



National Pollutant Inventory

Emission Estimation Technique Manual

for

Solvent Recycling

First published in July 1999

**EMISSION ESTIMATION TECHNIQUES
FOR
SOLVENT RECYCLING**

TABLE OF CONTENTS

1.0 INTRODUCTION	1
2.0 PROCESS DESCRIPTION AND EMISSIONS	2
2.1 Solvent Storage	3
2.2 Solvent Handling	3
2.3 Initial Treatment	3
2.4 Distillation and Purification	6
2.5 Spills	7
2.6 Equipment Leaks.....	7
3.0 EMISSION ESTIMATION TECHNIQUES: ACCEPTABLE RELIABILITY AND UNCERTAINTY.....	9
3.1 Direct Measurement.....	10
3.2 Mass Balance	10
3.3 Engineering Calculations.....	11
3.4 Emission Factors.....	11
4.0 ESTIMATING EMISSIONS	13
4.1 Emissions from Solvent Storage.....	13
4.2 Emissions from Solvent Handling.....	16
4.3 Emissions from Solvent Distillation.....	21
4.4 Emissions from Spills	24
4.5 Emissions from Surface Evaporation	27
5.0 REFERENCES	29

SOLVENT RECYCLING

LIST OF FIGURES, TABLES AND EXAMPLES

Figure 1 - General Processes in Solvent Recycling Operations.....	2
2 - Typical Fixed-Bed Activated Carbon Solvent Recycling System.....	5
3 - Distillation Process for Solvent Recycling.....	7
Table 1 - List of Variables and Symbols.....	13
2 - Pathways for VOC Emissions to Atmosphere from Solvent Storage Tanks.....	15
3 - Saturation (S) Factors for calculating Organic Liquid Loading Emissions.....	17
4 - Emission Factors for Solvent Recycling.....	23
Example 1 - Calculating Solvent Loading Emissions.....	20
2 - Calculating Solvent Distillation Emissions.....	23
3 - Calculating Spill Emissions.....	26
4 - Calculating Surface Evaporation Emissions.....	27

1.0 Introduction

The purpose of all Emission Estimation Technique (EET) Manuals in this series is to assist Australian manufacturing, industrial and service facilities to report emissions of listed substances to the National Pollutant Inventory (NPI). This Manual describes the procedures and recommended approaches for estimating emissions from facilities engaged in solvent recycling operations.

Solvent recycling activities covered by this Manual include facilities primarily engaged in the reclamation of waste and spent solvents to a condition that allows their reuse by industry. The recycling of solvents as fuels for kilns and furnaces is not covered in this Manual.

EET MANUAL: Solvent Recycling

HANDBOOK: Solvent Recycling

ANZSIC CODE : 2549

This Manual was drafted by the NPI Unit of the Queensland Department of Environment and Heritage on behalf of the Commonwealth Government. It has been developed through a process of national consultation involving State and Territory environmental authorities and key industry stakeholders.

2.0 Process Description and Emissions

Waste solvents are organic dissolving agents that are contaminated with suspended and dissolved solids, organics, water, other solvents, or any other substance not added to the solvent during its manufacture. Recycling is the process of restoring waste solvent to a condition that permits its reuse, either for its original purpose or for other industrial needs. Not all waste solvents generated by industry are recycled because the costs of reclamation may exceed the value of the recycled solvent, it is not always technically feasible to do so, and the manufacturers of new solvents often prevent their customers from utilising the recycled product.

Industries that produce waste solvents include solvent refining, polymerisation processes, vegetable oil extraction, metallurgical operations, pharmaceutical manufacture, surface coating, and cleaning operations (dry cleaning and solvent degreasing). The amount of solvent recovered from the waste varies from about 40 to 99 percent, depending on the extent and characterisation of the contamination and on the recovery process employed.

Design parameters and economic factors determine whether solvent reclamation is accomplished as a main process by a private contractor, as an integral part of a main process (such as solvent refining), or as an added process (as in the surface coating and cleaning industries). Most contract solvent reprocessing operations recover halogenated hydrocarbons, such as dichloromethane and trichloroethylene, from degreasing, and/or aliphatic, aromatic, and naphthenic solvents such as those used in paint, ink, and coatings industries. They may also reclaim small quantities of numerous specialty solvents, such as phenols, nitriles, and oils.

