UNITAR Series of PRTR Technical Support Materials - No. 2

Guidance for Facilities on PRTR Data Estimation and Reporting

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Table of Contents

Introduction to the Document

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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, as reported by individual facilities. Under a typical PRTR system, pollutant release and transfer data for listed chemicals are estimated by facilities and reported to the government which then compiles them into a database and makes the information publicly available.

Facilities faced with a requirement to report under such a system may find the prospect daunting and not know where to start, or even if they have to report. What types of information will be needed to estimate their releases and transfers? What is the best method for making such estimates? Where can a facility find more information on how to employ such methods? This brief guidance document attempts to outline the answers to these questions.

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 the PRTR data. **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 and provides some basic guidance and illustrations of its use. The document is not intended to be a complete guide; 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 which may already be available or readily attainable in order to estimate releases and transfers of pollutants for the purpose of PRTR reporting.

Appended to the document is a list of selected references which provide examples of the use of various estimation techniques, as well as other useful information. The references cited are predominantly issued by government or international organizations and are available free of charge or at low cost. There are more documents from the United States than from other countries, primarily because the U.S. PRTR (called the Toxics Release Inventory) has been in existence since 1987, with most others having been introduced more recently or still awaiting adoption.

Part A: Introduction for Company Managers

1. WHAT IS A PRTR?

A Pollutant Release and Transfer Register (PRTR) is a catalogue or database of releases and transfers of potentially harmful chemicals, including information on the nature and quantity of such releases and transfers. PRTRs are unique in that they provide data on releases to air, water, and land, and off-site transfers to various waste brokers in a single register, in contrast to single-media reporting requirements.

A PRTR system may include point source data reported from individual facilities, as well as information on releases and transfers from non-point sources 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 point source PRTR data by individual facilities.

2. DETERMINING IF THE FACILITY IS REQUIRED TO REPORT

The first step for the company manager is to determine if the facility has to report to the PRTR. This entails reviewing the 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 operate in more than one "industry," which can be defined on the basis of 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 facility size. 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? Reportable substances can vary by release medium. They can 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 or activity? Some PRTRs have "use" thresholds (i.e. a specified level of use) and/or waste thresholds that must be met before reporting is required. Total use is calculated by materials accounting (see Part B, section 3.6 and Part C, section 2).

PRTRs vary in the industries and facility sizes required to report, and some do not have 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, or inert ingredients often not tracked as part of normal record keeping.

A few problems typically arise for facilities 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, etc. In addition, a substance may be used in many ways at a facility and, in effect, be used in more than one “industry” with regard to reporting (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 and making that industry the basis for all 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.

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 based on the list of reportable substances, unless it is absolutely certain that none are present on site. It is also worth repeating this investigation every year, especially in case of changes in materials used on site or changes in reporting requirements.

3. 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 they probably do not measure on a routine basis, if they measure them at all. Fortunately, the majority of facilities collect some data that can be used to estimate quantities of releases and transfers for the purpose of 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 measurement or monitoring. Part C of this document introduces some of these estimation methods and provides references to sources of more in-depth information. In addition, facilities that are affiliated with companies in countries with PRTR reporting may be able to obtain guidance that is specific to their operations.

Many of the data used to estimate release and transfer quantities are already available on site or can be gathered with little effort and 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 in order 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, and 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 processes.

Non-process data, such as substances used in cleaning and maintenance. Most cleaning products end up as direct releases because of the way they are used.

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 efficiencies, especially in the absence of monitoring data.

Material and product specification data, including Material Safety Data Sheets (MSDSs). 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 at little or no cost.

Not all of these types of data will be collected by those responsible for environmental compliance. Environmental personnel are most likely to have 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 other personnel. For example, data on materials brought on site are usually available from the purchasing department, and information on products shipped would be available from shipping or accounting. Routine operating data are available from process or product managers, as is information on possible sources of releases.

4. 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. Developing an effective system for collecting and tracking PRTR data will not only ensure that reports are well prepared, but can also facilitate the use of PRTR data for other purposes, e.g. as an input into the company's efforts to reduce waste and emissions, streamline record keeping and cut costs. Following are some suggestions for organizing an effective PRTR reporting process.

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. A single coordinator provides a clear link within the facility, as well as with outside entities such as the government agencies to which the data is submitted and citizens of the surrounding community who may have an interest in the facility's record on 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 plant engineer is the person with this type of knowledge. Previous experience with environmental reporting is helpful for gathering 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.

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. Thus, these departments/personnel may need to provide a duplicate set of data to be stored with the PRTR coordinator. In some cases, the data collection forms used by various departments may have to be redesigned in order to include new data elements that are needed for PRTR reporting.
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 the estimation and reporting of annual PRTR data gets underway, the facility will want to track these data from year to year in order to identify trends, to highlight possible areas for improvement, and to document progress achieved in emissions and waste reduction.

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 consider 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 products produced at the facility contain any reportable substances?
- Do the production processes used to made the products use or produce any reportable substances?
- Are there any cleaning or maintenance activities at the facility that use reportable substances?
- Do the input materials used in producing the products or brought into the facility for other reasons contain any reportable substances?

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 will provide an estimate. 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 for 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 show improvements. For example, emission factors for fugitive air emissions depend only on the number of valves, fittings, etc. in the process and the particular substances flowing through them. If these do not change, then emission factors will show no improvement in fugitive air emissions even if the facility has instituted changes such as better worker education on materials handling. Similarly, engineering estimates may fail to reflect increases in efficiency or reductions in emissions which the facility may have achieved through instituting small changes in operating conditions.

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.

