

Unclassified

ENV/JM/MONO(2005)9



Organisation de Coopération et de Développement Economiques
Organisation for Economic Co-operation and Development

18-Apr-2005

English - Or. English

**ENVIRONMENT DIRECTORATE
JOINT MEETING OF THE CHEMICALS COMMITTEE AND
THE WORKING PARTY ON CHEMICALS, PESTICIDES AND BIOTECHNOLOGY**

Cancels & replaces the same document of 15 April 2005

**RESOURCE COMPENDIUM OF PRTR RELEASE ESTIMATION TECHNIQUES
PART 3: SUMMARY OF TECHNIQUES FOR OFF-SITE TRANSFERS**

JT00182559

Document complet disponible sur OLIS dans son format d'origine
Complete document available on OLIS in its original format

ENV/JM/MONO(2005)9
Unclassified

English - Or. English

ENV/JM/MONO(2005)9

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

No. 8

**RESOURCE COMPENDIUM OF
PRTR RELEASE ESTIMATION TECHNIQUES**

Part 3: Summary of Techniques for Off-site Transfers

IOMC



INTER-ORGANIZATION PROGRAMME FOR THE SOUND MANAGEMENT OF CHEMICALS

A cooperative agreement among **UNEP, ILO, FAO, WHO, UNIDO, UNITAR and OECD**

Environment Directorate
ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT
Paris 2005

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

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

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

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

PRTR Series No. 3: Presentation and Dissemination of PRTR Data: Practices and Experiences, Getting the Word and Numbers Out (2000).

PRTR Series No. 4: How Pollutant Release and Transfer Registers Differ: A Review of National Programmes (2001)

PRTR Series No. 5: Resource Compendium of PRTR Release Estimation Techniques, Part 1: Summary of Point Source Techniques (2002)

PRTR Series No. 6: Resource Compendium of PRTR Release Estimation Techniques, Part 2: Summary of Diffuse Source Techniques (2003)

PRTR Series No. 7: Uses of Pollutant Release and Transfer Register Data and Tools for Their Presentation: A Reference Manual (2005)

PRTR Series No. 8: Resource Compendium of PRTR Release Estimation Techniques, Part 3: Summary of Techniques for Off-site Transfers (2005)

© OECD 2005

Applications for permission to reproduce or translate all or part of this material should be addressed to Head of Publications Service, OECD, 2 rue André-Pascal, 75775 Paris Cedex 16, France.

ABOUT THE OECD

The Organisation for Economic Co-operation and Development (OECD) is an intergovernmental organisation in which representatives of 30 industrialised countries in North America, Europe and the Asia and Pacific region, as well as the European Commission, meet to co-ordinate and harmonise policies, discuss issues of mutual concern, and work together to respond to international problems. Most of the OECD's work is carried out by more than 200 specialised committees and working groups composed of member country delegates. Observers from several countries with special status at the OECD, and from interested international organisations, attend many of the OECD's workshops and other meetings. Committees and working groups are served by the OECD Secretariat, located in Paris, France, which is organised into directorates and divisions.

The Environment, Health and Safety Division publishes free-of-charge documents in nine different series: **Testing and Assessment; Good Laboratory Practice and Compliance Monitoring; Pesticides and Biocides; Risk Management; Harmonisation of Regulatory Oversight in Biotechnology; Safety of Novel Foods and Feeds; Chemical Accidents; Pollutant Release and Transfer Registers; and Emission Scenario Documents.** More information about the Environment, Health and Safety Programme and EHS publications is available on the OECD's World Wide Web site (<http://www.oecd.org/ehs/>).

This publication was produced within the framework of the Inter-Organisation Programme for the Sound Management of Chemicals (IOMC).

The Inter-Organisation Programme for the Sound Management of Chemicals (IOMC) was established in 1995 following recommendations made by the 1992 UN Conference on Environment and Development to strengthen co-operation and increase international co-ordination in the field of chemical safety. The participating organisations are FAO, ILO, OECD, UNEP, UNIDO, UNITAR and WHO. The World Bank and UNDP are observers. The purpose of the IOMC is to promote co-ordination of the policies and activities pursued by the Participating Organisations, jointly or separately, to achieve the sound management of chemicals in relation to human health and the environment.

This publication is available electronically, at no charge.

**For this and many other Environment,
Health and Safety publications, consult the OECD's
World Wide Web site (www.oecd.org/ehs/)**

or contact:

**OECD Environment Directorate,
Environment, Health and Safety Division**

**2 rue André-Pascal
75775 Paris Cedex 16
France**

Fax: (33-1) 45 24 16 75

E-mail: ehscont@oecd.org

FOREWORD

OECD began work on the PRTR Release Estimation Techniques project in 1999. That same year, an expert workshop was held in Australia to (1) identify what information is readily available on release estimation techniques for point and diffuse sources, and (2) recommend what can be done to improve the use and availability of such techniques. One of the recommendations from the workshop was to establish a Task Force to manage OECD work in this area. The Task Force on PRTR Release Estimation Techniques was established in February 2000 under the auspices of the Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology.

The work programme of the Task Force calls for the development of several technical documents to provide governments and industry - as well as others who are interested in this issue - with information and practical guidance for identifying, selecting and applying different techniques for estimating pollutant releases from point and diffuse sources and from transfers. The *Resource Compendium of PRTR Release Estimation Techniques* is the first in a series of documents created to help accomplish this goal. The intent of the *Resource Compendium* is to provide OECD countries with a basic information resource on estimation techniques typically used to quantify releases from point and diffuse sources and from transfers for a PRTR. It consists of three separate volumes: Part 1 summarises techniques used for point sources, Part 2 provides information about techniques used to quantify releases from diffuse sources and Part 3 summarises information about techniques used to calculate the amounts of chemicals found in transfers. ***This document provides Part 3 of the Compendium.***

During the development of Part 3 of the Resource Compendium, it became evident that the transfer terminology differs considerably in OECD member countries. To this end, the Task Force on PRTRs organised a special session in June 2004 on the transfer terminology, to be used in Part 3 of the Resource Compendium. The Glossary of Terms-section provides clarification on the terms used in this publication. Therefore, readers are encouraged to take a closer look at the used terms before starting to read Part 3 of the Compendium. Readers should note, however, that individual OECD members may nevertheless have different interpretations, applications or characterizations of the terms and/or RETs from the ones used in this publication.

The *Resource Compendium* was prepared under the auspices of the OECD Task Force on PRTR Release Estimation Techniques, recently renamed the Task Force on PRTRs. Part 3 of the Compendium was prepared at the US EPA, TRI Program, under the supervision of Ms. Maria Doa and Mr. John Dombrowski.

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

TABLE OF CONTENTS

FOREWORD	6
GLOSSARY OF TERMS	8
CHAPTER 1: INTRODUCTION	11
CHAPTER 2: SOURCES OF OFF-SITE TRANSFERS	13
2.1 Spent Catalyst Waste and Wastewater	13
2.2 Process Wastewater	14
2.3 Solid Waste and Wastewater	14
2.4 Ash, Residuals and Wastewater	15
CHAPTER 3: DESTINATION OF OFF-SITE TRANSFERS	17
3.1 Recycling	18
3.2 Energy Recovery	18
3.3 Treatment for Destruction or Disposal	19
3.4 Disposal	19
CHAPTER 4: ULTIMATE DESTINATION OF TRANSFERRED CHEMICALS.....	20
CHAPTER 5: IDENTIFICATION AND QUANTIFICATION OF OFF-SITE TRANSFERS	21
5.1 Direct Monitoring	21
5.2 Mass Balance	22
5.3 Chemical-Specific Emission Factors	24
5.4 Indirect Monitoring and Other Calculations	25
5.4.1 Indirect Monitoring	25
5.4.2 Modelling	25
5.4.3 Engineering Calculations	27
5.4.4 Non-Chemical Specific Emission Factors	30
5.5 Engineering Judgement	30
CHAPTER 6: GENERAL STEPS FOR DETERMINING RELEASES AND OFF-SITE TRANSFERS	31
6.1 Step 1: Prepare a Process Flow Diagram	31
6.2 Step 2: Identify Chemicals and Potential Sources of Chemical Releases and Off-site Transfers	33
6.3 Step 3: Identify Types of Releases and Off-site Transfers	33
6.4 Step 4: Determine the Most Appropriate Method(s) and Calculate the Estimates for Release and Transfer Quantities	34

GLOSSARY OF TERMS

Energy recovery

Energy recovery means the utilisation of the energy content of waste materials with or without pre-processing. Direct incineration is not energy recovery. Many countries even have minimum calorific values for chemicals/waste and only the combustion of such materials is considered energy recovery.