A solvent recycling process is illustrated by Figure 1. Industrial operations may not incorporate all of these steps. For example, initial treatment is necessary only when liquid waste solvents contain dissolved contaminants.

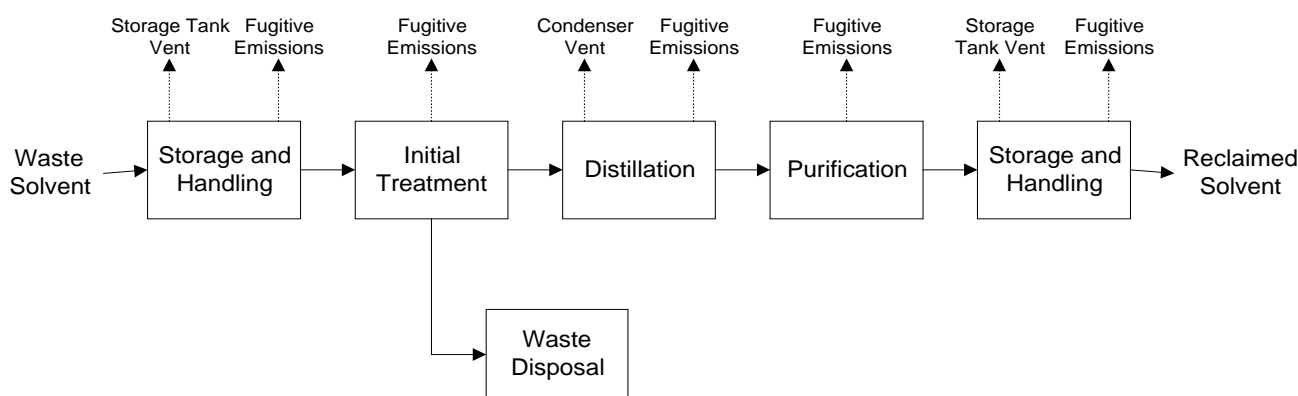


Figure 1 - General Processes in Solvent Recycling Operations

Source: USEPA AP-42 Section 4.7 1996.

2.1 Solvent Storage

Solvents are stored before and after recycling in containers ranging from 0.2 m³ (44 gallon drums) to tanks with capacities of 75 m³ or more. Various types and sizes of tanks are used for storage. Most of these tanks have a fixed-roof design. The two significant types of emissions from fixed-roof tanks are breathing and working losses. A breathing loss is the expulsion of vapour from a tank through vapour expansion and contraction that result from changes in ambient temperature and barometric pressure. This loss occurs without any liquid level change in the tank.

The combined loss from filling and emptying tanks is called the working loss. Evaporation during filling operations results from an increase in the liquid level in the tank. As the liquid level increases, the pressure inside the tank exceeds the relief pressure, and vapours are expelled from the tank. Evaporative emissions during the emptying process occur when air, drawn into the tank during liquid removal, becomes saturated with organic vapour and expands, expelling vapour through the vapour relief valve.

Emissions from tanks are characterised as a point source because volatile organic compounds (VOCs) are emitted through a vent. Please refer to *The Fuel and Organic Liquid Storage EET Manual* when estimating emissions from liquid storage facilities.

2.2 Solvent Handling

Handling includes loading waste solvent into process equipment and filling drums and tanks prior to transport and storage. The filling is most often done through submerged or bottom loading.

Emissions of VOCs to air may occur during material loading of solvents due to displacement of organic vapours. VOCs may be emitted from a tank when the vessel is uncovered or when a lid is open. Surface evaporation may occur during solvent recycling operations if containment vessels are exposed to the atmosphere. Surface evaporation emissions are generally fugitive in nature.

2.3 Initial Treatment

Waste solvents are initially treated by vapour recovery, or mechanical separation. Vapour recovery entails removal of solvent vapours from a gas stream in preparation for further reclaiming operations. In mechanical separation undissolved solid contaminants are removed from liquid solvents. Vapour recovery or collection methods employed include condensation, adsorption, and absorption. Technical feasibility of the method chosen depends on the solvent's miscibility, vapour composition and concentration, boiling point, reactivity, and solubility, as well as several other factors.