5. USES OF PRTR DATA BEYOND REPORTING

Facilities often find important uses for PRTR data other than satisfying reporting requirements. Keeping track of where materials go once they enter the facility is the quickest way to save money and resources. Releases and off-site transfers represent materials 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 profit. 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 in order to eliminate the need to have those substances on site at all. In certain cases, data on releases 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 better record keeping and increased awareness of operations and materials use. Therefore, developing PRTR data is often a wise thing to do, 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. Recorded 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

1. INTRODUCTION

The purpose of this part of the document is to assist the PRTR coordinator and other facility personnel in identifying reportable releases and transfers and generating 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 towards the identification and estimation of pollutant releases and transfers for the purpose of PRTR reporting.

2. 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 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. The difference between the two is based on intent. Point source air emissions come from equipment vents, 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, this document examines only production-related releases and those occurring from on-site storage and disposal.

Off-site transfers are wastes which facilities send off site for recycling, energy recovery, treatment, and disposal. In general, waste brokers require facilities 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.

3. 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 often 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.

- *Metals and metal compounds*

> Depending upon the specific features of the PRTR system, 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 substances, even though the releases and transfers of a metal and its compounds may be combined in public data releases.

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 can 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 color, odor, texture, stability, etc. Facilities are often unsure of exactly what goes into their products. This is especially true of consumer products, for which generally only the active ingredients are listed on content labels. 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 byproducts that did not get removed, and substances such as solvents that are not part of the product formula and which 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 color 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 specific contents.

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

Information on product content is available from many sources. Facilities may be required to provide Material Safety Data Sheets (MSDSs) to their customers and/or may receive MSDSs from their suppliers. An MSDS lists the name and amount of specific substances, either in the form of actual amount or concentration. The data listed on MSDSs may not be detailed enough to give the exact amounts of specific substances in a product, but is at least an indication that the material is present. Other useful data include in-house quality control measurements. Customers may require certification of product contents, and these certifications can be used to determine if the product contains specific substances.

Once products have been determined to contain reportable substances, it is time to gather as much data as possible 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.

Questions to answer:

- *What products are produced?*
- *Do these products contain reportable substances as formulation components?*
- *Do these products contain reportable substances as impurities, such as unremoved byproducts, solvents, or catalysts?*
- *Are any substances present as inert ingredients?*
- *Are any substances present in packaging materials?*
- *Is there any required documentation that will list the substances contained in the products, such as MSDSs 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 Used to Make These Products 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.

Processes that do not produce a product, such as wastewater treatment, may also use reportable substances that do not necessarily come from production processes. 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 take a walk-through of the plant, looking at each piece of equipment and flow stream, and consulting 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 assembling batch sheets, especially if several different products are made with the same equipment. Detailed batch sheets can provide information on the amount of input material in each batch, as well as amount of material produced. They can also provide other valuable information, such as clean-out procedures, that will need to be accounted for in the flow of material through the facility.

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, sources include valves, fittings, pumps, and compressors. These can be counted and recorded for use with emission factors. 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 discharge points that should be identified as well.

Finally, the walk-through is also the time for gathering available data that can be used to estimate potential releases. These include data on waste shipped off site, inventory data, discharges monitored for permits, and other hard data that would give amounts or concentrations of specific substances. Monitoring data can provide a check to the plant walk-through to see if any streams have been mischaracterized. Other data that should be gathered at this point are 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).

Questions to answer:

- *What production processes are used to produce each product?*
- *Do any non-production processes, such as storage or wastewater treatment, use reportable substances?*
- *Are any reportable substances added to the process that get completely consumed?*
- *Are any reportable substances produced in the process?*
- *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?*
- *Have possible sources of emissions been identified?*
- *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 gathered? Are batch production sheets available?*
- *Have all operating data been gathered, including down-times in production and other data such as spills and worker exposure?*

3.4 Are There Any Cleaning or Maintenance Activities Associated with These Products that Use Reportable Substances?

Cleaning and maintenance activities often use reportable substances, and the substances 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 cleanout, although the users of cleaning products are not always aware of the contents. The same is true of lubricating oils. Often, facilities contract out their cleaning and maintenance activities to local companies and have little idea of which products are actually used at the facility. Adding to this problem, those companies contracted for maintenance may not keep careful records of what was done in the facility, and facilities often change cleaning products depending on price or effectiveness.

Since almost all cleaning and maintenance products are brought on site, the same identification issues arise as with other materials brought on site (see section 3.5 below). The exception is that cleaners may be used in such small amounts that they may fall outside regular purchasing practices. An employee may be sent out to purchase a small bottle of cleaning fluid, for example, and if it costs less than the facility's minimum for record keeping, that purchase could go unrecorded.

If there is any doubt about cleaning and maintenance practices, the best way to determine if reportable substances are used is to observe some routing cleaning and maintenance, and then check every product used for reportable substances.

Questions to answer:

- *Are cleaning and maintenance done on site, or are they contracted out?*
- *Do cleaning and maintenance products contain reportable substances?*
- *Are there additional purchases of cleaning and maintenance products that are not accounted for in the regular purchasing system?*
- *Is vessel cleanout between batches included here or with the production process?*

3.5 Do the Input Materials Used for These Products or Brought into the Facility for Other Reasons Contain Any Reportable Substances?

Reportable substances may not be the main constituents of input materials, but nevertheless may be present in pigments, solvents, or other carriers. MSDSs from the manufacturers can be used to identify substances in 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 is useful to be able to test the coal quickly before burning it to determine if the sulfur content 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 easy option is to provide suppliers with a list of reportable substances and ask if their products contain them—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 the waste paper. However, multiple facilities, the industry associations, and the suppliers could work together to characterize waste paper feed at relatively little cost to all. 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.

Questions to answer:

- *Is content information available for each product brought on site, such as from MSDSs or other quality control information?*
- *Is it possible to get content information from suppliers?*
- *Are suppliers’ invoices accurate?*

3.6 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. Norway's PRTR is an example of one with no threshold: facilities that have to report must report releases of all reportable substances, even if those releases are zero and the amount used is small. Typically, however, PRTR reporting is based on the amount of the substance used in the reporting year. That is, there is usually a use threshold for reporting a particular substance. Canada's NPRI has a use threshold of 10,000 kilograms. If the facility's use of a substance meets that threshold, all releases and transfers must be reported, even if they are zero.

