factors). Speciation of these VOCs is based on fuel type and can be estimated by assuming that the VOCs released are unburned fuel and therefore, would have the same composition as the fuel. An alternative is the use of substance-specific emission factors from AP-42. VOCs for stationary fuel combustion for energy purposes, combustion of fuels for non-energy purposes, flaring and use of fuels for non-energy products and all other sources must be reported.

For Claus sulphur recovery units, the US EPA has published a new emission factor of 0.0014 lb/10<sup>6</sup> Btu for total hydrocarbons in 2015. This THC factor is for units equipped with combustion type tail gas emission control such as thermal oxidizers (Reference 4). However, as discussed in Section 15.2.1.3 (Sulphur Plant Incinerator Emissions), discretion is required in adopting this new EPA factor since the impacts of variations in unit configuration have not been fully considered during its development, especially with respect to the various tail gas treatment technologies used in the industry which varies depending upon the type of amine used, the desired chemical reactions, the catalyst and tail gas thermal oxidation/incineration design.

The default method for estimating VOCs emissions from flares is to use the AP-42 VOC emission factor (AP-42 Chapter 13.5, Table 13.5-2) which is based on firing capacity (BTU). An AP-42 VOC emission factor of 0.57 lb/10<sup>6</sup> BTU (LHV) was published by US EPA in 2015 based on a review of flare performance testing results. This factor applies to well operated steam-assisted or air-assisted flares, with at least 98% destruction efficiency (equivalent to 96.5% combustion efficiency), which comply with the General Provisions in the US Code of Federal Regulations (40 CFR Part 60) requiring >300 Btu/scf net heating value in the flare gas and a flare tip velocity of less than specified maximum (see Reference 1 in Section 9.5). As discussed in Section 9.3.3 (Other Substances in Stack Gases), in 2018, EPA AP-42 updated VOC emission factor at 0.66 lb/10<sup>6</sup> BTU (LHV) based on an average destruction efficiency of 98.9%. The 2018 AP-42 update was a final section for the industrial flares and should be used for VOC emission estimates. Alternatively, VOCs from flares can be estimated by assuming 2% of hydrocarbons in the flare gas remains as unburned hydrocarbon (See Reference 16, Section 15.7). Sample calculations for estimating emissions from flares are given in Appendix D.

Direct measurement of flare gas flowrate and compositions is deemed the most accurate estimation method. These flare parameters can be used, in conjunction with site-specific or AP-42 default combustion efficiency, to calculate the emission of pollutants in the flare exhaust. For facilities that measure either the flaring gas flowrate, composition, or neither parameters, engineering estimation/judgement may be used to determine missing parameters based on process knowledge.

#### **15.4.3.3. Refinery VOC Speciation**

Once the Total VOCs emission estimates have been determined, a facility must report all VOCs listed in Part 5 that were released to air in a quantity greater than or equal to 1 tonne. There are two methods to determine speciated VOCs:

1. Use process stream composition data,
2. Use generic speciation data in the form of weight fractions.

If site specific composition data is available, the first methodology is likely to give more accurate estimates than using generic weight fractions such as the speciation profiles developed by US EPA.

Canadian Fuels recommends using the following approach when estimating speciated VOCs from refineries, to ensure that double counting is avoided, and the greatest number of VOCs are speciated.

1. Estimate the Total VOCs from a refinery (see Section 15.4.3.1 for methodology).

There are VOC substances in the NPRI Part 1 substances list that are not on the Part 5 (Appendix C) list. If a facility is reporting a substance in Part 1 (e.g. MEK), it should also ensure that the tonnage is accounted for in the speciation calculator so that the maximum quantity of VOCs are captured.

2. Estimate all of the VOCs that are reportable to NPRI (referred to as NPRI-VOCs). Note: include all individual VOC substances reported to NPRI, not just the speciated list.

For substances that are in both Part 1 and Part 5 substances list, ensure that the same value (tonnes) is reported to NPRI. If the speciation calculator is used, this value should be entered in the calculator.

3. Compile any VOCs that may have been estimated but are not on the list of reportable NPRI substances (referred to as Estimated NON-NPRI VOCs).
4. Normalize and apply the speciation profile in Table 15-7 to the Total VOCs to determine the amount of VOCs on the speciation list by multiplying the percent value with the Total VOCs. For example, for Propane:

$$(Eq-A) \quad \text{Tonnes of Propane} = 3.98\% * \text{Total VOCs (tonnes)}$$

Normalize the speciation profile in Table 15-7 to exclude species that are in the default profile but have been quantified in steps 3 and 4 above. For example, if benzene was reported to NPRI, use that reported number and do not apply the benzene percentage in the speciation profile in Table 15-7. Apply the normalized profile to quantify the remaining VOC species.

The sum of the tonnes of each substance that a percentage was applied to constitutes the Speciated VOCs.

Do not apply the percentage in the profile to reported NPRI VOCs or estimated NON-NPRI VOCs. For example, if benzene was reported to NPRI, use that number and not the speciation profile in Table 15-7. If a substance was reported to NPRI as ‘zero’ emissions, do not apply the percentage in the profile to that substance.

If a substance was not reported to NPRI because it did not meet the threshold but is in Table 15-7, apply the speciation percentage to the substance.

5. The difference between the Total VOCs and the sum of the amount of individual VOCs reported to NPRI plus the estimated amount of the speciated VOCs is the amount of ‘unknown’ VOCs. The remaining “Unknown VOCs” can be classified as having a “low” reactivity, as the substances would consist of remaining heavy hydrocarbons.
6. Substances that appear in Part 5 (Appendix C) but are not in the speciation profile should be reported to Part 5 if they were reported in Part 1 to NPRI.



The method outlined above, assumes that the Total VOCs, the NPRI-VOCs, and the estimated NON-NPRI VOCs are solid numbers and will not change once the speciation calculations have been completed. Therefore, the “Unknown VOCs” will change according to the amount of available information of NPRI-VOCs and estimated NON-NPRI VOCs at each refinery.

Canadian Fuels developed the estimation tool identified above based on selected profiles from the US EPA SPECIATE database. These profiles were applied to 2001 NPRI data. Known species estimated via another technique (e.g. Benzene) and estimated via the test profiles were then compared for Canadian Fuels member refineries and the 2457/2459 profile statistically performed the best. The associated spreadsheet tool for refineries has been slightly modified from the 2003 version by normalizing the profiles based on user data to keep the species in proportion to each other.

**Table 15-7 Refinery Speciation Profile of Total VOCs\***

NPRI Name	NPRI Part I	NPRI Part 5	Percentage
1,2,4-Trimethylbenzene	YES	YES	0.31%
Benzene	YES	YES	1.72%
Cyclohexane	YES		1.73%
Ethylbenzene	YES		0.23
n-Hexane	YES	YES	3.11%
Propylene	YES	YES	1.40%
Toluene	YES	YES	2.03%
Xylene (All Isomers)	YES	YES	0.36%
Propane		YES	3.98%
Butane (All Isomers)		YES	34.92%
Butene (All Isomers)		YES	1.44%
Cycloheptane (All Isomers)		YES	0.20%
Cyclooctane (All Isomers)		YES	0.00%
Ethyltoluene (All Isomers)		YES	0.16%
Heptane (All Isomers)		YES	1.82%
Hexane (All Isomers Excluding n-Hexane)		YES	2.71%
Nonane (All Isomers)		YES	0.01%
Octane (All Isomers)		YES	0.48%
Pentane (All Isomers)		YES	8.56%
Pentene (All Isomers)		YES	2.06%
Trimethylbenzene (total of 1,2,3 and 1,3,5, Excluding 1,2,4)		YES	0.02%
UNIDENTIFIED			32.75%

\* Based on US SPECIATE profile 2457 (Misc. Chemical and Refining Plants in Texas)

**Table 15-8 Terminal Speciation Profile of Total VOCs\***

NPRI Name	NPRI Part I	NPRI Part 5	Percentage
1,2,4-Trimethylbenzene	YES	YES	0.08%
Benzene	YES	YES	1.18%
n-Hexane	YES	YES	1.85%
Toluene	YES	YES	1.35%
Xylene (All Isomers)	YES	YES	0.64%
Propane		YES	1.18%
Butane (All Isomers)		YES	35.87%
Butene (All Isomers)		YES	3.28%
Chlorobenzene	YES		0.01%
Cycloheptane (All Isomers)		YES	0.34%
Decane (All Isomers)		YES	0.04%
Heptane (All Isomers)		YES	4.46%
Hexane (All Isomers Excluding n-Hexane)		YES	7.80%
Hexene (All Isomers)		YES	1.35%
Nonane (All Isomers)		YES	0.23%
Octane (All Isomers)		YES	1.47%
Pentane (All Isomers)		YES	28.46%
Pentene (All Isomers)		YES	3.22%
Trimethylbenzene ( total of 1,2,3 and 1,3,5, Excluding 1,2,4)		YES	0.07%

\* Based on US SPECIATE profiles 1014/1015.

#### 15.4.3.4. Terminal VOC Speciation

As terminals do not usually know the concentrations of many of these substances within their products, an estimation tool, similar to the one described above for refineries was developed. This tool is based on the average of two profiles from the US EPA Speciate database, namely profile #1014 for gasoline-summer blend and #1015 for gasoline-winter blend. These profiles were deemed appropriate since they closely match the reported 2003 emissions of NPRI Part 1 substances, contain data for Part 5 substances, more closely match Canadian fuels formulation (e.g. no Methyl Tert-Butyl Ether or MTBE), and have the least quantity of unidentified components of US EPA Speciate profiles.

Canadian Fuels Association recommends use of the following approach when estimating the speciated VOCs from terminals to avoid double counting and to allow the estimation of the greatest number of VOC species.

1. Estimate the Total VOCs from tankage, loading and fugitive sources at a terminal (see Sections 4, 5 and 6 for methodologies).
2. The default VOC speciation profile for terminals, as shown in Table 15-8, can be applied to the estimated Total VOCs when the VOC speciation profiles of terminal products are not readily available.
3. If the product speciation profiles are available for some of the NPRI reportable VOC species, their respective speciated emissions can be determined according to the methodologies given in Sections 4.2.4, 5.2.3 and 6.2.2. Estimates of these known VOC species are reportable to NPRI (referred to as NPRI-VOCs. Note: include all individual VOC substances reported to NPRI, not just the speciated list).
4. Compile any VOCs that may have been estimated but are not on the list of reportable NPRI substances (referred to as Estimated NON-NPRI VOCs).
5. Normalize the speciation profile in Table 15-8 to exclude species that are in the default profile but have been quantified in steps 3 and 4 above. For example, if Benzene was reported to NPRI, use that reported number and do not apply the benzene percentage in the terminal speciation profile in the Table. Apply the normalized profile to quantify the remaining VOC species.