Condensation of solvent vapours is accomplished by water-cooled condensers and refrigeration units. For adequate recovery, a solvent vapour concentration well above 20 mg/m³ is required. To avoid explosive mixtures of a flammable solvent and air in the process gas stream, air is replaced with an inert gas, such as nitrogen. Solvent vapours that escape condensation are recycled through the main process stream or recovered by adsorption or absorption.

Activated carbon adsorption may also be used in capturing solvent emissions. Adsorption systems are capable of recovering solvent vapours in concentrations below 4 mg/m^3 of air. Solvents with boiling points of 200°C or more do not desorb effectively with the low-pressure steam commonly used to regenerate the carbon beds. Figure 2 shows a flow diagram of a typical fixed-bed activated carbon solvent recovery system. The mixture of steam and solvent vapour passes to a water-cooled condenser. Water-immiscible solvents are simply decanted to separate the solvent, whereas water-miscible solvents must be distilled, and solvent mixtures must be decanted and distilled. Fluidised bed operations are also in use.

Absorption of solvent vapours is accomplished by passing the waste gas stream through a liquid in scrubbing towers or spray chambers. Recovery by condensation and adsorption results in a mixture of water and liquid solvent, while absorption recovery results in an oil and solvent mixture. Further reclamation procedures are required if solvent vapours are collected by any of these three methods.

