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Series on Pollutant Release and Transfer Registers No. 9

FRAMEWORK FOR SELECTING AND APPLYING PRTR RELEASE ESTIMATION TECHNIQUES

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Series on Pollutant Release and Transfer Registers

No. 9

FRAMEWORK FOR SELECTING AND APPLYING PRTR RELEASE ESTIMATION TECHNIQUES

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Environment, Health and Safety Publications on Pollutant Release and Transfer Registers

Pollutant Release and Transfer Registers (PRTRs): A Tool for Environmental Policy and Sustainable Development. Guidance Manual for Governments (OECD/GD(96)32) (1996).

PRTR Series No. 1: Proceedings of the OECD International Conference on Pollutant Release and Transfer Registers (PRTRs). PRTRs: National and Global Responsibility. Tokyo, 9-11 September 1998. Part 1 (1999).

PRTR Series No. 2: Proceedings of the OECD International Conference on Pollutant Release and Transfer Registers (PRTRs). PRTRs: National and Global Responsibility. Tokyo, 9-11 September 1998. Part 2 (1999).

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FOREWORD

OECD began work on the PRTR release estimation techniques (RETs) in 1999. That same year, an expert workshop was held in Australia with objectives to identify what information is readily available on release estimation techniques for point and diffuse sources and to recommend what can be done to improve the use and availability of such techniques.

The work programme of the Task Force on PRTRs (previously Task Force on RETs) has called for the development of several technical documents to provide governments and industry with relevant and update information and practical guidance for identifying, selecting and using different techniques for estimating pollutant releases and transfers from point and diffuse sources.

This document*, Framework for Selecting and Applying PRTR Release Estimation Techniques* provides information on: i) the general principles for producing release data; and ii) the selection and application of the various release estimation techniques to different industrial sectors. The document can also be used for estimating transfers of pollutants.

The *Framework for Selecting and Applying PRTR Release Estimation Techniques* builds on and complements the information provided in the *Resource Compendium* that introduces the available RETs and where to find information on them (OECD PRTR Series, No. 5, 6, 8). The Resource Centre for Release Estimation Techniques (http://www.oecd.org/env/prtr) provides a clearinghouse of guidance manuals and other documents on release estimation techniques. The manuals and documents available at the Resource Centre include descriptive information on the sources of pollution and the pollutants that are released, as well as information on the different applicable estimation techniques worldwide.

Different aspects of this document have been addressed in several draft papers that were prepared under the OECD Task Force on Release Estimation Techniques. This final version is a compilation of selected parts of the earlier drafts and it was prepared by a small working group under the auspices of the OECD Task Force on PRTRs. The working group consisted of Ms. Kristina Saarinen, Finland (lead), Mr. Pieter van der Most, the Netherlands, Mr. John Dombrowski, US EPA, and Mr. Noriyuki Suzuki, Japan.

This document is published on the responsibility of the Joint Meeting of the Chemicals Group and Management Committee of the Special Programme on the Control of Chemicals of the OECD.

TABLE OF CONTENTS

EXECUTIVE SUMMARY

Background

The selection and applicability of release estimation techniques (RETs) has been on the agenda of the OECD Task Force on PRTRs since its establishment in 2000 (previously called Task Force on Release Estimation Techniques). Different aspects related to the selection and application of release estimation techniques have been addressed in several closely related draft documents, which the Task Force on PRTRs finally decided to combine under one title in the present document: "*Framework for Selecting and Applying PRTR Release Estimation Techniques*". The task was carried out by a working group with experts from Finland (lead country), Japan, the Netherlands and USA.

Context

The Framework for Selecting and Applying PRTR Release Estimation Techniques is intended to be useful for facility operators required to report to a PRTR, by providing guidance on the RET selection process and issues related to the application of RETs. The document is designed to assist PRTR project managers and policy analysts by providing an insight into the practical issues associated with the production of emission data on-site and the application of the bottom-up approach to estimation of releases. *The Framework for Selecting and application of PRTR Release Estimation Techniques* does not reintroduce the various release estimation techniques, but builds on and complements the information found in the *Resource Compendium of PRTR Release Estimation Techniques* and the *Resource Centre for Release Estimation Techniques* (www.oecd.org/env/prtr). The Resource Centre provides relevant material and useful websites addresses containing information on release estimation techniques and related guidance worldwide.

This framework document provides information on:

- the general principles for estimation of releases at an industrial site;
- the applicability of the various release estimation techniques;
- issues that need to be taken into consideration when applying the techniques; and
- issues that would support the evaluation of the release data.

Summary of the Content

Chapter 1 of this document leads the reader through the practical aspects of release estimation and introduces the elements of a release data production programme.

Chapter 2 provides information on the general principles in producing release data from point sources, as well as criteria for selecting the release estimation techniques. Quality considerations in the production of release data, as well as issues related to uncertainty in release data are also discussed in this chapter.

Chapter 3 leads the reader thoroughly through issues that are specific to each release estimation technique and that need to be taken into account when selecting the release estimation techniques, as well as when producing the input data and applying RETs.

Annexes 1-3 lead the reader through practical examples of applying release estimation techniques in three selected industrial branches.

GLOSSARY OF TERMS

Aerosols	Colloidal systems in which the dispersed phase is composed of either solid or liquid particles and in which the dispersion medium is some gas, usually air.
AP-42	Compilation of Air Pollutant Emission Factors.
BAT	Best Available Techniques.
Breathing loss	Breathing loss is the fugitive emission from the expulsion of vapour from a tank vapour space that has expanded due to daily changes in temperature and barometric pressure.
BREF	BAT Reference Document.
CEM	A continuous emission monitoring system is the total equipment necessary for the determination of a gas, particulate matter or liquid concentration or emission rate using pollutant analyser measurements and a conversion equation, graph or computer programme to produce the required data.
CH_4	Methane.
CO	Carbon monoxide.
CO_2	Carbon dioxide
CLRTAP	Convention on Long-Range Transboundary Air Pollution.
FRG	Flue gas recirculation.
EEA	European Environment Agency.
EFDB	Emission Factor Database (IPCC).
EMAS	Environmental Management and Audit System.
EMEP	Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe.
Entrainment	Mixing into pre-existing air.
EPER	European Polluting Emissions Register.

ESD	Emission Scenario Document.
ESP	Electrostatic precipitator: operates on the basis of electrostatic attraction and removes particles or mist from the flue gas flow.
EU	European Union.
Excess air	The amount of air available to react that is in excess of the air theoretically required to completely burn the combustible material
Fabric filtration	A method of particle collection that operates on the principle of collecting dust on one side of a woven or felted fabric, usually in the form of tubes (bags) that are suspended in a structure (baghouse).
FTIR	Fourier Transform Infrared Spectroscopy.
Fugacity	Measure of the tendency of a gas to escape or expand.
H_2S	Hydrogen sulphide.
HCl	Hydrochloric acid, hydrogen chloride.
Indirect monitoring	Parametric emission measurement, use of surrogate parameters, use of operation control parameters.
IPCC	Intergovernmental Panel on Climate Change.
IPPC	Integrated Pollution Prevention and Control.
ISO	International Standardisation Organisation.
LEA	Low excess air firing.
LNB	Low NO_x burners.
MSDS	Material Safety Data Sheet.
NH_3	Ammonia.
NMVOC	Non-methane volatile organic compounds, i.e. volatile organic compounds without methane (CH_4).
NO_x	Oxides of nitrogen. The primary combustion volatile product of nitrogen is nitrogen dioxide(NO_2). However, several other nitrogen compounds are usually emitted at the same time (most notably, nitric oxide (NO) and nitrous oxide (N_2O)). The convention is to report total NO_x on the basis of the molecular weight of NO_2.
NPI	National Pollutant Inventory (Australia).

NPRI	National Pollutant Release Inventory (Canada).
OECD	Organisation for Economic Co-operation and Development.
PEM	Parametric emission monitoring, equals to indirect monitoring, use of surrogate parameters and use of operation control parameters.
PM	Particulate matter.
Pollutant	A substance introduced into the environment that adversely affects the usefulness of a resource or the health of humans, animals, or ecosystems.
PRTR	Pollutant Release and Transfer Register.
RAP	Reduced air preheat.
Residence time	The average time spent by the molecules in a vessel.
RET	Release estimation technique.
SO_2	Sulphur dioxide.
SO_x	Oxides of sulphur. Oxides of sulphur can be sulphur dioxide (SO_2) and sulphur trioxide (SO_3). The convention is to report total SO_x on the basis of the molecular weight of SO_2.
Source testing	Single or periodic measurements.
Spray drying	A technique in which liquid is dried by spraying into a tower through which there is a down draft of hot gases.
Surrogate parameter	Surrogate parameters i.e. often operation control parameters which are used in determination of emissions (also called as parametric emission monitoring or indirect monitoring).
THC	Total hydrocarbon.
TRI	Toxics Release Inventory (USA).
UN	United Nations.
UNECE	United Nations Economic Council for Europe.
UNFCCC	United Nations Framework Convention on Climate Change.
UNITAR	United Nations Institute for Training and Research.
USEPA	United States Environmental Protection Agency.
VOC	Volatile organic compounds including methane (CH_4).

CHAPTER 1: INTRODUCTION

1.1 Practical Aspects of Release Estimation

In the framework for producing PRTR release data there are certain key issues that affect the transparency and comparability of the results and need to be taken into consideration when producing data for PRTR purposes.

To enable comparability of the release data in the PRTR registers worldwide, general principles in production of the release data need to be followed. The practical value of release data depends on well they represent the true releases, and how comparable they are with results from other plants in the same industrial branch, or with other branches, regions or countries. The comparability of the release and transfer data of an industrial site includes both the consistency in those release sources that are included in the sources from which releases are estimated, and the consistency and transparency of the methods and practices that have been used to produce the data.

The operator or owner of the facility is responsible for the quality of the information he reports to the national PRTR register. As release data from industrial installations are presented in various contexts, it is advisable that the same data, when available, is used for all reporting purposes to enable consistency between the different data sets. For instance, the installations report to the authorities according to the requirements set in the environmental permits (compliance assessment), and to the emission registers[1] or registers for emission trading, and present emission data in the companies' environmental reports. Many countries also use the release data reported by industrial installations in preparation of national emission inventories to the international conventions[2].

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[1] Emission registers, such as the OECD PRTR registers established according to the OECD Council Recommendation C(96)41/FINAL; UNECE PRTR registers according to the UNECE Convention on Access to Information, Public Participation in Decision-making and Access to Justice in Environmental Matters (1998); and, the European Pollutant Emissions Register (EPER) according to the European Commission Decision 2000/479/EC. The facilities report the releases only when their emissions exceed the thresholds set in the reporting requirements.

[2] National emission inventories are reported e.g. to the United Nations Framework Convention on Climate Change 1992, URL: http://www.unfccc.int and the United Nations Economic Council for Europe Convention on Long-Range Transboundary Air Pollution, 1979, URL: http://www.unece.org/env/lrtap/

1.2 Release Data Production Programme

Monitoring of releases may require both emission measurements and use of other release estimation techniques. In many cases measurements are used to determine the value of a measure or parameter that is used in calculation of the release data.

Many PRTRs require emission measurements. Others may include release and transfer data based on measurements only in cases where the measurement is required by another law. In all cases, quality control practices should be established to ensure reliability of the numerical values produced. To ensure reliable results it is often necessary to establish a release data production programme, which provides a detailed description of the generation of release data for each substance:

- It is essential to have good understanding of the processes and activities at the site and of their contribution to the releases. Organising and carrying out the practical monitoring tasks include various factors that affect the final results. Guidance for organizing the monitoring is presented for instance in the standard ISO 14001;

- The different release estimation techniques have different advantages and disadvantages that need to be taken into account when assessing their applicability to a specific case. The choice between the different release estimation techniques depends on the releases and their sources, the required accuracy as well as the relative costs of the estimation techniques. In cases where use of direct measurement is complex, costly and/or impractical, other methods can be used to find the best option. The relationship between the release to be estimated and the RET applied needs to be demonstrated, whenever direct emission measurements are not used. The principles listed in Section 2.4 (Release data production chain) should be followed both when using direct emission measurements and when using other release estimation techniques such as indirect monitoring, calculations, emission factors, or engineering judgement. This is due to the fact that usually the value of a measure or a parameter used in the calculations is determined by measurement.

- The sensitivity of the methods to the emission concentration, flow and their fluctuations, needs to be considered when selecting the RET.

- In the release data production programme it is often defined how the data should be produced. Consistency between the release data production programme and the actual release generating processes needs to be checked from time to time. In cases of process changes that would affect the releases, the programme needs to be modified accordingly. It is also important to collect enough information to enable estimation of releases under both normal and exceptional conditions;

- Monitoring frequency needs to be determined case-by-case, taking into account the applicability of the methods and equipment to the process, release source and the measurement location to be monitored.

- When deciding the monitoring method it is important to check that the method is applicable for the original reason for monitoring as shown, for example, by the limits and performance criteria for an installation. It is equally important to ensure that the technical equipment is adequate for the purpose and that the persons carrying out the tasks have the necessary knowledge and expertise. Guidance for these matters is presented for instance in the standard ISO 17025.

- In cases where the error in the result reaches the magnitude of the result itself the suitability of the estimation technique must be questioned. The factors affecting the applicability of the different release estimation techniques are considered in Chapter 3.

1.3 Structure of the Document

Chapter 1 of this document leads the reader through the practical aspects of the release estimation and introduces the elements of a release data production programme. This chapter highlights the key issues that affect the transparency and comparability of the estimation results and hence need to be carefully considered when producing data for PRTR purposes.

Chapter 2 provides information on the general principles in producing release data from point sources, as well as criteria for selecting the release estimation techniques. Quality considerations in the production of release data, as well as issues related to uncertainty in release data are also discussed in this chapter.

Chapter 3 leads the reader thoroughly through issues that are specific to each release estimation technique and need to be taken into account when selecting the release estimation techniques, as well as when producing input data and applying the RETs.

Annexes 1-3 lead the reader through practical examples of applying release estimation techniques in three selected industrial branches.

CHAPTER 2: GENERAL PRINCIPLES IN RELEASE DATA PRODUCTION

2.1 Total Releases from an Industrial Site

Total annual releases of a specific substance at an industrial site cover a wide range of releases originating from a wide range of sources under varying conditions, which are extremely installation specific. In addition to the channelled emissions during normal operation (end of pipe/stack releases) emissions, there are also other sources and prevailing conditions that generate releases. Especially at large industrial installations, where the majority of the regular releases are abated or treated on site, the relative share of releases during exceptional circumstances can be significant compared to normal releases. Diffuse emissions of certain substances[3] can also make a significant contribution to the total amount of releases. The range and scale of the activities at an industrial site, as well as the layout and age of the plant have an impact on the number of relevant release sources and the temporal variations of the releases. Thus, the total releases to be reported from a site include both the normal and exceptional channelled and diffuse emissions during the reporting period from all relevant activities in the site area. A compilation of the release types from point sources is presented in Table 1. [4, 9, 13]

2.1.1 Spatial Coverage of Releases

The sampling or measurement points have to be chosen to be representative for the true releases and the practical arrangements carried out accordingly. The releases at an industrial site are either channelled or diffuse:

- *Channelled releases*[4] include releases into the environment through a pipe, i.e. a stack or a sewer.

- *Diffuse emissions*[5] are due to releases of liquid, gaseous or solid substances from pumps, storages, filters or material transfer and maintenance. A specific type of diffuse emissions is the fugitive emissions caused by leakages of gaseous or liquid substances from, for instance flanges, pumps or storage facilities due to gradual loss of tightness of the equipment [4].

2.1.2 Temporal Coverage of Releases

Normal operation conditions at a plant cover the steady and characteristic conditions specific to the process type in question where the releases vary in a well known range in their volume flow, composition and concentration. The type and range of normal releases vary between different types of

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[3] For instance non-methane volatile organic compounds, NMVOCs

[4] In some OECD countries the terms "stack emission" can be used instead (see also Table 1).

[5] In some OECD countries the terms "fugitive emissions" can be used instead (see also Table 1).

processes. For instance, releases from batch and cyclic processes may have a wide temporal variance, but still fit within the expected range.

The measurement and sampling of releases during normal operation need to be planned carefully to give a representative picture of the releases and their characteristic fluctuations. In cases of fluctuating releases, the monitoring results need to be treated with statistical methods. The normal operation releases do not cover releases during start-ups or shutdowns, stoppages, maintenance, or unmanageable circumstances that affect the releases. [4, 9, 13]

Table 1. Different release types from point sources [4, 13]

Concept	Explanation
Channelled releases	Releases of pollutants into the environment are channelled through any kind of pipe, such as a stack or a sewer regardless of the shape of its cross-section. In some OECD countries the term "stack emissions" is used instead.
Diffuse releases	Diffuse emissions arise from a direct contact of volatile or light dusty substances with the environment under normal operating circumstances. These can result from inherent design of the equipment (e.g. filters, dryers), operating conditions (e.g. during transfer of material between containers), type of operation (e.g. maintenance activities) or from a gradual release to other media (e.g. to cooling water or waste water). Diffuse sources can be point, linear, surface or volume sources. Fugitive releases are a subset of diffuse emissions. In some OECD countries the term "fugitive emissions" is identical to the term "diffuse emissions".
Exceptional releases	Exceptional releases are generated due an event that deviates from regular operation, such as varying input or changing process conditions, start-ups or shutdowns, temporary stoppages, by-passes of treatment units due to malfunctioning of the installation, incidents. Exceptional releases can occur under both foreseeable and unforeseeable conditions.
Fugitive releases	Fugitive releases result from a gradual loss of tightness of a piece of equipment designed to contain an enclosed fluid (gaseous or liquid), typically this could be caused by a pressure difference and a resulting leak. Examples of fugitive releases include leakages from a flange, a pump or a piece of equipment and losses from the storage facilities of gaseous or liquid products. Fugitive releases are a subset of diffuse emissions. In some OECD countries the term "fugitive emissions" is identical to the term "diffuse emissions”.
Total releases	The total releases of an installation, or unit, are given not only by the normal releases arising from the stacks and pipes, but also by taking into account diffuse, fugitive and exceptional releases.

2.1.3 Exceptional Releases

As the normal operation time releases are, in general, continually decreasing due to modern technology and improved environmental performance, the relative significance of exceptional releases has increased. The release load from exceptional releases can in certain cases be significantly higher than the normal annual releases. For instance, the collecting efficiency of the electrostatic precipitator is 99–99.9 %. In a bad disturbance situation the particle concentration of the emission can be a thousand fold compared to the normal situation, thus corresponding significantly to the annual emissions. Despite this, the exceptional releases are not always included in the annually reported releases of the facilities. [9, 13]

An exceptional release causes the environmental load to exceed the expected level momentarily or for a longer period. A typical feature in exceptional releases is that they always induce a non-linear point in the release curve. The type and rate of the exceptional release depend on the process and installation in question. The exceptional releases are caused, for instance, by unsteady input or technical conditions, false functioning of a control circuit of a valve or an equipment breakdown. They can also be induced by human omissions, such as an unlocked valve. [9]

Exceptional releases are not regarded as accidental as long as the deviation from normal is not remarkable and the releases can be estimated at an adequate certainty. The quality and quantity of the deviation has to be assessed case-by-case against the possible consequences of the emitted substance and its volume. Accidental releases characteristically have human, environmental and economical consequences, such as serious danger to human health due to toxic or explosive character, or due to causing damage to the environment or material assets. Accidental releases need to be included in the annually reported emissions. [5]

Exceptional releases can occur both under foreseeable and unforeseeable conditions. Releases during foreseeable conditions are generated e.g. during routine start-up and shut-down periods, during maintenance or due to normal variations in the input or process conditions. Unforeseeable conditions include e.g. exceptionally varying input or process conditions or malfunction in the process or abatement technique, as well as due to human error. [4, 9, 13]

Best practices in monitoring of releases under both normal and exceptional conditions are presented in Section 2.5.

2.2 Release Estimation Techniques (RETs)

In this document the release estimation techniques (RET) are presented under the following five categories below. The order of presentation of the methods does not suggest any preference of the methods. More information on the different RETs can be found in the Resource Centre at: www.oecd.org/env/prtr.

For the purposes of this document the release estimation techniques (RETs) are:

- Direct monitoring (direct emission measurements)
- Indirect monitoring
- Calculations
- Emission factors
- Engineering judgement

2.2.1 Direct Monitoring/Direct Emission Measurements

Direct monitoring/measurements refer to direct emission measurements, which can be divided into continuous and periodic measurements:

- Continuous Emission Monitoring (CEM). A continuous emission monitoring system is the total equipment necessary for the determination of a gas, particulate matter or liquid concentration or emission rate using pollutant analyser measurements and a conversion equation, graph or computer programme to produce the required data.; and

- Periodic Emission Monitoring. Emissions can also be determined with short-term emission measurements (source testing), which can be periodical or single measurements. Monitoring frequency can vary between once or twice a year up to daily measurements.

2.2.2 Indirect Monitoring

Indirect monitoring relies on inherent relationships between process parameters and the resulting emissions. These parameters are usually monitored for operation control purposes. For example, emissions can be estimated with high accuracy for any process where those emissions depend directly on process conditions by measuring the process conditions that may be routinely monitored as a part of the production process. The same parameters can then be used to estimate releases. The operation control parameters (also called as surrogate parameters) used for indirect monitoring are usually in real time. Indirect monitoring is sometimes also referred to as parametric monitoring.

2.2.3 Calculations

2.2.3.1 Mass Balance

Releases are determined based on the amount of material that enters a process and the amount that leaves the process. Releases are estimated based on the difference between material input and material output across a vessel, process or entire facility. Mass balance approach relies on the "Law of Conservation of Mass" which states that the amount of chemical, which goes into the system must either come out in the form of a product or as a release or be chemically changed to some other compound.

The general form of mass balance model is as follows:

$$\text{Volume}_{\text{Input}} + \text{Volume}_{\text{Generated}} = \text{Volume}_{\text{Output}} + \text{Volume}_{\text{Destroyed}}$$

2.2.3.2 Models

Release models consider the detailed relationships that exist within an identified system. When using a model, knowledge is required on what is likely to happen to a chemical inside the system. Models are based on a combination of physicochemical and empirical relationships[6].

Engineering Calculations and Physicochemical Relationships

Engineering calculations include empirical relationships that are correlated to a set of observed or measured parameters. These equations can include multiple variables such as air temperature and vapour pressure. For example, emissions of non-methane volatile organic compounds (NMVOCs) from storage tanks vary as a function of the tank size, tank colour, temperature, barometric pressure and throughput and properties of the material stored.

Physicochemical relationships are derived from the fundamentals of chemistry and physics and based on the specific physical and chemical properties of the substances under consideration. Several of the most familiar and widely used physicochemical relationships include Antoine's Equation, the Ideal Gas Law, Raoult's Law and Henry's Law.

2.2.4 Emission Factors

Emission factors are numbers that can be multiplied by an activity rate or by throughput data from a facility (such as the production output, water consumption, etc.), in order to estimate the releases from the facility with the underlying assumption that a linear relationship exists between releases and the specified activity level over the probable range of application. The emission factors are usually expressed as the weight of a substance emitted divided by the unit weight, volume, distance, or duration of the activity emitting the substance, for instance kilogram of pollutant released per tonne of coal combusted.

The basic emission estimate equation using emission factor is:

$$E = A \times EF,$$

Where: E = the emission estimate;
A = the activity level or throughput; and
EF = the emission factor.

If the emission factor is for uncontrolled process, an additional factor to describe the removal efficiency of the abatement technique in place needs to be added into the equation above.

There are two major types of emission factors, namely chemical-specific emission factors and non-chemical-specific emission factors. For example, the emission factor for NO_x emissions is a chemical-specific emission factor and the emission factor for volatile organic compounds (VOCs) is a non-chemical-specific factor. Emission factors developed to take into account the removal efficiency of a specific

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[6] The most familiar model is USEPA's TANKS 4.0 developed for estimating organic emissions from storage tanks. The model has been developed, based on a combination of observations, measurements and physicochemical relationships.

control device for the specific substance are referred to as *"controlled emission factors"* and emission factors that are developed without control devices in place are referred as *"uncontrolled emission factors"*.

2.2.5 Engineering Judgement

Engineering judgements are intuitive methods that take advantage of the experience and professional knowledge of the estimator and knowledge over a specific process or device.

2.3 Selecting the Release Estimation Technique

2.3.1 Applicability of Release Estimation Techniques

The applicability of a specific release estimation technique needs to be determined case-by-case taking into account knowledge of the process to be monitored and the suitability of the monitoring technique to retrieve the desired information of the parameter to be monitored. At an industrial site, a combination of the various release estimation techniques can be used in production of information of the total releases from the site. [4, 9]

The different approaches and release estimation techniques have advantages and disadvantages that need to be taken into account when assessing their applicability to the specific case. The choice between the different release estimation techniques depends on the pollutants, their sources, the required accuracy, as well as the relative costs of the estimation techniques. Depending on the process or substance to be monitored, some of these possibilities may not be available. In cases where use of direct measurements is complex, costly and/or impractical, other methods can be used to find the best option. The use of other methods, such as indirect monitoring[7], mass balances and emission factors, transfer the burden of uncertainty and traceability from measurement of the actual emission to measurement of several other parameters or to the validation of a model, such as mass balance or emission factor. Each of these methods uses either input or output data of the process or a value of a parameter that is measured. The relationship between the estimation method used and the release parameter needs to be demonstrated, whenever direct measurements are not used. [4, 9]

The principles listed in Section 2.4 should be followed both when using direct measurements and when using rough release estimation techniques such as emission factors, mass balances or other calculations. In cases where the error in the result reaches the magnitude of the result itself the suitability of the estimation method needs to be questioned. [4] The factors affecting the applicability of the different release estimation methods are considered in Chapter 3.

The correspondence of the applied release estimation techniques to the reality needs to be checked from time to time and automatically in cases of any alterations having impact on them. Substitutive calculation methods must be established for conditions where measurements cannot be applied (for instance by-passes of the release treatment units or malfunction of the monitoring system). [4, 9]

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[7] As stated in Chapter 2.2 indirect monitoring is the general term used in this document for surrogate parameters operation control parameters and parametric emission monitoring.