If a substance was reported to NPRI as ‘zero’ emissions, do not apply the percentage in the profile to that substance.

If a substance was not reported to NPRI because it did not meet the threshold but is in Table 15-8, apply the speciation percentage to the substance.

6. The difference between the Total VOCs and the sum of the amount of individual VOCs reported to NPRI plus the estimated amount of the speciated VOCs is the amount of ‘unknown’ VOCs. The remaining “Unknown VOCs” can be classified as having a “low” reactivity, as the substances would consist of remaining heavy hydrocarbons.
7. Substances that appear in Part 5 (Appendix C) but are not in the speciation profile should be reported to Part 5 if they were reported in Part 1 to NPRI.

The method outlined above, assumes that the Total VOCs, the NPRI-VOCs, and the estimated NON-NPRI VOCs are solid numbers and will not change once the speciation calculations have been completed. Therefore, the “Unknown VOCs” will change according to the amount of available information of NPRI-VOCs and estimated NON-NPRI VOCs at each terminal.

#### **15.4.3.5. Stack Breakdown of VOC**

VOC emissions from an individual stack greater than 25 m must be reported if 0.25 tonnes or more of that speciated VOC is released from the stack.

**15.4.3.6. Improvement Options**

1. Estimate VOC emissions from spills where information is available (see Section 8.3.3).
2. Include emissions that are less than 1% MPO or 1 tonne in Part 5 for a more complete speciation profile.
3. Some Part 5 substances do not meet the 1 tonne threshold every year. Computation of industry-wide aggregate emission data for such Part 5 substances, based on omission of figures below 1 tonne threshold, leads to certain inconsistencies while examining the year-to-year emission trends of such Part 5 substances. Therefore, reporting of all emissions in the speciation profile of Part 5 substances has been suggested to eliminate the sources of inconsistencies in the emission trends. It has been confirmed that the SWIM software will accept an entry of <1 tonne.
4. Obtain more precise information about concentrations of non-VOC hydrocarbons and their inclusion in emission factors. Reflect the information in estimating VOC emissions.
5. If information is available, refinery specific or company specific profiles could be applied to individual facilities in place of Table 15-7 or Table 15-8. The same steps in 15.4.3.3 could still be followed where appropriate.
6. If information is available, data for each stack could be used (e.g. Total VOCs by stack, NPRI VOCs by stack), then apply the speciation and sum up the emissions to arrive at the speciated totals.

## 15.5. CARBON MONOXIDE (CO)

### 15.5.1. Scope

CO emissions from heaters, boilers, CCUs, flaring, and large combustion engines used for process purposes need to be considered.

### 15.5.2. Requirements

The US EPA has developed a range of emission factors to be used within the oil and gas sector (EPA AP-42, Volume I, 5<sup>th</sup> Edition, 1998 and updates). The AP-42 reference tables for common refinery equipment and processes are shown in Table 15-9. Sample calculations for estimating emissions from flares are provided in Appendix D.

**Table 15-9 CO AP-42 Reference Tables<sup>a</sup>**

Equipment/Process Type	EPA AP-42 Table Reference
Fuel/Natural Gas Combustion	Table 1.4-1
Fuel Oil Combustion	Table 1.3-1
Coker Coke Combustion/CCU	Table 5.1-1
Gas Turbines	Table 5.1-1
Reciprocating Engines	Table 5.1-1
Flares (Unknown fuel quantity)	Table 5.1-1
Flares (Known fuel quantity)	Table 13.5-2
Claus Sulphur Recovery <sup>b</sup>	Table 8.13-2

<sup>a</sup> Emission factors, except for sulphur recovery, are based on an average natural gas higher heating value of 1,020 Btu/scf. These may be converted to other natural gas heating values by multiplying the given emission factor by the ratio of the specified heating value to this average heating value.

<sup>b</sup> Emission factors are based on the quantity of sulphur produced and are applicable to sulphur recovery process equipped with combustion type controls such as thermal oxidizers. [Please refer to section 15.2.1.3 regarding the applicability of new emission factors provided in AP-42 Table 8.13-2 (2015 version).]

### 15.5.3. Improvement Options

Actual measurements of CO concentrations in stacks could be used to calculate emissions.

## 15.6. PARTICULATE MATTER (PM)

### 15.6.1. Scope

This section contains guidance for the estimation of primary PM, which includes total particulate matter under 100  $\mu\text{m}$  (TPM), under 10  $\mu\text{m}$  ( $\text{PM}_{10}$ ) and under 2.5  $\mu\text{m}$  ( $\text{PM}_{2.5}$ ). Only primary PM emissions are discussed (and will be referred to collectively as PM) in this section. Precursor particulate matter pollutants such as  $\text{NO}_x$ ,  $\text{SO}_x$ , and volatile organic compounds (VOCs) are discussed in previous sections of this document.

### 15.6.2. Requirements

The predominant petroleum refinery PM emission source is catalytic cracking units (CCUs) followed by external combustion. Other refinery processes, such as stationary internal combustion sources, may contribute negligible PM. Fugitive dust from roads and dust piles at typical refinery sites is normally a small percentage of total PM. The NPRI guidance on reporting PM stipulates that only the filterable fraction is reportable, and reporting should be on a dry basis. If the estimated release includes condensable PM or if it is unknown whether condensable PM are included, it must be indicated in the comments in the reporting system.

Almost all emission factors for fine PM ( $\text{PM}_{2.5}$ ) are estimated by applying a size distribution factor to total PM or  $\text{PM}_{10}$  data. There is currently a fair amount of uncertainty in the estimation of  $\text{PM}_{2.5}$  particulate emissions due to the difficulty of, and evolving methods for,  $\text{PM}_{2.5}$  measurement. Recommended  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  ratios are provided in the following sub-sections.

#### 15.6.2.1. Catalytic Cracking Units

PM emissions from catalytic cracking units (CCUs) stem primarily from catalyst fines entrained in the exhaust gas from the catalyst regenerator. Both  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  are a large fraction of the total particulate emissions from CCUs, but the magnitude of these emissions can vary substantially from refinery to refinery.

The recommended PM emission estimation method is to use a CCU catalyst mass balance approach as it is standard refinery practice to track catalyst losses. This approach ignores particulates related to the coke combustion particles but is still considered to be the preferred methodology. This calculation technique normally results in numbers significantly lower than those calculated by emission factors. The  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  size distributions can be estimated from AP-42 guidance as 70 and 40% of PM respectively.

An alternative method to the mass balance approach if catalyst losses are not known, is to use the AP-42 emission factors (Table 5.1-1). The AP-42 factors are based on two-stage cyclone units and for each additional stage a removal efficiency of 75% can be assigned. The  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  fractions can be estimated from the previously discussed AP-42 distributions of 70 and 40 % of PM for  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$ , respectively.

In addition, there are fugitive PM emissions that arise from catalyst handling operations. The US EPA Petroleum Refineries Protocol recommended the use of a predictive emission factor correlation, as provided in AP-42 Chapter 13.2.4 (Aggregate Handling & Storage Piles), to estimate these releases (US EPA, 2015).

#### **15.6.2.2. External Combustion Sources**

External combustion sources include:

- boilers,
- heaters,
- incinerators; and
- flares

PM emissions for gaseous fuels are typically much lower than for liquid fuel. Nearly all PM from the combustion of natural gas and most other gaseous fuels is assumed to be less than 1 µm in size. PM emissions can vary widely for fuel-oil combustion sources depending on fuel grade and composition, combustor type and size, and load. In general, PM emissions are dependent on the completeness of combustion and the inorganic ash content of the fuel. Heavier oils have PM emissions due to poorer combustion properties and increased ash content. The PM emissions for heavier oils are correlated with either ash or sulphur content because low sulphur (either natural or de-sulphurized) oils have substantially lower viscosity and reduced asphaltene and ash content. The lower viscosity oil has improved combustion due to better atomization.

The US EPA has compiled combustion emission factors for PM and size distribution (AP-42 Volume I, 5<sup>th</sup> Edition, 1998 & updates). The factors that may be of interest to the petroleum sector have been listed in Table 15-10 by fuel type. Previously, ECCC has used the same AP-42 PM emission factors in its Natural Gas Emissions Calculator to assist facilities in estimating releases from natural gas-fired combustion units. However, for the 2012 reporting year, these PM emission factors have been revised based on dilution tunnel tests rather than the traditional sampling test results used to develop the AP-42 PM factors. Results from the dilution tunnel tests are deemed to be more representative of actual PM emissions by ECCC for PM emission factors development. Hence, until future updates or revisions are published, these revised PM emission factors should be used for estimating emissions from natural-gas fired external combustion sources if site-specific data is not readily available. PM emission factors from flares are provided in Table 15-11.

**Table 15-10 PM Combustion Emission Factors<sup>a</sup>**

Fuel Type	EPA AP-42 Table 1.4-2 Emission Factors (Kg/10 <sup>3</sup> L liquid fuels or Kg/10 <sup>6</sup> m <sup>3</sup> gaseous fuel)		
	Filterable <sup>b</sup> PM	PM <sub>10</sub>	PM <sub>2.5</sub>
Gas (NG-RFG) <sup>c</sup>	30.4	100% of PM	100% of PM
Distillate	0.24	50% of PM	12% of PM
Fuel Oil # 6	1.2	86% of PM	56% of PM

<sup>a</sup> Emission factors are based on an average natural gas higher heating value of 1,020 Btu/scf. These may be converted to other natural gas heating values by multiplying the given emission factor by the ratio of the specified heating value to this average heating value.

<sup>b</sup> Filterable PM which is defined as the PM collected on or prior to a filter of an EPA method 5.

<sup>c</sup> - NG - Natural Gas; RFG - Refinery Fuel Gas. NG PM/PM<sub>10</sub>/PM<sub>2.5</sub> emission factors were revised for the 2012 NPRI reporting year.

Note for Table 15-10 – Low NO<sub>x</sub> burner air pollution control devices have no effect on PM emission factors.

For sulphur recovery units (SRUs), PM emissions should be calculated based on fuel combusted.

**Table 15-11 PM Emission Factors for Flares**

Flare Operation	Filterable PM Emission Factor		PM Size Fraction	
	µg/L Exhaust <sup>a</sup>	Lb/MMBtu <sup>b</sup> (LHV)	PM <sub>10</sub>	PM <sub>2.5</sub>
Non-smoking	0	0	100% of PM	100% of PM
Lightly smoking	40	0.027	100% of PM	100% of PM
Average smoking	177	0.12	100% of PM	100% of PM
Heavily smoking	274	0.19	100% of PM	100% of PM

<sup>a</sup> Data from US EPA AP-42 Chapter 13.5, 2015.