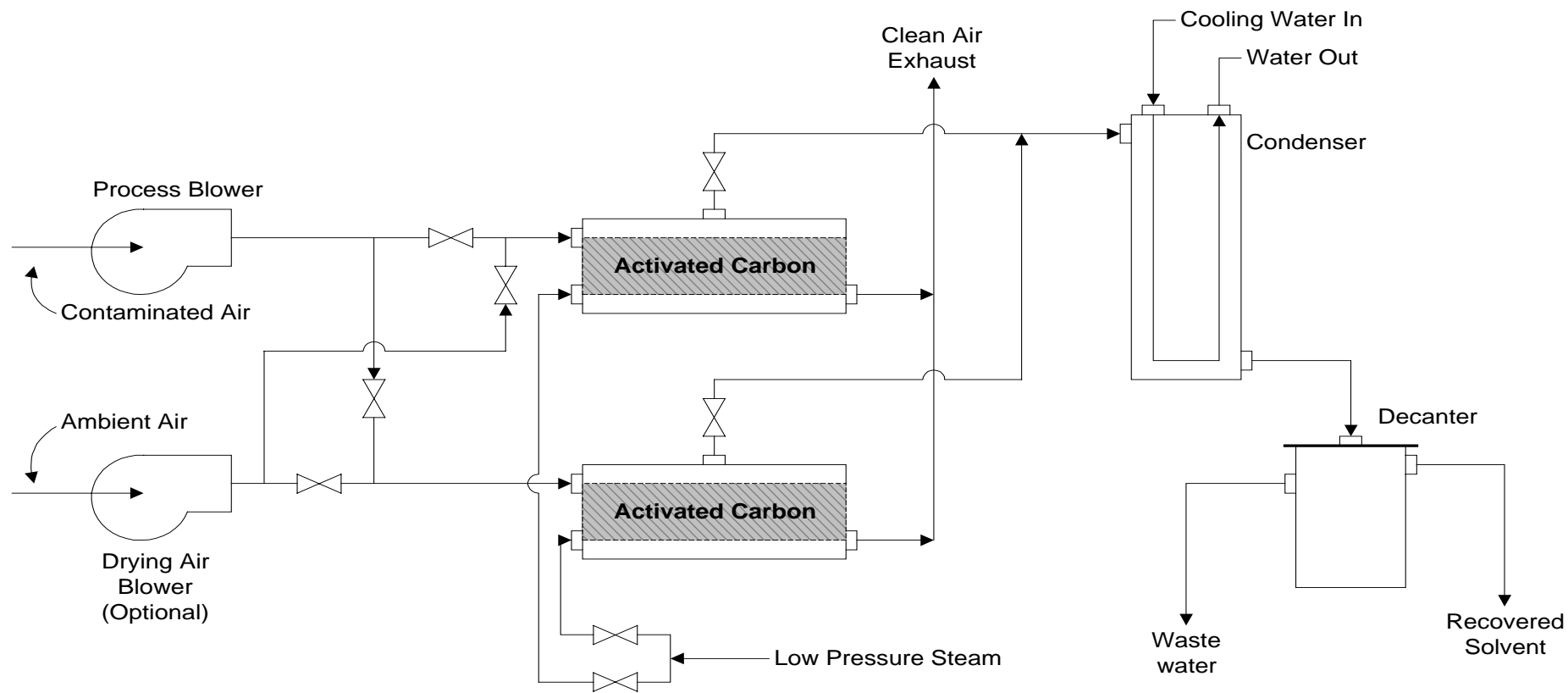


Figure 2 - Typical Fixed-Bed Activated Carbon Solvent Recycling System

Source: USEPA AP-42 Section 4.7, 1995.

Initial treatment of liquid waste solvents is accomplished by mechanical separation methods. This includes both removing water by decanting and removing undissolved solids by filtering, draining, settling, and/or centrifuging. A combination of initial treatment methods may be necessary to prepare waste solvents for further processing.

2.4 Distillation and Purification

After initial treatment, waste solvents are distilled to remove dissolved impurities and to separate solvent mixtures. Separation of dissolved impurities is accomplished by simple batch, simple continuous, or steam distillation. Mixed solvents are separated by multiple simple distillation methods, such as batch or continuous rectification. These processes are shown in Figure 3.

In simple distillation, waste solvent is charged to an evaporator. Vapours are then continuously removed and condensed, and the resulting sludge or still bottoms are drawn off. In steam distillation, solvents are vaporised by direct contact with steam, which is injected into the evaporator. Simple batch, continuous, and steam distillations follow Path I in Figure 3.

The separation of mixed solvents requires multiple simple distillation or rectification. Batch and continuous rectification are represented by Path II in Figure 3. In batch rectification, solvent vapours pass through a fractionating column, where they contact condensed solvent (reflux) entering at the top of the column. Solvent not returned as reflux is drawn off as overhead product. In continuous rectification, the waste solvent feed enters continuously at an intermediate point in the column. The more volatile solvents are drawn off at the top, while those with higher boiling points collect at the bottom.

Design criteria for evaporating vessels depends on the composition of the waste solvent. Scraped surface stills or agitated thin film evaporators are the most suitable for heat sensitive or viscous materials. Condensation is accomplished by barometric, or shell and tube, condensers. Azeotropic solvent mixtures are separated by the addition of a third solvent component, while solvents with higher boiling points (those in the range of high-flash naphthas at 155°C), are most effectively distilled under vacuum. The level of purity required in the reclaimed solvent determines the number of distillations, reflux ratios, and the processing time needed.

VOC emissions occur from loading solvent into the distillation equipment, operation of the distillation equipment, and spillage. Emissions from loading and spilling are classified as fugitive, while emissions from operation of the equipment are generally emitted through a condenser vent and are classified as a point source emission. NPI reporting requires partitioning of both air and water emissions into fugitive and point sources.

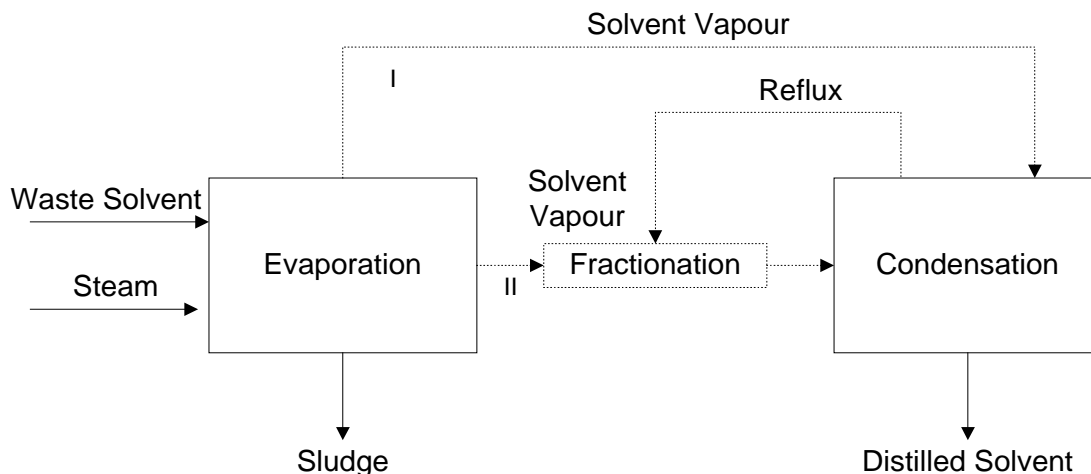


Figure 3 - Distillation Process for Solvent Recycling

Source: USEPA AP-42 Section 4.7, 1995.