Off-site release

This term appears in the US TRI, and is also reported in the “Taking Stock” report of the Commission for Environmental Cooperation in North America (CEC). The TRI Public Data Release (PDR) and the TRI Explorer tool (both accessible from www.epa.gov/tri) distinguish between the “off-site releases” of the site/facility of origin and releases of the receiving site/facility in such a way that releases from a facility are reported only once. Double counting is thereby avoided. Off-site release is also to be understood as a transfer for release/disposal. Due to the complexity of the term, it has been agreed that for the purposes of this document whenever a substance/pollutant/chemical is transferred from the site of origin for specified action outside the site/facility, the final destination of an off-site transfer can be release, disposal, recycling, energy recovery or treatment. The term “off-site transfer for release” is also used by some other OECD member countries for releases to land.

On-site release

On-site release means chemicals in waste released to air, water, underground injection, or on land at the location (site) of the reporting facility (CEC).

On-site release means a release of toxic chemicals occurring within the boundaries (site) of the reporting facility (USA).

On-site release means the emission or discharge of a substance from the facility site to air, surface waters, or under certain circumstances, to land, such as spills, leaks (Canada).

Recovery

For the purposes of this document, recovery includes material recovery (recycling) and energy recovery.

Recycling

For the purposes of this document, recycling means the recovery of a spent toxic chemical or waste material from a waste/wastewater stream for reuse.

Release to Land

This term is understood in two fundamentally different ways. Bringing a substance/pollutant/ chemical to a disposal site where full control of the site is provided (access, drain water, evaporation etc.), is by some countries understood as a release to land, and would by others be reported as a transfer for disposal. The level of control seems for some countries to exempt this kind of operation from being a release to land, whereas others would call everything placed on the ground a release to land regardless of the level of control. With regard to the spreading of waste/material containing substances/pollutants/chemicals of potential concern to farmland or green areas, there is a consensus that it is a disposal operation, and not a recovery operation. It is noted that this type of activity could be seen both as a transfer for release (transported far off the site of origin) and as a release to land (farmer applying manure from the own feedstock on her/his own fields). However, a line should be drawn between applying a product, even if containing chemicals of concern (such as treated sewage sludge), and material that is considered waste. A grey area is difficult to avoid, however, in this document all the final destinations described above are considered as release to land.

Site

For the purposes of this document, a site is a separate geographical location defined by map coordinates. Several owners and operators may be present at the same site and more than one (industrial) activity may take place at a particular site. For reporting purposes a site is often linked to a facility or company with PRTR reporting obligations. A site is for practical matters often understood to be the area inside the fence set up by a facility/company. The EU is proposing the following definition for the new European PRTR (E-PRTR): “Site means the geographical location of the facility including any adjoining land that is separated by a road, railway or water channel.”

Transfer

This term is considered to be equivalent to the term “off-site transfer”. However, to avoid any misunderstanding and to be in line with the text of the PRTR protocol of the Aarhus Convention and the future term to be used by the EU, it has been agreed that for the purposes of this document the term off-site transfer will always be used, also as a synonym for transfer.

Treatment

For the purposes of this document, treatment means a variety of processes that change the chemical in waste/wastewater into another substance, and/or reduce the environmental impact of a chemical and/or waste/wastewater. It includes treatment for destruction and treatment for disposal, but not disposal itself.

Treatment for destruction

For the purposes of this document, treatment for destruction means destruction of a toxic chemical subject to reporting to TRI. It excludes energy recovery (USA).

Treatment for disposal

Currently no OECD country requires PRTR reporting of transfers to this destination.

Wastewater

There is uncertainty whether wastewater is included in waste or not. Different practices have been identified in different member countries. To avoid any uncertainty, it has been agreed to use in the context of this document the term: “waste/wastewater”, unless it is specified or otherwise clear which one of the categories is referred to.

CHAPTER 1: INTRODUCTION

Reporting of transfers may vary from one Pollutant Release and Transfer Registers (PRTRs) to another. In principle, there are two ways of reporting transfers: i) the reporting of specific chemicals contained in the transferred waste; and ii) reporting of total waste transferred.¹ Both ways of reporting transfers provide valuable information for the management of wastes and the contained chemicals. PRTRs that require reporting of transfers covering both approaches are not common. In addition to the two ways of reporting of transfers, some PRTRs also distinguishes between on-site and off-site transfers. This document describes only the off-site transfers.

When a facility has an obligation to report on off-site transfers as part of its PRTR reporting, it must consider the potential sources of waste and wastewater streams, the types of these streams, the constituent chemicals and the methods by which the wastes are to be managed. Off-site transfers containing chemicals of concern may be destined for several types of management, such as recycling, energy recovery, treatment or disposal.

Data obtained by tracking wastes, wastewaters and the constituent chemicals in off-site transfers can be used in many ways including:

- Quantities of wastes, wastewaters and the included chemicals will provide information to governments and communities to assess environmental concerns;
- Having a record of chemicals in off-site transfers will facilitate comparisons of past and present transfer quantities to show environmental progress over time;
- Tracking chemicals in off-site transfers may be beneficial to industries that are analyzing the environmental performance and efficiency of their processes. In doing so, industries may identify opportunities to improve processes to minimize raw material and product losses;
- Tracking chemicals in off-site transfers is often necessary to fully characterize and understand on-site releases; and
- This information may prove useful to investors who wish to compare the environmental record of companies.

¹ In some member countries the definition of waste includes wastewater

PRTR Programme Benefit: For PRTR programmes that track data on recycling and energy recovery of waste streams transferred off site, including the chemical constituents, the initial years of reporting showed successive increases in quantities of such activities. As facility and industry managers became more conscious of the positive government and public perception of the performance of such activities, industries sought ways to beneficially recover more materials or energy from their waste streams.

To track the chemical composition and the quantities of chemicals in off-site transfers, release estimation techniques (RETs) are needed. With more and more countries developing PRTR programmes, it would be time consuming for one country to search for RETs already established in other countries, and resource intensive to develop its own techniques. The development of RETs can be considered a significant task for countries trying to establish a PRTR programme. Therefore, to facilitate PRTR implementation, the Organization for Economic Cooperation and Development (OECD) initiated a project to identify and review RETs in use and make the results widely available.

OECD's Resource Compendium on RETs consists of three separate parts: Part 1 focuses on point sources; Part 2 focuses on diffuse sources; and Part 3 (this document) focuses on off-site transfers. RETs include methods used for calculating releases of specific chemicals to air, water, and land, both on site and off site, from a broad range of industrial processes. A few general RETs have been developed that are applicable to both on-site and off-site releases and transfers from all facilities. However, industrial process-specific details for implementing these general RETs differ. Several of the same general RETs are described in each part of the compendium, followed by a discussion of how those RETs can be applied to point sources, diffuse sources, or off-site transfers.

This document provides an overview of example transfers that contain chemicals of concern, the sources of those transfers, the chemicals included and management methods for these transfers. In particular, Chapter 5 describes RETs that can be applied to estimate quantities of chemicals in transfers. A case study on oil refining is provided following the general description, including detailed descriptions of unit operations, identification of chemicals in waste/wastewater generated by industries, and calculations for determining the quantities of chemicals transferred off site.

CHAPTER 2: SOURCES OF OFF-SITE TRANSFERS

Off-site transfers containing an array of chemicals are generated by many sources. These sources may include both industrial processes as well as waste and wastewater management processes. The sources of waste and wastewater streams resulting in off-site transfers from a facility will vary greatly depending on the industry and the specific unit operations and engineering controls that are employed. Therefore, each facility should take the time to evaluate every unit operation, potential release point, and the chemicals in all waste and wastewater streams to identify and quantify the off-site transfers.

