

Emission Monitoring and Reporting Strategy – Summary and Background

In February 2002, the Canadian Council of Ministers of the Environment (CCME), Environmental Planning and Protection Committee, directed the National Air Issues Coordinating Committee (NAICC) to develop a multi-pollutant emissions reduction strategy for the petroleum-refining sector. This background study is foundational research for the *Emission Monitoring and Reporting (EM&R) Strategy* component of CCME's National Framework for Petroleum Refinery Emission Reductions (NFPRER).

The background study describes inventory practices and monitoring methodologies commonly used to monitor six polluting substances and categories of substances, and it summarizes current regulatory practices related to the monitoring and reporting of these substances by petroleum refineries across Canada. The authors compiled and compared information on air emissions of sulphur dioxide (SO₂), nitrogen oxides (NO_x), carbon monoxide (CO), particulate matter (total PM, direct PM₁₀, direct PM_{2.5}), volatile organic compounds (VOCs), and benzene. Two appendices provide details of measurement methodologies (i.e., source type, source characteristics, method, method uncertainty, measurement requirements, analytical considerations, and relative cost) and permit monitoring requirements (i.e., emitting unit and type, emission of interest, measurement method, and frequency) for each emission source at refineries. The usefulness of permit monitoring data can be limited where measurements are done to ensure compliance at a specific time, rather than to provide annual emission totals. A final section and third appendix take into consideration current *ambient* monitoring and reporting activities in the vicinity of Canada's refineries; however, this is not the focus of the study.

This study is one of two documents (the other being the strategy itself) prepared under the Emissions Monitoring and Reporting (EM&R) Strategy process, which was set up by the NFPRER Steering Committee, co-chaired by Alberta Environment and Environment Canada. An EM&R team, with representation from federal, provincial and local governments, industry, and non-governmental organizations, guided a consultative process for developing a strategy that will provide guidance and tools for refineries to monitor and report emissions of air pollutants and toxics and will, ultimately, allow jurisdictions to determine whether annual facility-wide emission limits are being achieved.

GENERAL FACILITY MEASUREMENT AND ESTIMATION METHODOLOGIES

Because of the diversity of operations and emission sources in a petroleum refinery, direct emissions data from all sources are difficult to obtain.

The monitoring methodologies most commonly used by large combustion installations, such as refineries, to estimate emissions to air are direct measurement methods: continuous emission monitoring systems (CEMs), predictive or parametric emission monitoring systems (PEMs), source testing; and indirect methods: mass balance calculations, emission models and factors, and engineering estimates.

CEMs are proven technologies. CEMs instrumentation monitors emissions directly and continuously, determines the flow rate, analyzes the gas, measures the contaminant concentration, and records the data. CEMs can be the most accurate method of quantifying emissions under certain circumstances but are the most costly alternative. In Canada, regulations in several jurisdictions require CEMs to monitor sulphur dioxide and nitrogen oxide emissions from sulphur plant incinerators, fluidized bed catalytic cracking units

(FCCUs), and boilers. Sulphur dioxide and nitrogen oxide emissions are perceived to be the most significant pollutants, and the three sources are generally the largest at refineries under normal operating conditions. The Ontario emission trading program generally requires CEMs but allows the development of emission curves from a suite of stack surveys. Most CEMs require certification and verification of quality assurance/control activities, as well as routine maintenance. Continuous monitoring can be done using either an “extractive CEMs,” in which case the sample gas is extracted from the emission stream and transported to a gas analyser for the measurement and recording of the contaminant concentration; or an “in-situ CEMs,” which measures and analyzes the emissions directly in a stack. The main benefits of an extractive CEMs is that the instruments are not subject to heat, vibration, and corrosive conditions; maintenance is easier at ground level; and analyzers for extractive CEMs are generally less expensive than those for in-situ systems. The disadvantages are that sample lines can leak, freeze, or clog, and pollutants can be lost to adsorption, scrubbing effects, or condensation. The main benefits of an in-situ CEMs are minimization of sample loss and elimination of the costly sampling and conditioning system. However, maintenance and replacement inside the stack are more difficult, and calibration gas must be taken to the analyzer location.