2.3.2 Selecting the Release Estimation Technique

The choice of the release estimation technique has an influence on the manner in which PRTR data can be used and on the credibility of the data provided in a PRTR. Some PRTR programmes allow the reporting facilities complete flexibility in the choice of the release estimation techniques, while others require that a certain technique, or one of a list of recommended techniques, be used. Given that increased costs are almost inevitably associated with increased accuracy, governments need to decide how much accuracy is necessary to achieve the objectives of their PRTR.

The estimation of releases and transfers is based on the fundamentals of science. Each of the techniques is valid under certain conditions. However, if there is more than one option, as is frequently the case, one of the methods becomes the preferred option and the others are considered alternative. There are several factors influencing what is determined to be the optimal approach. These factors include time and cost constraints, available data, required data quality and the ability of the estimation technique to best represent the release. Also the significance of the individual source in relation to other sources influence the selection of the RET. Figure 1 illustrates the relationship between these factors for each of the RETs. The end use of the PRTR is an extremely important consideration in the selection of methods. For instance, the supervision of emission limits and standards often require the use of continuous measurements for certain emissions, for which also a less costly RETs would provide the necessary data for the PRTR.

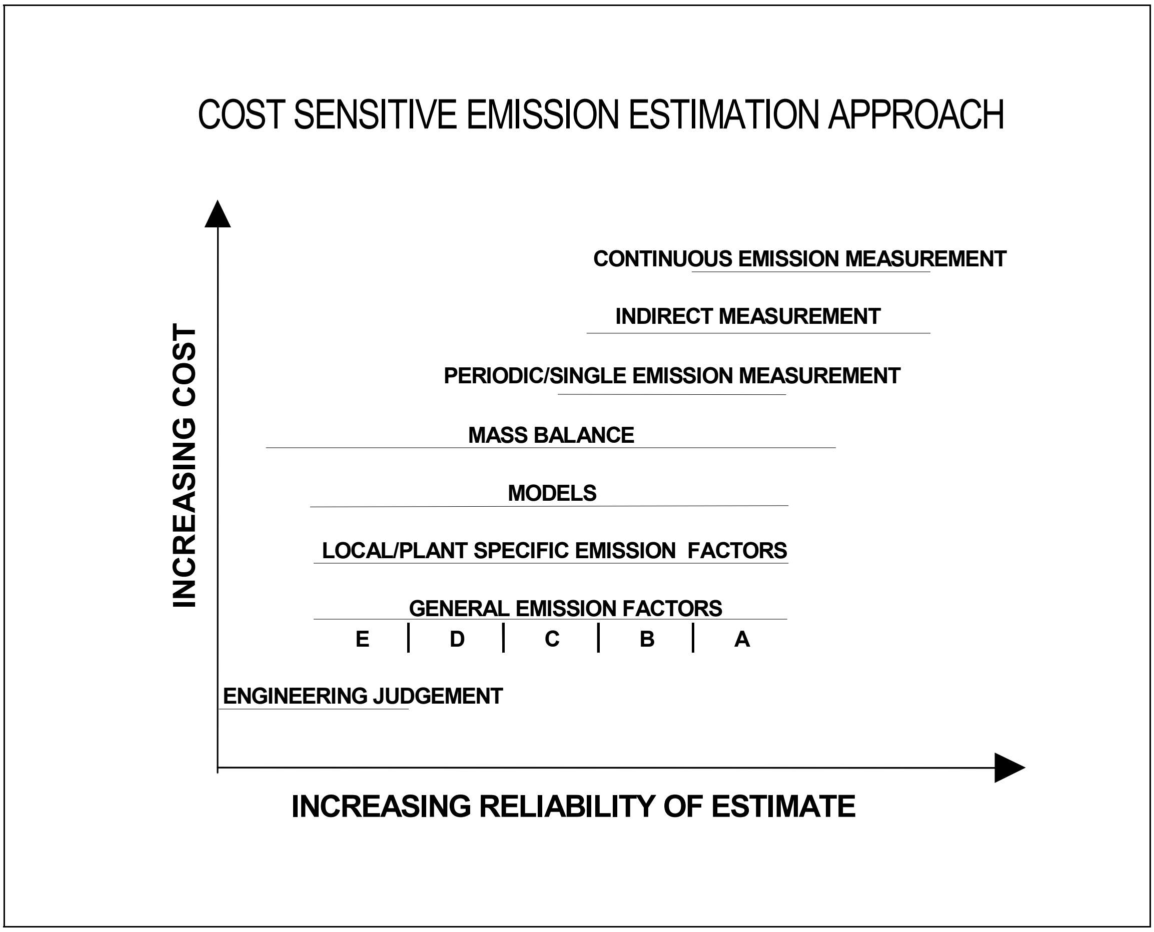

Figure 1: Relationship between cost and reliability of RETs modified according to USEPA, 1997 [27]

Bearing the above listed factors in mind, the following situations are generally encountered:

- The simplest case is where there is no time or cost constraints and the relevant data are available. In this situation, the RET providing the most accurate release data should be selected and used;

- Where the data are not available, but resources allow these data to be collected, the RET providing the most accurate release data should be selected and used. An example could be where monitoring for the specific pollutant is cost-effective but where monitoring of the specific source has not previously been conducted;

- Where adequate resources are not available for the necessary data collection required for the RET providing the most accurate release data, a next best RET would need to be selected. An example could be where monitoring is prohibitively expensive;

- When a particular source is likely to be insignificant compared to other sources considered in the PRTR, the use of the most accurate RET may not be warranted due to the extra time or cost associated with this RET; and

- Source specific data may not be available and, therefore, it may not be possible to use the RET providing the most accurate release data.

2.3.3 The RET Selection Process

The RET selection process is not mechanical and is usually done on a case-by-case basis. The selection process begins with determining the source type, emission characteristics and data needed for the application of the RET, as opposed to the data that are actually available. These factors affect the inherent uncertainty associated with the selected technique and, ultimately, affect the decision-making process in selecting appropriate release estimation techniques. It is important to note that often, it may not be entirely clear which RET is the preferred one. Frequently, the reliability of different methods may be comparable for a given situation and a *judgement* is required as to which method is most suitable for a particular application.

***First steps of the RET selection process*:**

- Determine source type and emission characteristics
- Assess data needs versus data availability
- Appropriate RETs to use for estimating releases
- Uncertainty associated with the use of the RETs

2.3.3.1 Releases and Their Sources

The first step in the RET selection process is to identify the key characteristics of each source for which releases are to be estimated. Point sources such as stacks, vents, or other discrete discharge points are generally associated with combustion or process releases at the facility. Usually, it is possible to measure the releases from such sources.

When a source is known to be significant, for instance from visual inspection for a specific dust source or an operator's opinion for process losses, it is appropriate to use a RET that provides more accurate data than for minor sources.

When selecting a RET for a source for which several options are available, a certain amount of discretion or crosschecking between the relevant sources of information need to be utilised. The estimates produced by the different RETs should also be compared with each other, as it may be that the more accurate RET gives several orders of magnitude larger emissions than the others. This type of qualitative check provides a potentially important means of ensuring that the calculated releases reflect the actual releases from a specific source or a specific facility. In addition, the estimates produced for each source at a facility should also be compared with each other. If, for example, the more accurate RET discussed above provides actually several orders of magnitude larger emissions than any other release estimated for the facility, then further investigation may be required.

Fugitive or diffuse emissions, on the other hand, are those that are emitted from processes or activities that are generally not technically or economically feasible to collect and control (e.g. storage piles, wastewater retention ponds). Release data are not usually available for these sources, although there are cases such as diffuse emissions to land or water, where measurement is the only reliable method to collect site specific data.

The selection of a RET also depends on whether the data utilised in developing the technique is specific to that region/country or whether it was developed elsewhere. When the selection or adaptation of a RET from another country is being considered, specific issues that should be taken into account in the process are:

- The consistency (or differences) in definitions of terms such as facility and sources covered by the PRTR;
- The scope of application of the RET;
- The specific characteristics of the source in question compared to the source(s) for which the RET was originally developed; and
- The data that are available for release estimation compared to the data that are required for the RET.

2.3.3.2 Assessing Data Needs versus Data Availability

The data required for release estimation relates to the source type and the substances released. The first step is the collation and review of all data available for the source.

Typically, the available measurement data are collected as part of a regulatory requirement and are principally used to indicate compliance with an environmental programme. Therefore, the quality of these data will reflect the standard imposed upon the facility for regulatory reasons. For pollutants that have been the subject of regulation for relatively long periods of time (e.g. SO_2, NO_x, CO), empirical relationships and emission factors are frequently available for many of the sources of such pollutants.

In some cases there may be very little data available and that data may be of low quality.

Assessing data to see if it can be used in a RET requires the user to develop an appreciation of the unit process as well as acquiring a 'feel' for what the values mean. Sometimes, there are very little or no measured data or the data that are available are not correlated to any process parameter, making it very difficult to assess if the data are representative of the releases to be estimated.

Stacks will usually have at least some monitoring data available for pollutants of concern whereas process vents may not have any monitoring data available. Data for use in empirical or physicochemical relationships may be available in these cases or activity data may be available for use together with emission factors.

For many pollutants, empirical relationships or emission factors do not exist for certain sources. In such situations, direct emission measurements may be the only way to obtain an estimate of releases of the pollutants from particular sources. The cost of sampling is a major factor in determining the viability of the estimation process. If the cost of sampling for a particular pollutant is prohibitive, then the application of any RET becomes difficult, as continuous, periodic or single emission measurements and mass balances all rely on sampling data. In such situations, alternative RETs, such as emission factors or engineering calculations and other methods, may still be possible. This will need to be evaluated on a case-by-case basis.

2.3.3.3 Appropriate RETs for Estimating Releases

Once the source type for each environmental medium (air, water, soil) has been identified, the RET can be selected. Sometimes, this step may include the evaluation of several RETs for a specific release type. The selection process is illustrated in Table 2 and Figure 2. Key questions that should be asked when considering which RETs should or could be used are listed below.

For process point sources, key questions are:

- Are measurement/monitoring data available? Use the available data to obtain the most reliable estimate using one, or a combination, of continuous, periodic or single emission measurements and mass balance.
- Can indirect monitoring be used to estimate releases?
- Is there an empirical/physicochemical relationship that applies to the source? Are the necessary process data available to apply the empirical/physicochemical relationship?
- Is there a site or industry specific emission factor available?
- Are other emission factors available?
- Can engineering judgement be employed?
- Can licence conditions be used to estimate worst-case releases?
- Can an Emission Scenario Document (ESD) be used to estimate worst-case releases?

Table 2: Features involved in the selection of the appropriate RET

Feature	Example
Understanding how to use the RET(s) available for the estimation for each pollutant under consideration.	For the estimation of air emissions from the boiler stack, the only data available are from measurement data. This narrows down the options to stack measurement data or emission factors.
Developing an understanding of the uncertainty involved in each of the RETs.	The available method is accepted by the regulatory authority or the emission factor is rated high quality e.g. by the USEPA's AP-42 system.
Gathering as much data as possible for use in each of the RET(s).	Annual stack emission data are available for 3 consecutive years for the criteria pollutants. No other data exists.
Assessing the quality of the data collected for use each of the RETs	Emission factors for criteria pollutants are representative of almost 20 years' worth of data over a wide range of releases for the given unit process and throughput data very well understood. Stack data have been collected quarterly over the past 3 years and correlate with the 'steady state' throughputs and furnace conditions.
Omitting through process of elimination, the RETs that cannot be used (e.g. due to lack of data).	Stack data will be used due to the repeatability of the measured data and the fact that the data has been collected 4 times per year over a 3 year period.
Applying the selected RET	Another RET, e.g. emission factors may be used to check the releases estimated with mass balance.

For diffuse releases, a similar approach is followed, although the questions differ slightly:

- Can mass balance techniques be used?
- Is there a suitable model that can be applied to the available data?
- Is there an empirical/physicochemical relationship that applies to the source? Are the necessary process data available to apply the empirical/physicochemical relationship?
- Is there a site or industry specific emission factor available?
- Are other emission factors available?
- Can engineering judgement be employed?
- Can licence conditions be used to estimate worst-case releases?
- Can an ESD be used to estimate worst-case releases?

To provide practical guidance on the selection of RETs, the reader is referred to the technical Annexes 1-3 in this document, where the decision-making framework is applied to the selection of RETs for three specific sectors: power generation, petroleum refining and incineration and cover all of the sources that could be covered by a PRTR and consider releases to air, water and land, and transfers.

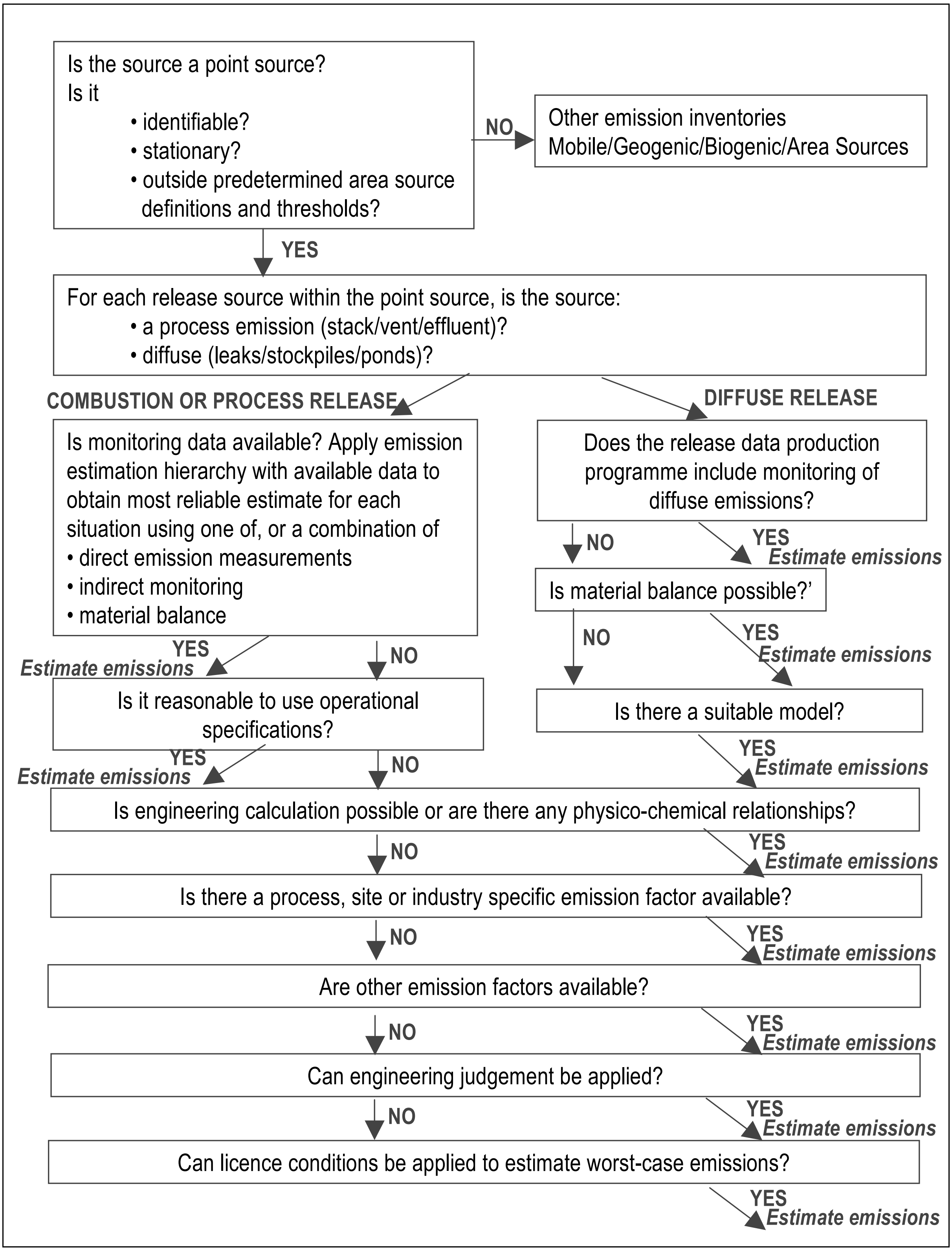

Figure 2. Selection process for RETs

2.3.3.4 Uncertainty Associated with the Use of RETs

2.3.3.4.1 Introduction

The quality of the release estimates in a PRTR is a function of both the data used and the inherent uncertainty in the estimation techniques used. Developing an understanding of the errors involved in release estimation will minimize the uncertainties of each computation. This, in turn, will help minimize the overall cumulative error in the PRTR.

Accuracy is hard to establish in PRTR data development efforts, since the ‘truth’ for any specific emission rate or the magnitude if releases are rarely known. Releases can be estimated with both confidence and reliability. Confidence can be defined as the term used to represent trust in a measurement or estimate [1]. Having confidence in PRTR estimates does not make those estimates accurate or precise, but will help to develop a consensus that the data can be incorporated into the PRTR. Since reliability is defined as ‘trustworthiness, authenticity or consistency’, then using reliable estimates in a PRTR will provide confidence in the data and RETs used in the PRTR.

2.3.3.4.2 Understanding Uncertainty in Release Estimation

The uncertainty associated with a particular release estimation technique is fundamentally reliant on the applicability of each release estimation technique to each particular situation. Direct continuous or periodical emission measurement data are typically of high reliability, but measurements or mass balance data may be just as applicable if taken under representative process conditions. Empirical relationships and models may be far more or far less reliable than emission factors depending on the situation.

The issues discussed in Section 2.4 must be taken into account when applying release estimation techniques to minimize the uncertainty related to the RETs. As long as the RET provides release data that meets the quality requirements of the specific PRTR these release estimation techniques may be used.

2.3.3.4.3 Sources of Error

There is a potential for systematic error or bias in release estimates. Bias results when one of the parameters used in the release estimation algorithm is based on unrepresentative data or does not consider some essential component of the estimation process. Bias in aggregated release estimates can also be caused by the failure to consider all of the sources or source categories that contribute to releases in an area. Systematic error in release estimates is difficult to predict and the effects of the bias introduced in release estimates as a result of systematic error can have significant effects on the data reported in a PRTR. Inherent variability in the release mechanisms and processes giving rise to releases needs to be considered as well.

Some of the key sources of error are:

- Inherent variability within a source activity;
- Inherent variability between sources within the same sector;
- Unrepresentative ‘source-specific’ data;
- Lack of source-specific data;

- Inconsistent or inappropriate measurement techniques;
- Calibration and drift in the instrumentation;
- Sampling errors (including inadequate sample size);
- Improper use of default values in estimation process;
- Miscalculation; and
- Improper data handling (e.g. defective interpretation of results, omission of relevant release data).

A large error in a small release may be insignificant on a relative scale. However, the additive effect in a PRTR can be appreciable. A small error in a large release may be appreciable at the facility level, however, the cumulative error for that source category within a PRTR may not be appreciable. Also, when an accurate data, e.g. concentration data, is multiplied with inaccurate data, e.g. wastewater volume, the resulting wastewater load is as inaccurate as the original volume data resulting in inaccurate information at facility level.

The uncertainty in release estimates may be assessed either qualitatively or quantitatively.

2.3.3.4.4 Qualitative Uncertainty Analysis

The simplest approach for estimating uncertainty is qualitative identification of the sources of bias and error in the release estimates. The easiest approach to take is to list all of the potential sources of bias and describe the direction, i.e. negative or positive, and the order of magnitude of the bias. Frequently, the specification of bias cannot be determined and all that can be provided is an assessment of the order of magnitude of the uncertainty.

2.3.3.4.5 Quantitative Uncertainty Analysis

There are several analytical methods available for the quantitative approach to uncertainty analysis. The end use of the PRTR will help establish what technique is the most appropriate. USEPA suggests the following methods: expert estimation, propagation of error and direct simulation [21].

- The expert estimation method is based on the fact that the statistical distribution of the release data generally does not fit within the realms of traditional statistical methods. Typically the data does not fit the normal, lognormal or other statistical distributions and there are no estimates or statistical parameters such as standard deviation available to assess the uncertainty. In such cases, expert judgement is needed. The Delphi method, a highly formalized approach, is based on the opinion of a panel of experts working separately, but with regular feedback, that ultimately converges into a single answer. The Delphi approach can be very powerful when used properly and the level of expertise is of high quality. Expert judgement outside the Delphi framework is also used for release estimation uncertainty analysis;
- Error propagation methods follow traditional statistical methodology to estimate the cumulative error introduced by the combination of a number of factors, each of which are

associated with a degree of uncertainty. The Intergovernmental Panel on Climate Change (IPCC) suggests that this approach only be applied when the ranges in the estimation technique and uncertainty do not exceed more than sixty percent above or below the mean release estimate [10]. The uncertainty in each component is first established using traditional statistical analysis, probabilistic modelling or a form of the expert estimation method; and

- Direct simulation methods are statistical methods incorporating uncertainty and confidence limits using statistical procedures such as the Monte Carlo regression, re-sampling techniques such as bootstrap and the Latin hypercube approach. Each of these techniques is discussed in [21]. The major drawback in using direct simulation methodologies is the computationally intensive nature of the techniques. Computational power as well as a high degree of competency in statistical analysis is needed to use these methods.

The IPCC has developed detailed guidance on uncertainty assessment for national greenhouse gas inventories [11]. The guidance provides two approaches to quantitative uncertainty assessment, namely the probability density function approach where the range and relative likelihood of possible values are described and confidence limits, the range within which there is a 95% probability of containing the true value. The IPCC guidance represents the likely long-term direction for PRTR data uncertainty characterisation. However, the approaches presented are resource and data intensive, in particular when considering the large number of pollutants in typical PRTRs.

2.4 Release Data Production Chain

The data production chain principle is applicable to all release estimation techniques where either the emission is measured directly or at least one of the values used in the calculations is measured. The data production chain for each release estimation technique and for each pollutant needs to be documented in a release data production programme as described in Chapter 1.

The data production chain consists of the following seven steps that are presented in Figure 3: i) Determination of the volume of effluent, flue gas or waste, as well as determination of the input volume of e.g. fuel or raw material; ii) Sampling of concentration or volume; iii) Sample pre-treatment; iv) Sample treatment; v) Sample analysis; vi) Data processing; and vii) Reporting. [4, 9, 13]

When monitoring releases, the first step relates to quantifying the volume flow and steps three to five to determining the concentration of the substance in the flow of the releases. In case of continuous measurements the steps can also be combined. The aspects presented for sampling apply both to sampling of volume and concentration. Information from all the previous steps is collected to steps six and seven (Data processing and Reporting), under which the information is processed and formulated to give a true and transparent value of the releases.

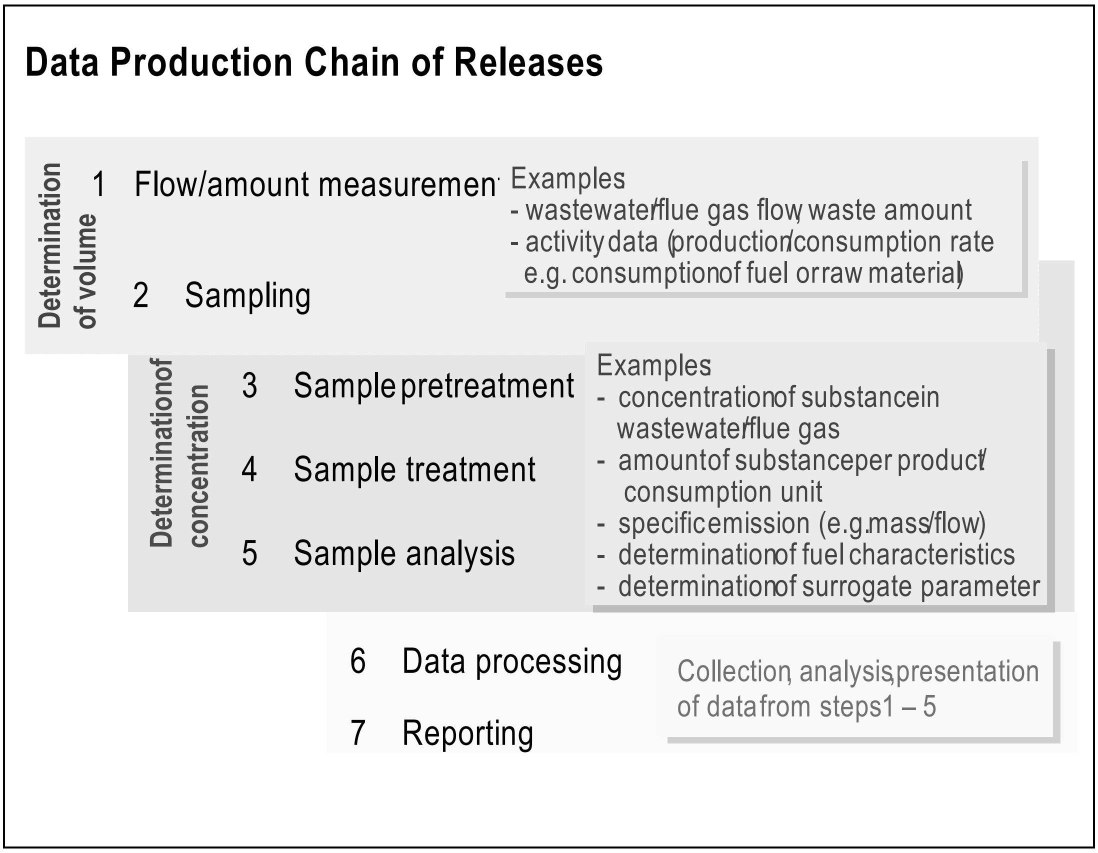

Figure 3. The elements of the data production chain in RETs [13]

The data production chain is applicable to all release estimation techniques where measurements are used to determine one or more of the measures used to produce the release data[8]:

- For direct emission monitoring all the items listed under the steps 1 to 7 need to be taken into account when carrying out the measurements.