This chapter provides examples for several industrial waste and wastewater streams that may result in off-site transfers. A few typical sources of off-site transfers include waste and wastewater streams generated from accidental spills that are subsequently collected and transferred off site; air pollution control devices (e.g., bag houses, electrostatic precipitators, and scrubbers); clean up and housekeeping practices; combustion by-products; container residues; process discharge streams; recycling and energy recovery by-products; and storm water runoff. The following paragraphs present examples of some waste and wastewater streams and their sources. These examples are not intended to be all-inclusive for the industries discussed; rather, they are intended to provide a starting point for a more detailed analysis that should be conducted by each facility, regardless of the industrial sector.

2.1 Spent Catalyst Waste and Wastewater

There are often many waste and/or wastewater streams generated from one process or source. For example, the catalytic cracking process utilized in petroleum refining uses heat, pressure and a catalyst to break larger hydrocarbon molecules into smaller, lighter molecules. There are typically two primary waste/wastewater streams generated from this unit operation that may be transferred off site:

- i) Spent catalyst waste; and
- ii) Wastewater.

A significant amount of fine catalyst dust is produced as a result of the constant movement of the catalyst grains against each other. Much of this dust, consisting primarily of alumina and relatively small amounts of nickel, is carried with the carbon monoxide stream to the carbon monoxide burner. The catalyst dust is separated out via engineering controls (e.g., cyclones and/or electrostatic precipitators) and is transferred off site for treatment or disposal. Depending on the type of container used to deliver the catalyst to the refinery, some fresh catalyst may also be transferred off site with the container as residue.

Wastewater is generated from the steam used to purge and regenerate catalysts. This wastewater may contain fuel oil, metal impurities and hydrocarbons remaining on the catalyst (Table 1), and is typically discharged to the wastewater treatment system.

Many industries, other than petroleum refining, incorporate catalysts in their processes and generate similar waste streams (e.g., spent catalysts, container residue, and dust).

Table 1. Chemicals commonly found in waste or wastewater streams transferred off site from catalytic cracking process in petroleum refining

Waste or wastewater stream	Chemicals commonly found in waste or wastewater streams from catalytic cracking process
Spent catalyst	Acenaphthene, acenaphthylene, anthracene, copper, naphthalene, nickel, phenol, toluene, vanadium, xylene, zinc,
Wastewater	Acenaphthene, acenaphthylene, anthracene, benzene, copper, ethylbenzene, flouranthene, flourene, naphthalene, nickel, phenol, pyrene, toluene, vanadium, xylene, zinc

2.2 Process Wastewater

Ethylene is the monomer used in polyethylene production. In many countries, most of the ethylene is produced by the thermal cracking of hydrocarbons, either as a primary product in ethylene units or as a by-product of petroleum-cracking processes.

Off-site transfers from ethylene manufacture may include process wastewater destined for treatment, and spent activated alumina catalyst destined for recycling. Process wastewater may contain many chemicals (Table 2) depending on the catalyst used for the cracking of hydrocarbons and the hydrocarbon feedstock used as a raw material.

Table 2. Chemicals commonly found in waste water streams transferred off site from polyethylene production

Waste water stream	Chemicals commonly found in waste water stream from polyethylene production
Process wastewater	Acenaphthene, acenaphthylene, anthracene, benzene, chromium, copper, ethylbenzene, flouranthene, flourene, naphthalene, phenol, pyrene, toluene

A facility would evaluate the quantity of wastewater that is transferred off site and determine the specific chemicals that are contained therein. Particular attention should be paid to contact water that may have absorbed chemicals during the industrial processes.

2.3 Solid Waste and Wastewater

Typically, the first step in plastic products manufacturing includes mixing additives with plastic materials to give the final product certain characteristics. Table 3 lists some of the

chemicals most commonly found in waste streams from certain operations of plastics product manufacturing.

Table 3. Chemicals commonly found in waste or wastewater streams transferred off site from plastics product manufacturing

Waste or wastewater stream	Chemicals commonly found in waste or wastewater streams from plastics product manufacturing
Compounding and mixing	Chloroform, dichloromethane, ethylbenzene, phenol
Thermoplastics and monomers	1,3-butadiene, ethylene, propylene, styrene, acrylonitrile, vinyl chloride
Heat stabilizers	Lead, zinc, barium, and cadmium compounds
Impact resistors	Acrylic acid, acrylamide
Flame retardants	Antimony compounds

There are typically two primary transfers generated from these operations:

- i) Solid waste; and
- ii) Wastewater.

Off-site transfers from the compounding and mixing step may include solids as well as aqueous streams that may be collected and destined for off-site treatments. These include particulate matter collected in air pollution control devices, wastewater and slurries from equipment cleaning, plastic pellet spills, and container residue. All of these off-site transfers are expected to contain specific chemicals that are used in the process (such as those listed above). Similar transfers can be found in most other industries.

2.4 Ash, Residuals and Wastewater

There are typically four primary off-site transfers from a coal-fired power plant that may be destined for off-site treatments:

- i) Bottom ash;
- ii) Fly ash;
- iii) Flue Gas Desulphurisation (FGD) system residuals; and
- iv) Wastewater.

Bottom ash comes from the boiler, usually as wet slurry (sometimes vitrified, called boiler slag). Fly ash may come directly from a catch in the boiler or from a dust collection system such as an electrostatic precipitator (ESP). FGD system residuals may be waste, or they may be directly sold as gypsum. Some electric power plants also sell their ash for the purpose of recycling the metals contained in the ash. Ash can be used as an ingredient in different types of concrete. Bottom ash, fly ash, boiler slag, and scrubber residuals (if wasted) would normally be buried in a landfill either on site or off site. These wastes are not exclusive to coal-fired power

plants, but may be found in any facility that utilizes combustion devices (e.g., a boiler or industrial furnace). Table 4 lists some of the chemicals commonly found in waste and wastewater streams transferred off site from fossil fuel combustion operations.

Table 4. Chemicals commonly found in waste or wastewater streams transferred off site from fossil fuel combustion operations

Waste or wastewater stream	Chemicals commonly found in waste or wastewater streams from fossil fuel combustion
Ash	Antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, mercury, nickel, selenium, thallium, vanadium and zinc compounds; dioxins, polycyclic aromatic compounds
Flue gas desulphurisation system residuals	Arsenic, barium, cadmium, chromium, cobalt, copper, lead, manganese, mercury, nickel, and zinc compounds
Wastewater	Ammonia, ethylene glycol, nitrate compounds, hydrogen fluoride, polycyclic aromatic compounds, antimony, arsenic, cadmium, chromium, copper, lead, nickel, selenium and zinc.

These are just a few examples of the sources of industrial wastes and wastewaters. Countries often have regulations affecting the industries generating wastes and wastewaters. These regulations will have a significant impact upon the waste and wastewater streams and the chemicals contained within them. For example, if a country has a regulation affecting the mass of particulate matter that can be emitted from a stack to the air, facilities may elect to install pollution control devices (e.g., electrostatic precipitators or bag houses). This will increase the amount of dust that is collected and possibly transferred off site for disposal.

CHAPTER 3: DESTINATION OF OFF-SITE TRANSFERS

Having discussed typical sources of waste and wastewater streams, it should be kept in mind that the primary objective of environmental policies is to avoid and reduce the generation of waste or wastewater containing chemicals of concern at the source. If this objective can not be met, activities resulting in reuse or recycling of materials should be considered. When the generation of waste or wastewater cannot be avoided measures should be taken to minimize their negative impacts on the environment. The substitution of chemicals of particular concern with relevant less hazardous alternatives contributes to reduced amounts of hazardous waste and wastewater. Energy recovery is also an option when reuse and/or recycling is not feasible. When no other possibilities can be obtained, environmentally sound treatment and/or final disposal must be considered carefully.

Facilities should note that the transfer of a pollutant from one medium to another is not considered pollution prevention. For example, a gaseous waste stream containing chemicals of concern may be sent through a scrubber. The scrubber may remove chemicals from the gaseous waste stream, not destroying them, but simply transferring them into the scrubber water. This scrubber water containing pollutants may now need to be sent off site for treatment. In this case, the chemicals have been transferred from an air waste stream to waste water. This may not alleviate the environmental concern, but rather may simply shift the risk from one medium (air) to another (water).

