GUIDANCE FOR FACILITIES ON POLLUTANT RELEASE AND TRANSFER REGISTER DATA ESTIMATION AND REPORTING

2020 Series 6



Welcome to UNITAR's Guidance Series for Implementing a National Pollutant Release and Transfer Register (PRTR) Design Project

Based on the lessons learned through ongoing activities supporting PRTR development worldwide, UNITAR has developed the following documents in a guidance series intended to facilitate the design and implementation of Pollutant Release and Transfer Registers (PRTRs):

- Implementing a National PRTR Design Project: A Guidance Document
- Series 1: Preparing a National PRTR Infrastructure Assessment
- Series 2: Designing the Key Features of a National PRTR System
- · Series 3: Implementing a PRTR Pilot Reporting
- · Series 4: Structuring a National PRTR Proposal
- · Series 5: Addressing Industry Concerns Related to PRTRs
- Series 6: Guidance for Facilities on PRTR Data Estimation and Reporting
- Series 7: Guidance on Estimating Non-Point Source Emissions

To access additional resources on various aspects of PRTR design and implementation, see:



UNITAR'S PRTR Platform highlights the activities of the UNITAR Chemicals and Waste Management Programme in support of the implementation of PRTRs. The site includes a library of Resources from UNITAR and other international organizations focused on supporting the development of PRTRs. The PRTR Platform also provides access to video training modules on different aspects of the development and implementation of national PRTRs through PRTR:Learn http:prtr.unitar.org

For additional information, please contact: Chemicals and Waste Management Programme United Nations Institute for Training and Research (UNITAR) email: cwm@unitar.org

Table of Contents

1. Introduction	6
PART A: Introduction for Company Facility Managers	7
1. What is a PRTR?	
2. Determining if the Facility is Required to Report	8
3. What Types of Information are Needed to Prepare a PRTR Report?	10
4. Organizing the PRTR Reporting Process	12
4.1 Assigning a PRTR Reporting Coordinator	12
4.2 Developing a System for Collecting/Tracking Data	12
4.3 Identifying and Estimating Pollutant Releases/Transfers	13
5. Uses of PRTR Data Beyond Reporting	14
PART B: Identifying and Estimating Pollutant Releases and Transfers for PRTR Repo	orting 15
1. Introduction	
2. What are Environmental Releases and Off-Site Transfers? An Introduction to	
Some Key Terms	16
3. Conducting an Inventory of Facility Releases and Transfers	19
3.1 Are Reportable Substances Used at the Facility?	
3.2 Do the Products Contain any Reportable Substances?	
3.3 Do the Production Processes Use or Produce Any Reportable Substances?	
3.4 Do the Input Materials Used or Brought into the Facility Contain Any	
Reportable Substances?	24
3.5 Reporting Thresholds	
4. Selecting Suitable Estimation Methods	27
5. Identifying Necessary Information	28
6. Conducting A Trial Run	29
PART C: Methods for Estimating and Generating PRTR Data	31
1. Direct Measurement	32
1.1 Measuring Fugitive Air Emissions	
1.2 Measuring Point Source Air Emissions	
1.3 Measuring Surface Water Discharges	
1.4 Measuring Releases to Land	

2. Materials Accounting and Mass Balance	37
2.1 Estimating Fugitive Air Emissions by Materials Accounting	41
2.2 Estimating Point Source Air Emissions by Materials Accounting	41
2.3 Estimating Surface Water Discharges by Materials Accounting	43
2.4 Estimating Releases to Land by Materials Accounting	43
3. Emission Factors	43
3.1 Estimating Fugitive Air Emissions with Emission Factors	44
3.2 Estimating Point Source Air Emissions with Emission Factors	46
3.3 Estimating Surface Water Discharges and Releases to Land with Emission Factors	46
4. Engineering Calculation	47
4.1 Estimating Fugitive Air Emissions by Engineering Calculation	49
4.2 Estimating Point Source Air Emissions by Engineering Calculation	51
4.3 Estimating Surface Water Discharges by Engineering Calculation	51
4.4 Estimating Releases to Land by Engineering Calculation	52
5. Choosing The Best Method For Estimating Releases	52
Sources	55

List of Acronyms

EMEP	European Monitoring and Evaluation Programme
EEA	European Environment Agency
OECD	Organization for Economic Cooperation and Development
PRTR	Pollutant Release and Transfer Register
SDSs	Safety Data Sheets
UNECE	United Nations Economic Commission for Europe
UNITAR	United Nations Institute for Training and Research
US EPA	United States Environmental Protection Agency
VOC	Volatile Organic Compound

Introduction

Countries around the world are adopting Pollutant Release and Transfer Registers (PRTRs) that characterize the quantity and nature of environmental releases and off-site transfers of specific chemical substances. Under a typical PRTR system, annual pollutant release and transfer data for listed chemicals are estimated by facilities and reported to the government, which then makes them publicly available, such as through an online searchable database and documents summarizing analyses of the PRTR data. As such, a PRTR is a tool for promoting efficient and effective policies for environmental protection and sustainable development.

Facilities and their staff faced with a requirement to report under such a system may find the prospect daunting and not know where to start. Do their operations trigger required reporting? What types of information will be needed to estimate their releases and transfers? What are the best methods for making such estimates? Where can a facility find more information on how to employ estimation techniques? This brief guidance document attempts to outline the answers to these questions to assist PRTR reporters.

The document is comprised of three sections:

Part A provides guidance to assist the facility manager in understanding the requirements of PRTR reporting, the types of information likely to be needed to estimate the data, and where such information can be found. Part A also provides some ideas on organizing the data collection and reporting process at the facility level.

Part B provides step-by-step guidance for the technical staff involved in identifying releases and transfers and estimating various PRTR data elements.

Part C provides an overview of the methods available to facilities to estimate their releases to air, water, and land. For each method, the document indicates the circumstances for which it might be most suitable, provides some basic guidance, and presents illustrations of its use. The document is not intended to be an exhaustive guide. That is, specific industrial processes are not discussed, nor are any methods definitively recommended for specific applications. The aim is to assist facilities in making effective use of data that may already be available or readily attainable to estimate releases and transfers of pollutants for the purpose of PRTR reporting.

Since the implementation of the first PRTR in the late 1980s, governments and international organizations have developed numerous guidance documents, either to support their own PRTR, or to assist others who are in the process of designing and implementing a PRTR. These documents are available through the UNITAR's PRTR Platform¹ or through the Resource Centre on PRTR. net².

¹ http://prtr.unitar.org/site/home

² https://prtr.unece.org/resource-centre

PART A: Introduction for Company Facility Managers

What is a PRTR?

A Pollutant Release and Transfer Register (PRTR) is a regional or national database of releases and transfers of potentially harmful chemicals, including information on the nature and quantity of such releases and transfers. A PRTR is a means for obtaining regular, periodic information about releases and/or transfers of chemical substances and for making this information publicly accessible. As such, a PRTR is a tool for advocating access to environmental information, as well as promoting efficient and effective policies for environmental protection and sustainable development.

A PRTR system may include data from point sources and non-point sources. Point sources are single, identifiable, stationary sources of pollutant releases, such as a manufacturing facility, a power plant, or a mine. In contrast, non-point sources are diffuse sources of pollutant releases such as agricultural operations and transportation activities. For countries that include non-point sources in their PRTR systems, the data are typically generated through government estimates. The focus of this document is on the estimation of PRTR data by individual facilities which are considered to be point sources.

Determining if the Facility is Required to Report

The first step for a company manager is to determine if the facility has to report to the PRTR. This entails reviewing the PRTR's reporting criteria and deciding if they apply to the facility. Although reporting criteria differ from one PRTR system to the next, in general there are four criteria to consider:

Industry: what products are produced, services provided, or specific activities undertaken? PRTR reporting may be required only for certain economic sectors, or alternatively, all sectors may be covered except for those which are specifically exempted. A single facility may have many operations. PRTRs typically specify how to determine a primary "industry" based on, for example, revenue, amount of production, or use of individual substances.

Facility size: how many employees work at the facility? Eligibility for reporting may be based on a minimum number of workers or some other indication of the size of the facility or business. Employee totals may or may not include non-production workers such as office staff.

Reportable substances: are reportable substances present or generated on-site, in the specified physical form or chemical state? A PRTR's list of reportable substances may vary by release medium. They may be individual substances (such as toluene), chemical groups (metal compounds, volatile organic chemicals), or types of emissions (particulates). A physical form, such as fume or dust, may be specified for a substance, which means that only that form is subject to reporting, even if other forms of the substance are present on-site.

Threshold: is the amount of a reportable substance on-site sufficient to trigger reporting to the PRTR, given the requirements for reporting based on level of use, activity, or releases? Some PRTRs have "use" thresholds (i.e., a specified level of use), while other PRTRs use the amount of listed substances released in threshold determinations.

PRTRs vary in the industries and facility sizes subject to reporting, as well as reporting thresholds. All, however, have specific lists of reportable substances, which may include substances that are brought on-site, generated on-site, consumed on-site, or shipped in product; they may be impurities, intermediates, cleaning products, combustion by-products, or inert ingredients, which may not be tracked as part of normal record keeping.

Facilities face a few common challenges when determining their reporting status. Many facilities operate in more than one industry, e.g., mining and primary metals manufacture, petroleum refining and chemical production, primary metals manufacture and metal fabrication. In addition, a substance may be used in many ways at a facility. For instance, a chemical may be used as a surface cleaner in primary metal operations and as a coating component in metal fabrication. PRTR reporting rules usually define the industry for reporting, either by determining which industry constitutes the majority of a facility's revenue or value-added, making that industry the basis for the facility's PRTR reporting, or on a substance-by-substance basis. Another issue which may arise is the need to define the system boundaries of a facility, for example in the case where a production or waste treatment plant is used jointly by several facilities. Ideally, the PRTR provides reporting guidance for the range of circumstances and configurations commonly found at industrial facilities.

Misreporting or failure to report to a PRTR may result in substantial penalties. Therefore, it is always worth investigating whether or not the facility has to report if any of the list of reportable substances are known to be present on-site. It is also worth repeating this investigation every year and documenting the process, especially in case of changes in materials used on-site or changes in PRTR reporting requirements.

What Types of Information are Needed to Prepare a PRTR Report?

As new PRTRs emerge, facilities are faced with the prospect of reporting data elements for which they probably do not gather information on a routine or even occasional basis. Fortunately, the majority of facilities collect some data that can be used to estimate quantities of releases and transfers for PRTR reporting. In this regard, it should be noted that most, if not all, PRTRs require only best estimates of their chemical releases and transfers and thus do not require facilities to undertake additional measurement or monitoring. Part C of this document introduces some of these estimation methods and provides references to resources with more in-depth information and guidance. In addition, facilities affiliated with companies with operations reporting to existing PRTRs may be able to obtain guidance that is specific to their own operations.