A PEMs can provide a less costly alternative to a CEMs. A PEMs calculates emissions based on their known correlation to operating parameters (e.g., fuel use), instead of by direct sampling. The authors of this study found that PEMs are not used at any petroleum refineries in Canada because of the complexity of the chemical reactions involved in some process units (FCCUs).

Source testing, also known as stack testing or stack sampling, is the regulatory standard. Done by trained and experienced staff during typical operating conditions, using accredited methods, and at appropriate intervals, source testing can provide accurate annual emission estimates. It is often required to determine compliance with provincial or regional air discharge permits. It is required for certification of a CEMs, and emission factors are often a collection of source tests at various operating rates.

A mass balance calculation applies the law of conservation of mass that the quantities of materials going in and out of a process unit remain unchanged provided there is no accumulation in the unit. *the report does not mention the deleted text*. The cost depends on the availability of accurate data and staff time. The general equation for the mass (M) balance calculation is

$$M_{in} = M_{out} + M_{accumulated/depleted}$$

A refinery example is the combustion of fuel oil containing sulphur. If one assumes all the sulphur converts to SO₂ then the following equation could be used to estimate SO₂ emissions.

$$SO_2 \text{ emissions (kg)} = \text{amount of fuel oil burned (m}^3\text{/d)} \times \text{sulphur content (mg/m}^3\text{)} \times (\# \text{ days units operates)} \times (\text{molecular weight of SO}_2\text{/S)} \times 1(\text{kg}) / 10^6 \text{ (mg)}$$

Emission models and factors are widely used to measure air emissions from refineries. If default data are not applicable to local conditions or type of facility, emission models do require detailed input of data, such as meteorological data or equipment specifications. Examples for the petroleum refining sector include the U.S. Environmental Protection Agency (EPA) TANKS and WATER9 models, both of which can be used to calculate VOCs and other air contaminants. An emission factor is a simplified emission model: it relates emissions from a source to some activity associated with the source. A large number of

published emission factors are available for many processes, and they are generally the least costly method and the easiest to apply. U.S.EPA provides ratings of reliability with its AP-42 emission factors.

Engineering estimates can be reliable or not depending on many factors, in particular the judgment of the expert involved. They can be used when there is a large data gap and neither emission test data nor published emission factors are available.

In Canada, regulatory agencies set out quality assurance/quality control (QA/QC) requirements to ensure that monitoring data from particular equipment meet quality standards and that data on total annual emissions by facility are complete. QA/QC methods include adherence to protocols, accreditation, training of staff, documenting activities, auditing and so forth.

Recordkeeping is essential. The study recommends that the methods used to monitor air emissions at refineries should be reported to the NFPRER. For each of the six pollutants considered in the study, it lists the types of records that should be retained for review by jurisdictions.

SOURCES OF EMISSIONS AT REFINERIES

Sulphur dioxide

Sources of sulphur dioxide emissions at Canadian petroleum refineries include process heat generation, sulphur recovery, catalyst regeneration, and flares.

Possible methods for monitoring sulphur dioxide emissions from refinery sources include mass balance calculations, emission factors, stack surveys, and CEMs. This study found that permits for monitoring sulphur dioxide emissions specify CEMs for four FCCUs and five sulphur plants, and it determined that stack surveys are performed on three heaters or boilers and four FCCUs. It recommends use of emission factors (with verification) or CEMs for FCCUs, mass balance calculations or CEMs for sulphur plants, mass balance calculations for boilers and heaters (solid and liquid fuels), and emission factors for flares.

Nitrogen oxides

Sources of nitrogen oxide emissions at Canadian refineries are combustion in heaters and boilers, flaring, incineration of waste gases from sulphur plants, and catalyst regeneration.