Use is calculated as follows:

amount of substance in inventory at the beginning of the year	+	amount of substance brought on site during the year	+	amount of substance produced on site during the year	-	amount of substance in inventory at the end of the year	=	amount of substance used during the year

Use can also be calculated from other process information:

amount of substance shipped as or in product during the year	+	amount of substance consumed on site during the year	+	amount of substance generated as waste during the year	=	amount of substance used during the year

In some cases 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 for substances produced or processed on site and a lower threshold of 10,000 pounds for substances that are otherwise used, such as solvents or production aids.

Some PRTRs also have a waste generation threshold for substances that are used in amounts that generate small amounts of waste. For the 1995 reporting year, the U.S. TRI added a new threshold based on waste generation: facilities generating less than 500 pounds of waste of a reportable substance do not have to report that substance to the PRTR unless total use exceeds one million pounds. In this case, waste generation is calculated as the sum of releases plus off-site transfers plus amount of waste managed on site during the year.

4. 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 easily available. Facilities routinely collect many different types of data for everyday operations. Some waste streams are 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 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, prior to TRI reporting in 1987 in the United States, few facilities estimated fugitive air emissions. One facility reporting to TRI tried materials accounting, but found that the uncertainty in measuring product streams and other losses left a relatively large amount as fugitive air emissions. An engineer from this chemical company reported that using emission factors reduced the amount of fugitive air emissions by half compared to mass balance estimates. Later, when the company instituted a programme to monitor its fugitive air emissions from equipment and piping, the estimate dropped another 50 percent—all through the choice of estimation method. Any one of the methods would have provided an estimate accurate enough for the PRTR, but 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.

5. GATHERING NECESSARY INFORMATION

The identification of releases and transfers at the facility is the starting point for generating PRTR data. The walk-though and data identification described in section 3 above are helpful for this process. Equally important is the collection of information that will be needed in applying the estimation methods. At this point, the facility should assemble in-house equipment operating data including manufacturers' specifications for process and pollution control equipment. Variables such as design yield, removal rate or treatment efficiency may be useful for calculating emissions, especially in the absence of monitoring data. Also, it is important to gather physical and chemical properties data on the individual reportable 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 calculation, such as for tank losses.

At this point, further identification of sources may be needed. The equipment design specifications will identify known sources for specific pieces of equipment. Two other technical references provide complete lists of sources from various types of equipment and processes. These two publications, both from U.S. EPA, entitled *Estimating Releases and Waste Treatment Efficiencies for the Toxic Chemical Release Inventory Form* and *Emission Factors for Equipment Leaks of VOC and HAP* are generally thorough enough to do a plant-wide estimate of emissions (see References). The first is a general guide with many examples of calculations, types of emission sources (some of them frequently overlooked), and other useful data. The second is the major reference for estimating fugitive air emissions from leaks in valves, fittings, pumps, and compressors. U.S. EPA has also produced guidance for individual industries (see References).

6. CONDUCTING A TRIAL RUN

One way to determine if enough data are collected to estimate releases for the PRTR is to attempt to estimate releases for the previous year. This trial estimate allows for the identification of release and data sources in the facility and provides an opportunity to institute new data collection and record keeping, if necessary, prior to actual reporting. Unexpectedly large releases can point the way to cost savings, offsetting the costs of monitoring or recovery equipment.

Small facilities may not routinely collect data that would allow them to report easily to a PRTR. For a facility facing this dilemma, the problem of reporting to the PRTR seems insurmountable. However, with a small amount of consistent record keeping, PRTR data can be estimated even for previous years as long as the facility keeps production records, as illustrated in the following case example.

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. If this information is not readily available, contact the supplier for information on substances used in the paints and their concentrations. Suppliers are usually willing to provide this information, since they are not being asked to divulge complete formulations.

- 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 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?

Continued on page 49

Part C: Methods for Estimating and Generating PRTR Data

1. 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 for PRTR reporting are outlined in Box 1.

Process Control Measurements:

- On-line sampling of concentration in process or exit streams to control process
- On-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
- Record of spills and leaks and what happened to those materials

Government Permit or Compliance Measurements:

- Air releases of specific chemicals from pollution control equipment or other vents
- Amounts of chemicals in surface water discharges from wastewater treatment or direct surface water discharges
- Amounts of chemicals disposed of in on-site landfills or surface impoundments
- Discharges to monitored injection wells

Very often, these measurements can be used directly 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 yearly emission. If operating conditions are relatively stable, the total quantity of the chemical in the waste stream is:

average concentration	x	average flow rate	x	operating time during the year	=	total quantity of chemical in waste stream

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 estimate of yearly releases.

Box 1. Estimating Releases by Direct Measurement

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

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 equipment, personnel training, maintenance, and record keeping.
- \- Facilities usually end up having to analyze large amounts of data.
- \- Monitoring every 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 measurement techniques. Consult the agency that collects monitoring data for information on specific monitoring techniques. U.S. EPA, industry associations and engineering societies are also good sources (see References).
- ▸ Equipment vendors can often provide information on measurement. Monitors may be 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, and many measurement errors combined can result in large uncertainties in the final calculation.

1.1 Measuring Fugitive Air Emissions

By nature, fugitive air emissions are difficult to measure. Because fugitive emissions come from many different sources, direct measurement can be costly and time consuming. However, facilities may already collect monitoring data that can 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 give 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. 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. U.S. EPA's *Emission Factors for Equipment Leaks of VOC and HAP* gives general instructions for measuring leak rates (see References). For valves, fittings, and small pumps, the equipment is "bagged" or fitted with a sealed enclosure. 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. This is essentially the procedure used to develop emission factors (see section 3 below).