Chemicals in waste and wastewater may be transferred off site for management (recovery, treatment or disposal) and their management may lead to releases into the environment. For many of the reasons stated above, it is important to track both the total waste and wastewater transferred as well as the included chemicals. Each of the different types of off-site transfers is discussed in the following section.

When developing a PRTR programme, it is useful to consider the destination of an off-site transfer and its management. As discussed previously in Chapter 1 some off-site transfers may be less detrimental to the environment than others, and are therefore categorized and tracked separately. With this in mind, four destinations of off-site transfers are discussed throughout this document:

- i) Recycling;
- ii) Energy Recovery;
- iii) Treatment for Destruction or Disposal; and
- iv) Disposal.

The following subsections define each destination of off-site transfers, and explain various examples of each transfer. Note that these four activities may also occur on site at industrial facilities (on-site transfers). Some PRTR programmes track the amount of chemicals in waste or wastewater that are transferred and managed on site as well as off site. While this

document focuses on off-site transfers, the same definitions, concepts, and RETs apply to these activities when they occur on site.

3.1 Recycling

Recycling (or material recovery) is the use of waste materials in the manufacturing of new products of an identical or similar nature of the original products. This includes extracting or removing a material (chemical) from a gaseous, aerosol, aqueous, liquid, or solid waste, and from wastewater. Recycling should be differentiated from the direct reuse of a product. For example, a solvent containing toluene may be used to degrease parts. The solvent will eventually become contaminated. The contaminated solvent may be sent to a distillation unit to be recycled so it can be reused (as a material) in the degreasing operation.

Some examples of off-site transfers for recycling include: i) the regeneration of acids, catalysts (e.g. spent nickel catalyst used in hydrogenation and reforming processes in petroleum refining); ii) recycling of solvents (e.g., hexane and isobutane for the manufacture of high-density polyethylene resin); iii) the recovery of metals from scrap (e.g., nickel, copper, zinc, and vanadium generated by secondary smelting processes); iv) regeneration of contaminated lubricants that will contain a variety of organic chemicals; and v) transfers to waste brokers who later sell the waste to off-site recyclers.

3.2 Energy Recovery

Energy recovery is the utilisation of the energy content of waste materials, or chemicals contained therein, with or without pre-processing. The waste and the chemicals contained are usually combusted in a boiler or an industrial furnace. Energy recovery has aspects of recycling because it results in the beneficial use of the waste and its contained chemicals, but also aspects of treatment because it results in destruction of such waste and chemicals. Consequently, it has been defined as a separate waste management activity whereby the calorific value of certain waste and chemicals are exploited.

In defining energy recovery and disposal, it should be noted that the same devices used to harness the energy generated by the combustion of waste (or chemicals), can also be used for treatment and disposal (destruction) of waste and chemicals without energy recovery. For instance, a distinction can be made by assessing the calorific value of the waste, or chemicals therein, and the intended use of the combustion device. Therefore, the calorific value of off-site transfers and the intended use of the combustion device should be considered when determining whether a transfer of waste containing certain chemicals is reported as destined for energy recovery, treatment or disposal.

Some examples of off-site transfers for energy recovery include: i) waste containing chemicals (e.g., spent organic solvents, used oil, etc.) with a sufficient calorific value to replace some of the fuel normally used in boilers or other combustion devices (e.g., cement kilns, blast furnaces, etc.); and ii) transfers to waste brokers who later sell the waste to off-site energy recovery facilities. For example, toluene may be used in coating operations in the finishing steps of plastic products manufacturing. The overspray of toluene could be collected and transferred off site for energy recovery. Metals cannot be combusted for energy recovery and would not be reported as transferred off site for energy recovery.

3.3 Treatment for Destruction or Disposal

In order to treat waste (and included chemicals) to reduce or eliminate the hazardous properties, various chemical and physical methods may be applied. The treatment aims to treat chemicals of particular concern in the waste, or wastewater, in such a way that the chemical is destroyed or converted into a form that is of less or no concern. Incineration is a typical example of such a treatment. As the principal focus is the chemical in the waste stream, treatment for destruction does not include the simple physical removal or separation of the chemical from the waste stream. Also, treatment for destruction does not include the off-site transfer of a chemical that cannot be destroyed. Note that metals cannot be destroyed and would not be reported as transferred off site for destruction.

Simple dissociation of a chemical in water (e.g., HCl that dissociates into H⁺ and Cl⁻ ions) is not considered treatment for destruction. When a chemical is dissociated in water, it has not been destroyed; it is still present in the solution. The quantity treated for destruction is the amount actually destroyed rather than the amount of the chemical that is removed from a waste (gaseous, aerosol, aqueous, liquid or solid) or wastewater.

Some examples of off-site transfers for treatment include: i) chemicals sent off site for incineration; ii) off-site wastewater treatment (e.g., process water from petroleum refining operations is usually highly contaminated with ammonia, hydrogen sulfide, and a variety of hydrocarbons such as xylene, toluene, hexane, and phenol); iii) container residue (if the container is cleaned before it is reused and the cleaning waste is subsequently treated for destruction); and iv) off-site transfers to waste brokers who later transfer it to off-site treatment.

3.4 Disposal

A facility may transfer waste or wastewater containing chemicals off site for disposal. Some examples of such off-site transfers include: i) underground injection; ii) landfilling and surface impoundments; iii) land treatment; and iv) off-site transfers to waste brokers who later transfer it to off-site disposal. Examples of wastes, containing chemicals, that may be transferred off site for disposal include: dusts, shavings, or sludge. For example, solid waste generated from spilled and unused plastic pellets and container residue in plastics products manufacturing contains metals and non-volatile chemicals captured in dust collection systems (air pollution control devices). This dust is typically collected and transferred off site for landfilling or other disposal.

CHAPTER 4: ULTIMATE DESTINATION OF TRANSFERRED CHEMICALS

Some PRTR programmes consider the ultimate destination (or fate) of the chemicals contained in waste or wastewater that are transferred off site, whereas others are tracking waste categories, and wastewater. Regardless of the approach care must be taken by the reporting of waste, wastewater and chemicals therein that double counting does not occur. The reporting requirements of a PRTR programme need to be defined carefully to avoid double counting of releases and transfers of various chemicals. Ultimately, one of the following six things happens to a particular chemical transferred off site:

- i) It is emitted to the air;
- ii) It is discharged to a receiving water body;
- iii) It is released into or onto the land;
- iv) It is destroyed through treatment;
- v) It is recycled and incorporated into another product (e.g., another metal product); or
- vi) It is recovered as energy.

An example of obvious double counting is the generation of a slurry waste stream containing a cyanide compound that is discharged to a surface impoundment. Eventually, much of the water evaporates, leaving behind a dried sludge. The sludge is subsequently dredged and ultimately transferred off site to a landfill. The landfill again may leak into nearby waters and also release gases into the air. The PRTR programme needs to be designed carefully to instruct facilities to report the chemical only once (i.e., released on site to a surface impoundment, or transferred off site with the sludge for disposal on a landfill).

The concept of the ultimate destination (or fate) of a chemical was alluded to in the descriptions and examples provided in the previous section. For example, a trace metal contained in a waste transferred off site for the purpose of energy recovery is not destroyed during combustion, nor is the trace metal recovered for energy. The metal is ultimately released from the combustion device to air through a stack, to water used to clean the combustion device, or to land if the ash generated during combustion is later released to land. A PRTR programme needs to define the end point of the process of tracking the disposal of each chemical to avoid double counting the releases and transfers of chemicals. The ultimate destination of the chemical is the most logical end point to choose.

CHAPTER 5: IDENTIFICATION AND QUANTIFICATION OF OFF-SITE TRANSFERS

This chapter describes the release estimation techniques (RETs) applicable to off-site transfers. These RETs have been presented in the other parts of the Resource Compendium, as they are also applicable to point sources and diffuse sources. Typically, off-site transfers of chemicals take place either in wastewater or waste. Off-site wastewater treatment plants receive wastewater from industrial and/or municipal sources for treatment. Most off-site transfers that occur via wastewater include dilute concentrations of chemicals. Off-site transfers of wastes for recovery or disposal are also very common.