After distillation, water is removed from the solvent by decanting or salting. Decanting is accomplished with immiscible solvent and water which, when condensed, form separate liquid layers, one or the other of which can be drawn off mechanically. Additional cooling of the solvent/water mix before decanting increases the separation of the two components by reducing their solubility. In salting, solvent is passed through a calcium chloride bed, and water is removed by absorption.

During purification, reclaimed solvents are stabilised, if necessary. Buffers are added to virgin solvents to ensure that pH level is kept constant during use. To renew it, special additives are added during purification.

2.5 Spills

Solvents may be accidentally spilled during handling, distillation, or purification activities. Materials that are spilled onto the ground may spread over an area, vaporise, and result in air, water, or land emissions.

2.6 Equipment Leaks

In order to transport stored organic solvents from storage tanks to the distillation and purification operation, a network of pipes, pumps, valves, and flanges is employed. As liquid material is pumped from the storage tanks to the particular process area, the pipes and supporting hardware (process line components) may develop leaks over time. When leaks occur, volatile components in the transported material are emitted into the atmosphere.

This generally occurs from the following process line components:

-
- pump seals;
 - valves;
 - compressor seals;
 - safety relief valves;
 - flanges;
 - open-ended lines; and
 - sampling connections.

Emissions from equipment leaks can be characterised as fugitive and are described in detail in the EET Manual for *Fugitive Emissions*.

3.0 Emission Estimation Techniques: Acceptable Reliability and Uncertainty

Emissions to the air, water and land are likely to be the primary emission points to consider. If water is treated on-site, sludges or other wastes containing listed substances may be created. Other emissions may come from discarded containers or samples, vessel washings, or from volatilisation to the air. Facility operators should ensure that all emissions are accounted for when reporting.

Estimates of emissions of listed substances to air, water and land should be reported for each substance that triggers a threshold. The reporting list and detailed information on thresholds are contained in *The NPI Guide* at the front of this Handbook.

In general, there are four types of emission estimation techniques (EETs) that may be used to estimate emissions from your facility.

The four types described in *The NPI Guide* are:

- sampling or direct measurement;
- mass balance;
- fuel analysis or other engineering calculations; and
- emission factors.

Select the EET, (or mix of EETs), that is most appropriate for your purposes. For example, you might choose to use a mass balance to best estimate fugitive losses from pumps and vents, direct measurement for stack and pipe emissions, and emission factors when estimating losses from storage tanks and stockpiles.

If you estimate your emission by using any of these EETs, your data will be displayed on the NPI database as being of ‘acceptable reliability’. Similarly, if your relevant environmental authority has approved the use of EETs that are not outlined in this handbook, your data will also be displayed as being of ‘acceptable reliability’.

This Manual seeks to provide the most effective emission estimation techniques for the NPI substances relevant to this industry. However, the absence of an EET for a substance in this handbook does not necessarily imply that an emission should not be reported to the NPI. The obligation to report on all relevant emissions remains if reporting thresholds have been exceeded.

You are able to use emission estimation techniques that are not outlined in this document. You must, however, seek the consent of your relevant environmental authority. For example, if your company has developed site-specific emission factors, you may use these if approved by your relevant environmental authority.

You should note that the EETs presented in this manual relate principally to average process emissions. Emissions resulting from non-routine events are rarely discussed in the literature, and there is a general lack of EETs for such events. However, it is important to recognise that emissions resulting from significant operating excursions and/or accidental situations (eg. spills) will also need to be estimated. Emissions to land, air and water from spills must be estimated and added to process emissions when calculating total emissions for reporting purposes. The emission resulting

from a spill is the net emission, ie. the quantity of the NPI reportable substance spilled, less the quantity recovered or consumed during clean up operations.

The **usage*** of each of the substances listed as Category 1 and 1a under the NPI must be estimated to determine whether the 10 tonnes (or 25 tonnes for VOCs) reporting threshold is exceeded. If the threshold is exceeded, **emissions** of these Category 1 and 1a substances must be reported for all operations/processes relating to the facility, even if the actual emissions of the substances are very low or zero.