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 individual valve types (such as 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 "sniffer" device. This is a portable monitor that is held near the piece of equipment to give a quick indication of the presence of certain types of chemicals over a set threshold. 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 sniffer shows no detectable leaks (or if the excessive leaks are quickly 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 fairly common since facilities are often required to monitor surface water discharges for various government programmes 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 direct discharges from individual pieces of equipment, such as filters, settling tanks, or sludge de-watering operations, the concentration of individual chemicals in the waste streams may be monitored to determine process yield. Monitoring is a common estimation method for many facilities because of concerns about landfill space: facilities want to know exactly how much material is deposited as part of future business planning for landfill space and alternative operations.

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 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/liter during 1,500 hours per year, and below the quantitation limit of $1*10^{-6}$ g/liter 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 $0.4*10^{6}$ gallons per day.

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

> ($6*10^{-3}$ g/liter) * (1 pound/453.59 g) * ($0.4*10^{6}$ gallons/day) * (1 day/24 hours) * (1500 hours/year) * (1 liter/0.264 gallons) = 1,252.6 pounds/year

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

> ($0.5 * 1*10^{-6}$ g/liter) * (1 pound/453.59 g) * ($0.4*10^{6}$ gallons/day) * (1 liter/0.264 gallons) * ((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 1,254 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

Materials accounting examines facility-wide inputs and outputs to calculate total releases (see Figure 1 in the Annex). In materials accounting, the inputs and outputs are usually quantities that facilities track for business reasons and include the amounts of materials brought on site, amounts in inventory, and amount of product shipped (see Box 2). A facility-wide materials accounting for Chemical A contains the following inputs and outputs:

Inputs	**Outputs**
Amount of Chemical A brought on site during the year	Amount of Chemical A shipped in product during the year
Amount of Chemical A in inventory at the beginning of the year	Amount of Chemical A in inventory at the end of the year
Amount of Chemical A produced on site during the year	Amount of Chemical A consumed on 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 byproducts. Total releases of Chemical A 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 product quality control:

- Material safety records may require monitoring of concentration of chemicals in products, such as pharmaceuticals.
- Customers may insist on regular monitoring of products to make sure that they meet specifications.
- Facilities may analyze 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 brokers usually insist on knowing the composition of waste brought on site.

Batch sheets or production logs often form the basis of an equipment mass balance or process-level materials accounting. Typical batch sheets list the amount of various chemicals put into each batch, the amount of product generated, and the amount of leftover chemicals put into inventory. If the product meets the usual specifications, then the operators can track various wastes based on whatever was put into a batch that did not end up in one place or the other. For example, if a paint manufacturer's batch sheet indicates that 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, as long as the paint contained the proper amount of xylene. The facility-wide sum of release amounts calculated from batch sheets for the year gives a good 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 constitutes a fugitive environmental release. Mass balances are performed for total mass and individual chemicals (component mass balances). A component mass balance for Chemical A in a reactor vessel would contain the following inputs and outputs (see Figure 2 in the Annex):

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

Box 2. Estimating Releases by Materials Accounting and Mass Balance

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

Benefits

+ 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 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 material safety sheets.
    - Amounts of chemicals stored in on-site inventories are frequently tracked.
    - Batch sheets and production logs 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.
- 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

- General information on performing mass balances is available from standard chemical engineering textbooks. Several examples of estimating releases by mass balance are given in EPA's *Estimating Releases and Waste Treatment Efficiencies for the Toxic Chemical Release Inventory Form* (see References).
- Although there is no comprehensive guide to materials accounting, the New Jersey Department of Environmental Protection collects facility-wide materials accounting data and has resources available on materials accounting. Industry associations and engineering societies are also good sources (see References).

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.

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 in New Jersey 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.

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 it 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.

3. 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 factor data. 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, although the World Health Organization (WHO) has published some emission factors for surface water discharge and land disposal for certain processes in *Rapid Inventory Techniques in Environmental Pollution* and the Netherlands' USES estimation system (see References).

Available emission factor data for 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

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.

Phosgene production data indicate that the plant produced 805,000 pounds of phosgene 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 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 the emissions come from process vents, the total amount would be reported as point source air emissions.

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 tool for calculating 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, 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, it's a simple multiplication 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 sources, facilities can calculate plant-wide leak rates for each reportable chemical.

The EPA publication *Emission Factors for Equipment Leaks of VOC and HAP* lists emission factors for many common pieces of equipment (see References). These emission factors were derived from leak rate measurements made at facilities in the synthetic organic chemicals manufacturing industry. 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 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.
- Most published emission factor data assume normal operation and no detectable leaks, and may not be appropriate for that reason.
- There are different published sources of emission factors for the same application and each gives a different result.
- 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, 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.
‣ There are two major sources of emission factor data from U.S. EPA: *Emission Factors for Equipment Leaks of VOC and HAP*, and the AP-42. USES and the WHO volume are more recent and use SI units (See References).
‣ 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, emission factors are seldom used. The reason is that pollution control equipment is rarely the same from facility to facility, while globe valves are the same the world over. There are two exceptions. The first occurs when facilities 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. The second exception is using process emission factors to estimate total air emissions, then subtracting out fugitive air 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 manual contains a wide variety of process emission factors for many types of manufacturing (see References).

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

Although WHO recently published emission factors for a small number of processes with surface water discharges and releases to land, emission factor data for these releases are not available for most applications. Equipment manufacturers may provide specific emission factors for individual pieces of equipment.

4. ENGINEERING CALCULATION

Three basic types of engineering calculation are used to estimate concentration and releases (see Box 4). The most common engineering calculations 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.