- Most of the release estimation techniques use either input or output data of the process or a value of a parameter that is measured. For instance, if the release estimation technique is related to the input, as can be the case when using indirect monitoring, emission factors, mass balance or physicochemical relationships and engineering calculations, the input, e.g. fuel, chemical or raw material consumption, needs to be measured. For the use of some emission factors, the output, e.g. the release flow or product volume, needs to be determined. For determining these data, at least the items listed under the data production chain steps 1-2 and 6-7 need to be taken into account.

- In case, the release estimation technique uses a value of a parameter such as pressure or temperature difference, the items listed under the DPC step 2 Sampling need to be taken into account when determining the value of the parameter.

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[8] For instance, determining the volume of activity data (e.g. fuel consumption, raw material or chemical use, production) and carrying out indirect monitoring (e.g. measuring pressure, temperature, velocity, pH etc.).

2.4.1 Determination of Volume (Step 1)

The determination of concentration in a sample can be very accurate. However, determination of the flow may not be as accurate. Small fluctuations in the flow measurements can potentially result in large differences in calculation of the load. In some situations the flow can also be calculated instead of measured. The accuracy of volume measurement has thus a significant impact on the accuracy of the release data. The same applies to measurement of activity data, which is needed when using emission factors. Therefore the accuracy of, for instance, fuel, raw material or chemical consumption needs to be determined at an adequate accuracy to obtain a reliable estimate of the release. [4, 9, 13]

2.4.2 Sampling (Step 2)

Sampling relates to both the determination of the emission flow or amount and the concentration of a substance in the emission flow, as well as to determination of physical parameters like, for instance, pH, pressure and temperature. [4, 9, 13]

- The sample must be representative in proportion to the composition and volume of the release over the given monitoring period (time representativeness). The frequency of sampling needs to be determined case-by-case to provide adequate information. The sample should represent the whole amount of the release from different operations at the site (space representativeness). If the material is homogeneous, sampling at a single point may be enough, however, for heterogeneous materials several samples from different points may be required in order to have a spatially representative sample;

- The location, suitability and construction of the measurement points, at which the samples are taken, should be such that the fluid at the sampling point is well mixed and be representative of the overall emission. It is important to select a sampling point that is practical to reach and where the flow can also be measured, or is known in advance. The samples should always be taken from the same defined locations; and

- The measurement method and equipment should be suitable for acquiring the information needed.

2.4.3 Sample Pretreatment (Step 3)

Sample pre-treatment includes all activities toward preserving the sample from any changes before it is taken to the laboratory, such as storage, fixation with chemicals or freezing. The value of some parameters of the sample may change over time, for example the pH or the oxygen content of a wastewater sample. In order to preserve the parameters that are to be measured during any storage and transporting of the sample, a time-proof pretreatment will generally be needed. The sample pretreatment method should not change the analysis of the sample. Any arrangement for chemically preserving, storing and transporting the samples should be clearly documented. [4, 9, 13]

2.4.4 Sample Treatment (Step 4)

Sample treatment includes operations in the laboratory prior to analysis such as dilution, concentration, pH adjustment and adding of chemical reagents. Sample treatment must not affect the analysis. The treatment method is usually determined by a standard. If the method is not determined by the standard or a published guideline, it has to be documented in detail. [4, 9, 13]

2.4.5 Sample Analysis (Step 5)

Sample analysis includes physical, chemical or biological determination of the parameter or pollutant.

As different methods can give different results from the same sample, it is important to indicate with the results the method used. Actually, release data can be fully comparable only in cases where the measurement and/or estimation of emissions from both the point and diffuse sources are consistent. The uncertainty of the results should be indicated together with the results.

When an external laboratory is used for the analysis of the samples, it is very important that the selection of the sampling and analytical methods is carried out in close co-operation with the external laboratory. This ensures that all relevant aspects such as method specificity and other limitations are considered before the sampling is performed.

Close co-operation between the personnel responsible for sampling and the laboratory is needed to ensure sufficient information to perform a correct analysis and the laboratory needs to provide relevant information to enable proper handling of the analysis results. [4, 9, 13]

2.4.6 Data Processing (Step 6)

Once the measurement results are produced, the data generated need to be processed and evaluated. All data handling and reporting procedures should be determined and agreed before the measurements. Data processing includes possible measurement device signal processing, statistical treatment of the data, interpretation of the measurement results and their validity, calculation of the results and uncertainty analysis. Data reduction is often necessary in order to produce the information in a format suitable for reporting. Statistical treatment of the data may include calculations from the data of means, maximum, minimum and standard deviations over appropriate intervals.

It is also important to check regularly

- that the calculation methods respond to the reality of the process, as well as take into account any process changes that may have taken place since the equation was last formed;
- that the monitoring results reflect the temporal and spatial coverage of the releases; and
- that the utilisation rates of the continuous measurements and the abatement techniques over the monitoring period correspond the reality.

Part of the data processing involves the validation of emission data. This is usually done by the laboratory by checking that all the procedures have been properly carried out. Validation may include the use of a thorough knowledge of monitoring methods and standardisation procedures, and may also involve, quality guarantees for certification methods and procedures. The validation process should include calibration of equipment as well as intra- and inter-laboratory checks. [4, 9, 13]

The uncertainties of the steps 1-6 of the data production chain need to be taken into account when determining the uncertainty of the final results.

2.4.7 Reporting (Step 7)

From the large amount of data generated when a parameter is monitored, a summary of the results over a certain period of time is usually generated and presented to the relevant stakeholders (authorities, operators, public, etc.).

Standardisation of reporting formats facilitates the electronic transfer and subsequent use of data and reports. The standard forms can be used to record whether data values are based on measurements, calculations or estimations, and may also identify the methods used for monitoring, sampling and analysis. [4, 9, 13]

2.5 Monitoring of Exceptional Releases

Monitoring of exceptional releases is not problematic if the source can be monitored continuously and the release concentration stays in the measurement range of the equipment used. However, in practice the exceptional emission concentrations usually exceed the measurement range of the equipment. Estimation of exceptional waste amounts is relatively easy if they exist in solid and/or immobile state. It is more complicated to estimate liquid or gaseous emissions. In all cases the exceptional releases have to be recognized. [9, 14]

At modern plants, monitoring of both the normal and exceptional releases is feasible. The estimation of total releases at old plants can be rather complicated due to the obsolete technical solutions. Also the number of both the point and diffuse emission sources can be high. Management of the monitoring of various release sources can be challenging or even impossible due to, for instance, difficult access to suitable measurement locations. [9, 14]

A comprehensive data production chain (as outlined in the previous Sections 2.4.1-2.4.7 can be planned to gather enough data for estimation of releases, both during situations where the measurements used to monitor under predictable conditions cannot follow the actual releases and in cases of sudden breakdown of the measurement devices. Substitutive calculation methods for the exceptional releases need to be established for the estimation of releases during these situations. Operation control plays an important role in providing information both in advance and during the exceptional situations. It is often possible to control the undesirable development of conditions well in advance, when detailed and immediate information of the process and abatement conditions is available. [9, 13]

However, it is necessary to establish the correspondence between the parameter (e.g. temperature) to be followed and the release or releases that the parameter indicate. In cases where the retention time is long, for instance at wastewater treatment plants, the frequency of monitoring needs to be intensified.

A compilation of suggested best monitoring practices in exceptional conditions is presented in Table 3. The table should be interpreted as follows: data from the reference installation (on line 6 in Table 3) is not applicable under normal operation conditions but it can be used in cases where the exceptional condition is related to disturbances in the process, process control and abatement technique.

Table 3. Best monitoring practices of releases in cases of normal and exceptional releases [9, 14]

Suggested Best Practice Monitoring Method		**In case of normal releases the monitoring method to be applied is:**	**In case of exceptional releases...**	
			...when the exceptional release is related to...	... the monitoring method to be applied is:
1	**Continuous emission measurements**	Continuous measurement of volume flow, concentration and process parameters	Process conditions Process control	Alarm or back-up systems that are calibrated *both to normal* and exceptional release ranges = Best practice when applicable
			Abatement technique	Continuous measurement before abatement equipment. Emission measurements have to be carried out also in cases of partial functioning of abatement technique.
2	**Periodic/ single emission measurements + calculation**	Justified in cases where continuous measurement is not available and the release is steady or can be adequately well defined between the measurements	Process conditions/ process control Abatement technique	Applicable periodic or single measurements in cases where they are applicable
3	**Indirect moni-toring/Operation control/Sur-rogate para-meters/PEM**	In situations where continuous/ periodic / single emission measur-ement is not applicable	Process conditions/ process control Abatement technique Measurement technique	Surrogate/operation control parameters such as e.g. pressure, pH, conductivity, temperature difference
4	**Material balance, engineering calculation**	Applicable to certain emissions such as CO_2 and SO_2; input measurement for fuel consumption needed	Abatement technique Measurement technique	Input measurements for e.g. fuel and raw material is needed
5	**Data from previous measurements**	Data used for comparison with the current measurement results to validate releases	Abatement technique Measurement technique	Measurement result from the previous direct measurements [e.g. kg/h] can be used and proportioned to the duration of the disturbance situation. The duration of the disturbance situation has to be known.
6	**Reference plant data**	Not applicable	Process conditions/ process control Abatement technique	To be used only under accidental conditions
7	**Emission factors**			
	- EFs for similar process and abatement technique & raw material	Emission factors are applicable in certain cases such as in calculation of greenhouse gas emissions. The emission factors used should preferably be plant specific based on previous measurements.	Process conditions/ process control Abatement technique	To be used only under accidental conditions
	- EFs for uncontrolled technique /similar process technique and inputs		Process conditions/ process control Abatement technique	To be used only under accidental conditions

2.6 Quality Considerations in Data Production

This section provides information on the data quality objectives and basic tools for the operator to ensure good quality of release data. [3, 10, 11]

2.6.1 Quality Objectives for Release Data

The international conventions and organisations[9] set quality requirements to the release data, such as accuracy, comparability, completeness, consistency and transparency. The following elements, which are listed as indicators of these data quality objectives, are relevant also to PRTR data:

- Accuracy includes that that the data does not include systematic over or under estimations and the uncertainty is as low as possible;

- Comparability includes elements such as a harmonised source nomenclature, standardised reporting formats, agreed estimation techniques and accepted methodologies and emission factors in production of the release data;

- Completeness includes all releases from the respective source are included in the reported data;

- Consistency includes unambiguous and uniform definitions, source identification and methodologies for the estimation of releases over several years to allow trend analysis; and

- Transparency includes information on how the data collection was performed, how the releases were measured or estimated, which methodology and emission factors were used to estimate releases as well as what the units of the reported data are.

2.6.2 How to Obtain Quality Data

The operator of the facility is responsible for the release data reliability. Proper organisation of the monitoring, responsibilities, information flow and the environmental files, as well as ensuring the competence of the personnel and application of suitable manners and methods, are all tools to improve the reliability of the monitoring.

Quality management systems[10] are useful for ensuring that the equipment and methods used in the measurements, as well as the various monitoring tasks, are carried out according to the requirements. Quality assurance includes also maintenance and calibration procedures related to the monitoring equipment.

Environmental management systems[11] assist in systematic management of monitoring data, for instance, in relevant documentation and in the practical organisation of the tasks. There are also standards

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[9] Quality assurance and control for estimation of emissions is dealt with, for instance, in the following documents: IPCC Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories [11], EMEP/Corinair Emission Inventory Guidebook [5]; and Guidance Document for EPER Implementation [3].

[10] Quality management systems are such as e.g. ISO 9000 series standards.

[11] Regulation (EC) No 761/2001 of the European Parliament and of the Council of 19 March 2001 allowing voluntary participation by organisations in a Community eco-management and audit scheme (EMAS).

for the competence requirements of the personnel carrying out the monitoring tasks and the laboratories participating in the work[12]. Competence requirements are also set in the IPCC Good Practice Guidance [11].

According to the European Union IPPC Reference Document on the General Principles of Monitoring [4], good practice in accessibility and quality in release data reporting can be achieved by considering the following items:

- Quality objectives and checks. Quality objectives for the technical standard and availability of reports should be set. Checks should be carried out to test how well these are being met. These may involve checks by both internal and external experts, and even certification under a formal quality management system;

- Competence. Reports should be prepared by competent and experienced teams who may maintain their skills by participating in relevant workshops and certification schemes;

- Archiving. Data can be systematically archived in a secure store, so that records of past performance are readily available;

- Contingency arrangements. Special contingency arrangements should be in place for rapid reporting and recording of abnormal and upset events, including off-scale conditions and breakdowns of monitoring equipment;

- Sign-off systems. It is desirable to nominate a responsible person for the authenticity and quality of the information in each report using a “sign-off” system, which may be manual or electronic;

- Retention of data. The operator should retain basic monitoring data and reports for periods to be agreed with the authority and make them available to the authority on request; and

- Falsification of data. Regulators should define procedures for dealing with any falsification of reported monitoring results. These can include unannounced audits and effective legal sanctions.

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[12] ISO/IEC17025 General requirements for the competence of testing and calibration laboratories and ISO, ISO/IEC Guides, ISO 9000 series, OECD and CEN (EN 45000 series) for Good Laboratory Practice.

CHAPTER 3: SELECTING AND APPLYING RETS

3.1 Introduction

Building on Chapter 2 of this document which provides a brief description of the different RETs and discusses the general issues that should be considered when selecting a specific RET, this chapter delves more fully into the suitability of a RET to specific circumstances. It elaborates on what input data is needed and what needs to be considered when applying a specific RET. Factors that generally affect the quality of emission data are presented in detail in Sections 2.5-2.6.

It is important to note that facilities normally use multiple RETs to calculate the releases of a specific pollutant. In addition to the suitability of a RET to a specific case, the quality of the input data also has a major impact on the quality of the release data produced. The input data can be activity data (e.g. volumes of process streams), process specific parameters (e.g. temperature, pressure differences, velocity) or emissions related data (e.g. specific emission quantities, emission factors).

3.2 Direct Monitoring/Measurements

3.2.1 When to Use This RET?

Direct monitoring aims to give the most representative, reliable and accurate release data possible with the current scientific knowledge and equipment available. The frequency of sampling needs to be determined case-by-case, taking into account pre-eminently the emission variations and the constraints set by the method.

Continuous monitoring, where applicable, or measurements at an adequate frequency and during a sufficiently long period improve representativeness of the results. Continuous monitoring techniques have the advantage over discontinuous measurement techniques because they provide a greater number of data points. They therefore provide data that is statistically more reliable and can highlight periods of adverse operation. In the case of continuous monitoring, exceptional releases will also be recorded in those instances where the measurement areas of the devices are sensitive to the exceptional concentration and volume.

For air emissions, the use of site-specific CEM data may be preferable for estimating NO_x, SO_2, CO, and total hydrocarbon (THC) releases because this data provides a detailed record of releases over time. Periodical or single measurements[13], which can be made periodically or on a single basis, is a common method of estimating for example, process releases.

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[13] i.e. source testing.

3.2.2 Input Data

Generally, input data used in RETs plays a considerable role in determining the quality of release data reported. Though there is no input data to be directly entered in direct monitoring, there are several aspects such as the data production chain (see Section 2.4), standardisation, and applicability that should be considered to ensure good quality of data. It is important to note that the measurement of concentration can be separate from the flow measurement. When evaluating the results, the quality of both flow and concentration measurement needs to be considered.

3.2.3 What to Consider?

The measurement method must be suitable for the specific process, release source and sampling or measurement point. In addition, the method must be sensitive to the magnitude and composition of the release. The physical state and properties of the sample as well as the magnitude and variability of the release volume have to be taken into consideration when choosing the monitoring techniques. The data production chain principles presented in Section 2.4 need to be taken into account when using direct measurements.

Reliability of emission measurements is affected by [4]:

- Relevant accuracy of the emission or waste volume includes accounting of all relevant release sources and conditions;

- Representativeness of sampling points and times need to be ensured in a way that produces information on the true annual releases. Operating conditions, process streams, control devices and temporal conditions that affect release estimates should be carefully considered; and

- Correct processing of the monitoring data includes statistical treatment and interpretation of the measurement results and their validity. The results should be reported in a way that enables unambiguous understanding of the release parameter and its numerical value in standard conditions.

Continuous monitoring techniques may also have some drawbacks such as cost or inapplicability for certain chemicals due to technical reasons or sensitivity of devices toward high and low concentrations. A single measurement result indicates only the releases at the respective measurement point and period, but does not reflect the annual total releases from the site during the reporting year. However, it is possible to extrapolate the periodic emission monitoring data to estimate long-term releases from the same or similar sources.

Two items should be noted when using measurement data to calculate releases. First, because most measurements are only conducted over several hours or days at most, adjustments may need to be made when using these data to estimate releases over longer time intervals. Release data from single measurements can be extrapolated to estimate annual releases only if the process stream does not vary and if the process and control devices are operated uniformly. Second, a measurement may not adequately describe a given facility's annual or seasonal operating pattern. For example, there may be variations in process operation throughout the year or the efficiency of control device performance may vary due to fluctuations in ambient temperature or humidity. In such cases, multiple measurements should be conducted in order to be useful in generating release estimates for time intervals to account for these annual variations.

Instrument calibration drift can be problematic for CEMs and the uncaptured data can create long-term incomplete data sets. Failure to include temporal conditions during calibration and data capture can also lead to unreliable release estimates. It is the responsibility of the source owner to properly operate, calibrate, and validate the monitoring equipment and the corresponding release data. [4]

Due to the time and equipment involved, the direct monitoring of emissions generally requires more resources than the other release estimation methodologies.

3.3 Indirect Monitoring/Measurements

3.3.1 When to Use This RET?

For a process that has been well characterised, indirect monitoring can be used to develop release estimates that are nearly as accurate as direct measurements for selected sources at a fraction of the cost. Releases can be estimated with high accuracy for any process where those releases depend directly on process conditions, by measuring the process conditions[14]. Parameters that are followed up for operation control purposes can also have a good correlation to the actual releases. A combination of parameters may result in a strong relationship to the pollutant to be monitored. [4]

Indirect monitoring can be applied in many cases for estimating air and water contaminants for industrial releases. For instance, the amount and nature of water pollutants that are released from industrial facilities are often directly related to one or more of the process-related operation control parameters. Estimates of releases to water can therefore be determined to a high degree of accuracy from measurements of those parameters. When using indirect monitoring, the relationship between the parameter to be monitored and the release needs to be demonstrated and documented.

Advantages in using indirect monitoring are cost effectiveness resulting in availability of more frequent information or possibilities to monitor more discharge points than with direct measurements. The operation control parameters can usually give on-line information and thus an early warning of possible upset conditions or abnormal releases.

3.3.2 Input Data

The parameters that have a correlation to the emission may be quantitative, qualitative or indicative [4]:

- Quantitative surrogates reflect the volume of the release and can substitute for direct measurements. Examples of a quantitative surrogate are, the assessment of the total organic compounds instead of the individual organic compounds, particulate matter measurements to indicate emissions of some heavy metals;

- Qualitative surrogates give qualitative information, such as information of the conductivity of wastewater; and

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[14] Indirect monitoring (or predictive emission monitoring) uses process parameters (surrogate parameters) in the determination of emissions, see Section 2.2.

- Indicative surrogates give information about the operation of an installation or process such as temperature, pressure drop or pH.

3.3.3 What to Consider?

When using indirect monitoring the relationship between the monitored parameter and the comparable release needs to be demonstrated and documented. The relationship between the parameter to be monitored and the release to be calculated needs to be checked and calibrated from time to time. However, the parameters may only be valid for a restricted range of process conditions.

3.4 Emission Factors

3.4.1 When to Use This RET?

The use of emission factors is recommended when the relationship between process data and releases is direct and relatively uncomplicated.

The primary limitation associated with the use of emission factors is that not all sources are designed or operated exactly the same. If facilities plan to use emission factors to predict releases from new or proposed sources, facilities are encouraged to review the latest literature and technology to determine whether such sources would likely exhibit release characteristics different from those sources from which the emission factors were derived.

While the releases calculated using emission factors might differ from actual releases for a specific facility, emission factors nevertheless provide a reasonable estimate of pollutant emissions across an entire source category. Because emission factors are typically averages obtained from data with wide ranges and varying degrees of accuracy, releases calculated this way for a given source are likely to indicate higher than actual releases for some sources and lower than actual releases for others.

Emission factors can be applied to any pollutant from a particular source that can be measured by some other method to obtain the information needed to develop the chemical-specific emission factor. Emission factors are generally developed by averaging measured emission rates during representative time interval and relating that to some other measure of the operating rate of the activity. That chemical-specific emission factor is then applied to all other similar sources whether or not they were included in the set of sources that were measured to develop the factor.

When the information used to develop an emission factor is based on national data, such as a wide range of measurements or national consumption estimates, you should be aware of potential local variations. Releases calculated using national emission factors might vary considerably from actual values at a specific source or within a specific geographic area.

National emission factors may be preferred when:

- No locally derived factor exists;
- The local mix of individual sources in the category is similar to the national average; and
- The source is a low priority in the inventory.

Locally derived emission factors may be preferred when:

- A national level emission factor does not account for local variations; and
- The category is a high priority in the area.

3.4.2 Input Data

Emission factors often require the input of site-specific data. If site-specific data are not available, default values may be used. The reliability of estimates obtained from using emission factors is usually greatly improved if site-specific data are used in place of default values.

To calculate releases using emission factors, the following basic inputs to the estimation algorithm are required:

- Emission factor, which is usually expressed as the weight of pollutant divided by a unit weight, volume, distance, or duration of the activity emitting the pollutant;
- Activity information for the process as specified by the relevant emission factor, for instance consumption of fuel, raw material, production rate, wastewater volume; and
- Information of the removal efficiencies of the abatement equipment when using an "uncontrolled" emission factor (an emission factor that indicates the emission when abatement technology is not in use).

3.4.3 What to Consider?

Emission factors are inherently prone to uncertainties as they are typically based on limited measurements of a potentially large source population. Information of the emission factor candidate should be carefully compared against the techniques and conditions at the process to be monitored. The uncertainty of emission data is affected by the accuracy of the activity data, the accuracy of the emission factor and of the possible conversion factor(s) as well as the factor used to estimate the removal efficiency of the control device. The following list indicates issues to be considered when using emission factors:

- When applying internationally developed release data to sources in another country, this uncertainty could potentially increase due to possible differences in process technologies, raw material and chemicals, operating conditions/practices and pollution control equipment;
- Emission factors tend to be based on measurement data collected over a relatively short sampling time period. In many cases the emission factor does not take into account likely releases during start-up or shut-down periods or process upsets and/or abnormal operation;
- The accuracy of the activity data, for instance consumption of fuel/raw material, production or wastewater volume, used in the calculation affects the final results;
- Facilities should make sure that their operational conditions fit 'controlled' or 'uncontrolled' emission factors. Use of incorrect emission factors might lead to a large error in release estimates. Control device efficiency may be determined for specific equipment by measuring pollutant concentrations before and after the application of a control device. As there are

possible variations in control device operation, such as potential malfunction or control device performance deterioration over time, the efficiency of the device should be checked from time to time. It may also be the case that the capture device efficiency is estimated on the basis of measurements performed on similar equipment at other facilities, rather than by measurements performed at the facility for which releases are being estimated. If measurement data are not available, published values in the literature or manufacturer's specifications are commonly used as defaults. These literature and/or manufacturer's specification values might not be specific to specific pollutants. Hence, the use of these numbers might result in a major error in release estimates. It is also necessary to modify the control device efficiency estimate based on considerations such as downtime or gradually deteriorating conditions, for example degradation of fabric filter bags. If the devices are shut down periodically for maintenance or by upset conditions, the releases during this time may far exceed the controlled releases over many hours of operation. Failure to account for excess releases resulting from downtime and deteriorated efficiency can be a major source of error in the release estimates.

3.5 Calculations

3.5.1 When to Use This RET?

3.5.1.1 Mass Balance

Mass balance is the most appropriate technique in cases where accurate measurements can be made of all but one release component, or when the release estimate will be used for screening purposes, provided that reasonable assumptions can be made about the fate of compounds. Use of mass balances involves the examination of a process to determine whether releases can be estimated solely based on the knowledge of operating parameters, material compositions, total material use and available sampling data.

Mass balances can be used for an estimation of the releases to the environment from a site, process, or piece of equipment. The use of mass balance involves examining a process to determine if releases can be estimated solely on knowledge of operating parameters, material compositions, total material use and available sampling data. Mass balance is an effective technique for estimating releases from evaporation sources and sources where the measurement of low-level, intermittent or fugitive exhausts streams would be difficult, costly or uncertain. It is particularly useful for processes such as solvent degreasing operations, and surface coating operations; and it is equally applicable to point and area sources. For any complex system, the conceptual simplicity of this approach is offset by fairly intense data requirements that often can only be adequately satisfied by direct measurement of the other processes. [4]

The mass balance approach should not be used for processes where

- Material reacts to form secondary products;
- The material otherwise undergoes significant chemical changes; or
- The releases are a small fraction of throughput.

If a mass balance is used to estimate releases, and if the actual releases are a small fraction of the throughput, the throughput estimate or measurement can be even more critical. A small percentage error in estimating the input or output can significantly affect the release estimate. For this reason, mass balances cannot be accurately employed at a reasonable cost for some evaporation processes because the amount of material lost is too small to be determined accurately. As an example, applying mass balances to petroleum product storage tanks is not generally feasible because the losses are too small relative to the uncertainty of any metering devices.

It is important to note, however, that the simplicity of this approach is offset by the potentially intense data requirements. Frequently, these data needs can only be adequately satisfied by direct measurement of other aspects of the process.

3.5.1.2 Models

Emission models may be used to estimate emissions in cases where the calculation approach is burdensome, or in cases where a combination of parameters have been identified which affect emissions but, individually, do not provide a direct correlation as the emissions are influenced by some other external factor that is not related to the activity. For example, the TANKS program incorporates variables such as tank colour, temperature, and wind speed to obtain an emissions estimate.

Release models consider the detailed relationships that exist within an identified system. The development of release models can be very expensive and, as a result, government agencies or industrial associations have developed most of the models in common use. Once developed, however, such models can usually be applied with limited effort to provide reasonable release estimates. Models tend to be available as software packages, with accompanying user manuals that describe the specific details of using such a model.