<sup>b</sup> Source: US EPA Emissions Estimation Protocol for Petroleum Refineries, 2015; Values shown have been converted from concentration by using the F-factor method on a dry basis with an assumed 3% O<sub>2</sub> in the exhaust gas stream.

### 15.6.2.3. Stationary Internal Combustion Sources (reciprocating internal combustion engines & turbines)

Stationary internal combustion sources are not normally as prevalent as external combustion sources and are not utilized to a significant extent at Canadian refineries. For natural-gas fired turbines, the PM emission factors have been revised based on dilution tunnel results, as discussed in the preceding section, and should be used for NPRI reporting for the 2012 reporting year and beyond. For natural gas-fired engines, emission results were not available from the dilution tunnel tests and there was no



change to the associated PM emission factors. Hence, if used, the preferred emission factors are the current AP-42 factors.

#### **15.6.2.4. Fugitive Road Dust**

Fugitive dust from unpaved refinery roads (road dust) within a facility boundary is an NPRI reporting requirement. Unpaved road types include gravel surfaced roads, roads with thin membrane bituminous surface treatments, and bituminous cold mix surfaces. When vehicles have travelled more than an annual total of 10,000 vehicle kilometres (VKT) on unpaved roads at the facility, the resulting PM emissions must be included in the mass reporting threshold calculations for total particulate matter (TPM), PM<sub>10</sub>, and PM<sub>2.5</sub>. According to the NPRI Guidance on Estimating Road Dust Emissions from Industrial Unpaved Surfaces, vehicles to be considered include those owned or operated by the facility, customer and contractor vehicles, as well as, any mobile equipment capable of self propulsion, such as loaders, dump trucks, forklifts, excavators, and bulldozers. A Road Dust Emission Calculator is available in the NPRI Toolbox to assist facilities in estimating their road dust emissions.

To calculate road dust emissions from unpaved roads, the following methodology is provided in the NPRI guidance and is consistent with those from AP-42 Chapter 13.2.2 (2006). An Unpaved Industrial Road Dust Calculator is available to assist NPRI reporters:

<https://www.canada.ca/content/dam/eccc/documents/xlsx/inrp-npri/road-dust-calculators/Road-dust-calculator.xlsx>

$$E_x = \text{VKT} * \text{EF}_x * \text{ADJ} * (1 - \text{CE}/100)$$

Where:

- $E_x$  = Emission of contaminant  $x$ , kg;
- VKT = Annual total vehicle kilometres travelled, km;
- $\text{EF}_x$  = Emission factor of contaminant  $x$ , kg/VKT;
- ADJ = Adjustment factor for precipitation, snow cover and frozen days;
- CE = Efficiency of dust control, %.

#### **Vehicle Kilometres Travelled, VKT**

The annual total VKT is dependent on traffic volume on a given length of unpaved road. It may be calculated using the equation given below.

$$\text{VKT} = \text{Average Daily Traffic} * \text{Length of Unpaved Roads} * \text{Operating Days/y}$$

The average daily traffic represents the total vehicle passes over the road segments per day. The NPRI guidance recommends the use of site-specific information such as odometer readings, length of roads within facility boundary, and the total count of vehicles entering the facility on a typical day.

**Emission Factors (EF<sub>x</sub>)**

The following size specific emission factor equation can be used to determine the respective factors for TPM, PM<sub>10</sub>, and PM<sub>2.5</sub>. In cases where a facility only has light vehicles (which means vehicle weights less than 2.7 tonnes) travelling on facility unpaved roads, an alternate emission factor correlation given in AP-42 Chapter 13.2.2.2 may be used.

$$EF = k * (s/12)^a * (W/2.72)^b$$

Where:

EF = Size-specific emission factor, kg/VKT;

s = Surface material silt content, %;

W = Mean vehicle weight, tonnes (metric);

k, a, b = Numerical constants (per Table 15-12)

**Table 15-12 Numerical Constants for Unpaved Industrial Road Dust Emission Factor**

Constant	PM <sub>2.5</sub>	PM <sub>10</sub>	TPM
k (kg/VKT)	0.042	0.423	1.381
A	0.9	0.9	0.7
B	0.45	0.45	0.45

For the silt content, s, a site-specific value is recommended. If this information is not available, a mean value from AP-42 Table 13.2.2-1 could be considered. The mean vehicle weight, W, should be representative of a weighted-average of the mix of vehicles travelling on the road.

**Adjustment Factor (ADJ)**

Precipitation, frozen roads, and snow cover contribute to the reduction of road dust emissions. Hence the climate adjustment factor, ADJ, needs to be taken into account in emissions calculations and the following equation can be used.

$$ADJ = (Working\ Days - (p+snow))/Working\ Days$$

Where:

ADJ = Adjustment factor for precipitation, snow cover, and frozen days;

Working Days = Number of operating days per year;

P = Estimated annual working days with precipitation > 0.2 mm;

Snow = Estimated annual working days when the roads were frozen, or snow covered and wet for winter.

On-site monitoring data should be used when available. Alternatively, a facility may obtain the precipitation data from a nearby ECCC meteorological station through its Climate Data Online website. The Climate Normals Data, ([https://climate.weather.gc.ca/climate\\_normals/](https://climate.weather.gc.ca/climate_normals/)), may also be used as appropriate to account for the days with precipitation exceeding 0.2 mm and the days with snow depth more than 1 cm. When using the ECCC climate data, the facility needs to ensure that the "P+snow" days for a specific month does not exceed the number of days worked for that month. If this occurs, the facility should use the number of days worked instead of the sum of "P" and "snow" for that month when calculating the adjustment factor.

**Control Efficiency (CE)**

Other than natural precipitation described above, periodic road watering and the application of dust suppressants are examples of ways to reduce road dust emissions. Table 15-13 below shows potential controls and their respective efficiencies for unpaved roads based on a review by Levelton (2008).

**Table 15-13 Emission Control Measures and Efficiencies for Unpaved Roads**

<b>Control Measure</b>	<b>PM<sub>10</sub> Control Efficiency</b>	<b>References/Comments</b>
Limit road speed to 40 km/h	44%	Assumes linear relationship between road speed and PM <sub>10</sub> emissions (WRAP, 2004)
Pave unpaved roads	99%	WRAP, 2004
Water roads twice a day	55%	MRI, 2001
Water roads more than twice a day	70%	NPRI Guidance
Chemical Suppressants	80%	NPRI Guidance
Apply dust suppressant annually to unpaved parking areas	84%	CARB, 2002

**15.6.2.5. Cooling Tower**

Suspended and dissolved solids in cooling water may be present in water droplets that are entrained in the cooling tower exit air stream (or liquid drift) and particulate matter (PM) is released to the atmosphere from the formation of salt crystals as the water evaporates in ambient air.

The following equation can be used to quantify uncontrolled PM emissions.

$$PM = TDS \times \text{Drift Loss (\%)} \times \text{Circulating Water Rate (m}^3\text{/hr)} \times D_{\text{water}} \times H \times 10^{-6}$$

Where:

- PM = total particulate (t/year)
- TDS = average concentration of dissolved solids (ppmw)
- D<sub>water</sub> = density of cooling water, 10<sup>6</sup> g/m<sup>3</sup>
- H = number of hours of operation of the cooling tower during the calendar year (h/year)
- 10<sup>-6</sup> = unit conversion factor from grams to tonnes

If the TDS data in the circulating cooling water is not available, ECCC suggests applying a concentration factor to the TDS concentration in the tower make-up water. The concentration factor is a ratio of a measured cooling water parameter, such as conductivity, calcium, chlorides or phosphates, to the same parameter in the make-up water. Although ECCC currently does not have any specific guidance on the sampling frequency of TDS or surrogate cooling water parameters for NPRI reporting, facilities are expected to use the most accurate data that can reasonably be obtained.

If tower-specific information is not readily available, the default values for TDS and drift rates, which are provided by ECCC and summarized in Table 15-14, may be considered.

**Table 15-14 Total Dissolved Solids Concentrations & Cooling Tower Drift Rates**

<b>Cooling Water</b>	<b>TDS (ppmw)</b>	<b>Tower Type</b>	<b>Drift rate (% water flow)</b>
Sea water	33,000	> 20-year-old towers (AP-42)	0.02
High dissolved solids (AP-42)	12,000	Standard new tower	0.001
Great Lakes water	3,000	New tower w/ best demister	0.0005

To estimate emissions of different particulate size fractions, a spreadsheet tool has been developed by ECCC for NPRI reporting. The tool estimates the particulate size distribution based on the assumption that dissolved solids will form a spherical particle after the water is evaporated, resulting in a conservative estimate of the smaller size particles since the spherical shape is the smallest shape that a particle can form (Reisman & Frisbie, 2001). The estimation of the respective percentage of PM<sub>10</sub> and PM<sub>2.5</sub> fractions in the total particulate is based on the known drift droplet size distribution (at a given drift rate) for three cooling towers equipped with selected drift eliminator types that are shown in Table 15-15.

**Table 15-15 Cooling Tower Drift Eliminator Types & Corresponding Drift Rate**

Eliminator Type	Drift Rate
Old Wood Herringbone Mist Eliminators	0.01%
Interpolated drift eliminator average (calculated)	0.005%
New Cellular Drift Eliminators	0.0003%

The following Table 15-16, taken from the ECCC NPRI Guidance, shows the summary results generated by the Spreadsheet Tool for various concentrations of cooling water TDS at different drift loss rates

**Table 15-16 Total Dissolved Summary Results of Particulate Emissions**

Drift Loss (%)	TDS (ppmw)	PM (mg/m <sup>3</sup> H <sub>2</sub> O)	PM-10 (%TPM)	PM-2.5 (%TPM)
0.02	3000	600	11.4	0.3
0.001	3000	30	27.8	0.2
0.0005	3000	15	50	0.2
0.02	12000	2400	4.1	0
0.001	12000	120	4	0.1
0.0005	12000	60	4.5	0.1
0.02	33000	6600	1.7	0
0.001	33000	329	1.2	0
0.0005	33000	165	0.6	0

In Table 15-16, the results shown for the 0.02% drift loss case are based on the droplet size distribution for the default 0.01% drift rate case as shown in Table 15-15 whereas the results for the 0.001% drift loss are based on drift data of 0.005%, and the results for the 0.0005% drift loss are based on 0.0003% drift data.