There are obvious benefits of knowing the quantities of chemicals in waste/wastewater streams that are transferred off site. For example, a facility may use a mass balance calculation to determine on-site chemical releases. Quantifying these releases by using the release estimation techniques described in the following sections may support the facility in maintaining compliance with any applicable regulations or tracking any potential occupational health and safety concerns. In addition, the facility may be able to identify opportunities to improve certain processes to minimise raw material and product losses. For example, in the plastics product manufacturing industry plastic parts are often coated, and there may be a significant amount of overspray during this process. The facility could quantify the amounts of raw materials lost during the process if the facility tracks the amount of chemicals in waste generated from the overspray. If the facility determines that there are significant losses, a cost-benefit analysis may prove that it is profitable to identify methods to improve the efficiency of the process (e.g., investing into new equipment to increase the transfer efficiency, or recycling the overspray).

The RETs that are described in the following sections include:

- i) Direct monitoring;
- ii) Mass balance calculations;
- iii) Chemical-specific emission factors;
- iv) Indirect monitoring/other calculations; and
- v) Engineering judgement.

5.1 Direct Monitoring

In fact, direct monitoring should be distinguished from all other RET-methodologies, since it produces direct measurements, while RETs provide more or less accurate estimates. However, direct monitoring is here listed along with other RET-techniques because, in many cases, a limited set of measurements is used to represent, or model, a broader range of emissions. A distinction should be drawn in the case of continuous monitoring (measuring), for which no modelling is needed (at least for the particular chemical that is monitored).

Direct monitoring techniques are in most cases limited to point sources and off-site transfers. However, measurement of ambient conditions can in some cases be used to make valid inferences about both discrete point sources and diffuse sources. Examples of direct monitoring of a chemical include: i) in-line chemical analyses; ii) continuous emissions monitoring; and iii) air, wastewater, and waste samples sent to a laboratory to provide concentrations of various chemical constituents of the release or off-site transfer.

Data obtained by continuous emissions monitors (CEMs) are usually not directly applicable in quantifying the amount of chemicals in off-site transfers (CEMs are typically installed to monitor on-site, point source releases to air or water). However, these data may be used in conjunction with a mass balance calculation or other technique to quantify chemicals in off-site transfers. For example, CEMs are utilized in the cement industry to measure the concentrations of specific chemicals (e.g., carbon monoxide, mercury, hydrochloric acid, chlorine) and general pollutants or chemical categories (e.g., total hydrocarbons and particulate matter) released to the air in stack gases from the cement kiln. These gases are continuously monitored and particulate matter in the gas is typically collected in one of two primary types of air pollution control devices: fabric filters or electrostatic precipitators. Using the known mass of chemicals that enter the system with raw materials along with concentration data obtained from the CEM, the quantity of chemicals in the cement kiln dust that is collected in the pollution control devices can be calculated by using a mass balance. This will allow the facility to estimate quantities of chemicals in the dust that is transferred off site. The mass balance release estimation technique is discussed in the following section.

A facility may utilize continuous or non-continuous direct monitoring to estimate concentrations of chemicals in various waste streams, including wastewater. For example, wastewater transferred off site is often periodically monitored. A facility may have flow-rate and concentration data from quarterly samples. To estimate the annual discharge of a chemical, the facility would first calculate the amount of a chemical (e.g., ethylene) discharged on each sample day by multiplying the concentration of the chemical in the discharge by the discharge flow rate for that day. The facility would similarly calculate the amount of chemical discharged on each sample day. The average daily amount of the chemical that is discharged would then be calculated by summing up the quantities calculated for each day and dividing by the number of days. The facility could estimate the amount of chemical discharged and transferred off site annually by multiplying the number of operating days by the average mass of the chemical discharged per day.

5.2 Mass Balance

In cases where it is not practical to measure the releases of the chemicals that are of direct interest, one must resort to an alternative model, explicit or implicit. Explicit models, other than empirical methods, rely on basic principles of chemistry and physics; hence they are often referred to as *first principles* models. The simplest conceptual form of such models, although in practice often the most complex to develop, is a mass balance model. These models rely on the fundamental fact that what goes into a system must either come out in the form of a product or as a release, or be chemically changed to some other compound. Thus, one can model a release from any system by knowing the amount of substance going into the system and the amount that is

generated or destroyed within the system. Any positive difference between inputs and net destruction in the system must therefore represent a release.

The general form of these models is as follows:

$$\Sigma (\text{inputs}) + \Sigma (\text{generation}) = \Sigma (\text{outputs}) + \Sigma (\text{destruction})$$

where:

- i) **Inputs** refer to the materials (chemicals) entering an operation. For example, chlorine added to process water as a disinfectant would be considered an input to the water treatment operation;
- ii) **Outputs** refer to the materials (chemicals) leaving an operation by various avenues. Outputs (avenues) may include on-site release and waste/wastewater management activities; transfers off site for recycling, energy recovery, treatment, storage, or disposal, or the amount of chemical that leaves the facility in or as a product;
- iii) **Generation** identifies those chemicals created during an operation (manufactured, including coincidental manufacturing). For example, when nitrogen sources are used in biological wastewater treatment systems, nitrate compounds and additional ammonia may be coincidentally manufactured; and
- iv) **Destruction** refers to the amount of chemical converted to another substance during the operation (e.g., reacted).

In practice, because most systems have multiple releases, one generally starts with a set of known parameters (e.g., the amount of the substance incorporated into the product and the amount in known waste streams) in order to model an unknown output (e.g., the air emissions). For a system of any complexity, the conceptual simplicity of this approach is offset by fairly intense data requirements that often can only be adequately satisfied by direct monitoring. Care should be taken to apply the mass balance approach to the media and chemical combinations that have the lowest uncertainty or the most benign potential effects. Moreover, the margin of error resulting from mass balance applications should be taken into account when considering this technique. For large inputs and outputs, a mass balance may not be the best estimation method, because slight uncertainties in mass calculations can yield significant errors in the release and other waste/wastewater management estimates.

It is also possible to apply an overall mass balance estimate as a check on the validity of the individual estimates of releases to the various media that are based on other techniques. A mass balance check may be particularly useful for source and chemical combinations that have relied on differing estimation techniques that have uncertainties that are either unknown or cannot be easily calculated. It is a relatively simple procedure to add up all of the release estimates of a chemical in the individual media and compare that to the known amount of that chemical that is

input to the process. The results will help to establish a measure or degree of reasonableness of the individual estimates. Section 6 presents more information to understand a mass balance through the use of schematics that identify a variety of possible release and off-site transfer sources for a facility or unit operation.

PRTR Programme Note: PRTR programmes usually allow facilities to estimate releases and off-site transfers using one or more release estimation techniques, including direct monitoring. Direct monitoring, except continuous monitoring, may not always be the most representative method, since it is often just a “snapshot” of measurements that must be extrapolated over the entire calendar year and adjusted to varying operating conditions. For certain releases and off-site transfers the use of a well established RET would give even more accurate results than the direct monitoring, in particular when continuous monitoring is not possible or feasible.

5.3 Chemical-Specific Emission Factors

Emission factors are ratios, generally expressed as the weight or volume of a chemical generated per unit measure of an input to the process or the production from that process (e.g., an emission factor for the amount of benzo (g, h, i) perylene released by combusting fuel oil No. 6 is 1.03×10^{-3} kilograms released per million gallons of No. 6 fuel oil burned in a boiler). Emission factors probably represent the most widely used method of estimating air emissions. Similar factors, perhaps more appropriately called release factors, can also be developed for chemicals released to other media.

While emission factors are most often applied to estimates of air emissions, air emissions are not typically transferred from one site to another. However, emission factors applied to air streams, along with other information, may still be useful for estimating quantities of chemicals transferred off site. An example is an air pollution control device that collects a chemical from an air stream, removing it from the air and incorporating it into a wastewater or solid waste that may then be transferred off site. For example, an emission factor may be used to determine the mercury in air emissions from a combustion process. The mercury in these emissions may subsequently be collected as part of the fly ash collected from an electrostatic precipitator (e.g. solid waste) and some may be collected in a scrubber (e.g. wastewater). This solid waste and wastewater may then be transferred off site and the emission factor can be used to determine the mass of mercury that was generated, and then transferred off site in waste or wastewater.