Many of the data used to estimate release and transfer quantities are already available on-site or can be identified with little effort and low cost. These include:

Existing data on quantities of direct releases and discharges of reportable and non-reportable substances, including data compiled for other environmental reporting requirements. Data on discharges of specific substances is likely to be directly applicable to PRTR reporting. Other environmental reporting data could provide useful information for estimating quantities released. These include total discharges, concentrations, and properties that relate to concentration such as pH or electrical conductivity.

Data generated through monitoring of ambient conditions, such as measurements of ambient air concentrations undertaken to ensure compliance with worker safety regulations.

Materials accounting data, specifically: amounts of substances brought on-site, amounts of substances produced on-site, consumed on-site, and shipped in product, as well as inventory data for reportable and non-reportable substances. These data can be used to calculate total use to determine if the facility meets a reporting threshold, as well as to estimate releases and transfers.

Process data, including inputs and outputs for each production process, specific sources of releases, and off-site transfers. This also includes an equipment inventory, since some fugitive air emissions can be estimated by the number of compressors, valves, and fittings in the facility's processes.

Non-process data, such as substances used in cleaning and maintenance, for on-site waste treatment, or in fuels combusted on-site. Most cleaning products end up as direct releases because of the way they are used on site.

General engineering data, including equipment specifications, general reference data for specific processes, and physical and chemical property data for reportable substances. These data are used to estimate loss quantities and efficiency, which is especially useful in the absence of monitoring data.

Material and product specification data, including Safety Data Sheets (SDSs). This information can be useful in identifying the composition of the chemical materials and products used at the facility.

General references on estimating releases. Most references are government publications developed by countries with existing PRTR systems and are available online at no cost.

Not all these types of data will be collected by those responsible for environmental compliance. Environmental personnel are most likely to have at hand data compiled for other environmental reporting requirements, as well as data from any monitoring conducted at the facility. However, additional types of information needed for PRTR data estimation will be found in other departments or with personnel working on non-environmental responsibilities. For example, data about quantities and types of materials brought on-site are usually available from the purchasing depart-

ment. Information on products shipped would be available from shipping or accounting. Routine operating data would typically be available from process or product managers, as is information on possible sources of releases.

Organizing the PRTR Reporting Process

Once it has been determined that the facility needs to report to the PRTR, management will need to decide how best to undertake the information collection, data estimation and reporting processes with the expectation that threshold determinations and PRTR reporting will be recurring obligations into the future. Developing an effective system for collecting and tracking PRTR data will not only ensure that reports are well prepared but can also support using the PRTR data for other purposes, e.g., as an input into the company's efforts to reduce waste and emissions, to streamline record keeping, and to improve process efficiency. Following are some suggestions for organizing an effective PRTR reporting process.

4.1 Assigning a PRTR Reporting Coordinator

Given the diversity of data used for reporting, it is usually worthwhile to assign PRTR responsibilities to a single person. Naming a single individual makes clear who is responsible for meeting PRTR obligations within the organization; they can serve as the primary focal point with outside entities, such as the government agencies to which the data is submitted, and with citizens of the surrounding community who may have an interest in the facility's pollutant releases and transfers.

The person designated to coordinate PRTR reporting should be familiar with the facility, its processes, and the products produced. Facilities usually find that the environmental manager or a plant engineer is the person with this knowledge. Previous experience with environmental reporting is helpful for identifying and estimating PRTR data, but not essential. What is essential is a commitment from senior management to allocate the time, resources, and assistance necessary.

PRTR coordination should be considered a long-term job for two important reasons. First, as with most tasks, PRTR reporting gets easier with each year, and it makes sense to capitalize on that experience. Equally important, however, is the goal of maximizing the utility of the PRTR data within the facility, both as a means of identifying and implementing reduction opportunities, and for assessing how changes in activities at the facility have led to changes in pollutant release and transfer levels from year to year. Frequent changing of coordinators tends to undermine these potential uses of the data. As with turnover in other areas such as process or product supervision, a great deal of "institutional memory" gets lost, robbing the facility of the full benefits of the PRTR data.

4.2 Developing a System for Collecting/Tracking Data

Facilities usually find it useful to develop a system for systematically collecting the information needed for PRTR reporting and for tracking PRTR data throughout the year. Much of the information, which will be used to generate the PRTR reports are data that are collected by various

.....

departments and for reasons other than PRTR reporting. Some facilities already have or purchase chemical management software where information on the chemicals entering the facility and those manufactured are tracked. Ideally, the chemical management system is integrated with key inputs such as purchasing, production, and inventory data. Alternatively, facilities may develop their own system, such as spreadsheets that can be shared with production and purchasing personnel, to track the information. Acquiring this chemical and production information throughout the year is always a more efficient approach than compiling the data months after the reporting year is concluded. If these data compiled from throughout the facility are shared and stored digitally, regular updates can be accomplished throughout the year with minimal effort.

As the necessary data are collected, it may be useful to undertake a few trial data estimations, using the previous year's data, both to test the data collection and tracking system and to see if there are any data gaps that need to be addressed.

Once a system for the estimation and reporting of annual PRTR data is in place, the facility will be able to analyze these data from year to year to identify trends, to highlight possible areas for improvement, and to document progress achieved in emissions and waste reduction.

4.3 Identifying and Estimating Pollutant Releases/Transfers

Particularly during the first reporting cycle, but also on a regular basis for each subsequent reporting year, the facility should systematically review its various processes and activities in order to identify all potentially reportable releases and transfers. Part B of this document provides a suggested step-by-step process to assist facility personnel in undertaking this assessment. Some of the key questions to be addressed in identifying reportable releases/transfers include:

• Do the input materials used in producing the products or brought into the facility for other reasons contain any reportable substances?

• Do the products produced at the facility contain any reportable substances?

• Do the production processes used to make the products use or produce any reportable substances?

• Are there any supporting activities (e.g., cleaning or maintenance, waste treatment) at the facility that use reportable substances?

2020 | Series 6

Once potential releases and transfers have been identified, facility personnel will need to select the appropriate method for estimating the quantity of these releases/transfers. In virtually all cases, more than one method may be suitable for making these estimates. However, some estimation methods are more accurate than others, while others may be simpler to perform. Just how refined the estimate has to be depends in part on how large the releases are, the quality of data already collected, the intended uses of the data, and the judgment of plant personnel about accuracy.

When choosing estimation methods, facilities may also want to keep in mind that not all methods will reveal actual changes in releases/transfers. For example, emission factors for fugitive air emissions may depend only on the types of equipment in the process and the particular substances flowing through them. If the emission factors and the base to which they are applied do not change, then the release estimate will not change year even if the facility has instituted changes such as better worker education on materials handling. Similarly, engineering estimates may fail to reflect increased operating efficiency or reductions in emissions which the facility may have achieved through instituting small changes in operating parameters.

The various methods should be considered in light of these tradeoffs in order to select the most suitable option(s). Estimating releases is an evolving process: facilities may decide to change methods as they learn which ones are feasible, most likely to provide accurate data, and best suited to their particular needs.

Uses of PRTR Data Beyond Reporting

Facilities often find beneficial uses for PRTR data in addition to satisfying PRTR reporting requirements. Keeping track of where materials go once they enter the facility and reducing wastes can help identify opportunities to reduce waste, thereby reducing production and waste management costs. Releases and off-site transfers represent wastes that do not end up in the facility's products. Thus, identifying sources of these losses can point the way to increased efficiency and improved profitability. Large amounts of PRTR substances present as impurities in input materials, which require the facility to undertake expensive removal processes, can spur the search for new suppliers or product reformulations to eliminate the need to have those substances on-site at all. In certain cases, release data can be used as the basis for potential exposure calculations and risk assessments for particular substances. Estimating PRTR data usually brings other benefits as well, such as an improved chemical management system, or better record keeping and increased awareness of operations and materials use. Therefore, compiling PRTR data often yields useful information for management decision-making, even if reporting is not required.

PRTR data can be useful in ways that extend beyond the facility boundaries. As PRTR data are made available to the public, they can serve as a basis for improved dialogue between the company and neighboring communities. Historical PRTR data also provide a recognized baseline against which the facility can demonstrate improvements in environmental performance, such as reductions in emissions/transfers or changes made at the facility which have eliminated the use of certain PRTR substances.

.....

PART B: Identifying and Estimating Pollutant Releases and Transfers for PRTR Reporting

Introduction

The purpose of this part of the document is to assist the PRTR coordinator and other facility personnel identify reportable releases and transfers and generate PRTR data. Following a section which defines some key terms, a series of questions and related guidance are provided to assist the facility in working through a systematic process for identifying and estimating pollutant releases and transfers for the purpose of PRTR reporting.

What are Environmental Releases and Off-Site Transfers? An Introduction to Some Key Terms

Any amount of a substance that is brought or produced on-site and does not end up in a product, is not consumed in processing, and is not stored in inventory is waste. Waste can be managed on-site, released to the environment, or transferred off-site for recycling, energy recovery, treatment, or disposal. A PRTR tracks the amounts and types of environmental releases and transfers of these substance-specific wastes from individual facilities.

Environmental releases are direct discharges to air, water or land, whether intentional or not. These releases include fugitive air emissions, point source air emissions, surface water discharges, injections of waste underground into deep wells, direct discharges to land, and disposal in on-site landfills. Under a PRTR system, facilities report the quantity of each reportable substance released to each environmental medium.



Air emissions are divided into point source air emissions and fugitive air emissions. Point source air emissions come from equipment vents, stacks, ducts, or pipes that are designed to be air discharge points. Fugitive air emissions are usually unintentional and occur because of equipment leaks or uncontained transfer or storage procedures. The word "losses" is often used to describe fugitive air emissions, as in storage tank losses or losses from holding ponds. Discharges from building ventilation systems are also fugitive emissions.



Surface water discharges are releases into bodies of water such as streams, lakes, oceans, and rivers. These include direct discharge of process waste streams as well as waste streams resulting from on-site waste management, such as wastewater treatment. Discharges to holding ponds are not surface water discharges but are on-site land disposal as long as the holding pond is the final destination. Discharges to publicly owned treatment works (POTWs) are generally reported as off-site transfers rather than as releases.



Releases to land include discharges of slurries, solids, sludges, and some non-aqueous liquids. These discharges may result from on-site waste treatment or direct discharges from production processes. Releases to land also include discharges to on-site landfills, surface impoundments, and land farms.