The mass percentages of the PM<sub>10</sub> and PM<sub>2.5</sub> fractions in total PM, as generated by the Spreadsheet Tool, can be applied to the total cooling tower PM emissions to estimate the emissions of these smaller size particles.

### **15.6.3. Improvement Options**

Actual measurements of PM could be used to estimate emissions. The sampling techniques need to be carefully controlled to ensure representative capture of primary PM without inadvertent precursor capture.

## **15.7. REFERENCES**

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## 16. OTHER NPRI REPORTING REQUIREMENTS

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### 16.1. SCOPE

This section provides guidance on reporting yearly breakdown of releases/temporal variation (mandatory by NPRI) and pollution prevention (P2) activities (mandatory by NPRI). Relevant NPRI publications are also listed in the Reference section of this section for member referral.

### 16.2. DEFINITIONS

#### **Pollution Prevention**

For the purposes of NPRI reporting, pollution prevention means: “The use of processes, practices, materials, products or energy that avoid or minimize the creation of pollutants and waste and reduce the overall risk to human health or the environment” and does NOT include on-site treatment (pollution control) activities; off-site recycling and disposal activities; waste treatment or dilution; and, transferring hazardous and/or toxic constituents from one environmental medium to another. See the ECCC NPRI reporting guide for further details. It should be noted that Canadian Fuels Association is committed to the concept of environmental protection which includes all of the hierarchy of options beyond just pollution prevention.

### 16.3. REQUIREMENTS

#### 16.3.1. Yearly Breakdown of Releases (Temporal Variations)

If reporting facilities operated on a continuous basis (24 hours a day 365 days a year), as is the normal operation for most refineries, it can be assumed that emissions do not vary significantly over time. If this is the case, then a yearly breakdown of releases by percentage in each month can be reported as 8.3%. However, if a facility only operates during certain hours of the day and/or certain days of the week or if operations are routinely shut down for maintenance, then the differences could be accounted for by dividing total releases by the typical operating schedule.

Terminals can also be considered (24 hours a day, 365 days a year) operations as described above.

##### 16.3.1.1. Improvement Option

For terminal operations, consideration of other data, for example, product throughputs, temperatures, and RVPs, could be utilised to attain a profile of emissions.



### **16.3.2. Pollution Prevention**

Qualitative reporting of pollution prevention activities for specific substances is a mandatory NPRI requirement. One or more pollution prevention activities can be selected as being relevant to the refinery and substance being reported.

Pollution prevention activities that can be selected include: materials or feedstock substitution; production design or reformulation; equipment or process modifications; spill, or leak prevention activities; on-site reuse, recycling, or recovery; improved inventory management or purchasing techniques; and, good operating practice and training. For each of these NPRI defined subsections, further information on the nature of the activity must also be provided. The NPRI reporting guide provides examples of each of the pollution prevention techniques given as options to choose from.

One of the choices allows a free format comment if none of the other choices are appropriate. “No pollution prevention activities” is also a choice although if “pollution prevention” has been chosen as the reason for a change in quantities released or transferred, then one of the other choices must be selected.

As an option, facilities can provide additional information on pollution prevention activities such as energy or water conservation. They can be entered into the free format comment area. Comments not pertaining to a particular substance that relate to a facility or are addressing pollution prevention initiatives for a different reporting year should be placed in the facility comments section.

Facilities that report implementing a pollution prevention plan must report the name of the Pollution Prevention Planning Notice for which the plan was prepared. If the Pollution Prevention (P2) Activities plan was prepared or implemented for another government jurisdiction or program, the name of the jurisdiction, program, or requirement must be reported. Facilities that report not implementing new pollution prevention activities during the year must report any existing barriers to implementing a plan. Facilities must specify if a substance is no longer being reported as a result of implementing pollution prevention activities at the facility. Beginning in the 2021 calendar year, facilities will be required to link their pollution prevention activities to specific substances.

## **16.4. REFERENCES**

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## **17. QUALITY ASSURANCE AND QUALITY CONTROL**

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### **17.1. PURPOSE**

Facilities generating an emission inventory should take steps to ensure that the data they report is true and accurate and thereby maintain credibility of the numbers reported. To this extent, implementation of a Quality Assurance/Quality Control (QA/QC) program ensures that the data collected is of sufficient accuracy and reliability to meet the data needs of the inventory and, where applicable, to demonstrate regulatory compliance with programs such as the annual facility-wide emission caps.

This section provides the framework to assist Canadian Fuels members in the design of a new QA/QC program or in the enhancement of an existing one. Based on the findings of a 2010 Canadian Fuels survey of member QA/QC programs, the guidance provided in the following sections is found to be consistent with those implemented, both formally and informally, at member refineries.

### **17.2. DEFINITIONS**

For the purposes of this section, the following definitions pertaining to data quality are adopted:

**Quality Assurance (QA)** refers to the management activities involving policy, planning, implementation, assessment, and reporting to ensure that the end product (e.g. environmental data) is of the type and quality needed to meet the needs of the user.

**Quality Control (QC)** is the overall system of operational procedures, techniques, and activities that are used to fulfill data quality requirements to ensure consistent high data quality. Quality control programs should include the use of approved standardized procedures, technical reviews, and accuracy checks.

**Quality Assurance Plan (QAP)** documents the QA policy and QC procedures and may include the following activities, which are consistent with recognized programs such as the ISO 9000 Quality Management System.

- Activity planning
- Activity implementation
- Activity performance audits
- Performance assessment which may lead to re-planning or modifying activity.

**Quality System (QS)** is a structured system that comprises the management level Quality Assurance policies and the working level Quality Control Procedures that are incorporated in a Quality Assurance Plan.

**Quality Management Plan** describes the organizational structure of a quality system, including quality assurance policies, quality control procedures, areas of application, roles and responsibilities, as well as, plan implementation and assessment.

### 17.3. REQUIREMENTS

The guiding principles for obtaining quality data with respect to emissions accounting and reporting should be consistent with industry standards (CCME, 2005; Battelle, 2003; CCPA (Chemistry Industry Association of Canada (CIAC) predecessor), 2004) and compose of the following aspects:

- Relevancy
- Comprehensiveness
- Transparency
- Consistency
- Competency
- Accuracy
- Continuous Improvement
- Validation
- Verification

These aspects should be reflected in the design and implementation of each member’s Quality System. Table 17-1 below summarizes the essential elements of such a system based on the CIAC model. Further description of each of the QA system elements presented in Table 17-1 is shown in Table 17-2 while Table 17-3 describes the QC procedural elements. The key verification and comparison components within the QA plan are summarized in Table 17-4. The information given below is for general guidance only and should be tailored to the business of each Canadian Fuels member company when formulating or updating its own QA policies.

**Table 17-1 Quality System Elements**

	<b>Quality System Elements</b>
Quality Assurance	Management System
	Preliminary Planning
Quality Control	Data Management
	Preparation, Documentation
	Data & System Assessment
	Emissions Quantification
Quality Assurance Plan	Verification & Comparison

**Table 17-2 Quality Assurance Policy Elements**

Elements	Descriptions
Management System	<ul style="list-style-type: none"> <li>• Individual &amp; organizational responsibilities defined and documented</li> <li>• Capability (knowledge &amp; competency) standards established</li> <li>• Procedures for emissions compilation &amp; reporting established</li> <li>• Emissions and estimation methods validated periodically</li> <li>• Emission estimates reviewed by operating unit and approved by senior management</li> <li>• Continuous improvement process established</li> <li>• Record Keeping</li> </ul>
Preliminary Planning	<ul style="list-style-type: none"> <li>• General requirements for reporting identified, such as reporting ID</li> <li>• Methodology or approach determined for reporting</li> <li>• Responsibilities identified &amp; delegated</li> <li>• Schedule established to meet set milestones or reporting deadlines</li> <li>• Resources identified for data collection, calculation, entry, presentation, verification, and approval</li> <li>• Estimation methods selected</li> </ul>

**Table 17-3 Quality Control Procedural Elements**

Elements	Descriptions
Data Management	<ul style="list-style-type: none"> <li>• Inventory requirements determined</li> <li>• Data platform (spreadsheets &amp; databases) identified</li> <li>• References reviewed</li> <li>• Rationale for choice of methods documented</li> <li>• Forecast methodology determined</li> </ul>
Preparation, Documentation, & Training	<ul style="list-style-type: none"> <li>• Prerequisites for report generators established</li> <li>• Training needs assessed</li> <li>• Past submissions reviewed</li> <li>• Procedures for calculations, documentation, and data storage followed</li> <li>• Working papers filed, complete with all relevant supporting information</li> <li>• References cited</li> <li>• Post submission checks performed</li> </ul>

<b>Elements</b>	<b>Descriptions</b>
Data & System Assessment	<ul style="list-style-type: none"> <li>• Quality control considered in planning, data collection, analysis, estimation, and reporting</li> <li>• Quality control elements incorporated</li> <li>• Databases archived and secured</li> <li>• Values verified by alternative methods or external party</li> </ul>
Emissions Quantification	<ul style="list-style-type: none"> <li>• Chemicals &amp; stream composition identified</li> <li>• Air, water, land, &amp; waste/recoverable streams identified</li> <li>• Construction maintenance &amp; other non-routine sources accounted for</li> <li>• Incident history reviewed and calculations documented</li> </ul>

**Table 17-4 Quality System Verification Elements**

<b>Elements</b>	<b>Descriptions</b>
Verification & Comparison	<ul style="list-style-type: none"> <li>• Data sources rationalized and documented</li> <li>• Reality/reasonableness checks performed</li> <li>• Peer review conducted</li> <li>• Data entry and emission software performance checked</li> <li>• Internal data checked</li> <li>• Comparisons to historical data made</li> <li>• Management signoff completed</li> <li>• Data consistency checked if posted elsewhere</li> </ul>

## **17.4. IMPROVEMENT OPPORTUNITIES**

- Given that the operation and management structures are unique to the business of each member company, any QA/QC program under development or revision should be site-specific.
- QA/QC programs and procedures should be reviewed, assessed, and updated if necessary, on a regular basis.