New emission factors may be developed for site-specific process. For example, an emission factor was recently developed showing that 6.03×10^{-3} kilograms of lead is emitted per short ton of bituminous coal burned. If new emission factors are developed, they should be based on a large number of similar operations over a long averaging time to provide better accuracy.

5.4 Indirect Monitoring and Other Calculations

Indirect monitoring and other calculations may be further subdivided into four sections:

- i) Indirect Monitoring;
- ii) Modelling;
- iii) Engineering Calculations; and
- iv) Non-Chemical Specific Emission Factors.

Each of these is discussed further in the following sections.

5.4.1 Indirect Monitoring

When data are routinely gathered from a source, not on emissions per se, but on factors that have a known predictive relationship to emissions, these approaches are sometimes referred to as “Indirect Monitoring”. Indirect monitoring methods rely on inherent relationships between process parameters and the resulting emissions. For example, release quantities can be estimated with high accuracy for any process where those release quantities depend directly on process conditions, by measuring the process conditions.

Indirect monitoring data may be readily available. Consider a process for which the release depends directly on the temperature and pressure within a reactor. In many cases, the product yield and/or product quality may also depend on those parameters, and therefore those parameters may be routinely monitored as a part of the production process. Those same parameters can then be used to estimate releases. For a well-characterized process, indirect monitoring methods can be used to develop release estimates that are nearly as accurate as direct measurements for selected sources or chemicals at a fraction of the cost. Typically, parametric monitoring is used to obtain enough measurements to adequately represent average conditions within the process. In some cases, periodic measurements of certain chemicals can be used to represent other chemicals by applying average ratios, or by using some other known conditions related to the source. It is important to note that measurement of a specific chemical concentration is usually defined as direct monitoring, while the measurement of a type of chemical, such as the concentration of volatile organic chemicals, is considered indirect monitoring.

One example of the use of indirect monitoring to estimate the amount of a chemical transferred off site is the use of the measurement of other parameters including biological oxygen demand (BOD), total suspended solids (TSS), or oil and grease as a surrogate to estimate the release of a specific chemical. The measurement of these parameters may already be required for wastewater discharge permits. If a facility does not have better data to measure the concentrations of organic chemicals found in wastewater to be transferred off site, the facility could use the concentration data obtained from measuring the oil and grease in the wastewater and assume the concentrations of the organic chemicals were similar.

5.4.2 Modelling

Another estimating approach is to develop a process-specific model, which in effect, replaces knowledge about what the inputs and outputs of a system are with knowledge about what

is likely to happen to an input or result in an output inside the modelled system. For example, while a mass balance model of a storage tank would likely address inflow and outflow to estimate breathing losses, a process-specific model could substitute knowledge about pressures inside the tank, vapour pressure of the liquid in the tank, and the operating parameters of relief valves. There is a wide range of possible models for a system. Ultimately, model development depends on the quality of theoretical knowledge and empirical data available that can be used to characterize the reactions and mass transfer processes that take place within the modelled system.

Several computer programmes are available for estimating emissions from storage tanks, landfills, water and wastewater treatment, and other processes. An example of a computer programme used to estimate quantities of chemicals in wastewater streams is WATER9 available at <http://www.epa.gov/ttn/chief/software/water/index.html>. WATER9 estimates the fate of chemicals that are processed through a wastewater treatment system. WATER9 allows the user to select the specific wastewater treatment unit operations that are employed in the process. Based on the selected unit operations, the specified sequence, and parameters of the inlet streams, WATER9 provides separate emission estimates for each individual compound that is identified as a constituent of the wastewater. The emission estimates are based upon the properties of the compound and its concentration in the wastewater. WATER9 will estimate the amount that is destroyed via biodegradation, volatilized (fugitive air emission), is transferred to sludge (which will ultimately be dredged and either disposed on site to land, or transferred off site), and passes through the system (an "off-site transfer" to a receiving water body or further wastewater treatment). Facilities can use WATER9 to estimate quantities of chemicals contained in sewage sludge or discharges that may be transferred off site. An example scenario using the WATER9 program is provided below.

Process Description and Required Inputs

The wastewater treatment process defined by the user consists of the following units: a bar screen, primary municipal clarifier, activated sludge unit and a circular clarifier, in that order. The sludge from the circular clarifier is recycled back to the activated sludge unit at a rate of 200 L/s. The wastewater enters the bar screen at 30°C and a rate of 300 L/s. The wastewater consists of 200 ppm solids, 1 ppm oil, 172 ppm dissolved solids, 10 ppm benzene, and 10 ppm toluene. Additional process parameters are required for the programme; however, default values that are based on typical wastewater treatment operations exist. Default values were used, but have not been listed here, to simplify the example.

Results

WATER9 produces various summaries and reports of the parameters and individual units. The results from the simulation are summarized below. 78.2% of the benzene and 83.4% of the toluene were removed from the wastewater stream by the activated sludge unit. 17.1% of the benzene and 12.5% of the toluene were lost to the air via fugitive releases. The remaining amounts remained in the exit streams. This information can be used to quantify the benzene and toluene that is partitioned to sludge, which may ultimately be transferred off site for release to land; and the quantity that passes through the system, which will be transferred to a receiving water body or to additional wastewater treatment.

Overall Summary

Compound	Flow Rate (gal/s)	Removal via Activated Sludge	Fugitive Air Emissions (% feed)	Remaining in exit stream (% feed)
Benzene	0.511	78.2%	17.0%	4.8%
Toluene	0.376	83.4%	12.5%	4.1%

5.4.3 Engineering Calculations

Engineering calculations are assumptions and/or judgments used to estimate quantities of chemicals. These calculations can be used to determine quantities of chemicals in waste/wastewater transferred off site, as well as quantities of chemicals released on site. The quantities are estimated by using physical and chemical properties and relationships (e.g., Ideal Gas law, Raoult's law), or by modifying an emission factor to reflect the chemical properties of the chemical in question. Engineering calculations rely on process parameters; therefore, a facility must have a thorough knowledge of facility operations to complete these calculations. Other examples include the use of purchase, sale, inventory, and process flow rate records that can be used to track a chemical in an off-site transfer.

An example of an engineering calculation is as follows. A facility may have stack monitoring data available for xylene but it is interested in quantifying the amount of toluene released. Toluene is used in the same application as xylene at the facility and the concentrations of the chemicals in the liquid feedstock are approximately the same. One could estimate the emissions of toluene by adjusting the monitoring data of xylene by a ratio of the vapour pressure for xylene to toluene. This example is an engineering calculation based on physical properties and process operation information.

Another example of an engineering calculation involves estimating the releases of shipping container residue. Off-site transfers for recycling or disposal may include container residue. Any residual chemicals in “empty” containers transferred off site should be reported as an off-site transfer. All containers (bags, totes, drums, tank trucks, etc.) will have a small amount of residual solids and/or liquid. On-site cleaning of containers should also be considered. If the facility uses a solvent (organic or aqueous) for cleaning purposes, the disposal of the waste solvent should be reported as appropriate.

COMMON ERROR - Shipping Container Residue

A common error is when a facility overlooks residual chemicals or chemical categories in containers. So-called “empty” drums may contain a few centimetres or more of liquid after draining and similarly “empty” bags may contain residues of dust and powder. Even though each individual drum or bag may only contain a small amount of a chemical, for facilities that receive hundreds or thousands of drums or bags each year the annual cumulative amount of a chemical can be substantial. The quantities that should typically be reported are shown in Table 5 for estimates of liquid drum residual. The text of this section addresses estimates of residual solids.

Actual data and knowledge of the unloading methods at a facility can be used to estimate the quantity of residual chemicals in containers. Table 5 provides results from a study of liquid residue quantities left in drums and tanks when emptied. These results are presented as the mass percent of the vessel capacity, and are categorized based on unloading method, vessel material, and bulk fluid material properties such as viscosity and surface tension. No testing was conducted for residual solids in this study. If data or site-specific knowledge is available to estimate the quantity of solid residual in containers, it should be considered. If no data are available, an estimate of 1% residual solid is reasonable.