3.5.1.3 Engineering Calculations and Physicochemical Relationships

Often, fugitive air emissions of volatile chemicals may be estimated only using their physico-chemical properties. Similarly, engineering calculations can be used to estimate the quantity released to land and/or transferred for waste management activities. However, sometimes there may not be any information available on the substance or substances in question, even though the relevant physicochemical relationship is known.

3.5.2 Input Data

3.5.2. Mass Balance

When facilities use material balance, they will determine releases by knowing the amount of a certain material that enters a process, the amount that leaves the process by all routes, and the amount shipped as part of the product itself. This involves the consideration of material inputs to the facility (i.e. purchases) and materials exported from the facility in products and wastes. The remainder is considered as a ‘loss’, or a release to the environment.

For releases of solvents, mass balances are greatly simplified and therefore accurate only in cases where all of the consumed solvent is emitted to the atmosphere, e.g. painting where the ‘drying’ process is due to solvent volatilization. However, many situations appear where a portion of the evaporated solvent is captured and routed to a control device such as an afterburner (incinerator) or condenser. In these cases, the captured portion must be measured or estimated by other means to avoid overestimating releases. The disposal of any recovered material must also be accounted for.

3.5.2.2 Models

Emission models may be based on measured or empirical values. The computer models may be based on theoretical equations that have been calibrated using actual data, or they may be purely empirical, in which case the equations are usually based on statistical correlations with independent variables.

The models require knowledge regarding what is likely to happen to an input or result in an output inside the system. For example, while a mass balance model for a storage tank may require data on inflows and outflows to estimate breathing losses[15], a process-specific model would include, but not necessarily be limited to, knowledge about pressures inside the tank, the vapour pressure of the liquid in the tank and the operating parameters of relief valves.

Release models require input data relating to each variable on which the relationship is based, i.e. partial pressure, temperature, concentration, as well as materials property information, such as that described in the section 3.5.2.3 below on physicochemical relationships. Once these input variables have been collected the models can then be used to estimate releases.

The input data can be source specific data, as well as non-source-specific data, e.g. meteorological data. Some models also provide default values. However, the more source specific data are included, the more accurate the final release estimates are likely to be. In some cases the models may require specific information that may not be readily available to the inventory developer.

3.5.2.3 Engineering Calculations and Physicochemical Relationships

Typically, these relationships rely on parameters such as partial pressure, temperature and wind speed. Sometimes these parameters include measured values as well as intrinsic values, such as molecular weight, partial pressure, density, fugacity[16], viscosity. The inclusion of source specific parameters tends to increase the accuracy of the release estimates. However, sometimes there may not be any information available on the substances in question, even though the relevant physicochemical relationship is known. This may be the case for substances typically not covered in chemical engineering, chemistry and physics handbooks.

There are computer programmes and spreadsheets available to assist in the application of these relationships.

3.5.3 What to Consider?

3.5.3.1 Mass Balance

Although mass balance is a valuable tool in estimating releases from many sources, its use requires that a measure of the substance in question is known at each point through the process. In the case where the actual releases are a small fraction of the throughput, the throughput estimate or measurement can be even more critical. Because the releases are estimated to be the difference between the material

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[15] Breathing loss is the fugitive emission from the expulsion of vapour from a tank vapour space that has expanded due to daily changes in temperature and barometric pressure.

[16] Fugacity is the measure of the tendency of a gas to escape or expand.

input and the known material output, a small percentage error in estimating the input or output can result in a much larger percentage error in the release estimate. For this reason, material balances are sometimes inappropriate for estimating relatively small losses. [4]

The accuracy and reliability of emission values calculated using the material balance approach are related to the quality of material use and speciation data, and knowledge of the different fate pathways for the material. Using a standardised method of measuring quantities can reduce the level of uncertainty. For certain applications, it may be more accurate to make these types of measurements monthly or annually, rather than after each application event. Another technique for determining the volume of consumption (of e.g. fuel, raw material and chemicals) would be to use purchase and inventory records.

The mass balance approach should not be used for processes where material reacts to form secondary products or where the material otherwise undergoes significant chemical changes.

Uncertainty of releases using the material balance approach is also related to the quality of material speciation data, which is typically extracted from Material Safety Data Sheets (MSDSs). If speciation data are not available on the MSDS, the material manufacturer should be contacted. A thorough knowledge of the amount of a material exiting a process through each fate pathway, including product, recycling, reuse, energy recovery, air emissions, wastewater discharges, land release and transfers for further waste management activities, is needed.

It is important to note, however, that the simplicity of this approach is offset by the potentially intense data requirements. Frequently, these data needs can only be adequately satisfied by direct measurement of other aspects of the process.

3.5.3.2 Models

The model needs to be based on valid assumptions and demonstrated by previous validations to show whether the scope of the model corresponds to the case studied and if the input data are reliable and specific to the conditions at the facility. A key weakness of calculation models is that these methods are sometimes inappropriately applied to sources that are operated differently than the sources that were used to develop the model. In other cases, the models may require specific information that may not be readily available to the inventory developer.

3.5.3.3 Engineering Calculations and Physicochemical Relationships

Assumptions are often made to simplify the estimation process by using a physicochemical relationship. This may add inaccuracy to the results. Sometimes there may not be any information available on the required input data.

3.6 Engineering Judgement

3.6.1 When to Use This RET?

An engineering judgement is made when the specific release estimation techniques presented in the previous Sections 3.1-3.6 are not feasible to use. Such estimates are usually made by an engineer familiar with the specific process and are based on whatever knowledge may be available.

While it is recognised that the use of engineering judgement methods has the potential for errors and inconsistencies, the method has practical advantages in developing release estimates quickly and inexpensively. Often, engineering judgement methods are used initially to provide estimates in the first year or two of a programme. The analysis and interpretation of these results then frequently leads to the use or development of more sophisticated methods that can improve the accuracy, specificity and uses of the data.

3.6.2 Input Data

The engineering judgement is based intuitive methods and information that are available in the specific case and conditions. Typically input data includes site-specific process parameters.

3.6.3 What to consider?

A best approximation or engineering judgement is a final option for estimating releases. It is generally considered the least desirable method. If releases must be estimated by best approximation, emission factors may be available to check the order-of-magnitude of the possible releases from the process in question.

CHAPTER 4: GUIDE TO ANNEXES 1-3

The objective of Annexes 1-3 is to provide specific guidance on the selection and application of RETs to a specific industrial sector. The industry sectors covered by these annexes are fossil fuel power generation, petroleum refining and incineration. Steps 1-3 cover the pollutants to be reported and their potential sources at the selected industrial branches. Steps 4-5 describe selecting and applying the release estimation techniques. The Annexes do not consider the effect of reporting thresholds for specific substances but assume that all pollutant releases will be reported and provide annual release estimates. Each of the three annexes follows the same structure.

The steps of the methodology are as follows:

1. The Scope of the Industry;
2. Pollutants;
3. Potential Release Sources;
4. Selection of and Application of Release Estimation Techniques; and
5. Quality Assurance.

ANNEX 1: FOSSIL FUEL POWER GENERATION

SELECTION AND APPLICATION OF RELEASE ESTIMATION TECHNIQUES

1. THE SCOPE OF THE INDUSTRY

2. POLLUTANTS

3. POTENTIAL RELEASE SOURCES
    - 3.1 Fuel Combustion in Boilers
        - 3.1.1 Coal-fired Boilers
        - 3.1.2 Oil-fired Boilers
        - 3.1.3 Natural Gas-fired Boilers
    - 3.2 Organic Liquid Storage and Transfer
    - 3.3 Wet Cooling Towers
    - 3.4 Flue Gas Desulphurisation
    - 3.5 Vehicles
    - 3.6 Open Areas
    - 3.7 Stockpiles
    - 3.8 Coal Handling
    - 3.9 Solvent Use
    - 3.10 Pipelines
    - 3.11 Ash Collection

4. SELECTION AND APPLICATION OF RELEASE ESTIMATION TECHNIQUES
    - 4.1 Combustion in Boilers
    - 4.2 Organic Liquid Storage and Transfer
    - 4.3 Wet Cooling Towers
    - 4.4 Flue Gas Desulphurisation Waste
    - 4.5 Vehicle Dust and Exhaust Releases
    - 4.6 Dust from Open Areas
    - 4.7 Dust from Stockpiles
    - 4.8 Coal Handling
    - 4.9 Solvent Use
    - 4.10 Leaks from Gas Pipelines
    - 4.11 Ash Collection and Disposal

5. QUALITY ASSURANCE

1. THE SCOPE OF THE INDUSTRY

For the purposes of this annex, a power generation facility is defined as any dedicated facility utilising steam to produce energy through the combustion of coal, oil or natural gas.

The major releases and their sources from power generation are illustrated below in Figure 1.1. Depending on the objectives of the PRTR, some of the releases shown in Figure 1.1 may not be reportable. Also, some of the release sources shown in Figure 1 are considered as diffuse sources. Depending on the scope of the inventory, some of these diffuse emissions may not be reportable in a point source inventory or may be required to be reported as part of a diffuse source inventory. The principal release sources to air, water and land from fossil fuel power generation facilities are shown in Table 1.1. The specific pollutant releases are further discussed in Step 3.

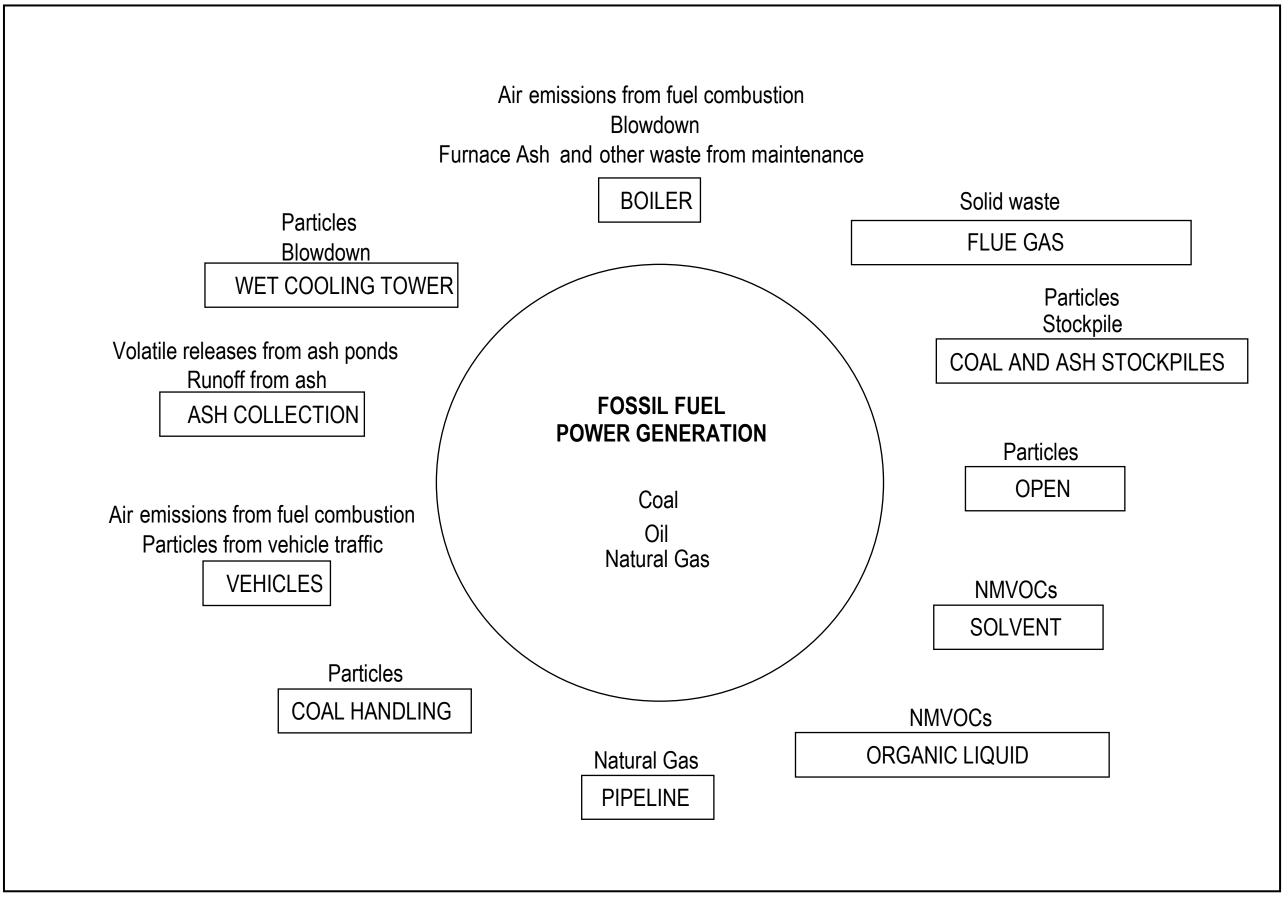

Figure 1.1. Releases and their sources from fossil fuel power generation

Table 1.1. Sources of releases from fossil fuel power generation

Emission Sources	Air	Water	Land
Fuel combustion in boilers	x		
Organic liquid storage and transfer	x		x
Wet cooling towers[1]		x	x
Flue gas desulphurisation			x
Vehicles	x		
Open areas	x		
Stockpiles	x		
Coal handling	x		
Solvent use	x		x
Pipelines	x		x
Ash collection	x		x

[1] Remark. The processes that lead to emissions from wet cooling towers do not occur in dry cooling towers.

2. POLLUTANTS

This step involves identifying releases at a combustion plant. The substances to be reported depend on the definitions and thresholds within the specific PRTR programme.

3. POTENTIAL RELEASE SOURCES

The potential releases from each of the sources identified in Table 1.1 need to be assessed. Resources, which can assist in determining the specific pollutants released from fossil fuel power generation can be found from the OECD website: http://www.oecd.org/env/prtr. Further information on the potential releases and the factors affecting these releases are presented below.

3.1 Fuel Combustion in Boilers

For the purposes of release estimation, combustion boilers are defined in terms of their shape, feed characteristics and operating conditions, as these all influence the releases, which result from fuel combustion. Combustion releases from boilers are also critically dependent on boiler type, boiler firing configuration, boiler operation, pollution control equipment and fuel properties.

Water (to produce steam) may be recirculated and eventually build up impurities in the boiler. This water is periodically purged from the system. Boiler blow-down[17] is typically alkaline, low in total dissolved solids and contains chemical additives used to control scale and corrosion. Blow-down also contains trace amounts of copper, iron and nickel.

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[17] The blow down is related to controlling the amount of solids and sludge in the boiler water and involves draining the boiler to remove sludge and to maintain pre-determined concentration levels of solids. As the water is turned into steam, the solids remain behind. Blow down is affected by the type of boiler, operating pressure, water treatment, and the amount and quality of make-up water.

In the case of coal and, to a lesser extent, oil combustion, ash forms at the bottom of the boiler and is periodically collected for treatment or disposal (See Section 3.11). Depending on the scope of the inventory, facilities may or may not be required to report on these substances.

3.1.1 Coal-fired Boilers

Coal ash may either settle out in the boiler as bottom ash or be entrained in the flue gas as fly ash. The distribution of ash, commonly referred to as partitioning, between the bottom ash and fly ash depends on the boiler firing method and furnace type (wet or dry bottom). Boiler load also affects particulate matter releases, since decreasing load tends to reduce releases. However, the magnitude of the reduction varies considerably depending on boiler type, fuel and boiler operation. Steam soot and air soot blowing is periodically used to dislodge ash from heat transfer surfaces in the furnace, convective section, economiser, and air pre-heater. Soot blowing may also be a source of intermittent particulate matter releases in coal-fired boilers. [28]

The oxides of sulphur (SO_x) from coal combustion are primarily sulphur dioxide (SO_2), with much lower quantities of sulphur trioxide (SO_3) and gaseous sulphates. These compounds form as the organic and pyritic sulphur in the coal are oxidised during the combustion process. The oxides of nitrogen (NO_x) formed in combustion processes are due either to the thermal fixation of atmospheric nitrogen in the combustion air (thermal NO_x), or to the conversion of chemically bound nitrogen in the fuel (fuel NO_x). Thermal NO_x concentration is exponentially dependent on temperature and is proportional to nitrogen concentration in the flame, the square root of oxygen concentration in the flame and the gas residence time. Fuel nitrogen can account for up to 80 percent of total NO_x from coal combustion [28]. NO_x production can be reduced by the design of low NO_x burners using low excess air and control techniques such as selective catalytic and non-catalytic reduction.

The rate of carbon monoxide (CO) releases from combustion sources depend on the fuel oxidation efficiency of the source. By controlling the combustion process, CO releases can be minimised. If a unit is operated improperly or is not well-maintained, the resulting concentrations of CO, as well as organic compounds, may be several orders of magnitude higher than from a well-operated boiler. Smaller boilers, heaters, and furnaces typically emit more CO and organics per unit of fuel consumed than larger combustion systems. This is because smaller units usually have less high-temperature residence time and, therefore, less time to achieve complete combustion than larger combustion systems. Combustion modification techniques and equipment used to reduce NOx can increase CO releases if the modification techniques are improperly implemented or if the equipment is improperly designed.

Carbon dioxide (CO_2) is formed as the major combustion product of coal-fired combustion.

Organic releases include volatile, semivolatile, and condensable organic compounds, either present in the coal or formed as a product of incomplete combustion. Organic releases are primarily characterised by the criteria pollutant class of unburned vapour-phase hydrocarbons. These releases include alkanes, alkenes, aldehydes, alcohols, and substituted benzenes, e.g., benzene, toluene, xylene, and ethyl benzene. Releases of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) also result from the combustion of coal. Dioxin and furan releases are influenced by the extent of destruction of organics during combustion and through reactions in the air pollution control equipment. The formation of PCDD/PCDF in air pollution control equipment is primarily dependent on flue gas temperature. The remaining organic releases are composed largely of compounds emitted from combustion sources in a condensed phase, such as polycyclic organic matter or polycyclic aromatic hydrocarbons.

Trace metals are also emitted during coal combustion. The quantity of any given metal emitted, in general, depends on the:

- Physical and chemical properties of the metal itself;
- Concentration of the metal in the coal;
- Combustion conditions;
- Presence of other pollutants which may affect metal volatilisation rates; and
- Type of particle control device used, and its collection efficiency as a function of particle size.

In addition to SO_2 and NO_x, the combustion of coal also results in releases of chlorine and fluorine, primarily in the form of hydrogen chloride (HCl) and hydrogen fluoride (HF). Small amounts of chlorine gas and fluorine gas may also be emitted. A portion of the chlorine and fluorine in the fuel may be absorbed onto fly ash or bottom ash. Both HCl and HF are water soluble and are readily controlled by acid gas scrubbing systems.

3.1.2 Oil-fired Boilers

Releases from oil combustion depend on the grade and composition of the fuel, the type and size of the boiler, the firing and loading practices used and stage in the maintenance cycle. There can be significantly different releases from the combustion of distillate and residual oils.

In general, particulate matter releases depend on the completeness of combustion as well as on the oil ash content. The particulate matter emitted by distillate oil-fired boilers primarily comprises of particles resulting from incomplete combustion of oil and is not correlated to the ash or sulphur content of the oil. However, particulate matter releases from residual oil burning are related to the oil sulphur content.

Boiler load can also affect particle releases in units firing heavier oils. However, no significant particle release reductions have been noted at low loads from boilers firing any of the lighter grades. At very low load conditions, such as approximately 30 percent of maximum rating, proper combustion conditions may be difficult to maintain and particle releases may increase significantly. Oxides of sulphur (SO_x) releases are generated during oil combustion from the oxidation of sulphur contained in the fuel. The releases of SO_x from conventional combustion systems are predominantly in the form of SO_2. Uncontrolled SO_x releases are almost entirely dependent on the sulphur content of the fuel and are not affected by boiler size, burner design, or grade of fuel being fired [29].

Oxides of nitrogen (NO_x) formed in combustion processes are due either to the thermal fixation of atmospheric nitrogen in the combustion air (thermal NO_x), or to the conversion of chemically bound nitrogen in the fuel (fuel NO_x). NO_x concentration is exponentially dependent on temperature and proportional to nitrogen concentration in the flame, the square root of oxygen concentration in the flame and the residence time. In general terms, an increase in flame temperature, oxygen availability and/or residence time at high temperatures leads to an increase in NO_x production. NO_x releases from tangentially (corner) fired boilers are, on average, less than those from horizontally opposed units. The firing practices employed during boiler operation also influence NOx formation. Low excess air (LEA) firing, flue gas recirculation (FGR), staged combustion (SC), reduced air preheat (RAP), low NO_x burners (LNBs), burning oil/water emulsions (OWE) or some combination of these measures may also reduce NOx emissions. Load reduction can likewise decrease NO_x production. It should be noted that most of these variables, with the exception of excess air, only influence the NO_x releases from large oil-fired boilers. Low excess air-firing is possible in many small boilers, but the resulting NO_x reductions are less significant [29].

The rate of carbon monoxide (CO) releases from combustion sources depends on the oxidation efficiency of the fuel. By controlling the combustion process, CO releases can be minimised. If a unit is operated improperly or not well maintained, the resulting concentrations of CO (as well as organic compounds) may be several orders of magnitude greater than in a well-controlled system. Smaller boilers, heaters and furnaces tend to emit more of these pollutants per unit of fuel consumed than larger combustion systems [29]. It should also be noted that carbon dioxide (CO_2) is formed as the major combustion product of oil-fired combustion.

The presence of CO in the exhaust gases of combustion systems is primarily a consequence of incomplete fuel combustion. Several conditions can lead to incomplete combustion, including insufficient oxygen (O_2) availability, poor fuel/air mixing, cold-wall flame quenching, reduced combustion temperature, decreased combustion gas residence time and load reduction, i.e. reduced combustion intensity. Since various combustion modifications for NO_x reduction can produce one or more of the above conditions, increased CO releases may be a result of reduction in NO_x releases [29].

Small amounts of organic compounds are released from oil combustion. As for CO releases, the rate of released organic compounds depends to some extent on the combustion efficiency of the boiler. Therefore, any combustion modification, which reduces the combustion efficiency will probably increase the concentrations of organic compounds in the flue gases.

Unburned hydrocarbon releases can include all alkanes, alkenes, aldehydes, carboxylic acids, and substituted benzenes, e.g. benzene, toluene, xylene, and ethyl benzene. The remaining organic releases are composed largely of compounds emitted from combustion sources in a condensed phase, such as polycyclic organic matter or polycyclic aromatic hydrocarbons. Formaldehyde is also formed during the combustion of oil [29].

Trace elements are also emitted from the combustion of oil. The quantity of trace metals emitted from the source depends on combustion temperature, fuel feed mechanism and the composition of the fuel. The temperature determines the degree of volatilisation of specific compounds contained in the fuel. The fuel feed mechanism affects the separation of releases into bottom ash and fly ash. In general, the quantity of any given metal emitted depends on the physical and chemical properties of the element itself, the concentration of the metal in the fuel, the combustion conditions and the type of particle control device used and its collection efficiency as a function of particle size [29].

3.1.3 Natural Gas-fired Boilers

The releases from natural gas-fired boilers and furnaces include oxides of nitrogen (NO_x), carbon monoxide (CO), and carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), non-methane volatile organic compounds (NMVOCs), trace amounts of sulphur dioxide (SO_2) and particulate matter (PM).

Release levels of thermal NO_x vary considerably with the type and size of combustion system and with operating conditions (e.g. combustion air temperature, volumetric heat release rate, load, and excess oxygen level). Another mechanism of NO_x formation, called prompt NO_x, occurs through early reactions of nitrogen molecules in the combustion air and hydrocarbon radicals from the fuel. Prompt NO_x reactions occur within the flame and are usually negligible when compared to the amount of NO_x formed through the thermal NO_x mechanism. However, prompt NO_x levels may become significant with ultra-low-NO_x burners. Releases of fuel NO_x from natural gas-fired boilers are generally insignificant [30]. The rate of CO releases from boilers depends on the efficiency of natural gas combustion. Improperly tuned boilers and boilers operating at off-design levels decrease combustion efficiency resulting in increased CO releases. In some cases, the addition of NO_x control systems such as low NO_x burners and flue gas recirculation (FGR) may also reduce combustion efficiency, resulting in higher CO releases relative to uncontrolled [30].

The rate of NMVOC releases from boilers and furnaces also depends on combustion efficiency. NMVOC releases are minimised by combustion practices that promote high combustion temperatures, long residence times at those temperatures and turbulent mixing of fuel and combustion air. Trace amounts of NMVOC species in the natural gas fuel (e.g. formaldehyde and benzene) may also contribute to NMVOC releases if they are not completely burnt in the boiler [30].

Releases of SO_2 from natural gas-fired boilers are low, because pipeline quality natural gas typically contains relatively low sulphur levels. However, sulphur-containing odorants are frequently added to natural gas to assist in detecting leaks. The combustion of these odorants may lead to small amounts of SO_2 releases. Boilers burning unprocessed natural gas may have higher SO_2 releases due to higher levels of sulphur in the natural gas. For these units, a sulphur mass balance should be used to determine SO_2 releases [30].

Particulate matter releases from natural gas combustion are typically low. Particulate matter from natural gas combustion systems are usually larger molecular weight hydrocarbons that are not fully burnt. Increased particulate matter releases may result from poor air/fuel mixing or maintenance problems.

CO_2, CH_4 and N_2O releases are all produced during natural gas combustion. In properly tuned boilers, nearly all of the fuel carbon (99.9 percent) in natural gas is converted to CO_2 during the combustion process. This conversion is relatively independent of boiler or combustion system type. Fuel carbon not converted to CO_2 results in CH_4, CO and/or NMVOC releases. N_2O releases are minimised when combustion temperatures are kept high and excess oxygen is kept to a minimum. Methane releases are highest during low-temperature combustion or incomplete combustion, such as the start-up or shut-down cycle for boilers. Typically, the conditions that favour the formation of N_2O also favour releases of methane [30].