* Usage is defined as meaning the handling, manufacture, import, processing, coincidental production or other uses of the substances.

This section describes the EETs available for estimating emissions from solvent recycling.

3.1 Direct Measurement

Because vent or other outlet testing is relatively uncommon for Australian solvent recycling facilities, emissions test data for these facilities is generally only available in the form of monitoring results for NPI-listed substances conducted for compliance with Worksafe Australia's *Exposure Standards for Atmospheric Contaminants in the Workplace Environment*. However, while this data may be used in conjunction with exhaust system flow rates to calculate total VOC or speciated organic solvent emissions from a room, floor, or building, emissions are often below reliable detection limits due to high flow rates and low concentrations of the pollutants of interest

3.2 Mass Balance

A mass balance approach may be used to estimate emissions when the quantities of a material used, recycled, emitted, and disposed of are known. Emissions from a solvent recycling facility can be estimated through knowledge of the amounts of dirty solvent purchased and the amounts recycled. The difference is assumed to have been emitted. Solvent usage figures would generally be in litres.

Similarly, estimating emissions for speciated VOCs would require knowledge of the types of solvents used and the weight percentages of NPI-listed materials in the solvents. Annual usage may be based on the gross amount purchased (in cubic metres). When operations have several formulas for different batches, a conservative emissions estimate for each listed substance may be based on the formula with the highest listed substance usage. This approach is suitable for speciated organics (xylenes, toluene) because they are not involved in chemical reactions and their usage rates may already be tracked for purchasing reasons or for reclamation procedures.

3.3 Engineering Calculations

Theoretical and complex equations or *models* can be used for estimating emissions from solvent recycling processes. EET equations are available for the following types of emissions found at a solvent recycling facility:

- material loading;
- surface evaporation;
- material storage; and
- spills.

Inputs for theoretical equations generally fall into the following categories;

- (1) chemical/physical properties of the material involved, such as vapour pressure and vapour molecular weight;
- (2) operating data, such as the amount of material processed and operating hours; and
- (3) physical characteristics and properties of the source, such as tank colour and diameter.

Use of emission equations to estimate emissions from solvent recycling facilities is a more complex and time-consuming process than the use of emission factors. Emission equations require more detailed inputs than the use of emission factors, but they do provide an emission estimate that is based on facility-specific conditions.

3.4 Emission Factors

An emission factor can be defined as a pollutant emission rate relative to a level of source activity. Emission factors are typically based on the results of source tests performed at an individual facility or at one or more facilities within the same or similar industries.

Emission factors may be used to calculate total VOC emissions from solvent recycling facilities, as well as emissions from specific types of equipment typically found at such a facility. These types of equipment include the following:

- process equipment;
- distillation and purification systems;
- parts washing equipment; and
- process piping.

Emission factors for solvent recycling processes are provided at Section 4. Using emission factors is more cost-effective than collection and analysis of air and water samples or use of emission equations. Additionally, there are potentially significant limitations with the mass balance approach for solvent recycling activities.

The reader should recognise that, in most cases, emission factors adopted for the NPI are averages of available industry-wide data with varying degrees of quality. Emission factors are, however, an acceptable technique for estimating emissions for the NPI where estimations of emissions are required to quantify medium to long-term emission trends.

Every emission factor has an associated emission factor rating (EFR) code. This rating system is common to EETs for all industries and sectors and therefore, to all Industry Handbooks. They are based on rating systems developed by the United States Environmental Protection Agency (USEPA), and by the European Environment Agency (EEA). Consequently, the ratings may not be directly relevant to Australian industry. Sources for all emission factors cited can be found in Section 5.0 of this Manual. The emission factor ratings will not form part of the public NPI database.

When using emission factors, you should be aware of the associated EFR code and what that rating implies. An A or B rating indicates a greater degree of certainty than a D or E rating. The less certainty, the more likely that a given emission factor for a specific source or category is not representative of the source type. These ratings notwithstanding, the main criterion affecting the uncertainty of an emission factor remains the degree of similarity between the equipment/process selected in applying the factor, and the target equipment/process from which the factor was derived.