## **17.5. REFERENCES**

1. “EPA Requirements for Quality Management Plans”, EPA/240/B-01/002, March 2001. <https://www.epa.gov/sites/production/files/2016-06/documents/r2-final.pdf>
2. “Petroleum Industry Guidelines for Reporting Greenhouse Gas Emissions”, Prepared by Battelle for the International Petroleum Industry Environmental Conservation Association (IPIECA), American Petroleum Institute (API) and the International Association of Oil & Gas Producers (OGP) Second Addition, May 2011 [https://www.api.org/~media/Files/EHS/climate-change/GHG\\_industry-guidelines-IPIECA.pdf](https://www.api.org/~media/Files/EHS/climate-change/GHG_industry-guidelines-IPIECA.pdf)
3. National Framework For Petroleum Refinery Emission Reductions (NFPRER), Canadian Council of Ministers of the Environment (CCME, 2005) <https://ccme.ca/en/res/nfprerpn1338esecure.pdf>
4. “Guideline for Quantifying Emissions from Chemical Facilities”, CIAC (Chemistry Industry Association of Canada, formerly the Canadian Chemical Producers Association (CCPA)), 2004.
5. “Quality Assurance Procedures and DARS software”, EPA Emissions Inventory Improvement Program (EIIP), Volume VI. <https://www.epa.gov/air-emissions-inventories/volume-6-quality-assurance-procedures-and-dars-software>

## APPENDIX A - SUBSTANCES COMMONLY REPORTED TO NPRI

In this section, substances are listed if they are likely to be present in the various refinery streams or processes. Most refineries should be reporting certain substances and should look carefully at other substances to determine if they should be reported. No suggested speciation is given for the many refinery streams and products because of the variation in refinery configuration and processes, and the potential confidential nature of the information.

### APPENDIX A - 1 - PURCHASED CHEMICALS

If an NPRI substance is present in a feedstock or purchased chemical at concentrations of 1 weight% or more and if at least 10 tonnes per year are handled at the refinery, then it must be reported, even if the releases are less than 10 tonnes or even zero. The following is a non-exhaustive list of typical chemicals used at a refinery that can be used as a guide to check if/whether reporting is required. Some refineries have specific needs for chemicals not listed below. The refineries purchased chemical list needs to be reviewed to capture any NPRI substances and determine if they meet 10 tonne per year limit.

**Table A - 1 Purchased Chemicals Often Used at a Refinery**

Substance	CAS Number	Use in Refinery
Ammonia	NA-16	Crude unit – corrosion control Refrigerant
Diethanolamine (DEA)	111-42-2	Gas Treating (sweetening) <ul style="list-style-type: none"> <li>Although losses occur, not clear if released to environment or destroyed in the process.</li> </ul>
Ethylene Glycol	107-21-1	Heat medium/tracing/ cooling
Lead and Compounds	NA-08	From the use of TEL in aviation gasoline. Releases very low or zero because of typical low concentration (<1 weight%) found in the aviation gasoline.
TEL	78-00-2	From the use of TEL in aviation gasoline. Releases very low or zero because of typical low concentration (<1 weight%) found in the aviation gasoline.
Methanol	67-56-1	Freeze protection
Methyl ethyl ketone (MEK)	78-93-3	Lube facilities
Methyl isobutyl ketone (MIBK)	108-10-1	Lube facilities

<b>Substance</b>	<b>CAS Number</b>	<b>Use in Refinery</b>
Sulphuric Acid	7664-93-9	Water treating; pH control <ul style="list-style-type: none"> <li>• Often neutralized so not counted as a release.</li> <li>• When sent off-site for regeneration, should be counted as recycling (see Section 11.3.1)</li> </ul>
Tetrachloroethylene	127-18-4	Used in reformer to chloride catalyst.

## **APPENDIX A - 2 - BY-PRODUCT EMISSIONS**

NPRI requires reporting of NPRI substances that are emitted as by-products. A “by-product” is an NPRI substance that is incidentally manufactured as a product of an unwanted side-reaction and is released on-site to the environment or transferred off-site for disposal. Under the “by-product” rule in NPRI, the release of a substance must be reported if 10 tonnes or more are emitted, regardless of the concentration. If less than 10 tonnes are emitted, the substance does not have to be reported (unless other emissions of the same substance are more than 10 tonnes). Heaters, boilers, and some process units utilize a variety of fuels including purchased natural gas, internally generated refinery gas, heavy fuel oil, and coke. Contaminants in these fuels (e.g. metals) are often present in heavy fuel oil and coke that may require reporting. Water effluent is another release source where low concentration substance release may fall under the by-product rule.

**Table A - 2 NPRI By-product Releases (Combustion/Water Effluent Sources)**

<b>Substance</b>	<b>CAS Number</b>	<b>Source in Refinery</b>	<b>Comments</b>
Ammonia	NA-16	<i>FCCU if no CO boiler</i>	<i>See AP-42 for factor. If CO boiler in operation with FCCU, no ammonia emissions.</i>
Anthracene	120-12-7	<i>HFO or coke burning</i>	<i>Generally, &lt; 10t</i>
Chlorine	7782-50-5	<i>Water Treating</i>	<i>Generally, only associated with non-routine releases</i>
Methanol	67-56-1	<i>Emitted from Steam Methane Reformers</i>	<i>Estimate emissions through stream analysis and engineering calculation and/or catalyst manufacturer</i>



<b>Substance</b>	<b>CAS Number</b>	<b>Source in Refinery</b>	<b>Comments</b>
Nickel	NA-11	<i>HFO or coke burning</i>	<i>Depends on concentration in HFO or coke.</i>
Nitrate Ion	NA-17	<i>Found in water effluent</i>	<i>Large variation in quantity released. Dependent on wastewater treatment operation and nitrogen containing streams feeding treatment plant.</i>
Phenol	108-95-2	<i>Primarily released to water in water effluent, but some fugitives also reported</i>	<i>Generally, refineries do not have phenol measured specifically, but have phenolic compounds and have used that number to estimate phenol.</i>
Vanadium	NA-40	<i>HFO or coke burning</i>	<i>Depends on concentration in HFO or coke.</i>

### **APPENDIX A - 3 - NPRI SUBSTANCES IN REFINERY STREAMS**

This section deals with NPRI substances that are present in refinery feedstocks or produced in the refinery processes. Most refinery products are complex hydrocarbon mixtures and potentially contain NPRI substances. However, in many instances the concentrations of these substances are below 1 weight%. Differences in refinery configuration lead to variations in the concentrations of some substances. Only through specific lab testing of streams can the concentration for a particular refinery be verified. Substances given in the three tables below have been reported by Canadian Fuels refineries since 1996 and are therefore, potentially present in other refineries. Note that if composition data is not available, NPRI does not require additional testing. Table A - 3 shows substances that can be expected to be present at NPRI reportable quantities for all conventional refineries.

Table A - 4 shows substances that are present at the majority of Canadian Fuels refineries and should be considered by all.

Table A - 5 shows substances that were reported only by a few refineries. All refineries should use the data presented to review their submission to ensure all required substances are being reported.

**Table A - 3 NPRI Process Substances Released by Most Refineries**

<b>Substance</b>	<b>CAS Number</b>	<b>Where Substance is Found in Refinery</b>
Benzene	71-43-2	<ul style="list-style-type: none"> <li>• Released to air from gasolines and components</li> <li>• Fugitive emissions from NHT, Reformers, FCCU, Hydrocracker</li> <li>• Storage and handling losses from gasoline</li> </ul>
Cyclohexane	110-82-7	<ul style="list-style-type: none"> <li>• Released to air from gasolines and components</li> <li>• Fugitive emissions from NHT, Reformers, FCCU, Hydrocracker</li> <li>• Storage and handling losses from gasoline</li> </ul>
Ethylbenzene	100-41-4	<ul style="list-style-type: none"> <li>• Released to air from gasolines and components</li> <li>• Fugitive emissions from NHT, Reformers, FCCU, Hydrocracker</li> <li>• Storage and handling losses from gasoline</li> </ul>
Hexane	NA-32	<ul style="list-style-type: none"> <li>• Released to air from gasolines and components</li> <li>• Fugitive emissions from NHT, Reformers, FCCU, Hydrocracker</li> <li>• Storage and handling losses from gasoline</li> </ul>
Hydrogen Sulphide (H <sub>2</sub> S) and Total Reduced Sulphur (TRS)	7783-06-4	<ul style="list-style-type: none"> <li>• Fugitive Process and Tank releases to air from sour gas and liquid streams (gasoline and distillates) primarily prior to desulphurization treatment (sweetening, hydrotreating)</li> <li>• Wastewater Treatment Fugitives</li> <li>• Stack Emissions</li> <li>• Flares</li> </ul>
Toluene	108-88-3	<ul style="list-style-type: none"> <li>• Released to air from gasolines and components</li> <li>• Fugitive emissions from NHT, Reformers, FCCU, Hydrocracker</li> <li>• Storage and handling losses from gasoline</li> </ul>
1,2,4 Trimethylbenzene	95-63-6	<ul style="list-style-type: none"> <li>• Released to air from gasolines and components</li> <li>• Fugitive emissions from NHT, Reformers, FCCU, Hydrocracker</li> <li>• Storage and handling losses from gasoline</li> </ul>
Xylene	1330-20-7	<ul style="list-style-type: none"> <li>• Released to air from gasolines and components</li> <li>• Fugitive emissions from NHT, Reformers, FCCU, Hydrocracker</li> <li>• Storage and handling losses from gasoline</li> </ul>

**Table A - 4 Some Key NPRI Process Substances Released by at least Half of Canadian Fuels Refineries**

<b>Substance</b>	<b>CAS Number</b>	<b>Where Substance is Found in Refinery</b>
Ammonia	NA-16	<ul style="list-style-type: none"> <li>• Underground injection; purchased chemical for corrosion control or cooling systems; generated in process units from nitrogen in crude – ends up in sour water stripper or effluent water.</li> </ul>
Ethylene	74-85-1	<ul style="list-style-type: none"> <li>• Air emissions. Ethylene produced in FCCU and released as fugitive. Large variation in releases depending if refinery produces ethylene as a product.</li> </ul>
Naphthalene	91-20-3	<ul style="list-style-type: none"> <li>• Air emissions. Found in gasoline and distillate product and components. Will have fugitive emissions from distillate units and storage and handling losses. Usually around 1 % + or - in streams.</li> </ul>
Propylene	115-07-1	<ul style="list-style-type: none"> <li>• Air emissions. Fugitive emissions from gas recovery units. Larger emissions usually associated with handling (loading and off-loading propylene tank cars) as a chemical feedstock.</li> </ul>

**Table A - 5 Some Key NPRI Substances Released By a Few Canadian Fuels Refineries**

<b>Substance</b>	<b>CAS Number</b>	<b>Where Substance is Found in Refinery</b>
Biphenyl	92-52-4	<ul style="list-style-type: none"> <li>• Generally released as fugitives to air. Found in distillate streams but often below 1 % concentration.</li> </ul>
1,3 Butadiene	106-99-0	<ul style="list-style-type: none"> <li>• Gasoline and components. Butane/butylene streams. Generally, from FCCUs. Often present below 1 %.</li> </ul>

## **APPENDIX B - 2022-2024 REVISIONS TO NPRI AND THE CODES**

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This Appendix serves to track changes to NPRI Reporting Requirements and a summary of revision 19 of the Codes. The Canada Gazette notices and updates published on the NPRI website must be reviewed to ensure understanding of actual requirements. To access the Gazette, go to <http://www.gazette.gc.ca/gazette/home-accueil-eng.php>.