3.2 Organic Liquid Storage and Transfer

Organic liquids at power generation facilities are usually stored in either floating-roof or fixed-roof tanks. Releases from fixed-roof tanks may be divided into two categories: working losses and breathing losses[18]. Working losses occur during both the filling and emptying of the storage tanks. Filling losses occur when the organic compounds contained in the air are displaced from a fixed roof vessel during loading. Emptying losses occur when air drawn into the tank saturates with organic compounds, then expands, exceeds the capacity of the vapour space and is forced out of the vessel. Breathing losses are the expulsion of vapour from a tank through vapour expansion caused by changes in temperature and pressure in the tank. The rate of losses from organic liquid storage tanks are influenced by the volatility of the liquid being stored (or components of the liquid being stored) and storage temperature and pressure [25].

Releases from floating roof tanks are either standing losses or withdrawal losses. Withdrawal losses occur when the liquid that clings to the tank wall is vaporised during the lowering of the floating roof during liquid withdrawal. Standing losses are caused by wind action at rim seals, deck fittings and deck seams. The control techniques for storage tanks can be divided into the modification of storage tank design to minimise losses and the incorporation of vapour recovery and recycle systems.

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[18] Breathing loss is the fugitive emission from the expulsion of vapour from a tank vapour space that has expanded due to daily changes in temperature and barometric pressure.

3.3 Wet Cooling Towers

Cooling towers are heat exchangers that are used to dissipate large heat loads to the atmosphere. They are used to transfer waste heat from cooling water to the atmosphere by allowing the water to cascade through a series of decks and slat-type grids [16].

The primary classification for cooling towers is into dry towers or wet towers, although some combinations of these also exist. Wet, or evaporative, cooling towers use water as their heat transfer medium and rely on the latent heat of water evaporation to exchange heat between the process and the air passing through the cooling tower. As cooling tower water comes in contact with the air passing through the tower, some of the liquid water may be entrained in the air stream and carried out of the tower as droplets. These aspirated droplets are dispersed into the atmosphere as aerosols (liquid dispersed in air). As the droplets evaporate in the atmosphere, particulate matter forms by crystallisation of the dissolved solids. Depending on the composition of the cooling water, these releases may contain heavy metals and salt compounds. This process does not occur in dry cooling towers. Therefore, only wet cooling towers are considered as sources of releases [16].

Wet cooling towers can be classified by draft type (atmospheric, natural, mechanical, induced) and/or the location of the draft relative to the heat transfer medium (counter flow, cross flow). To reduce the drift from cooling towers, drift eliminators may be incorporated into the tower design. Drift eliminators induce the particles to separate by forcing them to travel through a specially designed flow path prior to exiting the cooling tower. Hence, the quantity of droplets exiting the tower is controlled. The types of drift eliminator configurations include herringbone (blade-type), wave form and cellular (or honeycomb) designs. The cellular units, generally, are the most efficient. Drift eliminators are generally formed into closely spaced slats, sheets, honeycomb assemblies or tiles and may include features such as corrugations and water removal channels to enhance drift removal [16].

The liquid which remains after evaporation and needs to be released to the environment is known as cooling tower blow-down. The evaporation process causes the levels of impurities within the cooling water to concentrate as the water is continuously recycled. The water which is continuously purged from the process is known as cooling tower blow-down. The pollutants of concern in cooling tower blow-down discharges include chlorine, organic chemicals and trace metals from biofouling and corrosion control [24].

3.4 Flue Gas Desulphurisation

Flue gas desulphurisation control technologies result in the generation of solid wastes. Wet lime/limestone scrubbers produce slurry of ash, unreacted lime, calcium sulphate and calcium sulphite. Dry scrubber systems produce a mixture of unreacted sorbent, e.g. lime, limestone, sodium carbonates, calcium carbonates, sulphur salts and fly ash. Sludges are typically stabilised with fly ash. Sludges produced in a wet scrubber may be disposed of in impoundments or below-grade landfills, or they may be stabilized and disposed of in landfills. Dry scrubber sludges may be managed dry or wet. [24]

Blow-down from flue gas desulphurisation systems contains calcium sulphate, calcium chloride and sodium chloride and, depending upon fly ash carryover, may also contain metal ions.

3.5 Vehicles

The movement of vehicles over various surfaces leads to releases of particulate matter. Releases from vehicle exhausts contain a range of pollutants including carbon monoxide, volatile organic compounds, sulphur dioxide, various organic compounds and oxides of nitrogen. Releases of this type are often considered as part of diffuse source inventories.

3.6 Open Areas

Particulate matter may be generated by wind erosion of open exposed, dusty areas within an industrial facility.

3.7 Stockpiles

Storage piles of dry bulk solids are subject to wind erosion. In addition, there are releases from the materials (or aggregate) handling operations associated with these storage piles. Open storage of coal and/or ash allows contact with rain and/or other precipitation. This water can react with the minerals in the coal to produce a leachate contaminated with ferrous sulphate and sulphuric acid. The low pH of the leachate reacts with the coal and accelerates the dissolution of metals into the underlying groundwater.

3.8 Coal Handling

Any process operations that move or manipulate bulk solids can cause fugitive particle releases due to wind action. Fugitive releases occur when solids are loaded or unloaded into vehicles or moved around a facility.

3.9 Solvent Use

Ancillary operations such as equipment cleaning and related operations give rise to fugitive releases. These are usually evaporative losses and may be estimated using emission factors. These releases can usually be traced back to one point or to small area sources and can, therefore, be considered as point sources.

Gas-side metal and boiler cleaning wastes are produced during maintenance of the gas-side of the boiler, including the air pre-heater, economiser, superheater stack, and ancillary equipment. Residues from coal combustion, soot and fly ash, build up on the surfaces of the equipment and must be removed periodically and are typically removed with pressurised water, and these wastewaters may be neutralised and metals precipitated before being released or recycled. At coal plants, the wastewater is most often put into the ash ponds without treatment [24].

3.10 Pipelines

Leakage of liquids or gases can occur at equipment connections, joints and interfaces. The properties and conditions of these fluids can result in vapour releases through valve stems, pump seals and flanges.

3.11 Ash Collection

Two types of ash are generated during combustion of fossil fuels: bottom ash and fly ash. Ash that collects at the bottom of the boiler is called bottom ash and/or slag. Fly ash is a finer ash material that is born by the flue gas from the furnace to the end of the boiler. Bottom ash is collected and discharged from the boiler. Fly ash is collected in the economiser and air heaters or is collected by particle control equipment. Coal-fired facilities generate the largest quantity of ash. Gas facilities generate so little that separate ash management facilities are not necessary. Fly and bottom ash may be managed separately or together in landfills or in wet surface impoundments. [24]

Ashes differ in characteristics depending upon the content of the fuel burned. For coal, the chemical composition of ash is a function of the type of coal that is burned, the extent to which the coal is prepared before it is burned and the operating conditions of the boiler. These factors are very plant and coal specific. Generally, however, more than 95 % of ash is made up of silicon, aluminium, iron, and calcium in their oxide forms, with magnesium, potassium, sodium, and titanium representing the remaining major constituents. Ash may also contain a range of trace constituents in highly variable concentrations. Potential trace constituents include antimony, arsenic, barium, cadmium, chromium, lead, mercury, selenium, strontium, zinc and other metals.

Ash produced from the combustion of coal or oil is typically collected in sluice water that is then sent to settling ponds for disposal. The ash settling pond discharge may contain dissolved and suspended solids, heavy metals (nickel, iron, vanadium) and organ metallic compounds. Releases of pollutants from ash ponds to air may occur due to the volatile nature of some of the components of the ash. Particulate matter may also be released from dry ash ponds due to wind action. Pollutants may also be released to water or land if the ash ponds are not adequately contained.

4. SELECTION AND APPLICATION OF RELEASE ESTIMATION TECHNIQUES

4.1 Combustion in Boilers

Is the source a point source?

Yes.

Is the release a process point release (stack/vent/effluent) or a diffuse release?

It is a process point release through a stack.

Is monitoring data available? Use the available data to obtain the most reliable estimate using one, or a combination, of direct emission measurements or indirect monitoring and mass balance.

Monitoring data may be available for at least some of the pollutants released from fossil fuel boilers. A Continuous Emission Monitoring system (CEMs) is usually used to monitor releases of SO_2, NO_x, organic compounds and CO from boiler stacks. If CEM data are available and are of appropriate quality, these data will generally provide the most reliable estimate of releases for these substances. However, the cost of implementing a CEM system can be prohibitive. The use of a CEM may also be problematic at low concentrations. An example of application of CEM is presented in Annex 4.For uncontrolled emissions of metals and carbon dioxide, a CEM system may not be the preferred method. This is due to the fact that if the amount of metals or carbon in the fuel is monitored, uncontrolled, i.e. not accounting for pollutant controls, releases may be estimated based on the concentration in the fuel. For metals, an assumption is made on how much of the metal is partitioned between fly ash and bottom ash. It is assumed that metals pass untransformed through the combustion process and are partitioned at some determined ration between the fly ash and bottom ash. For carbon dioxide, it is assumed that all the carbon in the fuel is converted to CO_2. Therefore, for every kilogram of carbon (molecular weight of 12), 3.67 (44/12) kilograms of carbon dioxide (molecular weight of 44) is produced. Also uncontrolled emissions of SO_2 may also be estimated from the amount of sulphur in the fuel by assuming that there is complete conversion of sulphur to SO_2. Therefore, for every kilogram of sulphur (molecular weight of 32) burned, two kilograms of SO_2 (molecular weight of 64) are emitted. [21]

For SO_2 and metals, if control techniques are applied, either CEM or indirect monitoring becomes the preferred RETs [21]. Fuel analysis does not account for the removal of any pollutant from the control technology. However, fuel analysis may be used if the sulphur or metal content of the fuel is relatively homogenous and if site-specific pollution control efficiency data are available or can be determined with a reasonable accuracy, e.g. through measurements or equipment specifications. This is especially relevant if the only alternative release estimation technique is the use of emission factors. Furthermore, if measurement data or emission factors are available, they can be used to validate emissions estimates obtained through fuel analysis. CO_2 emissions are not generally affected by pollution control equipment.

Indirect monitoring is the preferred method used when a reliable, site-specific relationship between process parameters and release rates exists or can be developed. A typical example is the relationship between releases of SO_2 from a boiler equipped with a wet scrubber and parameters such as water pH, flow rate and fuel combustion rate [21].

Stack sampling is the preferred RET for particulate matter, speciated organics and sulphuric acid mist. Stack sampling may be used when the emission profile for a boiler is relatively homogenous. Fossil fuel power generation facilities generally have long periods of time at standard operating loads with consistent feedstock compositions. Provided that stack measurement data are available at each set of conditions throughout the reporting period, the data will provide reasonable estimates. This is often the case in the fossil fuel power generation industry and stack sampling is often used. Provided that the data are representative of boiler operations, stack sampling can provide reliable data for a PRTR at a relatively low cost. The accuracy of this method may be problematic at low pollutant concentrations [21].

Material balance may also be used to estimate the amount of particulate matter collected by pollution control equipment for disposal if inputs and outputs (estimated by one of the methods above) are known or can be estimated.

Is it reasonable to use operational specifications?

Operational specifications for boilers can be used to provide an accurate representation of releases from boilers at optimal conditions. Care should be taken when applying operational for different conditions, for instance, different unit age or differences in the maintenance cycle. Operational specifications may also not be representative of start-up or shutdown periods, in particular, when start-up or shutdown is a major part of the operating time in the reporting period. Operational specifications may also be validated with measurements to ensure applicability.

Are there an empirical/physicochemical relationship and necessary process data available?

Empirical/physicochemical relationships are generally not used for estimation of releases from boilers. These relationships may be developed for a particular facility for operational purposes.

Is there a site-specific or industry-specific emission factor available?

Emission factors are available for SO_2, NO_x, CO, NMVOC, hydrocarbons, particulate matter, trace metals and organic compound releases from boilers. Emission factors for fossil fuel combustion may be obtained from international databases listed on the OECD Resource Centre for Release Estimation Techniques: http://www.oecd.org/env/prtr.

The estimation of greenhouse gases such as CO_2, CH_4 and N_2O is mainly based on use of emission factors and oxidation factors determined for each fuel. The emission factor may be plant specific or retrieved from databases including suitable data for the purpose. For greenhouse gas emission factors the reader is referred to the IPCC Emission Factor Database[19]

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[19] The IPCC (Intergovernmental Panel for Climate Change) Emission Factor Database (EFDB) is a library for greenhouse gas emission factors and includes both IPCC default emission factors and country specific inputs evaluated and accepted by the EFDB editorial board.

When selecting emission factors for fuel combustion in boilers, the following specific issues need to be considered:

- Boiler configuration and whether this is the same configuration as specified in the emission factor. This is especially important for substances where emissions are heavily influenced by boiler configuration, i.e. NO_x, CO;
- Abatement technology used. The general approach is to use uncontrolled[20] emission factors with site-specific control efficiency data obtained from either stack measurements or manufacturer specifications, if applicable. Fossil fuel power generation facilities will often have some measurement data available for air pollution control equipment, either stack measurement data that, combined with fuel consumption data, may be used to determine the efficiency of the pollution control equipment, or specific upstream/downstream measurements to determine the efficiency of the pollution control equipment;
- Number of measurements used to compile the emission factor. In general, the greater the number of measurements, the more reliable the emission factor;
- Are the results consistent with any site-specific data, such as stack measurement data, fuel analysis data or process data, that could be used to provide an estimate of emissions;
- Age of the boiler relative to the age of facilities used to develop the emission factor;
- Does any possible variation in measurement methods produce significant variation in results; and
- Personnel performing the estimate should take these factors into account and use a combination of validation, comparison and expert judgement to arrive at a final decision on which emission factor is most appropriate.

Are other emission factors available?

Occasionally, other emission factors, e.g. for a different boiler type may need to be used in release estimation of particular substances. These emission factors may be used when emissions are not dependent on the parameter in question, e.g. boiler type. Depending on the substance, a validation of estimates with fuel analysis or measurement data may also be possible, as discussed above.

Can engineering judgement be employed?

Engineering judgement may need to be used to choose default values for parameters such as pollution control efficiencies or fuel compositions.

Can licence conditions be used to estimate worst-case releases?

In the absence of other information, licence conditions specifying either concentrations or release rates may be used to estimate worst-case releases. This assumes that licence conditions specify upper limits for releases and the facility is in compliance with these conditions.

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[20] Uncontrolled, i.e. abatement technology is not in use.

4.2 Organic Liquid Storage and Transfer

Is the source a point source?

Yes.

Is the release a process point release (stack/vent/effluent) or a diffuse release?

It is a diffuse release.

Is mass balance possible?

Technically, loss estimation of organic liquid during storage and transfer operations is possible, if data are available on purchases and material consumed. However, in most cases the losses are significantly less than throughput, which means that the uncertainties in measuring the throughput will be much larger than the losses being estimated. As a consequence, mass balance is rarely used for storage and transfer operations.

Is there a suitable model that can be applied to the available data?

There are commercial or public software programmes available if no site specific model exists. For instance, the TANKS computer software program is one example of a model that estimates volatile organic compounds (VOC) and other common air pollutant releases from fixed- and floating-roof storage tanks [36, 37]. TANKS uses chemical, meteorological, roof fitting and rim seal data to generate release estimates for several types of storage tanks, including:

- Vertical and horizontal fixed roof tanks;
- Internal and external floating roof tanks;
- Domed external floating roof tanks; and
- Underground tanks.

To use the models, specific information about storage tank construction and the stored liquid must be provided.

Are there an empirical/physicochemical relationship and necessary process data available?

Usually, for facilities with large number of tanks, an engineering model is used. The empirical/physicochemical relationships used for modelling purposes are readily available [37] and vary in complexity, depending on the site specific information which is available. For a small number of tanks, it may be preferable to simplify these relationships. A simplified methodology for estimating releases from storage operations using empirical relationships is presented in the *Emission Estimation Technique for Petroleum* [8].

Is there a site-specific or industry-specific emission factor available?

Due to the significant dependence of emissions on the physical properties of the liquids being stored, site specific or industry specific emission factors are generally not available.

Are other emission factors available?

Some inventories may provide emission factors for total emissions from storage facilities. Whether these emission factors are of acceptable quality is dependent on the objectives of the inventory.

Can engineering judgement be employed?

In the absence of emission factors, engineering judgement may need to be employed. An example is the air displacement technique developed for the Australian National Pollutant Inventory. The air displacement technique is an engineering equation that may be used in place of engineering models to estimate releases from storage tanks. This estimation technique assumes that the primary source of releases from a vessel occurs through the displacement of saturated vapour during addition of substances into the vessel, i.e. the volume of vapour released is equal to the volume of liquid added. It is also assumed that the volume of vapour displaced from a vessel during filling is saturated with the material filling the tank, i.e. the vapour displaced from the vessel is of the same composition as the liquid entering the vessel.

This assumption is valid for volatile single components and for some multiple component mixtures [6]. This is a crude RET which will tend to overestimate releases but is easy to use, especially for facilities with a small number of tanks.

The air displacement method for characterising releases from storage tanks has been recommended for storage tanks of less than 30 tonnes in capacity. For tanks of greater than 30 tonnes in capacity, the TANKS model is recommended. [7]

Can licence conditions be used to estimate worst-case releases?

In the absence of other information, licence conditions may be used to estimate worst-case releases. For example, some facilities have licences that specify upper limits on VOC releases. If using these data, it is assumed that upper limits for releases are specified and the facility is in compliance with these conditions.

4.3 Wet Cooling Towers

Is the source a point source?

Yes.

Is the release a process point release (stack/vent/effluent) or a diffuse release?

It is a process point release (stack) for air emissions and a process point release (effluent) for water emissions.

Is monitoring data available? Use the available data to obtain the most reliable estimate using one, or a combination, of direct emission measurements or indirect monitoring and mass balance.

It is difficult to measure particle releases from wet cooling towers. Water quality monitoring data may be available for the water entering the cooling tower, within the cooling tower and the wastewater discharges. This monitoring data may be useful for estimating metal or other pollutant emissions if the water flow is known. Information on total dissolved solids is also useful when using emission factors (see below).

Is it reasonable to use operational specifications?

Operational specifications for cooling towers generally include details of emission profiles, as emissions are dependent on the quality of the cooling tower water entering and exiting the tower.

Are there an empirical/physicochemical relationship and necessary process data available?

Empirical/physicochemical relationships are generally not used to estimate emissions from cooling towers.

Is there a site-specific or industry-specific emission factor available?

Emission factors for estimating particulate matter emissions to air from wet cooling towers are available. These emission factors are dependent on factors such as cooling tower type (induced draft or natural draft), total dissolved solid content of the water and water flow through the cooling tower. Default values for total dissolved solid content are also available [16]. Emission factors can be obtained through the links provided at OECD's Resource Centre website: http://www.oecd.org/env/prtr.

When applying emission factors, the following factors need to be considered:

- Whether pollutants emitted from wet cooling towers are reportable under the specific inventory;
- Whether the cooling tower type specified in the emission factor is consistent with the type being used;
- The availability of site-specific data for total dissolved solids content; and
- The availability of data for other pollutants contained within the total dissolved solids.

Emission factors are generally not available for wastewaters, although individual facilities may develop site-specific emission factors.

Are other emission factors available?

Particular inventories may have developed inventory wide emission factors for wet-cooling towers. This will depend on the objectives of inventory.

Can engineering judgement be employed?

Engineering judgement may be used to estimate total dissolved solid levels or flow of water through the cooling tower so that emission factors can be used to estimate releases.

Can licence conditions be used to estimate worst-case releases?

Licence conditions may specify upper limits for particulate matter releases to air, either as a concentration or a release rate, or for various substances that may be contained in the water discharges from cooling towers, either as a concentration or a release rate. When using licence conditions it is assumed that upper limits for releases are specified and the facility is in compliance with these conditions.

4.4 Flue Gas Desulphurisation Waste

Is the source a point source?

Yes.

Is the release a process point release (stack/vent/effluent) or a diffuse release?

It is a process point release (solid waste).

Is monitoring data available? Use the available data to obtain the most reliable estimate using one, or a combination, of direct emission measurements or indirect monitoring and mass balance.

Mass balance is generally the preferred method for estimating releases of flue gas desulphurisation waste due to the following factors:

- Records of inputs (i.e., flue gas flow rates) are usually kept;
- Captured material is usually analysed for composition because it is used to make other products[21] where the correct raw material specification is important. In addition, any material sent for landfill disposal usually has to meet certain specifications; and
- Records of the quantity of material sold or sent for disposal are usually kept.

Is it reasonable to use operational specifications?

Operational specifications may be used as the specifications for waste are usually of sufficient accuracy to allow mass balance to be performed.

Are there an empirical/physicochemical relationship and necessary process data available?

Stoichiometric relationships between sulphur removed and waste produced may be used to estimate releases, but are not usually performed due to the fact that mass balance is simpler to apply.

Is there a site-specific or industry specific emission factor available?

Emission factors are not usually used to estimate releases of flue gas desulphurisation waste.

Are other emission factors available?

Emission factors are not usually used to estimate releases of flue gas desulphurisation waste.

Can engineering judgement be employed?

In the unusual case that no other information is available or that there are limitations in the records of waste composition or material transferred, engineering judgement may need to be used to estimate this information.

Can licence conditions be used to estimate worst-case releases?

Agreements with solid or liquid waste treatment facilities may specify total amounts of waste annually treated or the composition of the waste. This can be used to estimate releases or transfers.

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[21] Such as construction material.

4.5 Vehicle Dust and Exhaust Releases

Is the source a point source?

Vehicle dust and exhaust releases may be required to be included in the emissions of the industrial site which is a point source.

Specific issues with characterising vehicle releases as part of the estimation of releases of point sources are as follows:

- If fuel composition and mass of fuel burnt is known, based on e.g. purchasing records, emissions of metals and sulphur dioxide from vehicle exhausts can be estimated using a material balance;
- Typically, emissions from vehicle exhaust are relatively minor compared to boiler emissions, so highly accurate emissions data may not be required;
- Empirical relationships for the estimation of vehicle generated dust are available [37]. These relationships are dependent on the mass of the vehicles, the moisture content of the ground surface and the surface silt loading of the ground;
- Site-specific data for moisture content and surface silt loading are sometimes available. Default values are available for these parameters, in case site-specific data is not available. The range in values for these parameters can be large, therefore it is recommended to make a first-estimate using default values, and if the results would indicate these emissions to contribute significantly to the emissions of the site, site-specific data should be obtained; and
- Emission factors to estimate vehicle exhaust emissions are available for a wide range of vehicle types [32]. Emission factors for vehicle exhaust emissions are also available by industry [1]. Emission factors can also be obtained through the links provided from OECD Resource Centre: http://www.oecd.org/env/prtr.

4.6 Dust from Open Areas

Is the source a point source?

Dust from open areas is a diffuse emission at the industrial site, which is a point source. Specific issues that characterise open area releases are listed below:

- Empirical relationships for estimating emissions of dust from open areas are available [17]. The relationships usually depend on wind speed and material characteristics such as moisture content, surface roughness and threshold friction velocity. These characteristics are highly site-specific and can significantly influence emission estimates. This uncertainty is usually not a major issue at fossil fuel power generation facilities because open area dust emissions are relatively minor compared to plant emissions; and
- Licence conditions are not usually applied to emissions of dust from open areas. However, it is possible that a site has dust deposition limits, which can be used to derive emission rates through back-calculation methods, e.g. by using engineering models.

4.7 Dust from Stockpiles

Is the source a point source?

Dust from stockpiles may be required to be included in the emissions of the industrial site which is a point source.

Specific issues for characterising stockpiles releases as part of the estimation of releases of point sources are as follows:

- Models, which estimate releases from stockpiles of coal or ash, are usually site-specific and are not usually publicly available. Therefore, models are generally not used to estimate these releases;
- Empirical relationships are available for estimating emissions from stockpiles [31]. These relationships are dependent on wind speed, material moisture content and mass of material transferred. These characteristics are highly site-specific and can significantly influence emission estimates. This uncertainty is usually not a major issue at fossil fuel power generation facilities because open area dust emissions are relatively minor compared to plant emissions;
- Due to the highly site-specific nature of the empirical relationships, which estimate stockpiling emissions, default emission factors are generally not used to estimate emissions. If these emission factors are used, they are of high uncertainty;
- If site-specific values are not available, engineering judgement may be used to estimate default values for wind speed, material moisture content and mass of material for use in empirical equations;
- Licence conditions are not usually applied to dust emissions from stockpiling operations; and
- If a site has dust deposition limits, those can be used to derive emission rates through back-calculation methods by using air dispersion models.

4.8 Coal Handling

Is the source a point source?

Yes.

Is the release a process point release (stack/vent/effluent) or a diffuse release?

It is a diffuse release.

Is mass balance possible?

Mass balance is not applicable.

Is there a suitable model that can be applied to the available data?

Models to estimate releases from coal handling are usually site-specific and are not usually publicly available. Therefore, models are generally not used to estimate these releases.

Are there an empirical/physicochemical relationship and necessary process data available?

Empirical relationships are available to estimate emissions from coal handling operations [33]. These empirical equations are dependent on material moisture content and material silt loading.

Is there a site-specific or industry-specific emission factor available?

Due to the highly site-specific nature of the empirical relationships, which estimate coal handling emissions, default emission factors are generally not used to estimate emissions. If these emission factors are used, they are of high uncertainty.

Are other emission factors available?

Emission factors are generally not used to estimate emissions (see above).

Can engineering judgement be employed?

In general, one of the RETs described above will be used. These RETs may require that some assumptions are made regarding suitable parameter values for use in equations.

Can licence conditions be used to estimate worst-case releases?

Licence conditions are not usually applied to dust emissions from coal handling operations. However, it is possible that a site has dust deposition limits, which can be used to derive emission rates through back-calculation methods by using air dispersion models.

4.9 Solvent Use

Is the source a point source?

Yes.

Is the release a process point release (stack/vent/effluent) or a diffuse release?

It is a diffuse release.

Is mass balance possible?

Mass balance can be used to estimate releases of NMVOC from solvent use. One approach is to assume that all the NMVOCs contained in the solvent are ultimately released directly to the atmosphere. This requires that information on the NMVOC content of solvents is obtained, e.g. from suppliers or material safety data sheets, and the total quantities of solvents used can be determined, generally from purchasing records.