The second type of engineering calculation is using equipment specifications, such as removal rate, efficiency, yield, or drying rate to estimate releases. These types of calculations are often used to calculate 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.

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

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 either methyl ethyl ketone or an equal mixture of toluene and xylene as solvents, and there is a dedicated line for each solvent. The polymer sheets are fed to a continuous dryer after extrusion and rolling. The dryers operate at a slightly negative pressure to prevent leaks. Exhaust from the dryers is compressed to greater-than-atmospheric pressure and fed to separate condensers, from which pure solvent or 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 each line 4000 hours per year. The weight fraction of solvent in the dryer exhaust streams averages 0.01, and the condensers are 80% efficient.

Process description and equipment inventory: Each 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 *Emission Factors for Equipment Leaks of VOC and HAP* provides emission factors for the calculations. Since all of the liquids are considered to be "light liquids" (vapor pressure greater than 0.1 psia at 100°F), use the light liquid emission factors.

Source	**Emission factor, pounds/hour**
Compressor seals (leaking)	3.54
Gas safety-relief valve	0.098
In-line valve (gas)	0.0132
In-line valve (light liquid)	0.0038

Calculations: Step through each piece of equipment and calculate the emissions for each chemical.

Compressor seals:

Methyl ethyl ketone: 3.54 pounds/hour/compressor * 0.01 pound solvent/pound air * 4000 hours/year = 141.6 pounds/year

The total for the toluene/xylene mixture is the same, but gets divided in half for each chemical because of the equal weight fractions in the mixture, so toluene and xylene each = 70.8 pounds/year.

Example C: Estimating Fugitive Air Emissions with Emissions Factors *(Continued from previous page)*

Gas safety relief valve:

Methyl ethyl ketone: 0.098 pounds/hour * 0.01 pound solvent/pound air * 4000 hours/year = 3.92 pounds per year

Again, the total for the toluene/xylene mixture is the same, but each chemical gets half the emissions, so toluene and xylene each = 1.96 pounds/year.

Gas valves before condenser:

Methyl ethyl ketone: 2 valves * 0.0132 pounds/hour/valve * 0.01 pound solvent/pound air * 4000 hours/year = 1.056 pounds/year

Toluene and xylene each = 0.528 pounds/year

Gas valves after condenser:

Methyl ethyl ketone: 12 valves * 0.0132 pounds/hour/valve * 0.01(1-0.8) pound solvent/pound air * 4000 hours/year = 1.27 pounds/year
Toluene and xylene each = 0.625 pounds/year

Liquid valves:

Methyl ethyl ketone: 18 valves * 0.0038 pounds/hour/valve * 4000 hours/year = 273.6 pounds/year
Toluene and xylene each = 136.8 pounds/year

SUM FOR TOTAL FUGITIVE AIR EMISSIONS

Methyl ethyl ketone = 141.6 + 3.92 + 1.056 + 1.27 + 273.6, or approximately 422 pounds per year
Toluene and xylene each approximately 221 pounds per 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 measurement. 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.

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 calculation are the only way to estimate certain small amounts of releases, because measurement may be difficult or mass balances are too uncertain.

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 *Estimating Releases and Waste Treatment Efficiencies for the Toxic Chemical Release Inventory Form* provides some of these correlations (see References).

Losses from holding ponds and other wastewater treatment operations are also 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 complicated air dispersion calculations.

Use of threshold concentration alarm monitoring is another common application of engineering 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, multi-chemical 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.

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. College Unit Operations textbooks, Perry’s *Chemical Engineering Handbook*, and many other standard engineering references are valuable resources. “My first year of completing TRI reports was like being back in college,” reported one chemical engineer for a small specialty chemical company. “It’s a good thing I didn’t throw my old textbooks away.”

4.3 Estimating Surface Water Discharges by Engineering Calculation

Facilities can discharge huge amounts of wastewater, especially when rainfall runoff is treated on site. Usually, however, facilities discharge only small amounts of reportable substances to surface water because of on-site wastewater treatment and discharges to POTWs. 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 is then multiplied by the water flow rate to give the amount discharged.

Known or measured treatment efficiencies can be used to calculate surface water discharges if the amount of specific chemicals sent to the water treatment operation is 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 from 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.

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.
‣ Dig out old college textbooks and engineering handbooks.
‣ See U.S. EPA’s *Estimating Releases and Waste Treatment Efficiencies for the Toxic Chemical Release Inventory Form* for examples of engineering calculation and commonly used correlations (see References).
‣ Contact industry associations and engineering societies for additional correlations and tips for use.

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.

5. 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 to determine if monitoring might be useful. 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 some data on sludge content 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 back to uncertainties in other materials accounting elements. The case example below, continued from page xx , describes how the fictional paint shop was able to estimate emissions quickly and how it then decided on additional data that would be useful for future years.

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 page 25)

Part 2: Estimating Releases and Transfers

Now that sources have been identified, the idea 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.

- If the necessary records do not exist, then begin keeping records now and make use of a few representative production runs to account for some of the data not previously collected. For example, overspray can be measured from a few pieces based on paint coverage per square meter— simply put some cardboard behind the first piece sprayed and measure the area covered by paint. If the facility is now making a run of the same metal painting described above, those data can be used as representative of the same production if there are no operating anomalies.

- The trick is to make 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 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 ft^3/minute * 60 minutes/hour * 4000 hours/year * 0.5 ft^3 MEK/10^6 ft^3 air = 3,000 ft^3/year for MEK and the solvent mixture

The density of MEK vapor can be calculated using the ideal gas law or from standard tables. With a molecular weight of 72.12 and standard temperature and pressure, the density of MEK vapor is approximately 0.18 pound/ft^3, so fugitive air emissions of MEK are:

3,000 ft^3/year * 0.18 pound/ft^3 = 540 pounds/year

For the toluene/xylene mixture, assuming that each chemical leaks at the same rate, calculate an average density based on molecular weights of the two components. The average density is 0.26 pounds/ft^3, so total emissions of the toluene/xylene mixture are:

3000 ft^3/year * 0.26 pounds/ft^3 = 780 pounds/year, with each chemical at 390 pounds/year

Note that these figures are higher than the estimates in Example C. They 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? In general, since the values are the same order of magnitude, report the higher values in the absence of better information.