### **Deletion of Substances:**

- Two substances were removed from the Part 1, Group A list:
  - Hexachloropentadiene (CAS RN 77-47-4)
  - Methyl iodide CAS RN (74-88-4)

### **Addition of Substances:**

- One substance was added to the Part 1, Group B list:
  - Chlorhexidine and its salts (CAS RN 55-56-1)

### **Changes to Reporting Requirements (from the Guide for Reporting to the NPRI 2022-2024):**

Facilities required to indicate the reason a substance is reported for the first time.

Facilities must provide applicable identification number(s) for their provincial or territorial operating permit, approval, authorization, license, or certificate or other applicable provincial or territorial environmental program identifier(s)

Two new bases of estimate have been added to the list of bases of estimate that facilities are permitted to use to estimate substance quantities: remote quantification and speciation profile

NPRI has made administrative name changes to categories of releases – see the Gazette (pages 44-45) for further details.

Facilities to report individual stacks higher than 25m, increasing the stack air release thresholds for six of the seven CACs; adding a stack exit temperature threshold; and adding exemptions for certain types of stacks and facilities. A requirement has been added to break down individual stack releases into several categories of combustion and fuel use activities, and to report the fuel types and basis of estimate associated with each category.

Facilities reporting stack or point releases of PM<sub>2.5</sub>, PM<sub>10</sub> or total particulate matter must now indicate if their reported releases include condensable particulate matter.

The 10-tonne total VOCs threshold no longer applies to reporting speciated VOCs. Instead, a speciated VOC must be reported if 1 tonne or more of that speciated VOC is released from the facility. The 5-tonne total VOCs threshold no longer applies to

reporting speciated VOCs from an individual stack. Instead, a speciated VOC must be reported for an individual stack if 0.25 tonnes or more of that speciated VOC is released from the stack. In addition, a basis of estimate, the monthly breakdown and reasons for changes in releases from the previous year must now be provided for speciated VOCs.

**Changes to Sections of the Codes:**

**All Sections** - Updated and Verified Applicable References and updated to changes in the 2022-2024 NPRI Gazette

**Section 4** – Process Fugitive Emissions – the Section is now based on the November 10, 2020 Gazette <http://www.gazette.gc.ca/rp-pr/p2/2020/2020-11-11/html/sor-dors231-eng.html>

**Section 9.4.1** Emission Factor changes for Mercury and Selenium

**Section 15.1** Updated to reflect lower stack height requirements and fuel types.

**Section 15.4** Changes to Speciated VOC reporting thresholds

**Section 15.6** Indication of whether Condensable PM is included in quantification

**Appendix B** - Applicable to the 2022 to 2024 years. For a history of changes to the codes or NPRI, please refer to previous versions of the codes by contacting CFA Ottawa office.

APPENDIX C - VOLATILE ORGANIC COMPOUNDS (VOC)

Table C - 1 Part 5 Individual Substances, Groups and Isomers

Name	Synonyms	CAS Registry Number
Acetylene	Ethyne	74-86-2
Benzene	Cyclohexatriene; Phenyl hydride	71-43-2
1,3-Butadiene	Vinyl ethylene; Biethylene; Bivinyll	106-99-0
2-Butoxyethanol	EGBE; Butyl Cellosolve; n-Butoxyethanol	111-76-2
<i>p</i> -Dichlorobenzene	1,4-Dichlorobenzene; PDCB; <i>p</i> -chlorophenyl chloride	106-46-7
1,2-Dichloroethane	Ethylene dichloride; Freon 150	107-06-2
Dimethylether	Methyl ether; Methoxymethane	115-10-6
Ethanol	Ethyl Alcohol; Ethyl hydroxide; Methylcarbinol	64-17-5
Ethyl acetate	Ethyl acetic ester; Acetoxyethane	141-78-6
Ethylene	Ethene	74-85-1
Formaldehyde	Methyl aldehyde; Methylene glycol; Oxomethane	50-00-0
Furfuryl alcohol		98-00-0
<i>n</i> -Hexane	Normal hexane; Dipropyl; Hexyl hydride	110-54-3
Isopropyl alcohol	2-Propanol; Isopropanol; Rubbing alcohol	67-63-0
D-Limonene	D-1,8- <i>p</i> -Menthadiene	5989-27-5
Methanol	Methyl alcohol; Wood alcohol; Monohydroxymethane	67-56-1
Methylcyclopentane		96-37-7
Methyl ethyl ketone	2-Butanone; Methyl acetone	78-93-3
Methyl isobutyl ketone	Hexanone; Isopropylacetone	108-10-1
Myrcene	7-Methyl-3-methylene-octadiene	123-35-3

**Canadian Fuels Association Codes of Practice – Refineries and Terminals**

Name	Synonyms	CAS Registry Number
Beta-Phellandrene	b-Phellandrene; 1(7)-2- <i>p</i> -Menthadiene	555-10-2
Alpha-Pinene	a-Pinene; Cyclic dextradiene	80-56-8
Beta-Pinene	b-Pinene; Nopinene	127-91-3
Propane		74-98-6
n-Propyl alcohol		71-23-8
Propylene	Propene	115-07-1
Styrene	Phenylethylene; Vinyl benzene	100-42-5
Tetrahydrofuran		109-99-9
Toluene		108-88-3
1,2,4-Trimethylbenzene	1,3,4-Trimethylbenzene; 1,2,5-Trimethylbenzene; Pseudocumene	95-63-6
Vinyl acetate	Acetic acid ethylene ether	108-05-4
<b>Isomer Groups, Other Compound Groups and Mixtures</b>		
Butane ‡	C4 Paraffins, C4 Alkanes	NA-24*
	n-butane (CAS 106-97-8)	
	Iso-butane (CAS 75-28-5)	
Butene ‡	C4 Olefin, C4 Alkenes, Butylene	25167-67-3
	1-butene (CAS 106-98-9) cis-2-butene (CAS 590-18-1) trans-2-butene (CAS 624-64-6) iso butene (CAS 115-11-7) 2-butene unspecified isomer (CAS 107-01-7)	
Butyl acetate Isomers†	n-butyl acetate (CAS 123-86-4)	NA-41*
	isobutyl acetate (CAS 110-19-0)	
	sec-butyl acetate (CAS 105-46-4)	
Cycloheptane ‡	C7 Cycloparaffins, C7 Cycloalkanes, C2 Cyclopentane, Methycyclohexane	NA-25*
	CAS 291-64-5	
	CAS 108-87-2	
	CAS 1640-89-7	
	CAS 1638-26-2	
	CAS 1192-18-3	
	CAS 1638-26-2	
	CAS 1759-58-6	
	CAS 2453-00-1	
	CAS 28729-52-4	
	CAS 2532-58-3	
CAS 822-50-4		

**Canadian Fuels Association Codes of Practice – Refineries and Terminals**

Name	<u>Synonyms</u>	CAS Registry Number
Cyclohexene ‡	C6 Cycloalkenes, Isomers of Cyclohexene, Methylcyclopentenes	NA-26*
	CAS 110-83-8	
	CAS 693-89-0	
	CAS 1120-62-3	
	CAS 1759-81-5	
	CAS 1501-58-2	
Cyclooctane ‡	C8 Cycloparaffins, C8 Cycloalkanes, C2 Cyclohexane, Dimethylcyclohexane	NA-27*
	CAS 292-64-8	
	CAS 4126-78-7	
	CAS 1678-91-7	
	CAS 2207-04-7	
	CAS 589-90-2	
	CAS 591-21-9	
	CAS 624-29-3	
	CAS 583-57-3	
	CAS 6876-23-9	
	CAS 27195-67-1	
	CAS 590-66-9	
	CAS 2207-01-4	
	CAS 2207-03-6	
	CAS 638-04-0	
	CAS 30498-64-7	
	CAS 4516-69-2	
	CAS 4850-28-6	
	CAS 4259-00-1	
	CAS 2613-69-6	
CAS 16747-50-5		
CAS 930-90-5		
CAS 930-89-2		
CAS 16747-50-5		
CAS 2040-96-2		
CAS 3875-51-2		
Decane ‡	C10 Paraffins, C10 Alkanes, Isomers of Decane	NA-28*
	CAS 124-18-5	
	CAS 34464-38-5	
	CAS 63335-87-5	
	CAS 871-83-0	
	CAS 5911-04-6	
	CAS 17301-94-9	
	CAS 15869-85-9	
	CAS 5881-17-4	
	CAS 15869-86-0	
CAS 7146-60-3		



**Canadian Fuels Association Codes of Practice – Refineries and Terminals**

Name	<u>Synonyms</u>	CAS Registry Number
	CAS 15869-87-1 CAS 15869-95-1 CAS 2051-30-1 CAS 4110-44-5 CAS 15869-93-9 CAS 1072-16-8 CAS 15869-94-0 CAS 52896-87-4 CAS 14676-29-0 CAS 17302-01-1 CAS 14720-74-2 CAS 20278-87-9 CAS 20278-89-1 CAS 2613-61-8 CAS 4032-93-3 CAS 7154-80-5 CAS 79004-85-6 CAS 1071-81-4 CAS 13475-81-5 CAS 16747-42-5 CAS 5171-84-6	
Ethyltoluene <sup>‡</sup>	2-ethyltoluene (CAS 611-14-3) 3-ethyltoluene (CAS 620-14-4) 4-ethyltoluene (CAS 622-96-8)	NA-42*
Heptane <sup>‡</sup>	C7 Paraffins, C7 Alkanes, Isomers of Heptane CAS 142-82-5 CAS 31394-54-4 CAS 73513-42-5 CAS 25495-88-9 CAS 589-34-4 CAS 591-76-4 CAS 617-78-7 CAS 38815-29-1 CAS 565-59-3 CAS 108-08-7 CAS 562-49-2 CAS 590-35-2 CAS 464-06-2	NA-31*
Hexane <sup>††</sup>	C6 Paraffins, C6 Alkanes, Isomers of Hexane [Excluding n-hexane (110-54-3)] CAS 43133-95-5 CAS 107-83-5 CAS 96-14-05 CAS 75-83-2 CAS 79-29-8-	NA-32*