Underground injection is purposeful injection of liquid waste underground into deep wells. Although there are different kinds of injection wells, the total quantity in all wells is generally summed to provide the total amount of underground injection.



Releases to the environment occur during all phases of the life cycle of raw materials and products, including mining or generation of raw materials, transportation to the facility, storage, processing, shipping of product, product use, and product disposal. Although all of these phases are potentially important sources of releases, PRTR reporting is typically defined as on a facility basis therefore this document examines only production-related releases and those occurring from onsite storage and disposal.

Off-site transfers are wastes which facilities send off-site for recycling, energy recovery, treatment, and disposal. In general, waste management facilities require their customers to tell them how much of specific chemicals are present in waste shipped off-site, so amounts of chemicals in off-site transfers are usually monitored and listed on waste shipping invoices.

Conducting an Inventory of Facility Releases and Transfers

PRTR reports typically contain estimates of releases by facilities based on their knowledge of the plant and its processes. Seldom if ever do PRTRs require facilities to measure their releases. Once the facility has determined that it is required to report to the PRTR (see Part A, section 2), a systematic assessment should be undertaken in order to identify reportable releases and transfers. Starting a facility-wide release inventory is no different from starting any other inventory: Find out what is known about the releases/transfers and look for information on the rest.

3.1 Are Reportable Substances Used at the Facility?

The first task is to identify on-site uses of reportable substances. Reportable substances are either produced on-site or brought on-site by the facility, but individual substances may also be present as impurities or inert ingredients and thus could be overlooked. Although most PRTRs specify reportable substances carefully, there are always questions about whether a specific substance actually has to be reported:

Physical Form or Chemical State

PRTR instructions may specify the form of a reportable substance such as zinc with the qualification "fume or dust". This means that large chunks of zinc deposited in on-site landfills would not be reported to the PRTR as releases to land. Other form qualifications include respirable, soluble, friable, and aerosol. The PRTR may also specify a chemical state, such as a particular valence of chromium, or organic versus inorganic. These designations are particularly important when there is a reporting threshold because the actual reportable substance, such as fume or dust, may not be used or produced on-site in sufficient quantity to trigger reporting, even if other forms of the substance are present in large amounts.

Part B ·····

Metals and Metal Compounds

Depending upon the specific features of the PRTR, metals may be reportable as pure substances, compounds, or both. When reported as compounds, only the weight of the reportable metal in the compound is actually reported to the PRTR. This is done to avoid double counting, as many metal compounds contain more than one metal. For example, lead chromate might be reportable as lead compounds and as chromium compounds, if both are substances reportable to the PRTR. In that case, the weight of the lead would be reported as lead compounds, and the weight of chromium as chromium compounds. Under some PRTRs, such as Canada's National Pollutant Release Inventory (NPRI), the weight of a reportable metal found in a metal compound is combined with the weight of the pure metal and these are reported as one number. Other PRTR systems, such as the U.S. TRI, list metals and metal compounds as separate, reportable substances, even though the releases and transfers of a metal and its compounds may be combined in the PRTR's data publications.

Once the actual reportable substance has been determined, the next step is determining how much and where the substance is present on-site. Essentially, this question requires knowledge of the flow of materials into the facility, through production and non-production processes, and out of the facility as product or waste. This knowledge also forms the basis of estimating releases, so a careful examination of the workings of the facility is useful on both counts. The best way to do this is to start with individual products shipped from the facilities and work backwards.

3.2 Do the Products Contain any Reportable Substances?

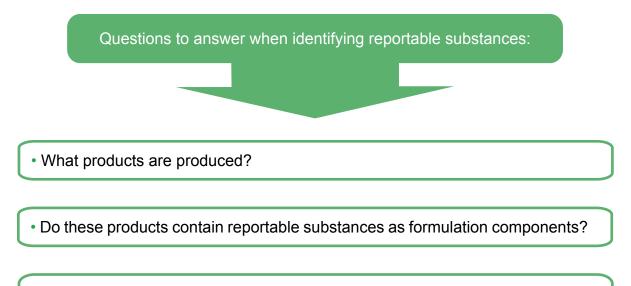
Chemicals may be present in products as part of the formulation or as impurities. Formulation components include "active" and "inert" ingredients, basically, ingredients that make the product do what it is supposed to do and other ingredients that either carry the active ingredients and/or provide other desirable qualities, such as colour, odour, texture, stability, etc. Complications occur when the inert ingredients vary either by substance or concentration—not an unusual situation, since these inert ingredients are usually carriers for the active ingredients and many different substances can work equally well: in these cases, price is usually the determining factor. Impurities include reaction by-products that did not get removed, and substances such as solvents that are not part of the product formula; these impurities may remain because they are too difficult or expensive to remove. Impurities can also be present in the raw material and thus can be carried along into the products.

When the product is an object or "article," reportable substances could be part of the product without specifically being included in the formulation. For example, if a metal shop that also coats its products has as its customer specification that the final product should have certain colour or surface durability properties, the specific formulation of the coating might not be as important to the shop manager as finding the coating with the required surface properties at the lowest available price. This is also true of non-articles such as petroleum products, which are usually rated by performance (such as "octane" level) rather than specified chemical content.

An additional source of reportable substances in product is packaging material. Facilities may bring packaging materials on-site without knowing their specific chemical components. Reportable substances could be present in adhesives, coatings, and the packaging material, such as corrugated cardboard.

Information on product content is available from many sources. Facilities may be required to provide Safety Data Sheets (SDSs) to their customers and/or may receive SDSs from their suppliers. An SDS lists the name and amount of specific substances, either in the form of actual amount or concentration. The data listed on SDSs indicates what chemicals are present in the product and provides some information on the concentration of each chemical in the product. The concentration provided may be a specific number or it may be a range. If a range is provided, either use the midpoint of the range, or contact the supplier to determine if a more precise value is available. Other useful data include in-house quality control measurements. Customers who require certification of product contents can use these certifications to determine if the product contains specific substances.

Once products have been determined to contain reportable substances, making a sound determination as to whether the chemical exceeds the reportable threshold requires accessing data on the amounts of individual products shipped throughout the year. These data will be useful for facility-wide materials accounting and for calculating total use levels and/or waste generation.



• Do these products contain reportable substances as impurities, such as unremoved by-products, solvents, or catalysts?

• Are any substances present as inert ingredients?

• Are any substances present in packaging materials?

Part B ·····

 Is there any required documentation that lists the substances contained in the products, such as SDSs or customer-required quality control measurements?

 Are any in-house measurements available for these products that will help determine if they contain reportable substances, such as process control or quality control monitoring?

3.3 Do the Production Processes Use or Produce Any Reportable Substances?

Even if reportable substances are not part of the product, they may be generated by the production process and removed before the product is shipped. Substances can also be produced and consumed in a single process, such as reaction intermediates. In addition, they might also be used in ways that do not end up in the final product, such as a solvent or catalyst.

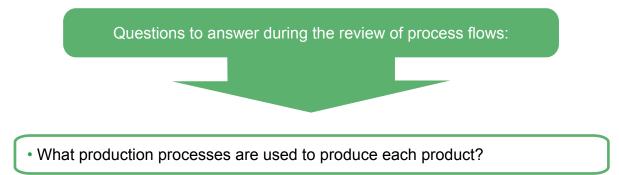
Non-production processes may also use reportable substances. For example, a reportable substance may be added to neutralize an acid in a facility's wastewater treatment process. Storage may also be considered as a separate process if it is not included in specific production processes.

> The best way to determine if substances are used or produced in a process is to take a walk-through of the plant.

The best way to determine if substances are used or produced in a process is to conduct a systematic assessment, starting with reviewing, updating, or developing a process flow diagram. A process flow diagram is a diagram commonly used in chemical and process engineering to indicate the general sequence and relationships of the plant's operations; such a diagram likely already exists for many facilities. To review, update or develop the process flow diagram, take a walk-through of the plant, inventorying each piece of equipment and the associated flow of materials, and consult with the plant personnel who operate the equipment and processes. This is also a good opportunity to determine if the piping and instrumentation diagrams are up to date. The basic procedure is to look at each piece of equipment, identify where input streams come from, where output streams go, and what materials they contain. Any measurements made on intermediate streams, such as process control measurements, could be useful in determining if reportable substances are generated or used in the process. Equally important is accessing production data, especially if several different products are made with the same equipment. Facilities typically have a system in place to track the types and quantities of products produced. Detailed production data can provide information on the amount of input material in each batch, as well as amount of chemicals incorporated into finished products.

The plant walk-through is also an excellent opportunity to take note of release sources, from individual pieces of equipment within a process to the whole plant. Otherwise, important sources of releases can be overlooked, particularly when chemicals go from one medium to another in processing—such as absorption of vapor from an air stream into water. This is particularly true of pollution control equipment. For fugitive air emissions, common sources include valves, fittings, pumps, and compressors. These can be counted and recorded during a walk-thorough and later combined with emission factors to estimate releases. Evaporation from wastewater treatment and storage tanks also creates fugitive air emissions. Sources of point source air emissions include all equipment vents. Surface water discharges and releases to land usually come from discrete release/discharge points that should be identified as well.

Finally, the process flow diagram review is also the time for identifying available data that can be used to estimate potential releases. These include data on waste shipped off-site, inventory data, discharges monitored for environmental or operating permits, and other data that would give amounts or concentrations of specific substances. Monitoring data is useful in providing an independent check to the plant walkthrough to see if any streams have been mischaracterized. Other data that should be identified at this point include: worker exposure data, accident and spill reports, and other in-house measurements made that can be related to concentration (see Direct Measurement, Part C, section 1 below).



• Are any reportable substances produced in the process?

• Are any reportable substances added to the process that get completely consumed?

• Are any reportable substances produced as intermediates (produced and consumed in the process)?

• Are any reportable substances used as solvents, as catalysts, or in other ways that do not end up in the final product?

2020 | Series 6

• Do any non-production processes, such as storage or wastewater treatment, use reportable substances?

· Have possible sources of emissions been identified?

• Has the source of production data been identified?

• Have all operating data been identified, including down-times in production and other data such as spills and worker exposure?

• What are the system boundaries of the facility? Does the way in which these are defined hold any implications for the identification of reportable substances/ transfers?

• Have all possible sources of data on specific substances been identified?