Table 5. Summary of Liquid Residue Quantities From Pilot-Scale Experimental Study^{a,b}**(Weight percent of drum capacity)**

Unloading Method	Vessel Type	Value	Material			
			Kerosene ^c	Water ^d	Motor Oil ^e	Surfactant Solution ^f
Pumping	Steel drum	Range	1.93 - 3.08	1.84 - 2.61	1.97 - 2.23	3.06
		Mean	2.48	2.29	2.06	3.06
Pumping	Plastic drum	Range	1.69 - 4.08	2.54 - 4.67	1.70 - 3.48	Not Available
		Mean	2.61	3.28	2.30	
Pouring	Bung-top steel drum	Range	0.244 - 0.472	0.266 - 0.458	0.677 - 0.787	0.485
		Mean	0.404	0.403	0.737	0.485
Pouring	Open-top steel drum	Range	0.032 - 0.080	0.026 - 0.039	0.328 - 0.368	0.089
		Mean	0.054	0.034	0.350	0.089
Gravity Drain	Slope-bottom steel tank	Range	0.020 - 0.039	0.016 - 0.024	0.100 - 0.121	0.048
		Mean	0.033	0.019	0.111	0.048
Gravity Drain	Dish-bottom steel tank	Range	0.031 - 0.042	0.033 - 0.034	0.133 - 0.191	0.058
		Mean	0.038	0.034	0.161	0.058
Gravity Drain	Dish-bottom glass-lined tank	Range	0.024 - 0.049	0.020 - 0.040	0.112 - 0.134	0.040
		Mean	0.040	0.033	0.127	0.040

^aFrom AReleases During Cleaning of Equipment.® Prepared by PEI Associates, Inc., for the U.S. Environmental Protection Agency, Office of Pesticides and Toxic Substances, Washington DC Contract No. 68-02-4248. June 30, 1986.

^bThe values listed in this table should only be applied to similar vessel types, unloading methods, and bulk fluid materials. At viscosities greater than 200 centipoise, the residue quantities can rise dramatically and the information on this table is not applicable.

^cFor kerosene, viscosity = 5 centipoise, surface tension = 29.3×10^{-5} newtons/cm²

^dFor water, viscosity = 4 centipoise, surface tension = 77.3×10^{-5} newtons/cm²

^eFor motor oil, viscosity = 97 centipoise, surface tension = 34.5×10^{-5} newtons/cm²

^fFor surfactant solution viscosity = 3 centipoise, surface tension = 31.4×10^{-5} newtons/cm²

5.4.4 *Non-Chemical Specific Emission Factors*

Non-chemical specific emission factors, industry-determined emission factors for processes or equipment, and site-specific emission factors also can be used to determine quantities of chemicals in waste/wastewater. For example, a facility may develop non-chemical specific emission factors for fugitive or stack emissions based on stack tests for various air permits.

An example of the use of non-chemical specific emission factors includes estimating fugitive releases of a category of chemicals, such as volatile organic compounds (VOCs) from different sources. Emission factors used to determine the releases of total VOCs are available for sources such as valves, flanges, pump seals, compressor seals, drains, cooling towers, etc. The total VOC emissions, combined with process knowledge regarding the concentration of various VOCs can be used to estimate the quantity of individual chemicals.

5.5 Engineering Judgement

All of the approaches discussed above are typically described as explicit techniques. That is, the parameters and assumptions used to make the prediction of a release can be stated unambiguously. Frequently, however, releases and off-site transfers are estimated using methods that are more implicit. Such implicit methods take advantage of the experience and professional knowledge of the estimator. Over time these approaches have been discussed collectively as methods based on engineering judgement. While it is recognized that the use of engineering judgement methods has the potential for errors and inconsistencies, the practical advantages of their role in developing release estimates quickly and inexpensively should not be undermined. Often, engineering judgement methods are used initially to provide estimates in the first year or two of a PRTR programme. The analysis and interpretation of these results then frequently leads to the use or development of more sophisticated methods that can improve the accuracy, specificity, and uses of the data.

An example of the use of engineering judgement is the use of an equipment design specification or system performance guarantee to estimate the quantity of a chemical removed from a waste/wastewater stream passing through that manufacturer's pollution control device. If a facility knows the amount of the chemical in the stream entering the pollution control device and the amount of the chemical removed, the facility can estimate the quantity of the chemical remaining in the stream that may be transferred off site.

CHAPTER 6: GENERAL STEPS FOR DETERMINING RELEASES AND OFF-SITE TRANSFERS

This section describes how the RETs presented above are applied in a systematic way at the facility level to estimate release and transfer quantities. Release and transfer quantities can be determined by completing the following four steps, described in detail in the following sections and as summarized in Figure 1.

- Step 1)* Prepare a process flow diagram;
- Step 2)* Identify chemicals and potential sources of chemical releases and off-site transfers;
- Step 3)* Identify release and transfer types; and
- Step 4)* Determine the most appropriate estimation method(s) and calculate the estimates for release and transfer quantities.

For the purposes of this document, “sources” refer to the streams or units that generate the releases and off-site transfers (such as process vents, container residue, or spills) and ‘types’ refers to the environmental media (for example, releases to fugitive air, releases to stack air, discharges to receiving water bodies or off-site wastewater treatment plants, or releases to land).

6.1 Step 1: Prepare a Process Flow Diagram

Preparing a process flow diagram will help identify potential sources and types of chemicals released and transferred off site from a facility. Depending on the complexity of the facility, a diagram of individual processes or operations may be more appropriate than a diagram of the entire facility. The diagram should show how materials flow through the processes and identify material input, generation, and output points. Looking at each operation separately will determine which chemicals are used and the medium to which they may be released or managed as waste/wastewater on site and off site. Identifying all potential release and transfer points will assist the facility in determining the amounts of chemicals released and transferred off site in waste/wastewater streams.