**Canadian Fuels Association Codes of Practice – Refineries and Terminals**

Name	<u>Synonyms</u>	CAS Registry Number
	CAS 38719-68	
Hexene ‡	C6 Olefins, C6 Alkenes, Isomers of Hexene, Methylpentenes	25264-93-1
	CAS 25264-93-1	
	CAS 592-41-6	
	CAS 592-43-8	
	CAS 592-47-2	
	CAS 7688-21-3	
	CAS 7642-09-3	
	CAS 37275-41-5	
	CAS 625-27-4	
	CAS 691-37-2	
	CAS 763-29-1	
	CAS 4461-48-7	
	CAS 760-20-3	
	CAS 27236-46-0	
	CAS 760-21-4	
	CAS 563-78-0	
CAS 563-79-1		
CAS 558-37-2		
Nonane ‡	C9 Paraffins, C9 Alkanes, Isomers of Nonane	NA-33*
	CAS 111-84-2	
	CAS 61193-19-9	
	CAS 3221-61-2	
	CAS 2216-33-3	
	CAS 2216-34-4	
	CAS 15869-80-4	
	CAS 2216-32-2	
	CAS 30498-66-9	
	CAS 4032-86-4	
	CAS 1072-05-5	
	CAS 2213-23-2	
	CAS 3074-71-3	
	CAS 106819-5	
	CAS 1071-26-7	
	CAS 2216-30-0	
	CAS 922-28-1	
	CAS 926-82-9	
	CAS 3074-75-7	
	CAS 3074-77-9	
	CAS 16789-46-1	
	CAS 26447-41-6	
	CAS 3522-94-9	
CAS 16747-26-5		
CAS 1069-53-0		

**Canadian Fuels Association Codes of Practice – Refineries and Terminals**

Name	<u>Synonyms</u>	CAS Registry Number
	CAS 16747-25-4 CAS 1068-87-7 CAS 16747-30-1 CAS 16747-31-2 CAS 921-47-1 CAS 1067-20-5 CAS 86571-39-3 CAS 1070-87-7 CAS 16747-32-3 CAS 60265-51-2 CAS 1186-53-4 CAS 7154-79-2 CAS 16747-38-9	
Octane ‡	C8 Paraffins, C8 Alkanes, Isomers of Octane, dimethylhexanes CAS 111-65-9 CAS 50985-84-7 CAS 589-81-1 CAS 592-27-8 CAS 589-53-7 CAS 111002-96-1 CAS 619-99-8 CAS 28777-67-5 CAS 584-94-1 CAS 589-43-5 CAS 563-16-6 CAS 590-73-8 CAS 592-13-2 CAS 583-48-2 CAS 79914-21-9 CAS 1067-08-9 CAS 609-26-7 CAS 29222-48-8 CAS 540-84-1 CAS 560-21-4 CAS 564-02-3 CAS 565-75-3 CAS 594-82-1	NA-34*
Pentane ‡	C5 Paraffins, C5 Alkanes, Isomers of Pentane, Includes 50% C5 Paraffin/Olefin CAS 109-66-0 CAS 78-78-4 CAS 463-82-1 CAS 102056-77-9	NA-35*

**Canadian Fuels Association Codes of Practice – Refineries and Terminals**

Name	<u>Synonyms</u>	CAS Registry Number
Pentene ‡	C5 Olefin, C5 Alkenes, Amylene, Includes Methylbutenes, 50% C5 Paraffin/Olefin	NA-36*
	CAS 109-67-1	
	CAS 25377-72-4	
	CAS 68527-11-7	
	CAS 109-68-2	
	CAS 513-35-9	
	CAS 627-20-3	
	CAS 646-04-8	
	CAS 563-46-2	
	CAS 563-45-1	
CAS 26760-64-5		
Propyl acetate‡	isopropyl acetate (CAS 108-21-4)	NA-43*
	propyl acetate (CAS 109-60-4)	
Trimethylbenzene ‡‡	1,2,3-trimethylbenzene (526-73-8)	25551-13-7
	1,3,5-trimethylbenzene (108-67-8)	
Xylene ‡	m-xylene (CAS 108-38-3)	1330-20-7
	o-xylene (CAS 95-47-6)	
	p-xylene (CAS 106-42-3)	
Analytically unresolved hydrocarbons (C10 to C16+)		NA - 44
Heavy aromatic solvent naphtha	Heavy Aromatics, Aromatic 150	64742-94-5
Hydrotreated heavy naphtha		64742-48-9
Hydrotreated light distillate		64742-47-8
Light aromatic solvent naphtha	Aromatic 100	64742-95-6
Mineral spirits		64475-85-0
Naphtha		8030-30-6
Other glycol ethers and acetates (and their isomers)	CAS 112-07-2	NA - 45
	CAS 112-15-2	
	CAS 112-25-4	
	CAS 112-34- 5	
	CAS 5131-66-8	
	CAS 107-98-2	
	CAS 109-59-1	
	CAS 111-90-0	
	CAS 124-17-4	
	CAS 1569-01-3	
	CAS 1569-02-4	
	CAS 2807-30-9	
	CAS 29911-27-1	
CAS 29911-28-2		

Name	<u>Synonyms</u>	CAS Registry Number
	CAS 34590-94-8 CAS 54839-24-6 CAS 623-84-7 CAS 88917-22-0, and their isomers	
Propylene glycol methyl ether acetate (all isomers)		108-65-6
Solvent naphtha light aliphatic		64742-89-8
Solvent naphtha medium aliphatic		64742-88-7
Stoddard solvent	White Spirits	8052-41-3
VM & P naphtha		8032-32-4

**Notes:**

‡ "all isomers."

† "all isomers", excluding tert-butyl acetate (CAS RN 540-88-5)

\* No single CAS RN applies to this substance.

†† "all isomers", excluding *n*-hexane (CAS RN 110-54-3).

‡‡ "all isomers", excluding 1,2,4-trimethylbenzene (CAS RN 95-63-6)

For the purposes of this Guideline, the definition of VOC “means volatile organic compounds as defined in the *Proposed Order Adding Toxic Substances to Schedule 1 to the Canadian Environmental Protection Act, 1999, published in the Canada Gazette, Part I, Vol. 136 No. 30 (Ottawa, Saturday, July 27, 2002)*”. Namely: “Volatile organic compound” or “VOC” means volatile organic compounds that participate in atmospheric photochemical reactions, excluding the following;

- a) methane;
- b) ethane;
- c) methylene chloride (dichloromethane);
- d) 1,1,1-trichloroethane (methyl chloroform);
- e) 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113);
- f) trichlorofluoromethane (CFC-11);
- g) dichlorodifluoromethane (CFC-12);
- h) chlorodifluoromethane (HCFC-22);
- i) trifluoromethane (HFC-23);
- j) 1,2-dichloro 1,1,2,2-tetrafluoroethane (CFC-114);
- k) chloropentafluoroethane (CFC-115);

- l) 1,1,1-trifluoro 2,2-dichloroethane (HCFC-123);
- m) 1,1,1,2-tetrafluoroethane (HFC-134a);
- n) 1,1-dichloro 1-fluoroethane (HCFC-141b);
- o) 1-chloro 1,1-difluoroethane (HCFC-142b);
- p) 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124);
- q) pentafluoroethane (HFC-125);
- r) 1,1,2,2-tetrafluoroethane (HFC-134);
- s) 1,1,1-trifluoroethane (HFC-143a);
- t) 1,1-difluoroethane (HFC-152a);
- u) parachlorobenzotrifluoride (PCBTF);
- v) cyclic, branched or linear completely methylated siloxanes;
- w) acetone;
- x) perchloroethylene (tetrachloroethylene);
- y) 3,3-dichloro-1,1,1,2,2-pentafluoropropane (HCFC-225ca);
- z) 1,3-dichloro-1,1,2,2,3-pentafluoropropane (HCFC-225cb);
- z.1) 1,1,1,2,3,4,4,5,5,5-decafluoropentane (HFC 43-10mee);
- z.2) difluoromethane (HFC-32);
- z.3) ethylfluoride (HFC-161);
- z.4) 1,1,1,3,3,3-hexafluoropropane (HFC-236fa);
- z.5) 1,1,2,2,3-pentafluoropropane (HFC-245ca);
- z.6) 1,1,2,3,3-pentafluoropropane (HFC-245ea);
- z.7) 1,1,1,2,3-pentafluoropropane (HFC-245eb);
- z.8) 1,1,1,3,3-pentafluoropropane (HFC-245fa);
- z.9) 1,1,1,2,3,3-hexafluoropropane (HFC-236ea);
- z.10) 1,1,1,3,3-pentafluorobutane (HFC-365mfc);
- z.11) chlorofluoromethane (HCFC-31);
- z.12) 1 chloro-1-fluoroethane (HCFC-151a);
- z.13) 1,2-dichloro-1,1,2-trifluoroethane (HCFC-123a);
- z.14) 1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy-butane (C<sub>4</sub>F<sub>9</sub>OCH<sub>3</sub>);
- z.15) 2-(difluoromethoxymethyl)-1,1,1,2,3,3,3-heptafluoropropane ((CF<sub>3</sub>)<sub>2</sub>CF<sub>2</sub>OCH<sub>3</sub>);
- z.16) 1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane (C<sub>4</sub>F<sub>9</sub>OCH<sub>2</sub>H<sub>5</sub>);

- z.17) 2-(ethoxydifluoromethyl)-1,1,1,2,3,3,3-heptafluoropropane ((CF<sub>3</sub>)<sub>2</sub>CF<sub>2</sub>OC<sub>2</sub>H<sub>5</sub>);
- z.18) methyl acetate and perfluorocarbon compounds that fall into the following classes, namely;
- (i) cyclic, branched, or linear completely fluorinated alkanes;
  - (ii) cyclic, branched, or linear completely fluorinated ethers with no unsaturation;
  - (iii) cyclic, branched, or linear completely fluorinated tertiary amines with no unsaturation, and
- (i) sulphur containing perfluorocarbons with no unsaturation and with sulphur bonds only to carbon and fluorine.
- z.19) \* 1,1,1,2,2,3,3-heptafluoro-3-methoxy-propane (HFE-7000);
- z.20) \* 3-ethoxy-1,1,1,2,3,4,4,5,5,6,6,6-dodecafluoro-2-(trifluoromethyl) hexane (HFE-7500);
- z.21) \* 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea);
- z.22) \* methyl formate (HCOOCH<sub>3</sub>);
- z.23) \* t-butyl acetate;
- z.24) \* 1,1,1,2,2,3,4,5,5,5-decafluoro-3-methoxy-4-trifluoromethyl-pentane (HFE-7300);
- z.25) \* propylene carbonate;
- z.26) \* dimethyl carbonate;
- z.27) \* trans-1,3,3,3-tetrafluoropropene (HFO-1234ze);
- z.28) \* HCF<sub>2</sub>OCF<sub>2</sub>H (HFE-134);
- z.29) \* HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>H (HFE-236cal2);
- z.30) \* HCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H (HFE-338pcc13);
- z.31) \* HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H;
- z.32) \* 2,3,3,3-tetrafluoropropene (HFO-1234yf);
- z.33) \* trans 1-chloro-3,3,3-trifluoroprop-1-ene [HCFO-1233zd(E)]; and
- z.34) \* 2-amino-2-methyl-1-propanol.