The PRTR may require reporting of either specific volatile organic compounds separately or as the sum of all non-methane volatile organic compounds (total NMVOCs). There are default speciation profiles for solvent evaporation available [38], if there is no site-specific information of the profiles.

If solvents are collected and sent for further treatment, e.g. to incineration, material balance may be possible if assumptions on the fate of the pollutants are made, e.g. assumed conversion to carbon dioxide and water. These assumptions can be validated with downstream measurements.

Is there a suitable model that can be applied to the available data?

Models are generally not used to estimate releases from solvent use.

Are there an empirical/physicochemical relationship and necessary process data available?

Empirical relationships are not applicable in this case.

Is there a site-specific or industry-specific emission factor available?

Emissions are highly dependent on the NMVOC content of the solvents, so emission factors are generally not used to estimate emissions from solvent use. If site-specific information is not available, there are default speciation profiles that can be used in stead [38]. Emission factors can be found through the links from the OECD Resource Centre: http://www.oecd.org/env/prtr.

Are other emission factors available?

Other emission factors are not available.

Can engineering judgement be employed?

Engineering judgement may be used to make assumptions regarding the volatility percentage of solvents or can be used to make assumptions regarding conversion or collection in extraction systems.

Can licence conditions be used to estimate worst-case releases?

Licence conditions are not generally applied to solvent use. An extraction system dedicated to solvent recovery may have associated licence limits, which can be used for release estimation.

4.10 Leaks from Gas Pipelines

Is the source a point source?

Yes.

Is the release a process point release (stack/vent/effluent) or diffuse release?

It is a diffuse release.

Is mass balance possible?

Mass balance is possible if records of inputs, e.g., fuel purchased and outputs, fuel burnt, are kept. Measurements, which may be used to estimate emissions from individual pieces of equipment, e.g., valves, flanges, compressors, are available [21]. These data can be used to develop emission factors for particular pieces of equipment.

Is there a suitable model that can be applied to the available data?

Models are generally not used to estimate releases from gas pipelines.

Are there an empirical/physicochemical relationship and necessary process data available?

A number of methodologies exist for estimating emissions from gas pipelines using empirical relationships [21]. These methodologies estimate losses from individual pieces of equipment depending on the amount of site-specific measurement data that is available. If no on-site measurement is available, default emission factors for equipment types can be used.

Is there a site-specific or industry-specific emission factor available?

Emission factors are available for particular types of equipment and gas types travelling through pipelines [21]. Emission factors can be found from OECD Resource Centre: http://www.oecd.org/env/prtr.

The estimation of greenhouse gases, such as CO_2, CH_4 and N_2O, is mainly based on the use of emission factors and oxidation factors determined for each fuel. The emission factor may be plant specific or retrieved from databases including suitable data for the purpose. For greenhouse gas emission factors the reader is referred to the IPCC Emission Factor Database[22]

Are other emission factors available?

Other emission factors are generally not used to estimate releases from gas pipelines.

Can engineering judgement be employed?

It may be possible to estimate gas consumption based on the quantity of energy produced and based on assumptions regarding the efficiency of the combustion system.

Can licence conditions be used to estimate worst-case releases?

Licence conditions are usually not applicable to estimation of releases from equipment leaks

4.11 Ash Collection and Disposal

Is the source a point source?

Yes.

Is the release a process point release (stack/vent/effluent) or a diffuse release?

It is a process point release (solid waste).

Is monitoring data available? Use the available data to obtain the most reliable estimate using one, or a combination, of direct emission measurements or indirect monitoring and mass balance.

Mass balance may be used to estimate releases of waste ash by using:

- Waste material composition data. Composition data are usually available for materials sent for landfill disposal; and
- Records of the total quantity of waste sent for disposal, e.g., number of truckloads per year.

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[22] The IPCC (Intergovernmental Panel for Climate Change) Emission Factor Database (EFDB) is a library for greenhouse gas emission factors and includes both IPCC default emission factors and country specific inputs evaluated and accepted by the EFDB editorial board.

The composition data are usually less reliable than data from flue gas desulphurisation because ash is not usually used in applications where these data are important.

Is it reasonable to use operational specifications?

Operational specifications may be used as specifications for waste are usually of sufficient accuracy to allow for mass balance to be performed.

Are there an empirical/physicochemical relationship and necessary process data available?

Empirical/physicochemical relationships are available but are not usually used due to the fact that mass balance is usually simpler to apply. Relationships which relate coal content to ash content may be available.

Is there a site-specific or industry-specific emission factor available?

Emission factors which estimate fly ash emissions can be used to estimate emissions of bottom ash using a material balance if the input is known and partitioning fractions are known or assumed. Emission factors can be found from OECD Resource Centre: http://www.oecd.org/env/prtr.

Are other emission factors available?

Emission factors are not usually used to estimate these releases.

Can engineering judgement be employed?

In the rare case that no other information is available, engineering judgement may need to be applied to estimate waste composition, disposal rates or ash partitioning fractions for use in mass balance release estimation.

Can licence conditions be used to estimate worst-case releases?

Licence conditions may specify the total amount of waste to be treated per year or the composition of the waste. This can then be used to estimate emissions.

5. QUALITY ASSURANCE

To ensure the reliability of release estimates, a process of quality assurance needs to be undertaken. Quality assurance and control is discussed in Section 2.6 of the main report.

ANNEX 2: PETROLEUM REFINING

SELECTION AND APPLICATION OF RELEASE ESTIMATION TECHNIQUES

1. THE SCOPE OF THE INDUSTRY

For the purposes of this annex, a petroleum refining facility is defined as a facility whose primary activity is the production of fuels (e.g. motor gasoline, diesel and distillate fuel oil, liquefied petroleum gas, jet fuel, residual fuel oil, kerosene and coke), finished non-fuel products (e.g. solvents, lubricating oils, greases, petroleum wax, petroleum jelly, asphalt, and coke) and chemical industry feedstocks (naphtha, ethane, propane, butane, ethylene, propylene, butylenes, butadiene, benzene, toluene and xylene) [31].

The major sources and releases from petroleum refining are illustrated in Figure 2.1. A number of the emission sources shown in Figure B.1 are considered as fugitive sources. Depending on the scope of the inventory, some of these fugitive emissions may not be reportable in a point source inventory or may be required to be reported as part of a diffuse source inventory. The processes that lead to emissions from wet cooling towers do not occur in dry cooling towers. The principal release sources to air, water and land from petroleum refining facilities are shown in Table 2.1. The specific pollutant releases are further discussed in Step 3.

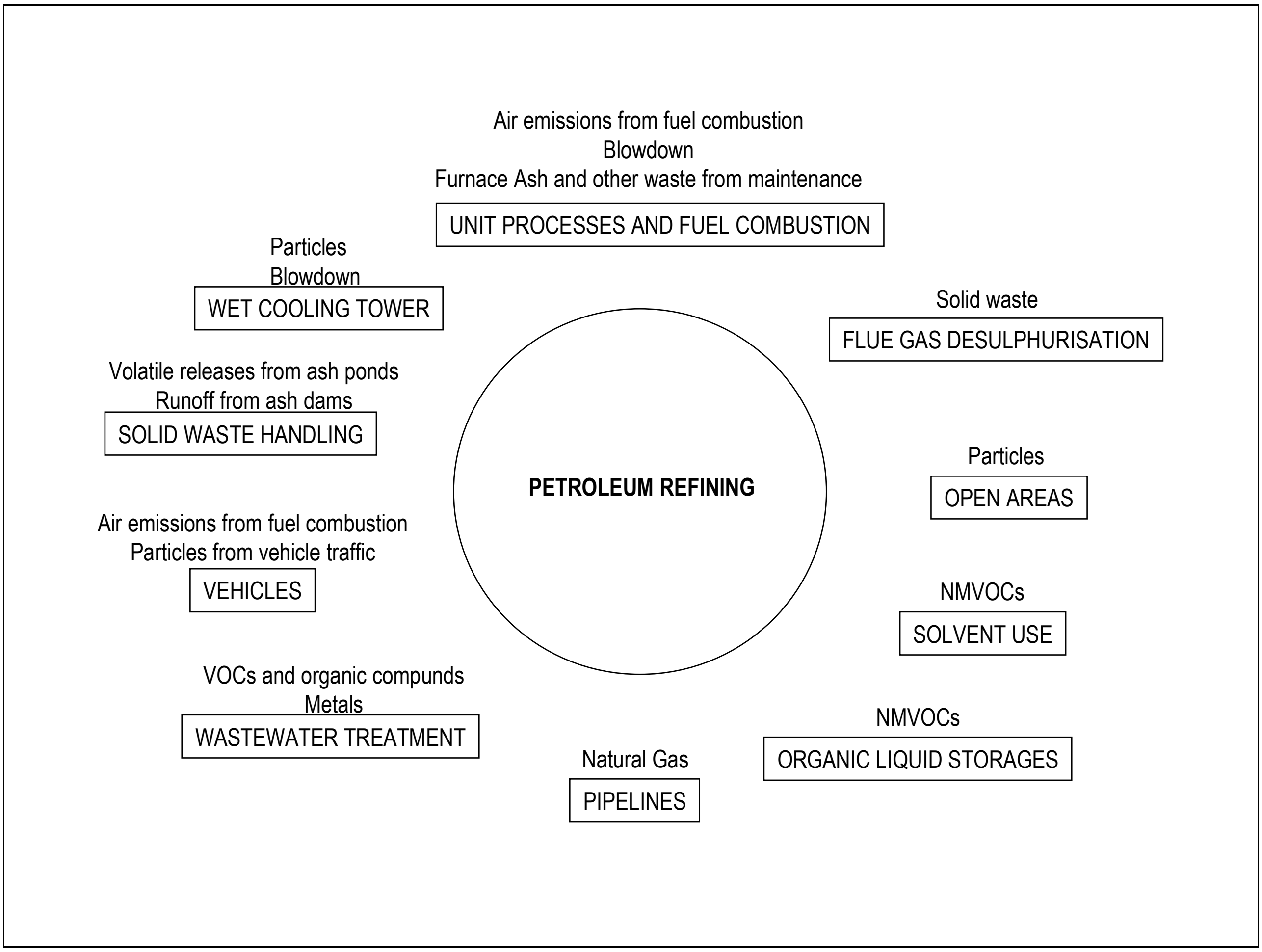

Figure 2.1: Releases from the petroleum refining industry

Table 2.1: Sources of releases from petroleum refining

Emission Sources	Air	Water	Land
Unit processes and fuel combustion	x		
Organic liquid storage and transfer	x		x
Wet cooling towers [1]		x	x
Wastewater treatment	x	x	x
Vehicles	x		
Open areas	x		
Solvent use	x		
Pipelines and equipment (leaks)	x		x
Solid waste handling	x		x

[1] The processes that lead to emissions from wet cooling towers do not occur in dry cooling towers.

2. POLLUTANTS

This step involves identifying releases at a petroleum refining site. The substances to be reported depend on the definitions and thresholds within the specific PRTR programme.

3. POTENTIAL RELEASE SOURCES

The potential emissions from each of the sources identified in Step 1 need to be assessed. This Annex will cover all pollutants which may be released by the petroleum refining industry. Resources, which can assist in determining the specific pollutants released from fossil fuel power generation can be found from the OECD website: http://www.oecd.org/env/prtr.

Further information on the potential releases and the factors affecting these releases are presented below.

3.1 Unit Processes and Fuel Combustion

A petroleum refinery consists of a large number of unit operations. These operations are necessary to produce the wide range of products, which a petroleum refinery typically manufactures. It should be noted that individual facilities may consider combustion emissions separately to process emissions when developing an inventory. This section considers total emissions from each unit. The factors, which influence these emissions are discussed below. Further information on the processes that lead to releases may be found in [20].

Another point to note is that a number of combustion processes occurring at petroleum refineries are similar to those at fossil fuel power generation facilities. Annex 1 of this report should be consulted when seeking further guidance on the estimation of emissions from combustion facilities.

Table 2.2: Emissions from the unit operations in petroleum refining [16]

Unit Operation	*Emission*
Crude oil desalting	CO, SOx,NOx, hydrocarbons and particles
Atmospheric distillation and vacuum distillation	CO, SOx,NOx, hydrocarbons and particles
Thermal cracking	CO, SOx,NOx, hydrocarbons and particles
Coking	CO, SOx,NOx, hydrocarbons and particles
Catalytic cracking	CO, SOx,NOx, hydrocarbons and particles
Catalytic hydrocracking	CO, SOx, NOx, hydrocarbons, particles and catalyst dust
Hydrotreating/hydroprocessing	CO, SOx,NOx, hydrocarbons and particles
Alkylation	CO, SOx,NOx, hydrocarbons and particles
Isomerisation	CO, SOx,NOx, hydrocarbons, HCl and particles
Polymerisation	Hydrogen sulphide
Catalytic reforming	CO, SOx,NOx, hydrocarbons and particles
Propane deashphalting	CO, SOx,NOx, hydrocarbons and particles
Gas treatment and sulphur recovery	SOx,NOx and H_2S
Merox treating	Hydrocarbons and disulphides
Heat exchanger cleaning	Hydrocarbons
Flaring	CO, SOx,NOx, hydrocarbons and particles

The specific releases from petroleum refining depend on the grade and composition of the crude oil, the type of combustion device, the firing and loading practices used and stage in the maintenance cycle. There can be significantly different releases from the combustion of distillate and residual oils.

In general, particulate matter releases depend on the completeness of combustion as well as on the oil ash content. The particulate matter emitted from distillate oil-fired combustion processes primarily results from the incomplete combustion of oil and is not correlated with the ash or sulphur content of the oil. However, particulate matter releases from residual oil burning are related to the oil sulphur content.

Oxides of sulphur (SO_x) are generated due to the oxidation of the sulphur in the fuel. The releases of SO_x from conventional combustion systems are predominantly in the form of SO_2. Uncontrolled SO_x releases are almost entirely dependent on the sulphur content of the fuel and are not affected by boiler size, burner design or grade of fuel being fired. Emissions of sulphur are reported as SO_2.

Oxides of nitrogen (NO_x) formed in combustion processes are due either to thermal fixation of atmospheric nitrogen in the combustion air (thermal NO_x), or to the conversion of chemically bound nitrogen in the fuel (fuel NO_x) [30]. NO_x concentration is exponentially dependent on temperature, and proportional to nitrogen concentration in the flame, the square root of oxygen concentration in the flame and the residence time. In general, an increase in flame temperature, oxygen availability and/or residence time at high temperatures leads to an increase in NO_x generation. The firing practices employed during boiler operation also influence NO_x formation. Low excess air (LEA) firing, flue gas recirculation (FGR), staged combustion (SC), reduced air preheat (RAP) or some combination of these measures may reduce NO_x emissions.

The rate of carbon monoxide (CO) releases from combustion sources depends on the oxidation efficiency of the fuel. By controlling the combustion process, CO releases can be minimised. If a unit is operated improperly or not well maintained, the resulting concentrations of CO, as well as organic compounds may be several orders of magnitude greater than in a well-controlled system. Smaller boilers, heaters and furnaces tend to emit more of these pollutants per unit of fuel consumed than larger combustion systems [29]. Carbon dioxide (CO_2) is formed as the major combustion product of oil-fired combustion.

The presence of CO in the exhaust gases of combustion systems is primarily a consequence of incomplete combustion. Several conditions can lead to incomplete combustion, including insufficient oxygen (O_2) availability, poor fuel/air mixing, cold-wall flame quenching, reduced combustion temperature, decreased combustion gas residence time and load reduction (i.e. reduced combustion intensity). Since various combustion modifications for NO_x reduction can produce one or more of the above conditions, increased CO releases may be a result of reduction in NO_x releases.

Small amounts of organic compounds are released from oil combustion. As with CO releases, the release rate of organic compounds depends, to some extent, on the combustion efficiency of the system. Therefore, any combustion modification, which reduces the combustion efficiency will probably increase the concentrations of organic compounds in the flue gases.

Unburned hydrocarbon releases can include all alkanes, alkenes, aldehydes, carboxylic acids, and substituted benzenes (e.g. benzene, toluene, xylene, ethyl benzene). The remaining organic releases are composed largely of compounds emitted from combustion sources in a condensed phase as polycyclic organic matter or polycyclic aromatic hydrocarbons. Formaldehyde is also formed during the combustion of oil. Trace elements are also emitted from the combustion of oil. The quantity of trace metals emitted from the source depends on combustion temperature, fuel feed mechanism and the composition of the fuel. The temperature determines the degree of volatilisation of specific compounds contained in the fuel. The fuel feed mechanism affects the separation of releases into bottom ash and fly ash. In general, the quantity of any given metal emitted depends on the physical and chemical properties of the element itself, the concentration of the metal in the fuel, the combustion conditions and the type of particle control device use and its collection efficiency as a function of particle size.

3.2 Organic Liquid Storage and Transfer

Organic liquids at petroleum refining facilities are usually stored in either floating-roof or fixed-roof tanks. Releases from fixed-roof tanks may be divided into two categories: working losses and breathing losses[23]. Working losses occur during both the filling and emptying of the storage tanks. Filling losses occur when the organic compounds contained in the air are displaced from a fixed roof vessel during loading. Emptying losses occur when air drawn into the tank saturates with organic compounds, then expands, exceeds the capacity of the vapour space and is forced out of the vessel. Breathing losses are the expulsion of vapour from a tank through vapour expansion caused by changes in temperature and pressure in the tank. The rate of losses from organic liquid storage tanks is influenced by the volatility of the liquid being stored (or components of the liquid being stored) and storage temperature and pressure [25].

Releases from floating roof tanks are either standing losses or withdrawal losses. Withdrawal losses occur when the liquid that clings to the tank wall is vaporised during the lowering of the floating roof during liquid withdrawal. Standing losses are caused by wind action at rim seals, deck fittings and deck seams.

The control techniques for storage tanks can be divided into the modification of storage tank design to minimise losses and the incorporation of vapour recovery and recycle systems.

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[23] Breathing loss is the fugitive emission from the expulsion of vapour from a tank vapour space that has expanded due to daily changes in temperature and barometric pressure.

3.3 Wet Cooling Towers

Cooling towers are heat exchangers that are used to dissipate large heat loads to the atmosphere. They are used to transfer waste heat from cooling water to the atmosphere by allowing the water to cascade through a series of decks and slat-type grids.

Cooling towers are either dry towers or wet towers, although some combinations of these also exist. Wet (or evaporative) cooling towers use water as their heat transfer medium and rely on the latent heat of water evaporation to exchange heat between the process and the air passing through the cooling tower. As cooling tower water comes in contact with the air passing through the tower, some of the liquid water may be entrained in the air stream and carried out of the tower as droplets. These aspirated droplets are dispersed into the atmosphere as aerosols, i.e. liquid dispersed in air. As the droplets evaporate in the atmosphere, particulate matter forms by crystallisation of the dissolved solids. Depending on the composition of the cooling water, these releases may contain heavy metals and salt compounds. This process does not occur in dry cooling towers. Therefore, only wet cooling towers are considered as sources of releases. [16]

Wet cooling towers can be classified by draft type (atmospheric, natural, mechanical, induced) and/or the location of the draft relative to the heat transfer medium (counter flow, cross flow). To reduce the drift from cooling towers, drift eliminators may be incorporated into the tower design. Drift eliminators induce the particles to separate by forcing them to travel through a specially designed flow path prior to exiting the cooling tower. Hence, the quantity of droplets exiting the tower is controlled. The types of drift eliminator configurations include herringbone (blade-type), wave form and cellular (or honeycomb) designs. The cellular units, generally, are the most efficient. Drift eliminators are generally formed into closely spaced slats, sheets, honeycomb assemblies or tiles ands may include features such as corrugations and water removal channels, to enhance drift removal.

The liquid that remains after evaporation and needs to be released to the environment is known as cooling tower blow-down. The evaporation process causes the levels of impurities within the cooling water to concentrate as the water is continuously recycled. The water that is continuously purged from the process is known as cooling tower blow-down. Pollutants of concern in cooling tower blow-down discharges include chlorine, organic chemicals and trace metals from bio fouling and corrosion control [24].

3.4 Wastewater Treatment

Wastewater streams are produced in a number of unit operations in a petroleum refinery. The design of wastewater treatment plants is influenced by the types of refinery pollutants, including oil, phenols, sulphides, dissolved solids, and toxic chemicals. Although the treatment processes employed by refineries vary greatly, they generally include neutralizers, oil/water separators, settling chambers, clarifiers, dissolved air flotation systems, coagulators, aerated lagoons and activated sludge ponds. Refinery water effluents are collected from various processing units and are conveyed through sewers and ditches to the treatment plant. Most of the treatment occurs in open ponds and tanks. The main components of atmospheric emissions from wastewater treatment plants are volatile organic compounds and dissolved gases that evaporate from the surfaces of wastewater residing in open process drains, separators, and ponds. Emissions to water and land may potentially contain all the pollutants released into the wastewater stream. These emissions are highly influenced by site-specific factors and will not be discussed further here. For further discussion on the processes that lead to wastewater emissions, please refer to [20].

Table 2.3 Wastewater emissions from petroleum refining operations

Unit Operation	**Wastewater Emissions**
Crude oil desalting	Oil, H_2S, NH_3, phenol, suspended solids, dissolved solids
Atmospheric distillation and vacuum distillation	Oil, H_2S, NH_3, suspended solids, chlorides, mercaptans, phenol
Thermal cracking	Oil, H_2S, NH_3, phenol, suspended solids
Coking	H_2S, NH_3, phenol, suspended solids
Catalytic cracking	Oil, suspended solids, phenols, cyanides,H_2S, NH_3
Catalytic hydrocracking	Suspended solids, H_2S
Hydrotreating/hydroprocessing	H_2S, NH_3, phenols, suspended solids
Alkylation	Suspended solids, dissolved solids, H_2S, NH_3, spent sulphuric acid
Isomerisation	Chloride salts, caustic wash, H_2S, NH_3
Polymerisation	H_2S, NH_3, caustic wash, mercaptans
Catalytic reforming	Oil, suspended solids, H_2S
Solvent extraction	Oil and solvents
Dewaxing	Oil and solvents
Propane deashphalting	Oil and solvents
Gas treatment and sulphur recovery	H_2S, NH_3, amines, Stretford solution
Heat exchanger cleaning	Oil
Storage tanks	Tank product
Wastewater treatment	Potentially all substances above

3.5 Vehicles

The movement of vehicles over various surfaces leads to releases of particulate matter. Releases from vehicle exhausts contain a range of pollutants including carbon monoxide, volatile organic compounds, sulphur dioxide, various organic compounds and oxides of nitrogen. Releases of this type are often considered as part of diffuse source inventories

3.6 Open Areas

Particulate matter releases may be generated by wind erosion of open exposed, dusty areas within an industrial facility.

3.7 Solvent Use

Ancillary operations such as equipment cleaning and related operations give rise to fugitive releases. These are usually evaporative losses and may be estimated using emission factors. These releases can, usually, be traced back to one point or to small area sources and can therefore be considered as point sources.

Wastes from the gas-side of the boiler (metals and cleaning wastes) are produced during maintenance, which includes the air pre-heater, economiser, super-heater, stack and ancillary equipment. Residues from coal combustion (soot and fly ash) build up on the surfaces of the equipment and must be removed periodically. This build-up is typically removed with pressurised water, containing no chemical additives. Wastewaters are sometimes neutralized and metals precipitated [20].

3.8 Pipelines and Equipment

Leakage of liquids or gases can occur at equipment connections, joints and interfaces. The intrinsic properties of these fluids (such as vapour pressure, temperature and pressure) can result in vapour releases through valve stems, pump seals and flanges.

3.9 Solid Waste Handling

Solid wastes are produced from a number of unit operations in a petroleum refinery. The formation of these wastes is dependent on the processes that lead to their formation. Further information on these processes is found in [20].

Table 2.4: Solid wastes produced at petroleum refineries

Unit Operation	Solid Wastes
Oil combustion processes	Bottom ash
Crude oil desalting	Sludge containing iron rust, clay, sand, emulsified oil, wax and metals
Coking	Coke dust (carbon particles and hydrocarbons)
Catalytic cracking	Spent catalyst (metals from crude oil and hydrocarbons), spent catalyst, fine particles from electrostatic precipitators (aluminium silicate and metals)
Catalytic hydrocracking	Spent catalyst fine particles (metals from crude oil and hydrocarbons
Hydrotreating/hydroprocessing	Spent catalyst fine particles (aluminium silicate and metals)
Alkylation	Neutralised alkylation sludge (sulphuric acid or calcium fluoride, hydrocarbons)
Isomerisation	Calcium chloride sludge from neutralised HCl gas
Polymerisation	Spent catalyst containing phosphoric acid
Catalytic reforming	Spent catalyst fines from electrostatic precipitators (aluminium silicate and metals)
Merox treatment	Spent Merox caustic solution, waste oil-disulphide mixture
Wastewater treatment	Separator sludge (phenols, metals and oil), chemical precipitation sludge (chemical coagulants, oil) DAF[24] floats, biological sludges (metals, oil, suspended solids, spent lime)
Gas treatment and sulphur recovery	Spent catalyst
Heat exchanger cleaning	Heat exchanger sludge (oil, metals and suspended solids)
Storage tanks	Tank bottom sludge (iron rust, clay, sand, water, emulsified oil, wax, metals)

4. SELECTION AND APPLICATION OF RELEASE ESTIMATION TECHNIQUES

4.1 Process and Combustion Emissions

Is the source a point source?

Yes.

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[24] Dissolved Air Flotation System (DAF).

Is the release a process point release (stack/vent/effluent) or a diffuse release?

It is a process point release through a stack/vent or effluent

Is monitoring data available? Use the available data to obtain the most reliable estimate for each source using one, or a combination, of direct emissions measurements or indirect monitoring and mass balance.

Monitoring data may be available for at least some of the pollutants released through stacks/vents at petroleum refineries. A Continuous Emission Monitoring System (CEM) can be used to monitor releases of SO_2, NO_x, organic compounds and CO from stacks. If CEM data are available and are of appropriate quality, these data will generally provide the most reliable estimate of releases for these substances. The cost of implementing a CEM system can be prohibitive and, beyond NO_x and CO, is not widely used in the industry. The use of CEM may also be problematic at low concentrations [21].