3.4 Do the Input Materials Used or Brought into the Facility Contain Any Reportable Substances?

In addition to the process operations, ancillary activities in the facility may also use reportable substances. Reportable substances may not be the main constituents of input materials, but nevertheless may be present in pigments, solvents, or other carriers. Cleaning and maintenance activities often use products with reportable substances, which typically end up as air emissions if not recovered, and as off-site transfers if they are recovered. Organic solvents are often used for cleaning machinery and batch clean-out, although the users of cleaning products are not always aware of the contents. The same is true of lubricating oils. Reportable substances may be used in on-site waste treatment operations, and in fuels combusted on-site for energy to power equipment (e.g., on-site motor vehicles) or support production processes.

SDSs from the manufacturers of inputs can be used to identify substances contained in their input materials. In addition, some facilities find it worthwhile to conduct their own assays of input materials to hold suppliers to their specifications. For example, if a supplier is supposed to deliver coal with a certain sulfur content, it can be useful to be able to test the coal before burning it to

2020 | Series 6

determine if the sulfur content reported by the supplier is accurate. This allows the facility to return the coal if it is substandard without even unloading it off the truck or train car. Another option is to provide suppliers with a list of reportable substances and ask them if their products contain any of the listed chemicals—and if so, in what concentration. Suppliers are usually willing to give out this kind of information as long as they are not being asked for complete formulations. If they are not willing to give the information, facilities should consider purchasing from other suppliers.

In some cases, input materials are not easily characterized. For example, paper facilities that use waste-paper feed as input may not be aware of the content of the waste paper purchased from suppliers. Very often, waste paper is graded by the amount of "white" office paper in the mixture, with more "white" paper being more desirable, since less bleaching is then necessary. It would be expensive for facilities to undertake multiple assays to determine if reportable substances are present in each delivery of waste paper. However, multiple facilities, the industry associations, and the suppliers could work together to characterize waste paper feed at relatively little cost to participating facilities. With access to such information, facilities might then decide that it is worthwhile to pay more for waste paper that does not contain reportable substances.

Consider All Sources of Potential Releases

- Accidental spills and releases
- Air pollution control devices (e.g., baghouses, scrubbers)
- Clean up and housekeeping practices
- Combustion by-products
- Container residues
- Fittings
- Flanges
- Maintenance activities
- Process discharge streams
- Process vents
- Pumps

- Recycling and energy recovery by-products
- Relief valves
- Stock pile losses
- Storage tanks
- Storm water runoff
- Tower stacks
- Transfer operations
- Treatment sludge
- Volatilization from process or treatment
- Waste treatment discharges

Questions to answer during the review of process flows:

• Is content information available for each product brought on-site, such as from SDSs or other quality control information?

Part B ·····

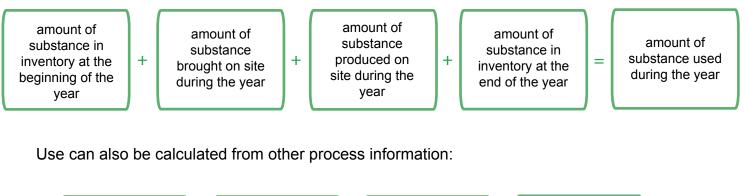
Is it possible to get content information from suppliers?

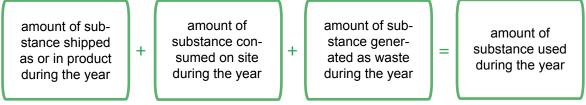
Are suppliers' invoices accurate and provide amounts of materials supplied?

3.5 Reporting Thresholds

Some PRTRs require facilities to report on any substance present on-site, no matter how small the amount or what the substance is used for. Typically, however, PRTR reporting is triggered by the amount of the substance used or released during the reporting year. That is, there is usually a use or release threshold for reporting a particular substance. The Kiev Protocol includes two options for reporting thresholds – one based on the quantity of the substance that the facility manufactures, processes, or uses with a threshold range of 0.0001 – 10,000 kg/year, depending on the substance; and another set of thresholds based on release quantities. If the facility's use of a substance meets the threshold, all releases and transfers must be reported to the PRTR, even if they are zero.

Use is calculated as follows:





For some PRTRs, there are different thresholds for specific types of uses. The U.S. TRI, for example, has a higher use reporting threshold of 25,000 pounds (11,340 kg) for substances that are manufactured or processed on-site and a lower threshold of 10,000 pounds (4,540 kg) for substances that are otherwise used, such as solvents or production aids.

For some PRTRs, there are different thresholds for specific types of uses. The U.S. TRI, for example, has a higher use reporting threshold of 25,000 pounds (11,340 kg) for substances that are manufactured or processed on-site and a lower threshold of 10,000 pounds (4,540 kg) for substances that are otherwise used, such as solvents or production aids.

Selecting Suitable Estimation Methods

The selection of methods for estimating releases from industrial facilities depends in large part on the type and quality of data already collected by the facility or which are readily available. Facilities routinely collect many different types of data for everyday operations. Some waste streams may be measured directly, but it is unusual to measure every waste stream. Thus, facilities also rely on three other methods of estimating releases: **materials accounting, emission factors, and engineering estimates**. A single release estimate reported to a PRTR can be a combination of any or all of these methods.

Estimating releases and transfer amount by the different methods gives different results, and facilities choose methods based on their knowledge of the plant, their degree of confidence in the data they collect, and the anticipated uses for the data other than PRTR reporting. For example, one facility reporting to the U.S. TRI tried materials accounting first, but found that the uncertainty in input and output values resulted in a relatively large amount of fugitive air emissions. An engineer at the plant found that using emission factors resulted in air emissions that were one-half that of the mass balance based estimates. Later, when the company instituted a programme to monitor its fugitive air emissions from equipment and piping, the revised estimate was another 50 percent lower—all through the choice of estimation method. Any one of the methods would have provided an estimate accurate enough for the PRTR, but PRTRs requires that facilities use their best available information. As more accurate data became available, the facility used those higher quality estimation methods and data to improve their release estimates. The facility also wanted to use the data for other purposes that required greater precision. These other uses ultimately were the impetus behind deciding to monitor fugitive air emissions.

Selecting the most appropriate release estimation technique for a specific release will be based on the data that are available or can be reasonably obtained with the time and resources available. Facilities strive to strike a balance between maximising the accuracy of the release estimate, while minimising effort and costs, as shown in the figure in the next page.

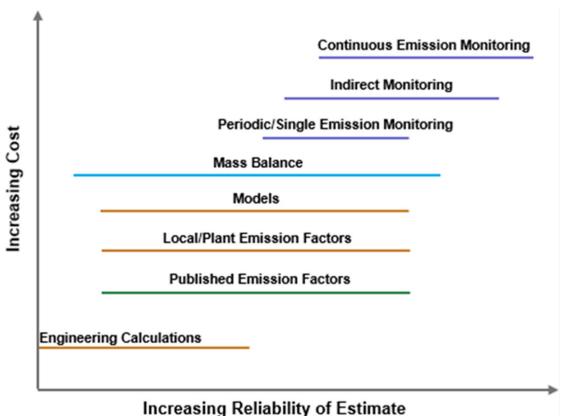


Figure 1: Cost Sensitive Emission Estimation Approach

increasing Reliability of Estimate

Facilities often use engineering estimates initially when they first start reporting to a PRTR, and over time, the facility obtains additional information to improve the accuracy of the estimate. The OECD document, Framework for Selecting and Applying PRTR Release Estimation Techniques³, provides additional insights into selecting release estimation techniques.

Identifying Necessary Information

The identification of releases and transfers at the facility is the starting point for generating PRTR data. The walk-though assessment and data identification described in section 3 above are help-ful when identifying processes where reportable chemicals are handled. Equally important is the identification of information that will be needed to apply the estimation methods. At this point, the facility should be aware of the equipment operating data available including manufacturers' specifications for process and pollution control equipment. Variables such as design yield, removal rate or treatment efficiency are often useful for calculating emissions, especially in the absence of monitoring data. An understanding of the information available at the plant will inform the selection of the best estimation technique. Also, depending on the estimation technique selected, the facility may need to access physical and chemical properties data on the individual reportable

³ http://prtr.unitar.org/site/document/1234

substances used at the facility. Particularly important are properties such as density and vapor pressure over a range of temperatures. These data are used in calculating emission factors and for engineering calculations, such as for tank losses.

Conducting A Trial Run

One way to determine if sufficient data have been collected to estimate releases for the PRTR is to attempt to estimate releases for the previous year. Such trial estimates help ensure that staff have identified release locations in the facility, associated data sources, and provides an opportunity to incorporate any additional data needs into the facility's chemical management system. If no chemical management system exists, the plant has time to develop and institute new data collection and record keeping, prior to actual reporting.

Small facilities may not routinely collect data that would allow them to report easily to a PRTR. However, a simple tracking system, even a spreadsheet-based system, and working with relevant personnel throughout the facility, will assist them in meeting their PRTR reporting obligations.

Case Example: Estimating Releases for a Small Paint Shop

Part 1: Identifying Reportable Releases/Transfers and Gathering Necessary Information

A small batch spray painting shop sets out to estimate its emissions for the previous year and determine what kinds of additional information will be necessary to estimate emissions for the current year. The layout is typical: paint is stored in in-plant storage tanks and pumped to the spray booths, and the facility uses a few different paints depending on the application.

< The first step is to look over the previous year's production and see how many individual jobs can be lumped together because of type of paint used and similarity of the type of units painted. The aim is to group into as few types of jobs or "job blocks" as possible. Then gather data on how much of each job was shipped during the year.

< Next, determine the types of paint used in each job block to see if they contained reportable substances. This information should be available from the Safety Data Sheet (SDS) for each product. If not, contact the supplier for information on the chemical constituents and their concentrations in the paints. Suppliers are typically required to provide this information on an SDS.

< Take stock of sources of emissions within the painting process. A paint shop typically has mostly air emissions. Sources include evaporation from the painted product, overspray, open containers, and equipment valves and fittings. Valves, fittings, and compressors should be identified to use with emission factors to calculate fugitive air

emissions. Any paint that does not end up on the product constitutes waste which, unless there are pollution controls, ends up as releases. If there are individual spray booths, there will probably be a common ventilation system for them-discharges from the vent will be point source air emissions. Otherwise, if the building ventilation takes care of everything, all emissions will be fugitive air emissions. Paint solids would constitute releases to land if they are disposed of on-site.

< Identify potential releases during cleaning and maintenance processes. How is painting equipment cleaned between batches? Is routine maintenance done during down times? Any solvent or cleaning product containing a solvent used to clean paint delivery lines and spray nozzles typically ends up as air emissions if it is not recovered.

< Are any other data collected that could be used for estimating emissions, such as worker exposure data? Are concentrations of organic solvents measured inside the spray booths? Are there any data on paint or cleaner spills?