6. REFERENCES

There are hundreds, perhaps thousands, of publications on estimating releases. Some are general, some are industry-specific, and some deal with only certain emissions like fugitive air emissions.

This list of references primarily contains U.S. EPA publications. For many U.S. facilities, the 1987 TRI was their first facility-wide inventory of releases. Prior to 1987, facilities had to report certain releases under the Clean Air Act and Clean Water Act. To help facilities prepare for reporting, EPA published a number of help guides. The first batch came in the early 1980s, and then a subsequent round of publications was released between 1985 and 1987. Refinements were made in the late 1980s and early 1990s, with more industry-specific publications. Most EPA publications are available from:

EPA/EPIC, Publications and Information Center
26 W. Martin Luther King Drive
Cincinnati, OH 45268
U.S.A.

The European Chemical Industry Council (CEFIC) is beginning to issue guidance for estimating releases in preparation for developing European PRTRs. Other international organizations, recognizing the need for publications that reflect industries in developing countries (not to mention SI units), are also developing guidelines. Industry associations and engineering societies in the United States and Europe are good resources for industry-specific publications on estimating releases.

6.1 General Publications

In 1981, U.S. EPA released a five-volume set called *Procedures for Emission Inventory Preparation*. These were developed by the Office of Air Quality Planning and Standards and were intended to help U.S. facilities comply with the Clean Air Act. The set contains a wide range of information on air emissions:

Volume I—Emission Inventory Fundamentals
Volume II—Point Sources
Volume III—Area Sources
Volume IV—Mobile Sources
Volume V—Bibliography

Much of the information is about chemicals that are not generally reported to current PRTRs (including TRI), such as CO, CO_2, SO_2, NO_X, total particulates, and general reporting of VOC emissions. Nonetheless, the publications provide a valuable resource for setting up PRTR reporting at facilities and estimating some air emissions. (EPA-450/4-81-026a,b,c,d, and e, September 1981). There have been revisions since 1981.

To prepare facilities for reporting to TRI, EPA published *Estimating Releases and Waste Treatment Efficiencies for the Toxic Chemical Release Inventory Form* in 1987. This is a good "how-to" manual with sample calculations and some limited tables of emission factors and engineering calculation correlations. The text is informative and easy to follow, and the bibliography is exhaustive. One current objection to the publication is that it is rather static and relies too much on using emission factors, rather than urging facilities to move toward more accurate estimation methods. This is not surprising, considering when it was published. However, many facilities could get by with this volume and nothing else. (EPA 560/4-88-002.) December, 1987.

As part of the European effort to develop PRTRs, the World Health Organization (WHO) commissioned a multi-part study called *Assessment of Sources of Air, Water, and Land Pollution: A Guide to Rapid Source Inventory Techniques and Their Use in Formulating Environmental Control Strategies*. Part one, *Rapid Inventory Techniques in Environmental Pollution,* was released in 1993. This volume is similar EPA's AP-42 (see Air Emissions, below) but also provides limited emission factors for surface water discharges and releases to land for various industries and processes. At present, the volume is available in English only, but it does use SI units. The bibliographies list many U.S. EPA publications, but also some European publications.

In 1994, the Government of the Netherlands published *USES: A Uniform System for the Evaluation of Substances, version 1.0*. USES is a system for calculating releases to air, water, and land by emission factors. These emission factors were developed for a wide variety of industries, process application, and type of use of different chemicals on site. For example, solvents are treated differently than formulation components; in addition, the range of processes is extremely specific. Information on USES is available from the National Institute of Public Health and the Environment, The Hague, The Netherlands.

6.2 Publications on Air Emissions

In 1985, U.S. EPA published *Compilation of Air Pollutant Emission Factors, Volumes I and II* (EPA AP-42). There have been several supplements since the initial release. Volume I has been called "The Bible of Air Emissions" and contains a wealth of information:

Chapter	*Air Emissions Sources*
1	External Combustion Sources
2	Solid Waste Disposal
3	Stationary Internal Combustion Sources
4	Evaporation Loss
5	Chemical Process Industry
6	Food and Agricultural Industries
7	Metallurgical Industry
8	Mineral Products Industry
9	Petroleum Industry
10	Wood Products Industry
11	Miscellaneous Sources

In general, the AP-42 contains process- and facility-wide emission factors for controlled and uncontrolled air emissions. The 1995 revision should contain more process-specific emission factors.

Going beyond the AP-42 to estimate fugitive emissions, U.S. EPA produced *Emission Factors for Equipment Leaks of VOC and HAP* (EPA-450/3-86-002, January, 1986). In addition to providing a set of emission factors for common pumps, valves, flanges, and compressors, the volume contains some chemical-specific information. Although some U.S. states and municipalities have developed their own emission factors, this is an exhaustive reference. It also provides details for developing in-house emissions factors. The use of this volume should be restricted to organic chemicals only.

Recognizing that facilities also needed to estimate fugitive emissions of inorganic chemicals, U.S. EPA commissioned *Measurement Techniques for Developing Emission Factors for Process Components in Inorganic Service* in 1991. The study quantifies the error in using organic emission factors for inorganic chemicals and presents a sampling method for developing emission factors.

Two documents relate to tank losses: *Evaporation Loss from External Floating Roof Tanks* (American Petroleum Institute Bulletin No. 2517, 1980) and *Evaporation Loss from Internal Floating Roof Tanks* (American Petroleum Institute Bulletin No. 2519, 1983). Both provide engineering estimate correlations for losses from various kinds of tanks for a range of chemicals.