Possible methods for monitoring nitrogen oxide emissions from refinery sources include emission factors, stack surveys, CEMs, and PEMS. In the case of flares, only emission factors can be used. From available permit data, this study found stack surveys are required for four boilers or heaters, five FCCUs, and one sulphur plant; and CEMs on one FCCU and two sulphur plants. The study recommends use of emission factors (with verification) or CEMs for FCCUs; emission factors (with verification) for sulphur plants; annual stack surveys (with continuous verification) for boilers and heaters with capacity of >250 MMBtu/hr, annual stack surveys for those with capacities from 100–250 MMBtu/hr, and AP-42 emission factors for the smaller ones; and emission factors for flares.

Carbon monoxide

Carbon monoxide emissions at Canadian refineries come from incomplete combustion in heaters and boilers, flares, incineration of waste gases from sulphur plants, and catalyst regeneration.

Possible methods for monitoring carbon monoxide emissions from refinery sources include emission factors, stack surveys, and CEMs for catalyst regeneration, and boilers and heaters; and emission factors for flares. CEMs are not usually warranted. Based on available permit data, this study found that stack surveys are used to measure carbon monoxide emissions from five FCCUs. One refinery performs stack surveys on heaters and the sulphur plant. It recommends use of emission factors or CEMs for FCCUs, emission factors for boilers and heaters, and emission factors for flares.

Particulate matter

Particulate matter (PM) can be primary or secondary; filterable or condensable; and total (TPM), total suspended (TSP), inhalable (PM₁₀), or respirable (PM_{2.5}). NPRI requires reporting of PM that is primary (released directly to air) and filterable (as determined by a U.S.EPA sampling train). Significant sources of PM emissions at Canadian refineries are external combustion (from boilers, heaters, and flares) and catalyst regeneration (in FCCUs).

Possible methods for monitoring PM emissions from refinery sources include emission factors and stack surveys. Based on available permit data, this study found that for this pollutant stack surveys are used for seven FCCUs, two boilers and heaters, and one sulphur plant. It recommends use of emission factors (with verification) or mass balance calculations (measured catalyst losses) for FCCUs; emission factors (with verification) for boilers and heaters that use solid and liquid fuels; emission factors alone for boilers and heaters that use gaseous fuels; and emission factors for flares.

Volatile organic compounds

In the background study, the term “volatile organic compounds” is used according to the definition from Environment Canada's National Pollutant Release Inventory (NPRI).

Sources of emissions of VOCs at Canadian refineries are incomplete combustion in heaters and boilers, catalytic cracking unit regenerators, catalytic reforming unit regenerators, steam methane reformers or hydrogen units, and flares; as well as fugitive emissions (i.e., leaks from equipment [valves]); storage tanks; loading operations; landfarm operations; wastewater sources; and non-routine releases, such as spills.

Possible methods for monitoring VOCs emitted are best limited to emission models and factors, because the sources of VOC emissions are numerous and do not lend themselves to direct monitoring. In addition, it is difficult to achieve accuracy using mass balance calculations, although these may be used to estimate total VOC emissions from fugitive or wastewater sources, whenever emission models or factors are not applicable.

Based on available permit data, VOC emissions are the only class of substances in this study for which permits have an emission inventory requirement: for this reason, the CCME code for fugitive and tank emissions is referenced for four facilities. Also stack surveys are required for some combustion sources, primarily FCCUs. The background study recommends use of CCME's “Fugitive VOC Code Monitoring Section – EPA leak rate/screening value

correlation equations for fugitive emissions” (with an exception for flanges); and it specifies emission model/factors for the following emission sources: storage tanks (a model from U.S.EPA TANKS); loading, wastewater, landfarms, and non-routine (factors from Canadian Petroleum Products Institute Code of Practice); and boilers and heaters, and flares (U.S.EPA AP-42 factors).

Benzene

Sources of benzene emissions include tankfarms, FCCUs, and fuel-oil or coke combustion.

Possible and recommended methods for monitoring benzene emissions are the same as those listed in the previous section for VOCs.

AMBIENT MONITORING

All Canadian refineries have some degree of ambient monitoring according to the information that was available and that was reviewed. The suite of contaminants, number of stations, and the frequency of monitoring and responsible agency vary widely across Canada. Appendix C of the background study summarizes the ambient monitoring currently conducted in airsheds influenced by refineries.