For uncontrolled emissions of metals and carbon dioxide, a CEM system may not be the preferred method [22]. This is due to the fact that if the amount of metals or carbon in the fuel is monitored, the uncontrolled releases may be estimated based on the concentration of a compound, for instance sulphur, in the fuel. For metals, an assumption is made on how much of the metal is partitioned between fly ash and bottom ash. It is assumed that metals pass untransformed through the combustion process and are partitioned at some determined ration between the fly ash and bottom ash. For carbon dioxide, it is assumed that all the carbon in the fuel is converted to CO_2. Therefore, for every kilogram of carbon (molecular weight of 12), 3.67 (44/12) kilograms of carbon dioxide (molecular weight of 44) is produced. Also uncontrolled emissions of SO_2 may also be estimated from the amount of sulphur in the fuel by assuming that there is complete conversion of sulphur to SO_2. Therefore, for every kilogram of sulphur (molecular weight of 32) burned, two kilograms of SO_2 (molecular weight of 64) are emitted.

For SO_2 and metals, if control techniques are applied, either CEM or indirect monitoring become the preferred RET [21]. Fuel analysis does not account for the removal of any pollutant from the control technology. However, fuel analysis may be used if the sulphur or metal content of the input stream is relatively homogenous and if site-specific pollution control efficiency data are available or can be determined with a reasonable amount of accuracy, e.g. through measurements or equipment specifications. This is especially relevant if the only alternative release estimation technique is the use of emission factors. Furthermore, if measurement data or emission factors are available, they can be used to validate emissions estimates obtained through fuel analysis. CO_2 emissions are not generally affected by pollution control equipment.

Indirect monitoring is the preferred method when a reliable, site-specific relationship between process parameters and release rates exists or can be developed. A typical example is the relationship between releases of SO_2 from fuel combustion in a boiler equipped with a wet scrubber and parameters such as water pH, flow rate and fuel combustion rate [21].

Stack sampling is the preferred RET for particulate matter, speciated organics and sulphuric acid mist. Stack sampling may be used when the emission profile for a unit is relatively homogenous. Petroleum refining facilities generally have long periods of time at standard operating loads, with consistent feedstock compositions. Provided that stack sampling data are available at each set of conditions throughout the reporting period, stack sampling data will provide reasonable estimates. This is often the case in the petroleum refining industry and stack sampling is often used. Provided that the data is representative of operations, stack sampling can provide reliable data for a PRTR at a relatively low cost. The accuracy of this method may be problematic at low pollutant concentrations [21].

Is it reasonable to use operational specifications?

Operational specifications for unit operations can be used to provide an accurate representation of releases from boilers at optimal conditions. Care should be taken when applying operational specifications at conditions of sub-optimal conditions, as units age or late in a maintenance cycle. Operational specifications may also not be representative of start-up or shut-down periods. This is of particular concern when start-up or shut-down are a major part of the operating time in a reporting period. Operational specifications may also be validated with measurements to ensure applicability.

Are there an empirical/physicochemical relationship and necessary process data available?

Empirical/physicochemical relationships are generally not used for estimation of releases from fuel combustion. These relationships may be developed for a particular facility for operational purposes.

Is there a site-specific or industry specific emission factor available?

Emission factors are available for SO_2, NO_x, CO, NMVOC, hydrocarbons, particulate matter, trace metals and organic compound releases from the unit operations at petroleum refining facilities. Emission factors can be found from the OECD Resource Centre: http://www.oecd.org/env/prtr. For instance, emission factors for combustion processes at petroleum refineries may be obtained from the USEPA [18] or the European Environment Agency [1].

The estimation of greenhouse gases such as CO_2, CH_4 and N_2O is mainly based on the use of emission factors and oxidation factors determined for each fuel. The emission factor may be plant specific or retrieved from databases including suitable data for the purpose. For greenhouse gas emission factors the reader is referred to the IPCC Emission Factor Database[25]

Section 3.5 of the main report discusses the general issues associated with selecting an appropriate emission factor. When selecting emission factors for fuel combustion in boilers, the following specific factors need to be considered:

- Unit operation configuration and whether this is the same configuration as specified in the emission factor: This is especially important for substances where emissions are heavily influenced by unit operation configuration (i.e. NO_x, CO);
- Abatement technology used: The general approach is to use uncontrolled emission factors with site-specific control efficiency data obtained from either stack measurements or manufacturer specifications (if applicable). Petroleum refining facilities will often have some measurement data available for air pollution control equipment, either stack measurement data which, when combined with fuel consumption data, may be used to determine the efficiency of the pollution control equipment, or specific upstream/downstream measurements to measure the efficiency of the pollution control equipment;
- Number of measurements used to compile the emission factor: In general, the greater the number of measurements, the more reliable the emission factor;
- Are the results consistent with available site-specific data (e.g. stack measurement data, fuel analysis data);

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[25] The IPCC (Intergovernmental Panel for Climate Change) Emission Factor Database (EFDB) is a library for greenhouse gas emission factors and includes both IPCC default emission factors and country specific inputs evaluated and accepted by the EFDB editorial board.

- Age of the unit relative to the age of facilities used to develop the emission factor; and
- Does any possible variation in measurement methods produce significant variation in results.

Personnel performing the estimate should take these factors into account and use a combination of validation, comparison and expert judgement to arrive at a final decision on which emission factor is most appropriate.

Are other emission factors available?

Occasionally, other emission factors, e.g. for a different furnace type, may need to be used for release estimation for particular substances. These emission factors may be used when emissions are not dependent on the specific characteristics of the source in question. Depending on the substance, a validation of estimates with fuel analysis or measurement data may also be possible (as discussed above).

Can engineering judgement be employed?

Engineering judgement may need to be used to choose default values for control efficiencies or fuel composition for use in release estimation calculations.

Can licence conditions be used to estimate worst-case releases?

In the absence of other information, licence conditions specifying either concentrations or release rates may be used to estimate worst-case releases. This assumes that licence conditions specify upper limits for releases and the facility is in compliance with these conditions.

4.2 Organic Liquid Storage and Transfer

Is the source a point source?

Yes.

Is the release a process point release (stack/vent/effluent) or a diffuse release?

It is a diffuse release.

Is mass balance possible?

Technically, estimating losses of organic liquid during storage and transfer operations is possible, if the initial and final mass of total material is measured. However, in most cases, the losses are significantly less than throughput, and as a consequence, mass balance is rarely used for storage and transfer operations.

Is there a suitable model that can be applied to the available data?

There are commercial or public software programmes available if no site specific model exists. For instance, the TANKS computer software program is one example of a model that estimates volatile organic compounds (VOC) and other common air pollutant releases from fixed- and floating-roof storage tanks [36, 37]. TANKS uses chemical, meteorological, roof fitting and rim seal data to generate release estimates for several types of storage tanks, including:

- Vertical and horizontal fixed roof tanks;
- Internal and external floating roof tanks;

- Domed external floating roof tanks; and
- Underground tanks.

To use the models, specific information about storage tank construction and the stored liquid must be provided.

Are there an empirical/physicochemical relationship and necessary process data available?

Usually, with facilities having large numbers of tanks, an engineering model is used. The empirical/physicochemical relationships used for modelling purposes are readily available [37] and vary in complexity depending on the site-specific information, which is available. For a small number of tanks, it may be preferable to simplify these relationships.

Is there a site-specific or industry-specific emission factor available?

Due to the significant dependence of emissions on the physical properties of the liquids being stored, site-specific or industry-specific emission factors are generally not available.

The estimation of greenhouse gases such as CO_2, CH_4 and N_2O is mainly based on the use of emission factors and oxidation factors determined for each fuel. The emission factor may be plant specific or retrieved from databases including suitable data for the purpose. For greenhouse gas emission factors the reader is referred to the IPCC Emission Factor Database[26]

Are other emission factors available?

Some inventories may provide emission factors for total emissions from storage facilities. Whether these emission factors are of acceptable quality is dependent on the objectives of the inventory.

Can engineering judgement be employed?

In the absence of emission factors, engineering judgement may need to be employed. An example is the air displacement technique developed for the Australian National Pollutant Inventory. The air displacement technique is an engineering equation that may be used in place of engineering models to estimate releases from storage tanks. This estimation technique assumes that the primary source of releases from a vessel is through the displacement of saturated vapour during addition of substances into the vessel, i.e. the volume of vapour released is equal to the volume of liquid added. It is also assumed that the volume of vapour displaced from a vessel during filling is saturated with the material filling the tank, i.e. the vapour displaced from the vessel is of the same composition as the liquid entering the vessel. This assumption is valid for volatile single components and for some multiple component mixtures [1].

The air displacement method for characterising releases from storage tanks has been recommended for storage tanks of less than 30 tonnes in capacity. For tanks of greater than 30 tonnes in capacity, the TANKS model is recommended [7].

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[26] The IPCC (Intergovernmental Panel for Climate Change) Emission Factor Database (EFDB) is a library for greenhouse gas emission factors and includes both IPCC default emission factors and country specific inputs evaluated and accepted by the EFDB editorial board.

Can licence conditions be used to estimate worst-case releases?

In the absence of other information, licence conditions may be used to estimate worst-case releases. For example, some facilities have licences, which permit the release of a certain quantity of VOCs per unit time.

4.3 Wet Cooling Towers

Is the source a point source? Is it identifiable, stationary and outside predetermined area source definitions and thresholds?

Yes.

Is the release a process point release (stack/vent/effluent) or a diffuse release?

It is a process point release (stack) for air emissions and a process point release (effluent) for water emissions.

Is monitoring data available? Use the available data to obtain the most reliable estimate for each source using one, or a combination, of direct emission measurements or indirect monitoring and mass balance.

It is difficult to measure particulate matter releases from wet cooling towers. Water quality monitoring data may be available for the water entering the cooling tower, within the cooling tower and the wastewater discharges. These monitoring data may be useful for estimating metal or other pollutant emissions if the water flow is known. Information on total dissolved solids is also useful when using emission factors (see below).

Is it reasonable to use operational specifications?

Operational specifications for cooling towers generally include details of emission profiles, as emissions are dependent on the quality of the cooling tower water entering and exiting the tower.

Are there an empirical/physicochemical relationship and necessary process data available?

Empirical/physicochemical relationships are generally not used to estimate emissions from cooling towers,

Is there a site-specific or industry specific emission factor available?

Emission factors for estimating particle emissions to air from wet cooling towers are available. These emission factors are dependent on factors such as cooling tower type (induced draft or natural draft), total dissolved solid content of the water and water flow through the cooling tower. Default values for total dissolved solid content are available [16]. Emission factors can be found through the links at the OECD Resource Centre: http://www.oecd.org/env/prtr.

When applying these emission factors, the following issues need to be considered:

- Whether pollutants emitted from wet cooling towers are reportable under the specific inventory;
- Whether the cooling tower type specified in the emission factor is consistent with the type being used;
- The availability of site-specific data for total dissolved solids content; and

- The availability of data for other pollutants contained within the total dissolved solids.

Emission factors are generally not available for wastewater discharges, although individual facilities may develop site-specific emission factors.

Are other emission factors available?

Particular inventories may have developed inventory wide emission factors for wet-cooling towers. This will depend on the objectives of inventory.

Can engineering judgement be employed?

Engineering judgement may be used to estimate total dissolved solid levels or flow of water through the cooling tower so that emission factors can be used to estimate releases.

Can licence conditions be used to estimate worst-case releases?

Licence conditions may specify upper limits for particulate matter releases to air, either as a concentration or a release rate, or for various substances that may be contained in the water discharges from cooling towers, either as a concentration or a release rate. When using licence conditions it is assumed that upper limits for releases are specified and the facility is in compliance with these conditions.

4.4 Wastewaters

Is the source a point source?

Yes.

Is the release a process point release (stack/vent/effluent) or a diffuse release?

It is a point source as effluent and diffuse emission source to air.

Is monitoring data available? Use the available data to obtain the most reliable using one, or a combination, of direct emission measurements or indirect monitoring and mass balance.

Measurement data are often available for process point releases to water when sampling is required as part of licence conditions. These data, together with information on effluent flow rates can be used to characterise releases to water.

Releases to air from wastewater treatment are usually diffuse releases of volatile organic compounds from units within the wastewater treatment system. Monitoring of these emissions is usually very difficult and/or expensive and is usually not performed.

Is it reasonable to use operational specifications?

Operational specifications are not applicable in this case.

Are there an empirical/physicochemical relationship and necessary process data available?

Due to the complex nature of the reactions that occur in wastewater treatment processes, models based on empirical/physicochemical relationships are often used to estimate releases from wastewater treatment systems. There are also publicly available models such as WATER8 and CHEMDAT8 [39, 34]. The models require information on the design specifications of the wastewater treatment system and the physical and chemical characteristics of the wastewater being treated.

Is there a site-specific or industry-specific emission factor available?

Emission factors are available for releases to air from oil water separator units at petroleum refineries [18]. Emission factors can be found through the links at OECD Resource Centre: http://www.oecd.org/env/prtr.

Are other emission factors available?

Emission factors from other industries are generally not applicable due to the site-specific nature of the releases from wastewater treatment.

Can engineering judgement be employed?

Engineering judgement is often employed to estimate input parameters, e.g. physical and chemical characteristics of wastewater that can then be used in models used to estimate releases.

Can licence conditions be used to estimate worst-case releases?

Licence conditions for releases to water in terms of concentration or total release may be used to estimate worst-case releases to water. This assumes that licence conditions specify upper limits for releases and the facility is in compliance with these conditions.

4.5 Vehicle Dust and Exhaust Releases

Is the source a point source?

Vehicle dust and exhaust releases may be required to be included in the emissions from the industrial site, which is a point source.

Specific issues with characterising vehicle releases as part of the estimation of releases of point sources are as follows:

- If fuel composition and mass of fuel burnt is known (e.g. purchasing records), emissions of metals and sulphur dioxide from vehicle exhausts can be estimated using mass balance techniques;
- Typically, emissions from vehicle exhaust are relatively minor compared to emissions from combustion, so highly accurate emissions data may not be required;
- Empirical relationships for the estimation of vehicle-generated dust are available [37]. These relationships are dependent on the mass of the vehicles, the moisture content of the ground surface, and the surface silt loading of the ground. It should be noted that the emission factors for vehicle-generated dust have usually been derived from measurements that cover all PM_{10} emissions associated with a unit operation, including exhaust emissions. To add the exhaust PM_{10} emissions to the fugitive emissions any result in some double counting for those activities;
- Site-specific data for moisture content and surface silt loading are sometimes available. Default values are available for these parameters if site-specific data is not available. The range in values

for these parameters can be large, therefore it is recommended to make a first-estimate using default values, and if the results would indicate these emissions to contribute significantly to the emissions of the site, site-specific data should be obtained; and

- Emission factors to estimate vehicle exhaust emissions are available for a wide range of vehicle types [32]. Emission factors for vehicle exhaust emissions are also available by industry [1]. International databases for emission factors can be obtained through the OECD Resource Centre: http://www.oecd.org/env/prtr.

4.6 Dust from Open Areas

Dust from open areas may be reported under point source inventories but are generally considered as diffuse sources.

When characterising open area releases from point sources the following specific issues need to be considered:

- Empirical relationships for estimating emissions of dust from open areas are available [17]. The relationships usually depend on wind speed and material characteristics such as moisture content, surface roughness and threshold friction velocity. These characteristics are highly site-specific and can significantly influence emissions estimates. This uncertainty is usually not a major issue at petroleum refineries because open area dust emissions tend to be relatively minor compared to plant emissions; and
- Licence conditions are not usually applied to emissions of dust from open areas. However, it is possible that a site has dust deposition limits that can be used to derive emission rates through back-calculation methods by using air dispersion models.

4.7 Solvent Use

Is the source a point source?

Yes.

Is the release a process point release (stack/vent/effluent) or a diffuse release?

It is a diffuse release

Is mass balance possible?

Mass balance can be used to estimate releases of NMVOCs from solvent use. One approach is to assume that all the NMVOCs contained in the solvent are released directly to atmosphere. This requires that information on the NMVOC content of solvents is obtained from suppliers or from material safety data sheets and the total quantities of solvents used can be determined, generally from purchasing records.

Depending on the scope of the PRTR, emissions may need to be reported for individual substances as well as for total NMVOCs. Default speciation profiles for solvent evaporation are available [38], if site specific data are not available.

If solvents are collected and sent for further treatment, e.g. for incineration or energy recovery, mass balance may be possible if assumptions on the fate of the pollutants are made, e.g. assumed conversion to carbon dioxide and water. These assumptions can be validated with downstream measurements.

Is there a suitable model that can be applied to the available data?

Models are generally not used to estimate releases from solvent use.

Are there an empirical/physicochemical relationship and necessary process data available?

Empirical relationships are not applicable in this case.

Is there a site-specific or industry-specific emission factor available?

Emissions are highly dependent on the NMVOC content of the solvents, so emission factors are generally not used to estimate emissions from solvent use. Emission factors are available that specify the NMVOC contents of typical surface coatings [38]. International databases for emission factors can be obtained through the OECD Resource Centre: http://www.oecd.org/env/prtr.

Are other emission factors available?

Other emission factors are not available.

Can engineering judgement be employed?

Engineering judgement may be used to make assumptions regarding the volatility percentage of solvents or regarding conversion or collection rates in extraction/treatment systems.

Can licence conditions be used to estimate worst-case releases?

Licence conditions are not generally applied to solvent use. An extraction system dedicated to solvent recovery may have associated licence limits, which can be used for release estimation.

4.8 Leaks from Pipelines and Equipment

Is the source a point source?

Yes.

Is the release a process point release (stack/vent/effluent) or a diffuse release?

It is a diffuse release.

Is mass balance possible?

Mass balance may be possible if records of inputs (fuel purchased) and outputs (fuel burnt) are kept. Measurement methods that may be used to estimate emissions from individual pieces of equipment, e.g. from valves, flanges, compressors are available [21]. Mass balance techniques may be used to develop emission factors for particular pieces of equipment. Mass balance is, generally, not used for large scale estimation of losses.

Is there a suitable model that can be applied to the available data?

Models are generally not used to estimate diffuse releases from gas pipelines.

Are there an empirical/physicochemical relationship and necessary process data available?

A number of methodologies exist for estimating emissions due to equipment leaks by using empirical relationships [21]. These methodologies estimate losses from individual pieces of equipment depending on the amount of site-specific measurement data that are available. If no on-site measurement data are available, default emission factors for equipment types are used.

Is there a site-specific or industry-specific emission factor available?

Emission factors are available for particular types of equipment and physical properties travelling through pipelines [21]. Emission factors can be obtained through links provided at OECD Resource Centre: http://www.oecd.org/env/prtr.

The estimation of greenhouse gases such as CO_2, CH_4 and N_2O is mainly based on the use of emission factors and oxidation factors determined for each fuel. The emission factor may be plant specific or retrieved from databases including suitable data for the purpose. For greenhouse gas emission factors the reader is referred to the IPCC Emission Factor Database[27]

Are other emission factors available?

Other emission factors are generally not used to estimate releases from gas pipelines.

Can engineering judgement be employed?

Engineering judgement is not generally applicable in this case.

Can license conditions be used to estimate worst-case releases?

Licence conditions for total fugitive emissions may be available and can be used to estimate releases if a reasonable assumption can be made regarding what fraction of total fugitive releases are comprised of leaks from gas pipelines.

4.9 Solid Waste

Is the source a point source?

Yes.

Is the release a process point release (stack/vent/effluent) or a diffuse release?

It is a process point release (solid waste).

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[27] The IPCC (Intergovernmental Panel for Climate Change) Emission Factor Database (EFDB) is a library for greenhouse gas emission factors and includes both IPCC default emission factors and country specific inputs evaluated and accepted by the EFDB editorial board.

Is monitoring data available? Use the available data to obtain the most reliable using one, or a combination, of direct emissions measurements or indirect monitoring and mass balance.

Mass balance may be used to estimate releases of waste ash by using:

- Waste material composition data. Facilities are generally required to collect composition data for any material sent for landfill disposal; and
- Records of total quantities of material sent for disposal. Records of this information are generally kept.

Is it reasonable to use operational specifications?

Operational specifications may be used as specifications for waste are usually of sufficient accuracy to allow for mass balance to be performed.

Are there an empirical/physicochemical relationship and necessary process data available?

In instances where chemical reactions are used to remove waste from air streams, stoichiometric relationships may be used to estimate quantities of waste generated.

Is there a site-specific or industry-specific emission factor available?

Emission factors, which estimate fly ash emissions, can be used to estimate emissions of bottom ash using a material balance if the input is known and combustion system partitioning fractions are known or assumed. International databases for emission factors can be obtained through the OECD Resource Centre: http://www.oecd.org/env/prtr.

Are other emission factors available?

Emission factors are not usually used to estimate these releases.

Can engineering judgement be employed?

In the rare case that no other information is available, engineering judgement may be needed to estimate waste composition, disposal rates or ash partitioning fractions for use in mass balance.

Can license conditions be used to estimate worst-case releases?

Licence conditions may specify total amount of waste to be treated per year and/or the composition of the waste. This can be used to estimate emissions assuming that licence conditions specify upper limits for releases and the facility is in compliance with these conditions.

5. QUALITY ASSURANCE

To ensure the reliability of release estimates, a process of quality assurance and control needs to be undertaken. The key elements of an effective quality assurance procedure are discussed in Section 2.6 of the main report.

1.

ANNEX 3: INCINERATION

SELECTION AND APPLICATION OF RELEASE ESTIMATION TECHNIQUES

1. THE SCOPE OF THE INDUSTRY

For the purposes of this annex, an incineration facility is defined as any facility which primary activity is the burning of municipal solid waste (MSW), medical waste or sewage sludge.

The major sources and releases from incineration are illustrated in Figure 3.1. Depending on the objectives of the PRTR, some of the releases shown in Figure 3.1 may not need to be reported.

One of the releases: “Vehicle dust and exhaust releases” shown in Figure 3.1 is considered as diffuse release. Depending on the scope of the inventory, some of these diffuse emissions may not be reportable in a point source inventory or may be required to be reported as part of a diffuse source inventory.

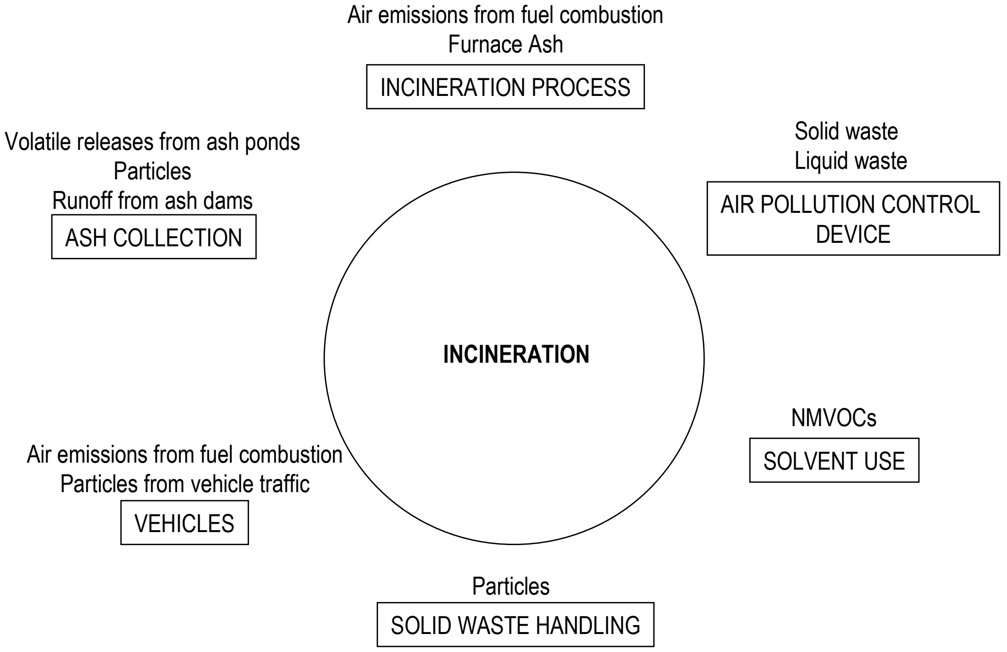

Figure 3.1. Releases from incineration

The principal release sources to air, water and land from incineration facilities are shown in Table 3.1. The specific pollutant releases are further discussed in Step 3.

Table 3.1: Sources of releases from incineration

Emission Sources	Air	Water	Land
Furnace	x		
Ash collection and disposal			x
Air pollution control device		x	x
Vehicles	x		
Solvent use	x		x
Solid waste handling	x		x

2. POLLUTANTS

This step involves identifying releases at a petroleum refining site. The substances to be reported depend on the definitions and thresholds within the specific PRTR programme.

3. POTENTIAL RELEASE SOURCES

The potential emissions from each of the sources identified in Step 1 need to be assessed.

Resources, which can assist in determining the specific pollutants released from incineration can be found from the OECD Resource Centre: http://www.oecd.org/env/prtr.

Further information on the potential releases and the factors affecting these releases are presented below.

3.1 Furnace

Furnace emissions from incineration are dependent on the furnace type and the characteristics of the material being burned. The furnace type varies depending on the material being burnt and there are a number of different technologies available for each type of material. The factors affecting the emissions from each of these technologies are discussed below.

3.1.1 Municipal Solid Waste Incineration

The methods of incineration (combustion) used for municipal solid waste (MSW) are:

- Mass burn;
- Refuse derived fuel; and
- Modular combustion.

The pollutants emitted from municipal solid waste combustion include particulate matter, metals, as part of particulate matter, except mercury, acid gases, carbon monoxide (CO), oxides of nitrogen (NOx), various organic compounds, such as dioxins and furans.