*\*The volatile organic compound (VOC) definition as listed on Schedule 1 of the Canadian Environmental Protection Act, 1999 was amended as of June 15, 2016. This amendment added these 16 compounds to the exclusion list of the VOC definition.*

For NPRI threshold determination and reporting, ECCC also uses the physical chemistry definition of a VOC, which defines it as any compound that contains carbon and at least one other element and has a vapour pressure of greater than or equal to 2 mm Hg (Seaman,

2004). Substances with vapour pressures greater than 2 mm Hg, such as COS and CS<sub>2</sub>, are deemed to be VOCs by ECCC in this physical chemistry definition.

**NPRI Part 5 Substances – Selected VOCs with Additional Reporting Requirements**

**Table C - 2 Individual Substances**

Name	CAS Registry Number	Listed on NPRI Part 1
Acetylene	74-86-2	
Benzene	71-43-2	√
1,3-Butadiene	106-99-0	√
2-Butoxyethanol	111-76-2	√
<i>p</i> -Dichlorobenzene	106-46-7	√
1,2-Dichloroethane	107-06-2	√
Dimethylether	115-10-6	
Ethanol	64-17-5	
Ethyl acetate	141-78-6	
Ethylene	74-85-1	√
Formaldehyde	50-00-0	√
Furfuryl alcohol	98-00-0	
<i>n</i> -Hexane	110-54-3	√
Isopropyl alcohol	67-63-0	√
D-Limonene	5989-27-5	
Methanol	67-56-1	√
Methylcyclopentane	96-37-7	
Methyl ethyl ketone	78-93-3	√
Methyl isobutyl ketone	108-10-1	√
Myrcene	123-35-3	
Beta-Phellandrene	555-10-2	
Alpha-Pinene	80-56-8	
Beta-Pinene	127-91-3	
Propane	74-98-6	
<i>n</i> -Propyl alcohol	71-23-8	
Propylene	115-07-1	√



Name	CAS Registry Number	Listed on NPRI Part 1
Styrene	100-42-5	√
Tetrahydrofuran	109-99-9	
1,2,4-Trimethylbenzene	95-63-6	√
Toluene	108-88-3	√
Vinyl acetate	108-05-4	√

**Table C - 3 Isomer Groups**

Name	CAS Registry Number	Listed on NPRI Part 1
Butane ‡	NA-24*	
Butene ‡	25167-67-3	
Butyl acetate‡	NA-41*	
Cycloheptane ‡	NA-25*	
Cyclohexene ‡	NA-26*	
Cyclooctane ‡	NA-27*	
Decane ‡	NA-28*	
Ethyltoluene‡	NA-42*	
Heptane ‡	NA-31*	
Hexane ††	NA-32*	
Hexene ‡	25264-93-1	
Nonane ‡	NA-33*	
Octane ‡	NA-34*	
Pentane ‡	NA-35*	
Pentene ‡	NA-36*	
Propyl acetate‡	NA-43*	
Propylene glycol methyl ether acetate‡	108-65-6	
Trimethylbenzene ††	25551-13-7	
Xylene ‡	1330-20-7	√

**Table C - 4 Other Groups and Mixtures**

Name	CAS Registry Number
Analytically unresolved hydrocarbons (C <sub>10</sub> to C <sub>16</sub> <sup>+</sup> )	NA-44*
Heavy aromatic solvent naphtha	64742-94-5
Hydrotreated heavy naphtha	64742-48-9
Hydrotreated light distillate	64742-47-8
Light aromatic solvent naphtha	64742-95-6
Mineral spirits	64475-85-0
Naphtha	8030-30-6
Other glycol ethers and acetates	NA-45*
Propylene glycol methyl ether acetate (All isomers)	108-65-6
Solvent naphtha light aliphatic	64742-89-8
Solvent naphtha medium aliphatic	64742-88-7
Stoddard solvent	8052-41-3
VM & P naphtha	8032-32-4

**Notes:**

‡ "all isomers."

\* No single CAS RN applies to this substance.

†† "all isomers", excluding *n*-hexane (CAS RN 110-54-3).

‡‡ "all isomers", excluding 1,2,4-trimethylbenzene (CAS RN 95-63-6)

**APPENDIX D - SAMPLE CALCULATIONS**

**Example 1: CAC and H<sub>2</sub>S Emissions from Flaring**

**Assumptions:**

- 1) Flared gas composition (assumed for demonstration purposes only)

Components	Mol %	MW (g/gmol)
C <sub>1</sub>	88.24	16
C <sub>2</sub>	3.98	30
C <sub>3</sub>	1.48	44
C <sub>4</sub>	0.78	58
C <sub>5+</sub>	0.79	72+
CO <sub>2</sub>	2.35	44
H <sub>2</sub> S	2.18	34
N <sub>2</sub>	0.20	28
	100.00	18.82

- 2) Flared gas volume of 100,000 scf

$$= 100,000 \text{ scf} \times 0.0283 \text{ m}^3/\text{ft}^3 = 2,830 \text{ m}^3$$

$$= 2,830 \text{ m}^3 / 0.0236 \text{ m}^3/\text{gmol} (15^\circ\text{C}) = 119,759 \text{ gmols}$$

- 3) Flared gas heating value = 1,000 Btu/scf (LHV)

Note: Adjust to other gas heating value by multiplying emission factors by the ratio of the specified heating value to the average heating value 1,020 Btu/scf.

- 4) Combustion efficiency = 98%

- 5) CO emission factor = 0.31 lb/10<sup>6</sup> Btu (AP-42 Table 13.5-2)

- 6) NO<sub>x</sub> emission factor = 0.068 lb/10<sup>6</sup> Btu (AP-42 Table 13.5-1)

- 7) PM emission factor\* = 0.19 lb/10<sup>6</sup> Btu (AP-42 Table 13.5-1 for heavily smoking flares)

- 8) VOC emission factor = 0.66 lb/10<sup>6</sup> Btu (AP-42 Table 13.5-2, if appropriate)

**Emission Calculations:**

$$\begin{aligned} \text{CO emissions} &= 0.31 \times 10^{-6} \text{ lb/Btu} \times 100,000 \text{ scf} \times (1,000 \text{ (BTU/scf)}/1,020 \text{ (LHV} \\ &\text{adjust factor (lb/BTU))}) = 0.03 \text{ lbs} = 0.03 \text{ lb} * 0.4536 \text{ kg/lb} = 0.014 \text{ kg} = 0.014 \\ &\text{kg} * 0.001 \text{ tonne/kg} = 0.000014 \text{ tonne} \end{aligned}$$

$$\begin{aligned} \text{NO}_x \text{ emissions} &= 0.068 \times 10^{-6} \text{ lb/Btu} \times 100,000 \text{ scf} \times (1,000 \text{ (BTU/scf)}/1,020 \text{ (LHV} \\ &\text{adjust factor (lb/BTU))}) = 0.0067 \text{ lbs} = 0.0067 \text{ lbs} * 0.4536 \text{ kg/lb} = 0.003 \text{ kg} = \\ &0.003 \text{ kg} * 0.001 \text{ tonne/kg} = 0.000003 \text{ tonne} \end{aligned}$$

PM emissions =  $1.9 \times 10^{-6}$  lb/Btu x 100,000 scf x (1,000 (BTU/scf)/1,020 (LHV adjust factor (lb/BTU))) = 0.19 lbs = 0.19 lbs \* 0.4536 kg/lb = 0.08 kg = 0.08 kg \* 0.001 tonne/kg = 0.00008 tonne

PM<sub>10</sub> emissions = 0.00008 tonne (100% of PM)

PM<sub>2.5</sub> emissions = 0.00008 tonne (100% of PM)

SO<sub>x</sub> emissions = 119,759 (moles) x 98% (combustion efficiency) x (2.18/100) (sulphur content in gas stream) x 64 (molecular weight of SO<sub>2</sub>, g/mole) = 163,746 g = 0.16 tonne

H<sub>2</sub>S emissions = 119,759 (moles) x (1-0.98 (combustion efficiency)) x (2.18/100) (sulphur content in gas stream) x 34 (molecular weight of H<sub>2</sub>S, g/mole) = 1,775 g = 0.0017 tonne

VOC emissions – Emission Factor approach =  $0.66 \times 10^{-6}$  lb/Btu x 100,000 scf x (1,000 (BTU/scf)/1,020 (LHV adjust factor (lb/BTU))) = 0.065 lbs = 0.065 lbs \* 0.4536 kg/lb = 0.03 kg = 0.00003 tonne

VOC emissions – using 98% destruction efficiency approach = C<sub>3</sub> emissions = 119,759 (moles) x (1-0.98 (combustion efficiency)) x (1.48/100) (C<sub>3</sub> content in gas stream) x 44 (molecular weight of C<sub>3</sub>, g/mole) = 1,559.7 g = 0.0016 tonne

\* emission factor for soot has been assumed to be PM<sub>2.5</sub> (filterable) and the value shown is from the EPA Emissions Estimation Protocol for Petroleum Refineries, Version 3, April 2015. This PM factor corresponds to a concentration of 274 µg/L in the exhaust, as given in AP-42 Table 13.5.1, for heavily smoking flares.

### Example 2: Benzene Reporting

#### Assumptions:

- a facility emitted a total of 25 tonnes of VOCs to air in 2014.
- 7 tonnes of benzene were from facility process vents and 5.5 tonnes were present in boiler exhausts
- all boiler exhausts are vented through a common stack of 35 m.

#### Benzene reporting:

- reportable under Part 1A since the total of benzene from process vents (7 tonnes) and as combustion by-products (5.5 tonnes) exceeded the Part 1A 10-tonne reporting threshold
- reportable under Part 5 and the amount of benzene (5.5 t) exceeded the speciated Part 5 substance threshold of 1 tonne.
- reportable under facility stack-specific emissions since the quantity of benzene emitted (5.5 tonnes) through the 35 m stack exceeded the stack height threshold of 25 m.