Example continues in Part C

PART C: Methods for Estimating and Generating PRTR Data

Part C presents the four release estimation techniques (RETs) commonly used in PRTR reporting: direct measurement, materials accounting, use of emission factors, and engineering calculations. The application of each technique is described for estimating: 1) fugitive air emissions; 2) point source air emissions; 3) surface water discharges; and 4) releases to land. Additional information and examples for each of the RETs is available in the OECD guidance document, Resource Compendium of PRTR Release Estimation Techniques. Part 1: Summary of Point Source Techniques⁴

Direct Measurement

Facilities often measure the composition of waste streams for reasons other than PRTR reporting. These reasons include process control, measuring worker exposure, or fulfilling government requirements. Some general considerations regarding the use of direct measurement data for PRTR reporting are outlined in Box 1.

Process Control Measurements:

In-line sampling of concentration in process or exit streams to control process

• In-line sampling of properties directly related to concentration, such as pH or electrical conductivity

Worker Exposure Measurements

 Direct measurement of ambient concentration of various chemicals in the plant

Records of spills and leaks and descriptions of remedial actions applicable to those materials

Government Permit or Compliance Measurements

• Air releases of specific chemicals from pollution control equipment or other vents

• Amounts of chemicals discharged to surface water directly or to an off-site wastewater treatment facility

 Amounts of chemicals disposed of in on-site landfills or surface impoundments

Discharges to monitored injection wells

,.....

Part C

⁴ http://www.oecd.org/officialdocuments/publicdisplaydocumentpdf/?cote=env/jm/mono(2002)20/rev1&doclanguage=en

2020 | Series 6

Very often, these measurements can be used in a straightforward manner to estimate releases. As long as monitoring data are taken frequently enough to account for normal variations in operating conditions throughout the year, an average concentration can be used with an average flow rate to calculate the annual emission amounts. If operating conditions are relatively stable, the total quantity of the chemical in the waste stream is:



Even if operating conditions are not stable, measurements can still be used if the facility has confidence that the monitoring data have accounted for the range of conditions. For example, the vapor concentration leaving a distillation column condenser may vary significantly because of seasonal changes in cooling water temperatures. In this case, breaking the calculation into smaller time periods (such as quarters of the year or months), calculating total emissions for each time period, and summing for the year can provide an accurate estimate of annual releases.

Box 1. Estimating Releases by Direct Measurement

Direct measurement is usually used for estimating air emissions from point sources, surface water discharges, and releases to land. Measuring fugitive air emissions is more difficult, and is done less frequently.

Benefits

+ Facilities often measure waste streams, releases, and process streams for reasons other than PRTR reporting.

+ If the monitoring data are good, direct measurement is probably the most accurate estimate of releases.

+ Direct measurement is the method most likely to give unexpected results, which not only gives a more accurate estimate of releases but also alerts plant personnel to changes in operating conditions.

+ It is not always necessary to monitor for a specific chemical if there is only one reportable substance (e.g. one organic chemical) in use. It may also be possible to monitor for certain properties, such as pH or electrical conductivity, that relate to concentration.

+ Direct measurement of releases may satisfy government monitoring requirements for permits and compliance.

Drawbacks

- Direct measurement can be expensive, requiring specialized equipment, personnel training, maintenance, and record keeping.

- Facilities often have large amounts of monitoring data to analyse.

- Monitoring every source of release is not possible; practical technology is not always available.

- If monitoring data are not reliable (not representative of operating conditions), direct measurement may give a poor estimate of releases.

How to Begin

• Government regulations may provide appropriate measurement techniques. Consult the agency that collects monitoring data for information on specific monitoring techniques. Industry associations and engineering societies are also good sources.

•Equipment vendors can often provide information on measurement. Some monitors are relatively inexpensive and easy to use.

 Consult equipment manufacturers for tips on measuring inlet and outlet streams for specific pieces of equipment.

In general, facilities find that it is better to make a few measurements at strategic discharge points in the plant than to make many measurements on intermediate process streams. There is a certain amount of error in each measurement; combining errors associated with multiple measurements can result in large uncertainties in the final calculation.

1.1 Measuring Fugitive Air Emissions

Fugitive emissions are chemical releases to the air that are not released through stacks, vents, ducts, pipes, or any other confined air stream. By their nature, fugitive air emissions are more difficult to measure. Because fugitive emissions may come from many different sources, direct measurement can be costly and time consuming. However, some monitoring data that facilities already collect may be used to estimate fugitive air emissions. For example, ambient concentrations of specific chemicals may be monitored in various places throughout the plant to estimate worker exposure. If so, these concentrations can be used along with the air exchange rate of the plant's ventilation system to generate an estimate of fugitive air emissions. It is not always necessary to have a specialized monitor for a specific chemical if there is only one reportable substance present or if the chemical the facility wants to measure is unique. For example, a pharmaceutical company that uses chloroform as the only organic solvent in an extraction process can monitor total hydrocarbons to measure the ambient chloroform concentration.

Facilities can also measure routine leaks from valves, fittings, pumps, compressors, or even from individual pieces of process equipment. Specific measurement methods have been developed, and many are publicly available. For instance, U.S. EPA's Protocol for Equipment Leak Emission Estimates⁵ gives general instructions for measuring leak rates. Methods for doing so include using a portable monitoring instrument to sample air from potential leak interfaces on individual pieces of equipment, and "bagging" the equipment with a sealed enclosure. Once bagged, a sampling pump is used to remove material from the enclosure at regular intervals, and concentration measurements of the samples are recorded. A leak rate can be calculated from these measurements.

Monitoring equipment leaks can give a good estimate of fugitive air emissions and, depending on the processes, may be cost-effective. It is not necessary to monitor each valve in the plant, for example, but enough measurements should be made on each type of valve to get a reasonable average for each valve type (e.g., gate valves, globe valves, etc.). Leak rates may depend on the flow rate through the equipment or the chemicals in use, so measurements should be taken that account for these variations, at least enough to determine that the leak rate is independent of chemical or flow rate.

Because the age and condition of the equipment also influence the amount of fugitive emissions, facilities often routinely monitor for detectable leaks (as opposed to normal fugitive emissions) with a portable monitoring device. The instrument is held near the piece of equipment to give a quick indication of the presence of certain types of chemicals if over a threshold concentration. Unexpected detectable leaks indicate that the equipment needs to be repaired or replaced, and if they continue for too long, average leak rate measurements for that particular piece of equipment will not be accurate. If the device shows no detectable leaks (or if the excessive leaks are guickly repaired), then the average leak rate will be a good estimate of fugitive air emissions.

1.2 Measuring Point Source Air Emissions

Point source air emissions are usually the vapor output streams of specific pieces of equipment. Because they occur at known discharge points and are essentially confined before discharge, they are easier to monitor than fugitive air emissions. A few well-placed sample ports and flowmeters can provide a plant-wide estimate of point source air emissions, especially if only a few chemicals are present in the vapor streams. Even if it is not possible to monitor emissions of individual chemicals, monitoring of total point source air emissions can be used as a basis for estimating individual components: for example, total volatile organic compounds (VOC) emissions should be the sum of the individual VOC components. Point source air emissions are the air emissions most frequently monitored by facilities for reasons other than PRTR reporting, such as process control or government regulations.

1.3 Measuring Surface Water Discharges

Most facilities have only a single discharge point, which makes monitoring surface water discharges easier than measurement of some other releases (at least from a sample-collection point of view). If only one reportable substance is present in the wastewater stream, monitoring may be a reasonable choice of estimation method. Other indicators of concentration, such as pH or electrical conductivity, can also be measured to calculate surface water discharges. Measurement is fair-

ly common since facilities are often required to monitor surface water discharges for a government programme, such as a permit requirement, or to report water treatment efficiencies.

1.4 Measuring Releases to Land

As with surface water discharges, facilities usually have only one waste stream that is released to land on-site, making measurement a reasonable task if the waste stream contains few reportable substances. They may also monitor these waste streams for other reasons. For example, facilities may measure concentration in sludges to determine wastewater treatment efficiency, especially for large volumes of wastewater with small concentrations of contaminants. They may also monitor holding ponds directly to measure worker exposure because concentrations of individual chemicals may be high. If the releases to land are a result of direct discharges/disposal from individual pieces of equipment, such as filters, settling tanks, or sludge dewatering operations, the concentration of individual chemicals in the waste streams may be monitored to determine process yield. Monitoring is a common estimation method for land disposal because of facility concerns about landfill space and cost: facilities want to know exactly how much material is deposited as part of future business planning for landfill space and alternative waste management options.

Example A: Estimating Surface Water Discharges Using **Direct Measurement**

Task: Use plant monitoring data to estimate discharges of cadmium compounds from a cadmium plating line after wastewater treatment. The on-site treatment process receives cadmium compounds from the rinse water used to clean finished pieces and from the spent plating solution.

Process description and equipment inventory: Although the plant is a batch operation averaging 2000 hours per year, the treatment operation runs continuously (24 hours per day, 350 days per year). Plant personnel monitor discharges of total cadmium continuously for permit compliance. The monitoring data indicate that the average cadmium concentration is 6*10-3 g/litter during 1500 hours per year, and below the detection limit of 1*10-6 g/litter the rest of the time (these are measurements of cadmium only and do not include other substances present in the cadmium compounds). Average discharge flow rate does not vary and is 0.4*106 gallons per day.

How to begin: Calculate the amount of discharge when there is a measurable concentration.

(6*10-3 g/litter) * (1 pound/453.59 g) * (1 litter/0.264 gallons) * (0.4*106 gallons/day) * (1 day/24 hours) * (1500 hours/year) = 1,252.6 pounds/year

To be conservative, assume that the discharge level is half the detection limit when there is no measurable concentration in the discharge.

(0.5 * 1*10⁻⁶ g/litter) * (1 pound/453.59 g) * (1 litter/0.264 gallons) * (0.4*10⁶ gallons/ day) * ((350 days/year - (1500 hours/year * 1 day/24 hours)) = 0.48 pounds/year

This additional amount is quite small but brings the total discharge to approximately 1,253 pounds/year. The actual amount reported to the PRTR will depend on the number of significant figures required. Most require only two significant figures, so 1,300 pounds would be reported.

2

Materials Accounting and Mass Balance

Facilities often measure the composition of waste streams for reasons other than PRTR reporting. These reasons include process control, measuring worker exposure, or fulfilling government requirements. Some general considerations regarding the use of direct measurement data for PRTR reporting are outlined in Box 1.