The amount of particulate matter exiting the furnace of MSW combustion system depends on the waste characteristics, the physical design of the combustion system and the combustion system operating conditions. Under normal combustion conditions, solid fly ash particles formed from inorganic, noncombustible constituents in MSW are released into the flue gas to be mostly captured by the facility's air pollution control equipment. [23]

The level of particulate matter emissions at the inlet of the air pollution control equipment will vary according the combustion system design, air distribution, and waste characteristics. For example, facilities that operate with high underfire/overfire[28] air ratios or relatively high excess air levels may entrain greater quantities of particulate matter. For incinerators with multiple-pass boilers that change the direction of the flue gas flow, part of the particulate matter may be removed prior to the air pollution control equipment. Lastly, the physical properties of the waste being fed and the method of feeding both influence particulate matter levels in the flue gas. Typically, refuse derived fuel units have higher particulate matter carryover from the furnace due to the suspension-feeding of the refuse derived fuel.

However, controlled particulate matter emissions from refuse derived fuel plants do not vary substantially from other MSW combustion systems, because the particulate matter is efficiently collected in the air pollution control equipment.

Due to the variability in MSW composition, metal concentrations are highly variable and are essentially independent of the combustion system type. If the vapour pressure of a metal is such that condensation onto particles in the flue gas is possible, the metal can be effectively removed by the particulate matter control device. With the exception of mercury, most metals have sufficiently low vapour pressures to result in almost all of the metals being condensed. Therefore, removal in the particulate matter control device for these metals is generally greater than 98 %. Mercury, on the other hand, has a high vapour pressure at typical air pollution control device operating temperatures and the rate of capture of mercury by the particulate matter control device is highly variable. The level of carbon in the fly ash appears to affect the level of mercury control. A high level of carbon in the fly ash can enhance mercury adsorption onto particles removed by the particulate matter control device.

The chief acid gases of concern from the combustion of MSW are hydrochloric acid (HCl) and sulphur dioxide (SO_2). Hydrogen fluoride (HF), hydrogen bromide (HBr) and sulphur trioxide (SO_3) are also present, but at much lower concentrations. The concentrations of HCl and SO_2 in MSW combustion flue gases are directly related to the chlorine and sulphur content of the waste. The chlorine and sulphur content can vary considerably based on seasonal and local waste variations. Emissions of SO_2 and HCl from MSW combustion depend on the chemical form of sulphur and chlorine in the waste, the availability of alkali materials in combustion-generated fly ash that act as sorbents and the type of emission control system used. Acid gas concentrations are considered to be independent of combustion conditions [22]. The major sources of chlorine in MSW are paper and plastics. Sulphur is contained in many constituents of MSW, such as asphalt shingles, gypsum wallboard and tyres. Because refuse derived fuel processing does not generally impact the distribution of combustible materials in the waste fuel, HCl and SO_2 concentrations for mass burn and refuse derived fuel units tend to be similar.

Carbon monoxide emissions result when all of the carbon in the waste is not oxidized to carbon dioxide (CO_2). High levels of CO indicate that the combustion gases were not held at a sufficiently high temperature in the presence of oxygen (O_2) for long enough to convert CO to CO_2. As waste burns in a fuel bed, it releases CO, hydrogen (H_2), and unburned hydrocarbons. Additional air then reacts with the gases escaping from the fuel bed to convert the CO and H_2 to CO_2 and H_2O respectively. Adding too much air to the combustion zone will lower the local gas temperature and quench (retard) the oxidation reactions. If too little air is added, the probability of incomplete mixing increases, allowing greater quantities of unburned hydrocarbons to escape the furnace. Both of these conditions would result in increased emissions of CO.

CO levels also vary between combustion system types. For example, semi-suspension-fired RDF units generally have higher CO levels than mass burn units, due to the effects of carryover of incompletely burnt

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[28] Overfire/underfire are air adjustments to optimise the burning in the combustion process.

materials into low temperature portions of the system, and, in some cases, due to instabilities that result from fuel feed characteristics.

Nitrogen oxides are formed during combustion through oxidation of nitrogen in the waste and fixation of atmospheric nitrogen. Due to the relatively low temperatures at which MSW combustion furnaces operate, 70 to 80 % of NO_x formed is associated with nitrogen content of the waste.

A variety of organic compounds, including chlorinated dioxins and furans, chlorobenzene (CB), polychlorinated biphenyls (PCBs), chlorophenols (CPs), and polyaromatic hydrocarbons (PAHs), are present in MSW or can be formed during the combustion and post-combination processes depending on combustion conditions. Organics in the flue gas can exist in the vapour phase or can be condensed or absorbed on fine particles. The control of organics is accomplished through the proper design and operation of both the combustion system and the air pollution control equipment.

3.1.2 Medical Waste Incineration

The methods of incineration (combustion) used for medical waste are:

- Controlled air incineration;
- Excess air incineration; and
- Rotary kiln incineration.

The pollutants emitted from medical waste incineration systems include particulate matter, metals, acid gases, oxides of nitrogen, (NO_x), carbon monoxide (CO), organic compounds and various other materials present in medical wastes such as pathogens, cytotoxins, and radioactive diagnostic materials. [15]

Particulate matter is emitted as a result of incomplete combustion of organics and by the entrainment of noncombustible ash due to the turbulent movement of combustion gases. Particulate matter may exit as a solid or an aerosol and may contain heavy metals, acids and/or trace organic compounds. Uncontrolled particulate emission rates vary widely, depending on the type of incinerator, the composition of the waste and the operating practices employed. Entrainment of particulate matter in the incinerator exhaust is primarily a function of the gas velocity within the combustion chamber containing the solid waste. Controlled air incinerators have the lowest turbulence and, consequently, the lowest particulate matter emissions. Rotary kilns have highly turbulent combustion and, therefore, tend to have the highest particulate matter emissions.

The type and amount of trace metals in the flue gas are directly related to the metals contained in the waste. Metal emissions are related to the removal rate of particle emissions and the flue gas temperature. Most metals, except mercury, exhibit fine-particle enrichment and are removed by maximising small particle collection. Mercury, due to its high vapour pressure, does not show significant particle enrichment, and removal is not a function of small particle collection rates at temperatures greater than 150°C.

Acid gas concentrations of hydrogen chloride (HCl) and sulphur dioxide (SO_2) in medical waste incineration flue gases are directly related to the chlorine and sulphur content of the waste. Most of the chlorine, which is chemically bound within the waste in the form of polyvinyl chloride (PVC) and other chlorinated compounds, will be converted to HCl. Sulphur is also chemically bound within the materials making up medical waste and is oxidised during combustion to SO_2 .

Oxides of nitrogen are formed by oxidation of nitrogen chemically bound in the waste and the reaction between molecular nitrogen and oxygen in the combustion air. The formation of NO_x is dependent on the quantity of fuel-bound nitrogen compounds, the flame temperature and the air/fuel ratio.

Carbon monoxide (CO) is a product of incomplete combustion. Its presence can be related to insufficient oxygen, residence time, temperature and turbulence (fuel/air mixing) in the combustion zone.

Failure to achieve complete combustion of organic materials evolved from the waste can result in emissions of a variety of organic compounds. These products of incomplete combustion range from low molecular weight hydrocarbons, such as methane or ethane, to high molecular weight compounds like chlorinated dioxins and furans. In general, combustion conditions required for the control of CO, i.e. adequate oxygen, temperature, residence time and turbulence, will also minimise emissions of most organic compounds Emissions of dioxins and furans are presently believed to follow one of the four general mechanisms. The first is where trace quantities of dioxins and furans present in the refuse feed are carried over, unburned to the exhaust. The second mechanism involves the formation of chlorinated dioxins and furans from chlorinated precursors with similar structures. The conversion of precursor material to chlorinated dioxins and furans can, potentially occur either in the combustion system at relatively high temperatures or at lower temperatures such as in wet scrubbing systems. The third involves the synthesis of chlorinated dioxin and furan compounds from a variety of organics and a chlorine donor. The fourth mechanism involves catalysed reactions on fly ash particles at low temperatures.

3.1.3 Sewage Sludge Incineration

Sewage sludge incineration (combustion) generally occurs in the following three furnace types:

- Multiple hearth;
- Fluidised bed; and
- Electric.

Sewage sludge incineration systems typically emit particulate matter, metals, carbon monoxide, oxides of nitrogen, sulphur dioxide (SO2) and unburned hydrocarbons. Partial combustion of sludge can result in emissions of intermediate products of incomplete combustion including toxic organic compounds. [19]

Uncontrolled particle emission rates vary widely depending on the type of incinerator, the volatile and moisture content of the sludge, and the operating practices employed. Generally, uncontrolled particle emissions are highest from fluidised bed incinerators because suspension burning results in much of the ash being carried out of the incinerator with the flue gas. Uncontrolled emissions from multiple hearth and fluidised bed incinerators are extremely variable. Electric incinerators appear to have the lowest rates of uncontrolled particle release of the three major furnace types, possibly because the sludge is not disturbed during firing. In general, higher airflow rates increase the opportunity for particulate matter to be entrained in the exhaust gases. Sludge with low volatile content or high moisture content may require more supplemental fuel to burn. As more fuel is consumed, the amount of air flowing through the incinerator is also increased. However, no direct correlation has been established between airflow and particle emissions.

Metal emissions are affected by metal content of the sludge, fuel bed temperature and the level of particulate matter control. Since the metals that are volatilised in the combustion zone condense in the exhaust gas stream, most metals, except mercury, are associated with fine particles and are removed as the fine particles are removed.

Carbon monoxide is formed when available oxygen is insufficient for complete combustion or when excess air levels are too high, resulting in lower combustion temperatures.

Emissions of nitrogen and sulphur oxides are primarily the result of oxidation of nitrogen and sulphur in the sludge. Therefore, these emissions can vary greatly based on local and seasonal sewage characteristics.

Emissions of non-methane volatile organic compounds (NMVOCs) also vary greatly with incinerator type and operation. Incinerators with countercurrent airflow such as multiple hearth designs provide the greatest opportunity for unburned hydrocarbons to be emitted. In multiple hearth furnaces, hot air and wet sludge feed are contacted at the top of the furnace. Any compounds distilled from the solids are immediately vented from the furnace at temperatures too low to completely destroy them.

3.2 Ash Collection and Disposal

Two types of ash are generated during combustion: bottom ash and fly ash. Ash that collects at the bottom of the furnace is called bottom ash. Fly ash is a finer ash material that is borne by the flue gas from the furnace to the end of the boiler. Fly ash is collected by the particle control equipment [24].

3.3 Air Pollution Control Device

Air pollution control devices that remove impurities from the flue gas generate waste. The volume and quality of the waste depends on the process and the inputs to the process, the efficiency of the control device as well as the operating conditions of the control device. Recent studies have indicated that dioxins and furans (PCDD/PCDF) may be formed downstream of the furnaces in air pollution control devices. Aromatic structures associated with the carbon in the fly ash can be converted to chlorinated dioxins and furans through reactions with inorganic chlorine [27].

The following control devices are typically used at incineration facilities [36]:

- Electrostatic precipitators, venturi scrubbers, baghouse filters and fabric filters for particulate matter removal;
- Spray drying, dry sorbent injection and wet scrubbing for acid gas control;
- Staged combustion, low excess air, flue gas recirculation, selective non-catalytic reduction, selective catalytic reduction and natural gas re-burning; and
- Injection of activated carbon or sodium sulphide, or the use of activated carbon filters for mercury control.

Combinations of these technologies may also be used. Depending on the control technology, the waste stream may be solid (electrostatic precipitators) or liquid (wet scrubbers).

3.4 Vehicles

The movement of vehicles over various surfaces leads to variable releases of particulate matter. Releases from vehicle exhausts contain a range of pollutants including carbon monoxide, volatile organic compounds, sulphur dioxide, various organic compounds and oxides of nitrogen. Releases of this type are often considered as part of diffuse source inventories.

3.5 Solvent Use

Ancillary operations such as equipment cleaning and related operations give rise to diffuse releases. These are usually evaporative losses and may be estimated using emission factors. These releases can be traced back to one point or to small area sources and can therefore be considered as point sources.

3.6 Solid Waste Handling

The handling and transfer of large quantities of solid waste can lead to uncontrolled emissions of particle matter. At incineration facilities, this often occurs indoors and may be controlled by extraction systems leading to air pollution control devices.

4. SELECTION AND APPLICATION OF RELEASE ESTIMATION TECHNIQUES

4.1 Furnace Emissions to Air

Is the source a point source?

Yes.

Is the release a process point release (stack/vent/effluent) or a diffuse release?

It is a process point release through a stack.

Is monitoring data available? Use the available data to obtain the most reliable estimate using one, or a combination, of continuous emission measurement, indirect monitoring and mass balance.

Monitoring data may be available for at least some of the pollutants released by incinerators. A Continuous Emission Monitoring System (CEM) can be used to monitor releases of SO_2, NO_x, organic compounds and CO from furnace stacks. CEM data are usually not available for incinerators. However, if CEM data are available and are of appropriate quality, these data will generally provide the most reliable estimate of releases of these pollutants. The cost of implementing a CEM can be prohibitive and, in addition to monitoring NO_x, SO_2 and CO, CEM is not widely used. The use of a CEM may also be problematic at low concentrations [21].

For metals and carbon dioxide CEM may not be the preferred method [21]. This is due to the fact that if the amount of metals or carbon in the fuel is monitored, uncontrolled (i.e. not accounting for pollutant controls) releases may be estimated based on the concentration in the fuel. This release estimation technique relies on the assumption that the feedstock sampling is sufficient to provide a reasonable characterisation of the sulphur, metal and carbon content of the feedstock. At many incineration facilities, the feedstock composition varies over a large range and care is required to ensure that feedstock sampling captures this variation. For SO_2, this assumes that there is complete conversion of sulphur to SO_2. Therefore, for every kilogram of sulphur (molecular weight of 32) burned, two kilograms of SO_2 (molecular weight of 64) are emitted. For metals an assumption is made on how much of the metal is partitioned between fly ash and bottom ash. It is assumed that metals pass untransformed through the combustion process and are partitioned at some determined ratio between the fly ash and bottom ash. For carbon dioxide, it is generally assumed that all the carbon in the fuel is converted to CO_2. Therefore, for every kilogram of carbon (molecular weight of 12), 3.67 (44/12) kilograms of carbon dioxide (molecular weight of 44) is produced.

For SO_2 and metals, if control techniques are applied, either CEM or indirect monitoring becomes the preferred RET [19]. Fuel analysis does not account for the removal of pollutants by pollution control technology. However, fuel analysis may be used if the sulphur or metal content of the fuel is relatively homogenous and if site-specific pollution control efficiency data are available or can be determined with a reasonable amount of accuracy, e.g. through measurements or equipment specifications. This is especially relevant if the only alternative release estimation technique is the use of emission factors. Furthermore, if measurement data or emission factors are available, they can be used to validate emission estimates obtained through fuel analysis. CO_2 emissions are not generally affected by pollution control equipment. Indirect monitoring is the preferred method used when a reliable, site-specific relationship between process parameters and release rates exists or can be developed. A typical example is the relationship between releases of SO_2 from a furnace equipped with a wet scrubber and parameters such as water pH, flow rate and waste combustion rate [21].

Stack sampling is the preferred RET for particulate matter, speciated organics and sulphuric acid mist. Stack sampling may be used when the release profile for a furnace is relatively homogenous. This may be problematic at incineration facilities since the exact composition of the waste is often not known and feedstock characteristics can be quite variable. Provided that the data is representative of furnace operations, stack sampling can provide reliable data for a PRTR at a relatively low cost. The accuracy of this method may be problematic at low pollutant concentrations.

Material balance may also be used to estimate the amount of particulate matter collected by pollution control equipment for disposal if inputs and outputs (estimated by one of the methods above) are known or can be estimated.

Is it reasonable to use operational specifications?

It is generally difficult to use operational specifications for incineration facilities due to the variable nature of the feedstock.

Are there an empirical/physicochemical relationship and necessary process data available?

Empirical/physicochemical relationships are generally not used for the estimation of releases from furnaces. These relationships may be developed for a particular facility for operational purposes.

Is there a site-specific or industry-specific emission factor available?

Emission factors are available for SO_2, NO_x, CO, NMVOCs, hydrocarbons, particulate matter, trace metals and organic compound releases from incineration facilities. Emission factors for incineration may be obtained from the USEPA [15, 16, 22] or European Environment Agency [1]. International databases for emission factors can be obtained through the OECD Resource Centre: http://www.oecd.org/env/prtr.

The estimation of greenhouse gases such as CO_2, CH_4 and N_2O is mainly based on use of emission factors and oxidation factors determined for each fuel. The emission factor may be plant specific or retrieved from databases including suitable data for the purpose. For greenhouse gas emission factors the reader is referred to the IPCC Emission Factor Database[29]

Section 3.4 of the main report discusses the issues to be taken into account when using an emission factor. When selecting emission factors, the following specific issues need to be considered:

- Furnace configuration and whether this is the same configuration as specified in the emission factor. This is especially important for substances where emissions are heavily influenced by furnace configuration, i.e. NO_x, CO;

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[29] The IPCC (Intergovernmental Panel for Climate Change) Emission Factor Database (EFDB) is a library for greenhouse gas emission factors and includes both IPCC default emission factors and country specific inputs evaluated and accepted by the EFDB editorial board.

- Control technology used: The general approach is to use uncontrolled emission factors with site-specific control efficiency data obtained from either stack measurements or manufacturer specifications, if applicable. Incineration facilities will often have some measurement data available for air pollution control equipment, either stack measurement data that, combined with fuel consumption data, may be used to determine the efficiency of the pollution control equipment, or specific upstream/downstream measurements to measure the efficiency of the pollution control equipment;
- Number of measurements used to compile the emission factor: In general, the greater the number of measurements, the more reliable the emission factor;
- Are the results consistent with any site-specific data, e.g. stack measurement data, fuel analysis data or process data, that could be used to provide an estimate of emissions;
- Age of the furnace relative to the age of facilities used to develop the emission factor; and
- Does any possible variation in measurement methods produce significant variation in results.

Personnel performing the estimate should take these factors into account and use a combination of validation, comparison and expert judgement to arrive at a final decision on which emission factor is most appropriate.

Are other emission factors available?

Occasionally, emission factors for a different boiler type may need to be used for release estimation for particular substances in lack of better methods. These emission factors may be used when emissions are not dependent on the parameter in question, e.g., furnace type. Depending on the substance, a validation of estimates with fuel analysis or measurement data may also be possible, as discussed above.

Can engineering judgement be employed?

Engineering judgement may be used to choose default values for control efficiencies or fuel composition.

Can licence conditions be used to estimate worst-case releases?

In the absence of other information, licence conditions specifying either concentrations or release rates may be used to estimate worst-case releases. This assumes that licence conditions specify upper limits for releases and the facility is in compliance with these conditions.

4.2 Ash Collection and Disposal

Is the source a point source?

Yes.

Is the release a process point release (stack/vent/effluent) or a diffuse release?

It is a process point release (solid waste).

Is monitoring data available? Use the available data to obtain the most reliable using one, or a combination, of continuous emission measurement, indirect monitoring and mass balance.

Mass balance may be used to estimate releases of waste ash by using:

- Waste material composition data, since such data are generally available for incinerators; and
- Records of total quantities of material sent for disposal.

Is it reasonable to use operational specifications?

Operational specifications may be used as specifications for waste are usually of sufficient accuracy to allow for mass balance to be performed.

Are there an empirical/physicochemical relationship and necessary process data available?

Empirical/physicochemical relationships are available but are not normally used due to the fact that mass balance is usually simpler to apply.

Is there a site-specific or industry-specific emission factor available?

Emission factors which estimate fly ash emissions (see Section 4.1 above in this Annex) can be used to estimate the quantity of bottom ash if partitioning ratios between fly and bottom ash are known or can be assumed. International databases for emission factors can be obtained through the OECD Resource Centre: http://www.oecd.org/env/prtr.

Are other emission factors available?

Emission factors are not usually used to estimate these releases.

Can engineering judgement be employed?

In the case that no other information is available, engineering judgement may be needed to estimate waste composition, disposal rates or ash partitioning fractions for the use in mass balance release estimation.

Can licence conditions be used to estimate worst-case releases?

Licence conditions may specify the total amount of waste to be annually treated or the composition of the waste. This can be used to estimate emissions.

4.3 Air Pollution Control Device Waste

Is the source a point source?

Yes.

Is the release a process point release (stack/vent/effluent) or a diffuse release?

It is a process point release (solid or liquid waste).

Is monitoring data available? Use the available data to obtain the most reliable estimate using one, or a combination, of continuous emission measurement, indirect monitoring and mass balance.

Mass balance may be used to estimate releases of waste ash by using:

- Waste material composition data. Any material sent for landfill disposal usually has composition specification; and

- Records of total quantities of material sent for disposal. Records of this information are generally kept by incinerator facilities.

Is it reasonable to use operational specifications?

Operational specifications may be used as specifications for waste are usually of sufficient accuracy to allow for mass balance to be performed.

Are there an empirical/physicochemical relationship and necessary process data available?

In instances where chemical reactions are used to remove waste from air streams, stoichiometric relationships may be used to estimate quantities of waste produced.

Is there a site-specific or industry-specific emission factor available?

Emission factors which estimate fly ash emissions can be used to estimate the quantity of bottom ash if partitioning ratios between fly ash and bottom ash are known or can be assumed. International databases for emission factors can be obtained through the OECD Resource Centre: http://www.oecd.org/env/prtr.

Are other emission factors available?

Emission factors are not usually used to estimate these releases.

Can engineering judgement be employed?

In the case that no other information is available, engineering judgement may be needed to estimate waste composition, disposal rates or ash partitioning fractions for the use in mass balance release estimation.

Can license conditions be used to estimate worst-case releases?

Licence conditions may specify the total amount of waste to be treated per year or the composition of the waste. This can be used to estimate emissions assuming that licence conditions specify upper limits for releases and the facility is in compliance with these conditions.

4.4 Vehicle Dust and Exhaust Releases

Is the source a point source?

Vehicle dust and exhaust releases may be required to be included in the emissions of an industrial site, which is a points source.

Specific issues with characterising vehicle releases as part of the estimation of releases from point sources are as follows:

- If fuel composition and the mass of fuel burnt are known, e.g. from purchasing records, emissions of metals and sulphur dioxide from vehicle exhausts can be estimated using a material balance;
- Typically, releases from vehicle exhausts are relatively minor compared to furnace emissions, so highly accurate emissions data may not be required;
- Empirical relationships for the estimation of vehicle-generated dust are available [37]. These relationships are dependent on the mass of the vehicles, the moisture content of the ground surface and the surface silt loading of the ground. It should be noted that the emission factors for vehicle-

generated dust have usually been derived from measurements that cover all PM_{10} emissions associated with a unit operation, including exhaust emissions. To add the exhaust PM_{10} emissions to the diffuse emissions may involve some double counting of releases from those activities;
- Site-specific data for moisture content and surface silt loading are sometimes available. Default values are available for these parameters if site-specific data are not available. The range of values for these parameters can be large. In case the release estimate obtained by using a default value gives a relatively significant release compared to other sources, site specific data should be obtained; and
- Emission factors to estimate vehicle exhaust emissions are available for a wide range of vehicle types [32]. Emission factors for vehicle exhaust emissions are also available [1].

4.5 Solvent Use

Is the source a point source?

Yes.

Is the release a process point release (stack/vent/effluent) or a diffuse release?

It is a diffuse release.

Is mass balance possible?

Mass balance can be used to estimate releases of NMVOCs from solvent use. One approach is to assume that all the NMVOCs contained in the solvent are, ultimately, released directly to atmosphere. This requires that information on the NMVOC content of solvents is obtained from suppliers or from material safety data sheets and that the total quantities of solvents used can be determined. In general, this can be determined from purchasing records. Emissions may need to be reported for individual substances as well as for total NMVOCs, depending on the scope of the PRTR. If site-specific data are not available, default speciation profiles for solvent evaporation are available [38].

If solvents are collected and sent for further treatment, e.g. to incineration systems, material balance may be possible if assumptions on the fate of the pollutants are made, e.g. assumed conversion rates to carbon dioxide and water. These assumptions can be validated with downstream source measurements.

Is there a suitable model which can be applied to the available data?

Models are generally not used to estimate releases from solvent use.

Are there an empirical/physicochemical relationship and necessary process data available?

Empirical relationships are not applicable in this case.

Is there a site-specific or industry-specific emission factor available?

Emissions are highly dependent on NMVOC content of the solvents, so emission factors are generally not used to estimate emissions from solvent use. Emission factors are available that specify NMVOC contents of typical surface coatings [37]. International databases for emission factors can be obtained through the OECD Resource Centre: http://www.oecd.org/env/prtr.

Are other emission factors available?

Other emission factors are not available.

Can engineering judgement be employed?

Engineering judgement may be used to make assumptions regarding the volatility percentage of solvents or regarding conversion or collection rates in extraction systems.

Can licence conditions be used to estimate worst-case releases?

Licence conditions are not generally applied to solvent use. An extraction system dedicated to solvent recovery may have maximum emission limits or defined removal efficiency. These data may be used for release estimation.

4.6 Solid Waste Handling

Is the source a point source?

Yes.

Is the release a process point release (stack/vent/effluent) or diffuse release?

It is a diffuse release.

Is mass balance possible?

Mass balance is not applicable.

Is there a suitable model that can be applied to the available data?

Models which estimate releases from waste handling are usually site-specific and are not usually publicly available. Therefore, models are generally not used to estimate these releases.

Are there an empirical/physicochemical relationship and necessary process data available?

These releases are highly material and operation specific and there are no empirical relationships presently available for these releases.

Is there a site-specific or industry-specific emission factor available?

No.

Are other emission factors available?

Emission factors are generally not used to estimate these emissions (see above).

Can engineering judgement be employed?

Releases from waste handling are extremely difficult to characterise and are highly site-specific. If data are available on materials composition, e.g., presence of volatile substances, it may be possible to make some estimate, based on physicochemical properties of the substances contained in the wastes.

Can licence conditions be used to estimate worst-case releases?

Licence conditions are not usually applied to dust emissions from waste handling. However, sites may have dust deposition limits that may be used to derive emission rates through back-calculation by using air dispersion models.

STEP 5: QUALITY ASSURANCE

To ensure the reliability of release estimates, a process of quality assurance needs to be undertaken. Quality assurance is discussed in Section 2.6 of the main report.

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