The European Chemical Industry Council (CEFIC) has begun asking its members to provide general guidance on matters related to PRTRs. In January 1995, CEFIC released a study of fugitive air emissions factors prepared by DSM. These factors are based on average conditions in the Netherlands and are not chemical specific.

6.3 Publications on Surface Water Discharges and Releases to Land

U.S. EPA has produced several documents on surface water discharges for complying with the Clean Water Act and the National Permitted Discharge Elimination System (NPDES, EPA's water permitting system). There are also many publications on hazardous and solid waste, as well as the Superfund project. These documents are available from various EPA offices; for a complete list of offices contact EPA's Public Information Center (Mail Code PM-211B, 401 M St., SW, Washington, DC 20460 USA). *Access EPA*, a publication listing EPA resources, is available from this office and is especially valuable for locating information clearinghouses and hotlines throughout the agency.

Estimating Chemical Releases from Formulation of Aqueous Solutions is one of the guidance documents EPA prepared to help facilities complete their TRI reporting forms. This document includes surface water discharges and air emissions from aqueous solutions. Although less specific than *Estimating Releases and Waste Treatment Efficiencies for the Toxic Chemical Release Inventory Form*, it provides more sample calculations and is easier to follow. (EPA 560/4-88-004f, March, 1988).

6.4 Publications on Mass Balance and Materials Accounting

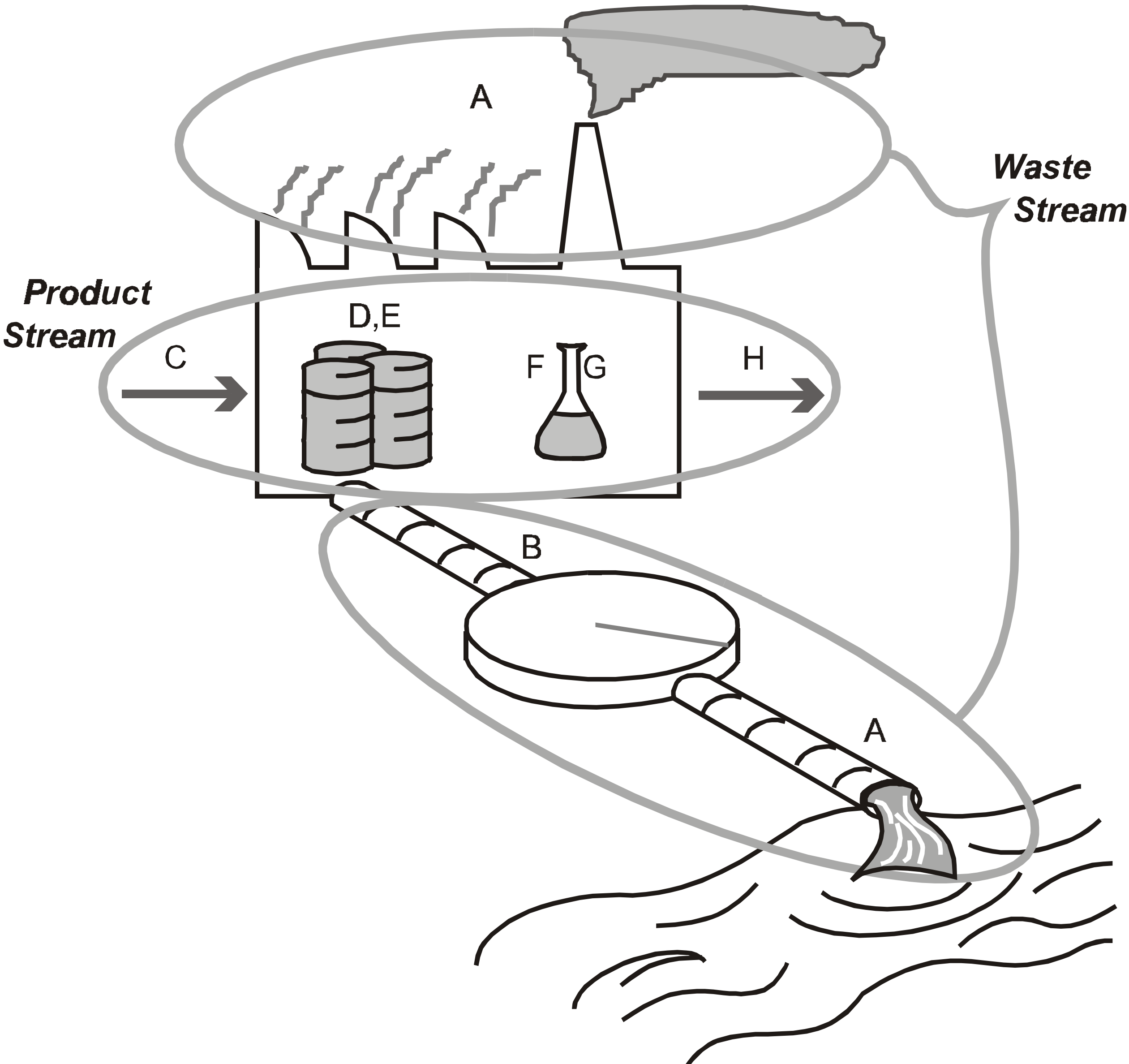
In the United States, the State of New Jersey requires facilities to report quantities of hazardous substances brought on site during the year, produced on site, consumed on site, shipped in product, and stored on the first and last day of the reporting year. Although the state has not produced specific guidance on materials accounting—that is, using batch sheets, production logs, shipping and receiving manifests, and other data to do a facility-wide mass balance—the New Jersey Department of Environmental Protection's Office of Pollution Prevention has produced a guidance document for pollution prevention planning that discusses aspects of mass balances and materials accounting. It also lists U.S. industry associations that provide technical assistance. The document is called *Industrial Pollution Prevention Planning: Meeting Requirements under the New Jersey Pollution Prevention Act* and is available from the Information Resource Center of the New Jersey Department of Environmental Protection. The address is 432 East State St., Trenton, NJ 08625, USA.