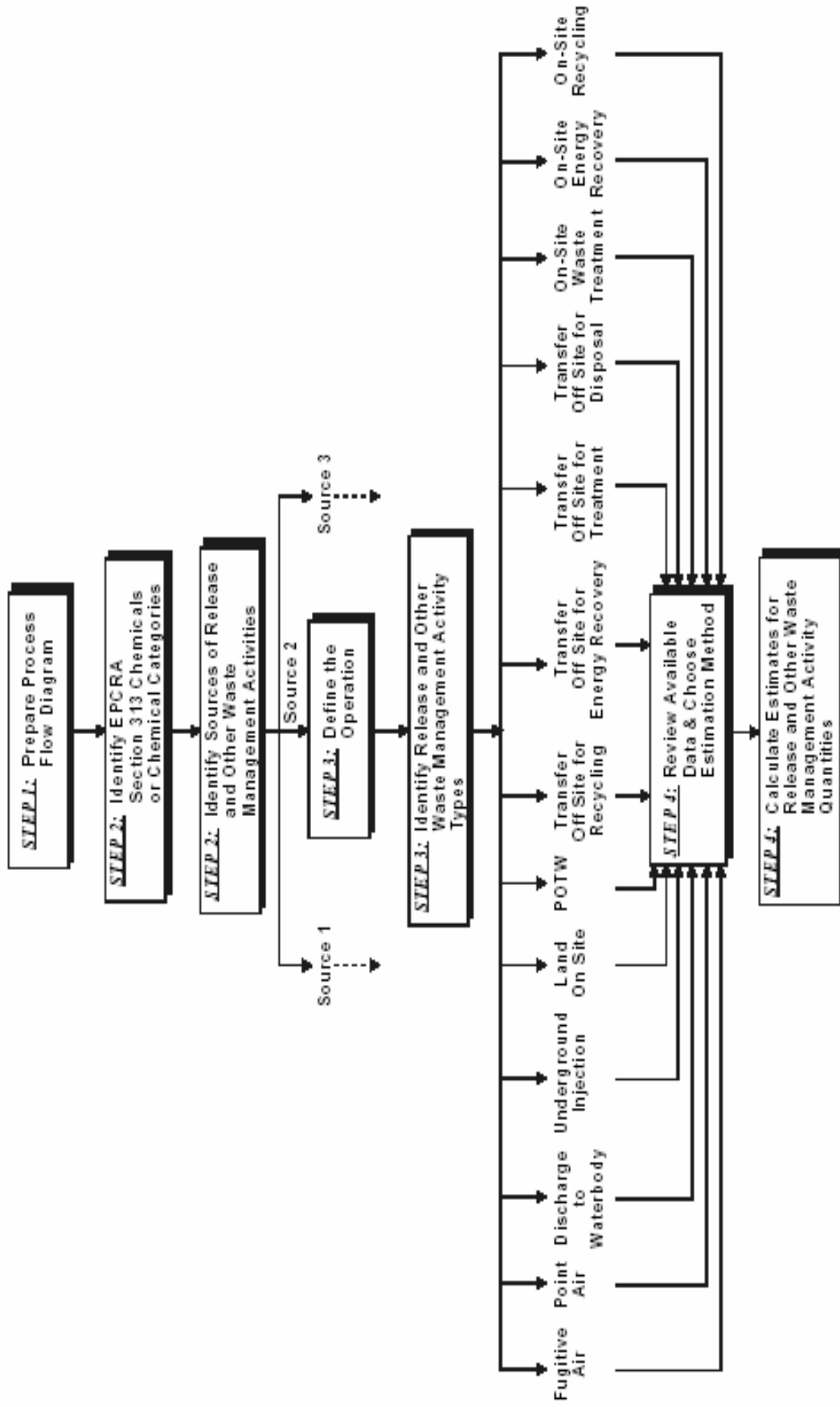


Figure 1. Release and Off-site Transfer Calculation Approach

6.2 Step 2: Identify Chemicals and Potential Sources of Chemical Releases and Off-site Transfers

Once a process flow diagram has been developed, sources of chemical releases and off-site transfers from each unit operation and process must be developed. This normally includes upsets and routine maintenance activities. Potential sources are listed below:

- Accidental spills and releases;
- Air pollution control devices (e.g., baghouse, electrostatic precipitator, and scrubber);
- Clean up and housekeeping practices;
- Combustion by-products;
- Container residues;
- Fittings;
- Flanges;
- Process discharge stream;
- Pumps;
- Recycling and energy recovery by products;
- Relief valves;
- Process vents;
- Stock pile losses;
- Storage tanks;
- Storm water runoff;
- Tower stacks;
- Treatment sludge;
- Volatilization from process or treatment; and
- Waste treatment discharges.

Next, the chemicals released or transferred off site from each source must be identified. A thorough knowledge of the facility operations and processes is required for this determination. Chemicals that are coincidentally manufactured at the facility (e.g., during combustion) should also be considered.

6.3 Step 3: Identify Types of Releases and Off-site Transfers

For each identified source of chemicals, the next step is to examine all possible release and transfer types (i.e., releases to air, water and land). Figure 2 schematically presents the possible release and transfer types. Remember to include both routine operations and accidental spills when identifying transfer types. This diagram can be used as a checklist to make sure all possible types of releases and off-site transfers have been considered. As the diagram illustrates, a facility may have both fugitive and stack air emissions, discharges to water bodies, releases to land, on-site waste management (i.e., for recycling, energy recovery, treatment, or release), and transfers off site for waste/wastewater treatment.

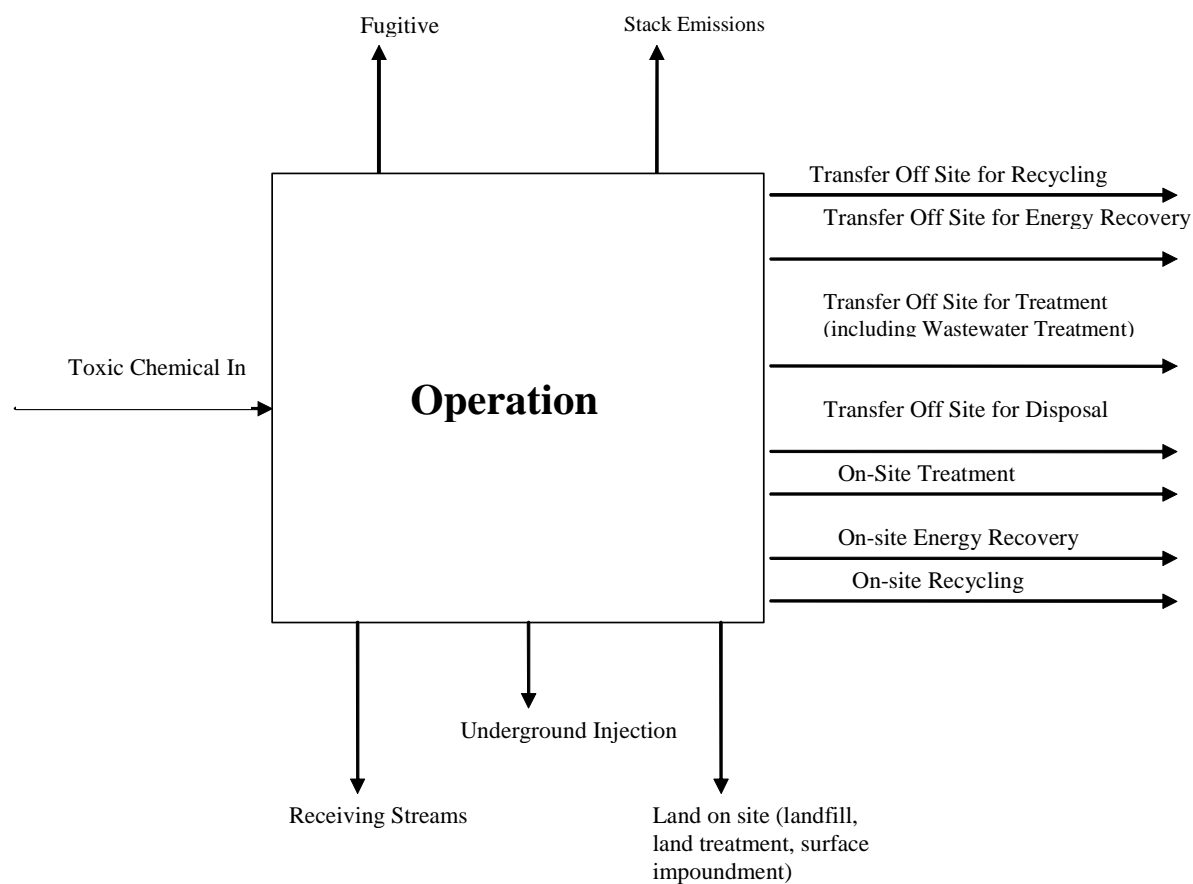


Figure 2: Possible Release and Transfer Types

6.4 Step 4: Determine the Most Appropriate Method(s) and Calculate the Estimates for Release and Transfer Quantities

After all potential sources and types of releases and off-site transfers have been identified, the quantities of each chemical released and transferred must be calculated. While many PRTR programmes do not require facilities to conduct sampling or testing to perform reporting, facilities are generally required to use readily available data, or where such data are not readily available, reasonable estimates to determine the method that will result in the most accurate estimate. For example, it may not be appropriate to use emission factors or engineering calculations if more accurate data, such as stack testing results, are available.

Many potential sources of data exist for these (and other) methods of developing estimates. Table 6 presents potential data sources and the estimation methodology in which they are most likely to be used. Based on site-specific knowledge and potential data source availability, the best method for calculating each release and transfer quantity can be determined.

Table 6. Potential Data Sources for Off-Site Transfer Calculations

DATA SOURCES	
Direct Monitoring	Indirect Monitoring/Other Calculations
<ul style="list-style-type: none"> • Air, water, land release permits • Wastewater discharge monitoring data • Continuous emissions monitoring data • pH for acids and bases • Solid waste analyses, manifests • Industrial hygiene monitoring data 	<ul style="list-style-type: none"> • Facility <u>non-chemical specific</u> emission factors. • Henry's Law • Raoult's Law • Solubilities • Volatilization rates
Mass Balance	Engineering Judgement
<ul style="list-style-type: none"> • Hazardous material inventory • Material Safety Data Sheets • Pollution prevention reports • Spill event records • Supply and purchasing records 	<ul style="list-style-type: none"> • Process operator knowledge • Technical/process consultant knowledge • Process design specifications • Equipment manufacturer specifications
Chemical-Specific Emission Factors	
<ul style="list-style-type: none"> • AP-42² chemical-specific emission factors • Facility or trade association derived chemical-specific emission factors 	

² Compilation of Air Pollutant Emission Factors AP-42, Fifth Edition, Volume I: Stationary Point and Area Sources. <http://www.epa.gov/ttn/chief/ap42/index.html>