Inputs	Outputs
 Amount of Chemical A brought on-site	 Amount of Chemical A shipped in prod-
during the year	uct during the year
 Amount of Chemical A in inventory at	 Amount of Chemical A in inventory at
the beginning of the year	the end of the year
 Amount of Chemical A produced on-site	 Amount of Chemical A consumed on-
during the year	site during the year
	 Total on-site releases of Chemical A during the year
	 Total off-site transfers of Chemical A (as waste) during the year

In this plant-wide materials accounting, the amount of Chemical A consumed on-site (used as a reactant or changed to another substance) during the year includes non-production consumption such as on-site treatment or energy recovery. The amount produced includes unintentional production, such as reaction by-products. Total releases of Chemical A are not identified using materials balance, but are the sum of fugitive air emissions, point source air emissions, surface water discharges, underground injection, and releases to land.

Facilities measure many of the quantities used in plant-wide materials accounting or equipment mass balances for various reasons, such as:

 Material safety records may require monitoring of concentration of chemicals in products, such as pharmaceuticals.

• Customers may require regular monitoring of products to make sure that they meet specifications.

• Facilities may analyse raw materials to prevent contamination or check that suppliers are meeting delivery specifications.

 Concentrations of certain process streams may be monitored as part of process control.

 Shipping logs and manifests can be used to identify amounts brought on-site, shipped in product, or transferred off-site as waste.

 Off-site transfers of waste may be monitored, since waste management facilities usually require information on the composition of waste brought on-site.

Production data forms the basis of an equipment mass balance and process-level materials accounting. Typical production data includes the amount of various chemicals put into the process, the amount of product generated, and the amount of leftover chemicals put into inventory. If the product meets its specifications, then the operators can track various wastes based on whatever was put into a process that did not end up in the product or back in inventory. For example, if a paint manufacturer's production data indicates that a) the paint contained the proper amount of xylene and b) 100 pounds of xylene are unaccounted for in the weight of the paint produced in that batch, then the xylene was probably released as a fugitive air emission. The facility-wide production data for the year serves as the basis for the materials accounting estimate of releases.

It is also possible to do a materials accounting calculation or mass balance for individual pieces of equipment. An equipment mass balance is the calculation of the amounts of material contained in input and output streams of that particular piece of equipment. The inputs include any material

generated in the equipment, such as reaction products (either intended or unintended), as well as the amount of the specific chemicals contained in input streams. Likewise, the outputs include any material consumed in the equipment, such as the amount consumed by reaction or destroyed in treatment, in addition to waste streams, process streams, and product streams. Since total inputs must equal total outputs, any material accounted for in the inputs but not the outputs constitute a fugitive environmental release. Mass balances are performed for total mass and individual chemicals (component mass balances). For example, a component mass balance for Chemical A in a reactor vessel would contain the following inputs and outputs:

Inputs	Outputs
 Amount of Chemical A in all streams flowing into the reactor Amount of Chemical A produced by 	 Amount of Chemical A in the product stream and other streams flowing out from the reactor
reaction within the reactor	 Amount of Chemical A consumed by reaction within the reactor
	 Total amount of Chemical A released from the reactor

Total releases from the reactor include liquid leaks, fugitive emissions, and waste streams such as pressure relief valves (unless these materials are counted as an output stream). A series of mass balances on all pieces of equipment within a process can account for total releases from that process. In turn, these process mass balances can be summed for the entire plant to account for every waste stream and yield the plant's releases to air, water, and land.

Box 2. Estimating Releases by Materials Accounting and Mass Balance

Mass balance and materials accounting are used regularly in most plants. Many types of releases can be estimated with these techniques, either from individual pieces of equipment or for the entire facility.

+ In theory, it's possible to estimate nearly the entire release inventory for the plant by mass balance and materials accounting.

+ Since mass balance and materials accounting are mathematical exercises, capital costs for this estimation method are low.

+ In addition to process monitoring data, many of the inputs and outputs in mass balances and materials accounting are already available from operating and finance data:

 Amounts of chemicals brought on-site during the year are available from receiving invoices and material safety sheets.

 Amounts of chemicals shipped in product are available from shipping receipts and safety data sheets.

• Amounts of chemicals stored in on-site inventories are frequently tracked.

 Production data provide inputs and outputs for equipment and process mass balances.

Drawbacks

- Releases estimated by mass balance and materials accounting are only as precise as the other inputs and outputs in the equation.

- The environmental media receiving releases may have to be determined by additional analysis.

 Small errors or uncertainties in input and output quantities can make huge differences in the amounts of releases estimated by mass balance and materials accounting.

- If the quantity of releases is small, mass balance and materials accounting may miss it altogether.

- Releases estimated by mass balance probably do not satisfy government monitoring requirements, although they are acceptable for PRTR reporting.

How to Begin

 Resources on release estimation techniques, including mass balance, are available through international organizations and PRTRs worldwide and are consolidated in the Resource Centre for Release Estimation Techniques accessed through PRTR. net. Experiences from existing PRTR systems, such as Chile, developed their own national guidelines on Release Estimation Techniques.

The aim is to end up with a single unknown quantity in each mass balance or materials accounting and to have reasonable confidence in all the other quantities, whether they are measured or estimated by other methods. It is probably not an exaggeration to say that most facilities would like their facility-wide materials accounting to balance within 5 – 10 percent. Unfortunately, it is often difficult to characterize inputs and outputs that accurately, and uncertainties in inputs and outputs can obscure small amounts of releases in a mass balance. Thus, materials accounting and mass balance are most appropriate when process losses are large compared to use (e.g., a solvent bath with large evaporative losses).

2.1 Estimating Fugitive Air Emissions by Materials Accounting

The ideal situation for calculating fugitive emissions by mass balance or materials accounting would be to quantify all other releases, inputs, and outputs first. Fugitive air emissions then would be whatever is left over. If fugitive air emissions for a particular piece of equipment or the entire facility are large in comparison to other releases, calculation by mass balance or materials accounting may be possible. Otherwise, variations in the amount of any input or output quantity, such as the amount of a chemical brought on-site, can have a huge impact on the amount of calculated fugitive air emissions, both in terms of amount and percent. For example, a large pharmaceutical company had used receiving invoices to determine the amount of material brought on-site. Outputs other than releases were well characterized, especially the amount shipped in product, since measurements had to be taken to satisfy federal regulations. Subsequently, the facility decided to spot-check the amount of material delivered and found that the supplier had actually delivered 20 percent less than stated on the invoices. This made a difference of much more than 20 percent in the estimate of fugitive air emissions by mass balance, translating to tens of thousands of pounds over the course of a year. This is an extreme example, but even a small error, say 5 percent in a large input or output stream, can end up disproportionately increasing or decreasing estimates of fugitive air emissions estimated by materials accounting.

2.2 Estimating Point Source Air Emissions by Materials Accounting

In some facilities, point source air emissions may be large enough to calculate by mass balance or materials accounting, especially if fugitive air emissions are small in comparison and can be estimated by another method. Point source air emissions may be the single unknown in an equipment mass balance if there is a discharge vent. If point source air emissions are much larger than fugitive air emissions, small uncertainties in other input and output streams will have little impact.

Example B: Estimating Air Emissions by Materials Accounting

Task: Use materials accounting information to calculate total air emissions of phosgene from a processing plant. The phosgene is produced on-site and is subsequently used to create the product. In addition, the facility buys some phosgene to keep a small inventory in case of problems with phosgene production.

Assemble plant-wide data:

Items needed for the calculation include the following:

 Amount of phosgene brought on-site during the year—available from purchasing records:

 Amount of phosgene in inventory on-site at the beginning and end of the year—may be available from inventory records or can be estimated if inventory remains constant;

Amount of phosgene produced on-site— available from production records;

 Amount of phosgene consumed on-site— may be available from production records or based on amount or product produced.

How to begin: An inventory of the plant records yields the following data:

The plant purchased 432,000 pounds of phosgene during the year.

Inventory data are not available, but plant personnel estimate that inventory is relatively constant at 30,000 pounds on any given day.

Production data indicate that the plant produced 805,000 pounds of phospene during the year.

No data are available on the amount of phosgene consumed on-site, but the plant produces a single product with a constant product specification. Shipping records indicate that the amount of product produced should have consumed 1,229,000 pounds of phosgene.

Sum the inputs and subtract the outputs:

432,000 pounds purchased + 30,000 pounds starting inventory + 805,000 pounds produced - 30,000 pounds ending inventory - 1,229,000 pounds consumed = 8,000 Guidance on PRTR Data Estimation and Reporting

2020 Series 6

pounds of phosgene unaccounted for.

These 8,000 pounds can be assumed to be total air releases if there is no pollution control on-site. If these air emissions come from process vents, the total amount would be reported as point source air emissions.

2.3 Estimating Surface Water Discharges by Materials Accounting

The same caveat for estimating point source air emissions by mass balance and materials accounting applies to surface water discharges. If the amount of chemical discharge is small compared to other releases or other inputs and outputs, the mass balance may not pick it up or calculate releases accurately. This is especially true if the facility discharges treated wastewater: the amount of reportable substances in the wastewater discharge stream may be so small that the concentration can't even be measured and may be hidden by uncertainties in other inputs and outputs. On the other hand, if the surface water discharge is an exit stream from a specific piece of equipment, an equipment mass balance may be the best way to calculate the quantity.

2.4 Estimating Releases to Land by Materials Accounting

Again, facilities have to consider the relative amount of releases to land and the uncertainty in other inputs and outputs when deciding whether or not to estimate them primarily by mass balance or materials accounting. Take the wastewater treatment example again-it would be difficult to calculate the amount of chemicals in treatment sludge if the amount of chemicals discharged to surface water is small. However, if the discharge to land occurs from a specific piece of equipment, such as a filter press or centrifuge, then equipment mass balance may be appropriate.

Emission Factors

Emission factors are, as the name implies, factors that are multiplied by flow rate, quantity of production, or other measures to yield releases, usually air emissions. A facility can calculate emission factors for its own use based on measurement or rely on published emission factors. Emission factors can be flow-rate or chemical dependent and should be carefully selected to fit the situation. They are most generally used for air emissions, and available emission factors air releases range from leak rates for valves and fittings to emission factors for entire processes or plants. Some facilities use a process or plant emission factor to calculate their total air emissions and then use leak rate emission factors to calculate fugitive emissions-the difference is the point source air emissions.

Although there are many types of published emission factors, they do not exist for every process. Facilities often use data for similar processes or chemicals to estimate emissions, especially when good mass balance or materials accounting data are not available. Even when a reliable mass balance can be performed, facilities may still use emission factors to check to see that their results are reasonable. The other drawback is that since emission factors are equipment dependent, unless changes in equipment are made, releases estimated by emission factors will not show the effects of reduction projects such as improvement in materials handling.