6.5 Industry-Specific Publications

U.S. EPA produced a number of guidance documents in 1988 to help facilities in specific industries complete their TRI reports. These are industries that use hazardous substances rather than producing them:

Electrodeposition of Organic Coatings (EPA 560/4-88-004c)
Electroplating Operations (EPA 560/4-88-004g)
Formulation of Aqueous Solutions (EPA 560/4-88-004f)
Leather Tanning and Finishing Processes (EPA 560/4-88-004l)
Monofilament Fiber Manufacture (EPA 560/4-88-004a)
Paper and Paperboard Production (EPA 560/4-88-004k)
Presswood & Laminated Wood Products Manufacturing (EPA 560/4-88-004i)
Printing Operations (EPA 560/4-88-004b)
Roller, Knife, and Gravure Coating Operations (EPA 560/4-88-004j)
Rubber Production and Compounding (EPA 560/4-88-004q)
Semiconductor Manufacture (EPA 560/4-88-004e)
Spray Application of Organic Coatings (EPA 560/4-88-004d)
Textile Dyeing (EPA 560/4-88-004h)
Wood Preserving (EPA 560/4-88-004p)

Figure 1. Chemical Waste and Product Streams at Industrial Facilities.



A = Environmental Releases of Chemical

B = Nonproduct Releases and Transfers of Chemical

C = Amount of Chemical Brought On-Site for Each Different Use

D,E = Amount of Chemical at Start and End of Inventory Period

F,G = Amount of Chemical Produced, Consumed at Facility

H = Amount of Chemical in Products (by Type) Shipped from Facility

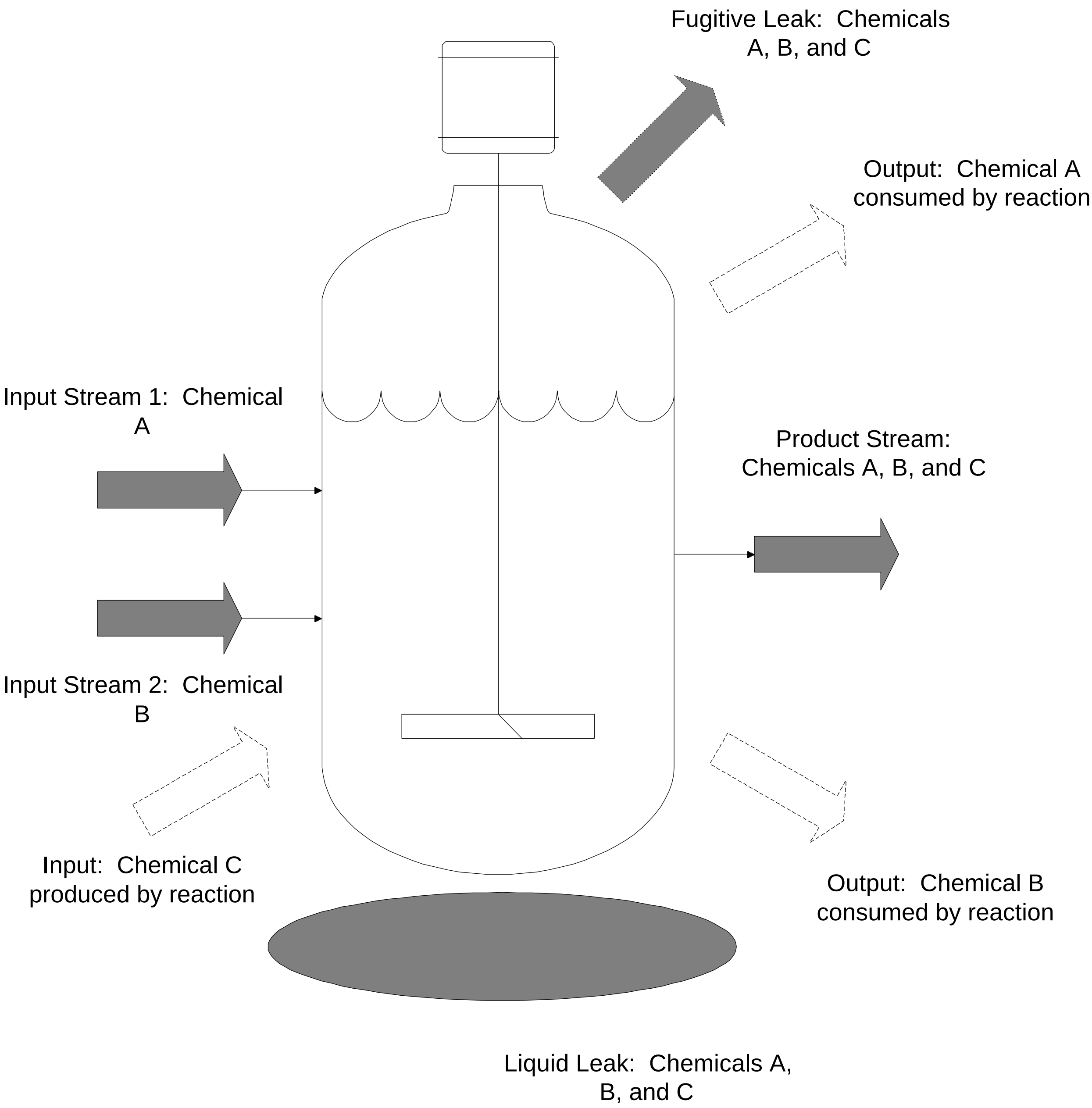


Figure 2: Component Mass Balance