3.1 Estimating Fugitive Air Emissions with Emission Factors

Emission factors are the most common method of estimating fugitive air emissions and are probably the quickest way to calculate leaks from fittings, valves, pumps, and other equipment (see Box 3). Most published emission factors for leak rates are independent of flow rate and depend only on the type of chemicals in use, so emission factors are convenient as well.

To calculate fugitive air emissions from leaks, facilities first prepare an inventory of all pumps, compressors, valves, fittings, flanges, and similar equipment in use on-site. After identifying the appropriate emission factors for each piece of equipment, it's a simple calculation to estimate the leak rate. To calculate leak rates for valves, for example, multiply the total number of valves by the valve emission factor. To obtain the leak rate for each chemical involves only multiplying the total leak rate for the valves by the weight fraction of that chemical in the streams going through the valves. With a similar calculation for each of the different types of leaks/equipment with leaks, facilities can calculate plant-wide leak rates for each reportable chemical.

The EPA publication Protocol for Equipment Leak Emission Estimates⁶ lists emission factors for many common pieces of equipment. These emission factors were derived from leak rate measurements made at facilities in the synthetic organic chemicals manufacturing industry, petroleum refineries, oil and gas production operations, and other sectors. They do not depend on flow rate, but they are chemical-specific to the extent that liquids are divided into "light" and "heavy" based on vapor pressure. Emission factors for gasses are the same regardless of chemical. Some of the emission factors are different for "leaking" and "non-leaking" sources—the definition of leaking is based on average measurements from "bagging" the equipment. If packings and seals are well-maintained, it's usually safe to assume they are not leaking. If there is any doubt, it is better to assume they are leaking and use the leaking emission factors, if available.

At their best, emission factors for leak rates are average values and cover a wide range of operating conditions. In addition, many sets of published emission factors may exist for the same applications, so they may not be appropriate for every facility. For example, a large U.S. oil company with refineries in Washington State and Southern California set about estimating fugitive air emissions using emission factors. Local regulations in Southern California required the use of specific emission factors developed for the region, while the refinery in Washington State used emission factors developed by the U.S. EPA. The California refinery's fugitive air emissions were estimated to be more than 50 percent lower than those of the Washington refinery, although the two refineries had similar operating conditions for the year. Because of this type of discrepancy in

⁶ https://www3.epa.gov/ttnchie1/efdocs/equiplks.pdf

published sources, facilities often choose to develop their own emission factors by monitoring. The distinction between calling the estimate a direct measurement and an emission factor calculation is not always clear, but the implication is that direct measurement is performed more often than a one-time measurement to calculate an emission factor.

Box 3. Estimating Releases with Emission Factors

Although some emission factors are available for surface water discharges and releases to land, they are most often used for estimating air emissions, especially fugitive air emissions such as leaks from valves, fittings, pumps, and compressors.

Benefits

+ Emission factors are quick and easy to use.

+ The most commonly used emission factors require only two pieces of information: the number of valves, fittings, pumps, and compressors, and the chemicals flowing through them.

 Emission factors are extremely useful for estimating small amounts of emissions that might be missed by mass balance.

+ Estimated releases from emission factors can also be fairly accurate if done for the proper chemicals in specific processes.

+ Process and plant emission factors can provide an upper bound for air emissions, even if another estimation method is used.

Drawbacks

- Most published emission factors for leak rates apply only for organic chemicals. Very little data exist on emission factors for inorganic chemicals.

- Most published emission factors for leak rates were derived from measurements in the synthetic organic chemicals industry and may not be applicable to other processes.

- Different published sources of emission factors for the same application can yield different results.

- Other than counting specific pieces of equipment, use of emission factors does not require much in the way of identification of sources-major sources could be overlooked. Also, unless equipment or substances change in a way that affects selection of the most appropriate emission factor, releases estimated with emission factors won't change either, so reduction projects might go unnoticed.

How to Begin

< Take an inventory of valves, fittings, pumps, and compressors even if the emission factors references are not on hand.

< Think about measuring for detectable leaks—there are emission factor data for leaking equipment as well as for leaks in normal operation.

< Sources of emission factor data are available through the OECD's **Resource** Centre for PRTR Release Estimation Techniques.

< Many companies have developed emission factors for their own use, as have some industry associations.

3.2 Estimating Point Source Air Emissions with Emission Factors

Since point source air emissions are usually equipment-specific, any emission factors used to estimate emissions also need to be equipment-specific. Process emission factors can be used estimate point source air emissions, if the emission factor was derived for a process that is similar to the process to which the emission factor is applied. Process emission factors estimate total air emissions, then fugitive air emissions are subtracted to estimate point source emissions. For example, if an average air emission rate for a plant producing phthalic anhydride is available in pounds released per pound of phthalic anhydride produced, then the total air releases can be calculated. If fugitive air emissions are estimated from leak rate emission factors, then they can be subtracted from the total air emissions to yield an estimate of point source air emissions by emission factors. EPA's AP-42 manual⁷ contains a wide variety of process emission factors for many types of manufacturing operations, as does the European Monitoring Evaluation Programme/ European Environment Agency's EMEP/EEA air pollutant emission inventory guidebook⁸. Facilities may also use emission factors developed by equipment manufacturers for their outlet vents. These emission factors usually depend on flow rate and chemical loading, so in that sense they are more like efficiencies.

3.3 Estimating Surface Water Discharges and Releases to Land with Emission Factors

Emissions factors for surface water discharges and releases to land are not available for most applications. Equipment manufacturers may provide specific emission factors for individual pieces of equipment.

⁷ https://www.epa.gov/air-emissions-factors-and-quantification/ap-42-compilation-air-emissions-factors ⁸ https://www.eea.europa.eu/themes/air/emep-eea-air-pollutant-emission-inventory-guidebook/emep

Engineering Calculation

Three basic types of engineering calculation are used to estimate releases (see Box 4). The most common engineering calculation are published correlations for fugitive air emissions developed for tank losses, losses from holding ponds, and losses from wastewater treatment processes. These correlations are widely used, since measuring evaporation losses is difficult to measure directly.

The second type of engineering calculation uses equipment specifications, such as removal rate, efficiency, yield, or drying rate to estimate releases. These types of calculations are often used to estimate point source air releases from pollution control equipment. The equipment specifications may be actual values derived from measurement or supplied by the manufacturer, or they may be published average values for the types of equipment and processes in use. For example, if a baghouse is designed to remove 99 percent of particulates by weight from an air stream, then 1 percent will be released to air. If the chemical composition of the particulates is known or can be calculated, then those values can be used to estimate the individual chemical air releases.

Example C: Estimating Fugitive Air Emissions with Emission Factors

Task: Estimate fugitive air emissions from a polymer processing plant. The plant produces sheets of polymers of various formulations. The formulations use an equal mixture of toluene and xylene as solvents. The polymer sheets are fed to a continuous dryer after extrusion and rolling. The dryer operates at a slightly negative pressure to prevent leaks. Exhaust from the dryer is compressed to greater-than-atmospheric pressure and fed to a condenser, from which solvent mixture is extracted and returned to the process. The remaining solvent vapor is either used for energy recovery on-site or burned in the flare.

The plant operates the line 4000 hours per year. The weight fraction of solvent in the dryer exhaust stream averages 0.01, and the condenser is 80% efficient.

Process description and equipment inventory: The dryer exhaust line leads directly to a compressor. There is a gas safety relief valve immediately following the compressor and two in-line valves before the condenser. There are 18 liquid valves after the condenser in the lines leading to the storage tanks and back to the process, and another 12 gas valves from the condenser leading to storage and the flare. Assume that the compressor seals are leaking but that all other fugitive emission sources are non-leaking.

How to begin: U.S. EPA's <u>Protocol for Equipment Leak Emission Estimates</u> provides emission factors for the calculations. Since all of the liquids are considered to be "light liquids" (material in a liquid state in which the sum of the concentration of individual constituents with a vapor pressure over 0.3 kilopascals (kPa) at 20°C is greater than or equal to 20 weight percent), use the light liquid emission factors.

.....

Example C continued

Source	Emission factor, kg/hour
Compressor seals	0.228
Gas safety-relief valve	0.104
Valve (gas)	0.00597
Valve (light liquid)	0.00403

Calculations: Review operations of each piece of equipment and calculate emissions for each chemical.

Compressor seals:

Toluene/xylene mixture: 0.228 kg/hour/compressor * 0.01 kg solvent/kg air * 4000 hours/year = 9.12 kg/year

The total for the toluene/xylene mixture is divided in half for each chemical because of the equal weight fractions in the mixture, so toluene and xylene each = 4.56 kg/ year.

Gas safety relief valve:

Toluene/xylene mixture: 0.104 kg/hour * 0.01 kg/kg air * 4000 hours/year = 4.16 kg/ year

Again, the total for the toluene/xylene mixture is divided in half for each chemical, so toluene and xylene emissions each = 2.08 kg/year.

Gas valves before condenser:

Toluene/xylene mixture: 2 valves * 0.00597 kg/hour/valve * 0.01 kg solvent/kg air * 4000 hours/year = 0.4776 kg/year

Toluene and xylene each = 0.2388 kg/year

Gas valves after condenser:

Toluene/xylene mixture: 12 valves * 0.00597kg/hour/valve * 0.01(1-0.8) kg solvent/ kg air * 4000 hours/year = 0.573 kg/year

Toluene and xylene each = 0.287 kg/year

Liquid valves:

Toluene/xylene mixture: 18 valves * 0.00403kg/hour/valve * 4000 hours/year = 290.16kg/year

Toluene and xylene each = 145.08 kg/year

Some caveats in these calculations: These emission factors were developed for the synthetic organic chemicals manufacturing industry and may not be accurate for the polymer processing example. This is not to say that the result is inaccurate: it is probably adequate in the absence of measurements. However, note the difference in result estimating fugitive air emissions by engineering calculation in the next example.

The energy recovery equipment and flare each have their own efficiencies, and these efficiencies would have to be used in calculating point source air emissions for the plant.

Physical, chemical, and equilibrium properties of chemicals are often used to estimate concentration and releases in the absence of measurement. For example, the vapor pressure of a chemical can be combined with the ideal gas law and an appropriate diffusion coefficient to calculate the concentration of that chemical in air. Chemical solubility in water is a frequent measure of concentration used to calculate surface water discharges, and reaction stoichiometry can also be used to estimate concentration. Often, these kinds of engineering calculations are the only way to estimate certain small amounts of releases, because measurement may be difficult and mass balances may be too uncertain, as described previously.

4.1 Estimating Fugitive Air Emissions by Engineering Calculation

Tank losses are commonly estimated using engineering calculation because they are difficult to measure. Correlations for fugitive emissions from many types of tanks have been developed and are widely used. Other published correlations, such as for amounts of liquid remaining in "empty" drums, are also used to estimate fugitive air emissions from open empty storage containers or from solvent washout between batch operations. EPA's TANKS⁹ is a computer software program that estimates volatile organic compound and hazardous air pollutant emissions from fixed-roof and floating-roof storage tanks.

Losses from holding ponds and other wastewater treatment operations are usually estimated from published correlations.

Other fugitive air emissions estimated by engineering calculation include losses from loading and unloading tank cars. Even if some measurement data are available, such as worker exposure measurements in the area of the tank car, some sort of estimate of the effects of diffusion and ambient conditions has to be made. Models for losses range from simple diffusion calculations to box models and more complex air dispersion calculations.

Use of threshold concentration alarm monitoring is another common application of engineering

⁹ https://cfpub.epa.gov/si/si public record Report.cfm?dirEntryID=198287

calculation in estimating fugitive air emissions. If the plant operates for the entire year without setting off the air monitoring alarms, then as long as there are dedicated alarms for specific substances, facilities often assume half the threshold value as the ambient concentration of those chemicals. This ambient concentration is combined with the building air exchange rate to estimate fugitive air emissions. If facilities have a general, multichemical alarm, such as one for total hydrocarbons, then half the threshold value may be used as the total ambient VOC concentration.

Engineering calculation based on physical and chemical properties of substances is often the best way of estimating fugitive air emissions from open containers or channels. The calculations usually assume equilibrium between the liquid and air and must be adjusted for temperature. These are standard mass transport calculations and are often quite accurate for certain well-studied chemicals such as methanol/water mixtures.

Box 4. Estimating Releases Using Engineering Calculation

Engineering calculation is used to estimate releases to all media, particularly when direct measurement is not possible. There are many commonly used correlations for releases, as well as typical mass transfer calculations to estimate amounts of chemicals in various process and waste streams.

Benefits

+ Engineering calculation tools are available from a wide variety of sources, including equipment manufacturers, textbooks, and engineering handbooks.

+ They are an inexpensive way of estimating releases and can be quite sophisticated and accurate depending on the application, but especially for small amounts of releases.

 Engineering calculation correlations for losses from storage tanks are commonly used and are the best way for estimating storage losses.

+ There are a wide range of engineering calculation tools for many applications, including material remaining in empty containers, evaporation losses, and losses from water treatment plants.

These are the kind of calculations chemical and mechanical engineers are trained to perform.

Drawbacks

- Many of the engineering calculation tools such as published efficiencies and removal rates are averages for many applications and should be chosen carefully.

- Many mass transfer parameters are temperature specific and can't always be adjusted accordingly.

- Engineering calculation can be removed from reality, like emission factors, and may overlook obvious emission sources by working from paper instead of the equipment.

- Engineering calculation estimates of releases are generally not acceptable as monitoring data for government requirements.

How to Begin

< Contact the equipment manufacturers to get equipment specifications useful for engineering calculation.

- < Refer to engineering handbooks.
- < See U.S. EPA's chemical-specific and industry-specific guidance documents for examples of engineering calculation and commonly used correlations.
- < Contact industry associations for additional correlations and tips for use.

4.2 Estimating Point Source Air Emissions by Engineering Calculation

Engineering calculation plays a significant role in estimating point source air emissions. Facilities can use efficiency specifications from pollution control equipment such as scrubbers, absorbers, adsorbers, cyclones, baghouses, and filters as the basis of estimating air discharges when loading rates are known. If the equipment specifications are not available, facilities often rely on published values from many sources. Unit Operations textbooks, Perry's Chemical Engineering Handbook, and many other standard engineering references are valuable resources.

4.3 Estimating Surface Water Discharges by Engineering Calculation

Facilities can discharge large amounts of wastewater, especially when rainfall runoff is diverted to treatment on-site. Usually, however, facilities discharge only small amounts of reportable substances to surface water because of on-site wastewater treatment and discharges to offsite

sewage treatment plants. Wastewater treatment systems are sometimes so efficient that concentrations of chemicals known to be in the residual wastewater stream are undetectable and must be estimated by engineering calculation. Facilities usually use half the quantitation limit for the chemical (lowest detectable amount) as the basis for engineering calculation for undetectable chemicals. This concentration, multiplied by the water flow rate yields the amount discharged.

Known or measured treatment efficiencies can be used to calculate surface water discharges if the amounts of specific chemicals sent to the water treatment operation are known or can be estimated. Engineering calculation can be used to estimate those amounts in various ways:

• Since water solubility is a common chemical property, it may be used to estimate the amount of specific chemicals in individual waste streams.

• Certain pollution control devices, such as scrubbers, remove chemicals from air streams and transfer them to the scrubber liquid. Equipment specifications (either actual specifications or average published values) can be used to estimate the amount of chemicals transferred to the liquid.

• Reaction stoichiometry can be used to predict the amounts of specific chemicals generated in chemical reactions, and if waste chemicals are generated, then their amounts can be estimated based on the amount of product generated in the same reaction.

4.4 Estimating Releases to Land by Engineering Calculation

Because releases to land usually occur as a result of specific unit operations, engineering calculation is an important estimation method, particularly for sludges and slurries. Equipment specifications for filters and centrifuges can be used to estimate the amount of various substances removed from liquid streams. These specifications are available either from the manufacturer or from published values. Amounts of specific chemicals in wastewater treatment sludges may also be estimated from treatment efficiencies for certain types of treatment processes.

Baghouse residue, incinerator ash, and other particulate remains from pollution control equipment such as electrostatic precipitators and cyclones are often disposed of on-site. These amounts are usually estimated from equipment specifications, either published or provided by the manufacturer.

CHOOSING THE BEST METHOD FOR ESTIMATING RELEASES

So, which method is best for estimating emissions? Each has its benefits and drawbacks, but there are some general rules. In most circumstances, these four guidelines apply:

• Measurement works well with stable operating conditions for streams that don't vary much in flow rate and chemical concentration.

• Materials accounting and mass balance are better for facilities and processes with large ratios of releases to use and for large quantities of releases.

• Emission factors work well for relatively small amounts of releases, especially fugitive air emissions, that would be missed by materials accounting.

• Engineering calculation is best for estimating tank losses and releases from pollution control equipment, especially when measurement is difficult.

Another rule of thumb for facilities setting out to estimate emissions for the first time is that once sources are identified, emission factors can be used for as many estimates as possible, and the balance can be calculated by materials accounting. This provides a "quick and dirty" estimate that can be refined in subsequent reporting years and is especially useful for small facilities that typically would not monitor emissions. For example, a plating facility might learn from materials accounting that its sludge from plating operations contains large amounts of metals. A decision to undertake monitoring might then be made if the cost of acquiring data on sludge constituents was relatively low in comparison to the cost of lost metal. These measurements in turn might make the facility decide that the materials accounting had given an inaccurate estimate of releases to land from sludge, pointing to uncertainties in other materials accounting elements used previously. The case example below, continued from Part B, describes how the fictional paint shop was able to estimate emissions quickly and how it then decided on additional data that would be useful when estimating releases in the future.

The challenge is to select the methods that are best for each facility, based on the knowledge of its processes and products. The choice of estimation method may change as plant personnel gain more experience in estimating releases and as facilities seek to use their release data for uses other than PRTR reporting.

Case Example: Estimating Releases for a Small Paint Shop (continued from Part B)

Part 2: Estimating Releases and Transfers

Once the sources of release have been identified, the facility determines that the best method for estimating releases and transfers is to use emission factors for fugitive air releases from the paint delivery system (tanks, pumps, compressors, valves, and fittings) and use a facility-wide materials accounting for the rest.

< If records exist for how much of the various materials were brought on-site and used during the year, they can be used for the calculations. Say that a certain job block of metal painting ends up with x kilograms of paint per piece. Since the paint solvents evaporate, x will be solid content. Based on the known composition of the paint, the amount of solvents that evaporated can be calculated. Knowing how much total paint was put into the batch means that the amount of waste solids can be calculated based on the actual amount that ended up on the metal pieces.

< The facility will need to make, and document educated guesses for unknowns. It may not be possible to collect data for each job block, but the facility may be able to estimate emissions based on their similarity to other job blocks: more or less emissions based on the composition of the paint and the quantity that ends up on the product.

While this seems like an oversimplification, and may be for some facilities, the idea is the same: find out what data are known, quickly gather as much new information as possible, and make reasonable, educated guesses on the rest. Then begin making plans for routine data collection that will make annual reporting easier.

Example D: Estimating Fugitive Air Emissions by Engineering Calculation

Task: Calculate fugitive air emissions for the polymer processing plant described in Example C using an engineering calculation method.

Process description and equipment inventory: The plant is divided into two operating areas, each with its own ventilation system. Each area has an alarm monitoring total VOCs that will sound at one part per million. The air exchange rate for each side of the plant is 25,000 acfm at 70°F.

Calculate releases: Since the alarms have not sounded during the year, assume that the actual concentration is one-half the alarm limit, or 0.5 ppm. Since 70°F is standard operating temperature and the exhaust system operates at atmospheric pressure, no adjustment for temperature or pressure is needed.

Chemical emissions: $25,000 \text{ ft}^3/\text{minute} * 60 \text{ minutes/hour} * 4000 \text{ hours/year} * 0.5 \text{ ft}^3 \text{ toluene/xylene mixture/} 10^6 \text{ ft}^3 \text{ air} = 3,000 \text{ ft}^3/\text{year}$ for the solvent mixture

For the toluene/xylene mixture, assuming that each chemical leak at the same rate, calculate an average density based on molecular weights of the two components. The average density is 0.26 pounds/ft³, so total emissions of the toluene/xylene mixture are:

3000 ft³/year * 0.26 pounds/ft³ = 780 pounds/year, with each chemical at 390 pounds/year or 177 kg/year

.....

Note that this figure is 16% higher than the estimates in Example C. The value could be even more conservative if the alarm limit of 1 ppm were used instead of half that value. The question is, which values to report? The facility should consider the assumptions made in each method, and decide which method best reflects the facility operations, and then document the basis for the decision.

Sources

Cover page: Photo by Markus Distelrath from Pexels

Icons:

Page 18 - Chemistry flask by Bluetip Design from the Noun Project

Page 19 - Chain by faisalovers from the Noun Project

Images:

Page 15 - Photo by Pixabay from Pexels

Page 16 - Photo by Pixabay from Pexels

Page 17 - Photo by Matthew Barra from Pexels

Page 17 - Photo by Jahoo Clouseau from Pexels