The EFR system is as follows:

A	-	Excellent
B	-	Above Average
C	-	Average
D	-	Below Average
E	-	Poor
U	-	Unrated

4.0 Estimating Emissions

After the NPI-listed substances and emission sources at the reporting facility have been identified, the procedures for estimating emissions can proceed. The usual approach is first to estimate emissions from sources across a facility for all substances triggering a threshold and then, based on the disposal method used, determining whether emissions from a particular emission source are to air, water, land, or an off-site disposal facility. (The off-site transfer of NPI-listed substances, including listed substances contained in wastes, does not require reporting, but may nevertheless require characterisation and estimation if emissions are being estimated from a mass balance).

Table 1 lists the variables and symbols used in the equations and examples throughout this section and indicates the level of information required in applying the EETs illustrated.

Table 1 - List of Variables and Symbols

Variable	Symbol	Units
Total VOC emissions	$E_{kpv, VOC}$	kg/yr
Standing losses from storage tanks	E_S	kg/yr
Working losses from storage tanks	E_W	kg/yr
Saturation Factor	S	dimensionless
Volume of material loaded	Q	1000 kL/yr
Temperature	T	K
Vapour pressure of the material loaded at temperature T	P	kPa
Concentration of pollutant i	C_i	mass %
Molecular weight	MW	kg/kg-mole
Emission factor for pollutant i	EF_i	kg/units
Amount of solvent reclaimed	Q_{VOC}	tonnes/yr
Emission of species i	E_i	kg/hr
Gas-phase mass transfer coefficient for VOC species i	K_i	m/sec
Partial vapour pressure of VOC species i	P_i	kilopascals, kPa
Liquid mole fraction of VOC species i	m_i	mole/mole
Vapour mole fraction of VOC species i	y_i	mole/mole
Henry's Law constant for VOC species i	H_i	kPa
True vapour pressure of VOC species i	VP_i	kPa
Liquid mass fraction of VOC species i	z_i	kg/kg
Molecular weight of VOC species i	MW_i	kg/kg-mole
Vapour mass fraction of VOC species i	x_i	kg/kg
Duration of spill	HR	hr/event
Surface area of spill or tank	area	m^2
Universal gas constant	R	$8.314 \text{ kPa} \cdot \text{m}^3 / (\text{kgmol} \cdot \text{K})$
Mass percent of species i in mixture	X_i	mass %
Volume percent of species i in mixture	Y_i	mass %
Number of species in mixture	n	no units
Diffusion coefficient for VOC species i	D_i	cm^2/sec
Batch time	H	hr/batch
Wind speed	U	km/hr
Number of batches	B	batches/yr

Source: Queensland Department of Environment and Heritage, 1998.

4.1 Emissions from Solvent Storage

Table 2 shows the pathways for VOC emissions from three types of solvent storage tanks commonly found at recycling facilities.

As the table indicates, there are a number of pathways for evaporated VOCs to escape from solvent storage tanks and enter the atmosphere. Accurate calculation of emissions escaping through each of these pathways requires information on the tank structure, solvent type, meteorology, and operating practices. In general, fixed-roof tanks tend to be older and result in the greatest atmospheric emissions.

The presence of a volume of vapour space above the level of liquid in the tank promotes evaporation of the solvent VOCs and their subsequent emission to the atmosphere through the breather valve. Tanks equipped with a floating roof are able to reduce evaporative emissions by eliminating the vapour space between the liquid level in the tank and the tank roof. However, some emissions do occur through various seals and openings and also because solvent clings to the tank walls as the liquid level and roof are lowered.

A technique for estimating the sum of VOC emissions from above-ground and below-ground storage tanks is provided in the *Fuel and Organic Liquid Storage* EET Manual. A wide range of storage tanks is covered in this document, including fixed roof, internal floating roof, external floating roof, variable vapour space, and pressure tanks. The general methodology is to identify each of the major pathways for VOCs to escape from storage tanks to the atmosphere, and use available information to estimate emissions through each pathway. An overview of information requirements is given below. The two main categories of emissions are standing storage emissions, which result from changes in the surrounding temperature and barometric pressure, and working emissions, which result from the loading or withdrawal of solvent. In both cases, emissions result from higher pressure inside the tank than outside, causing the solvent vapour, containing VOCs, to escape through any available opening. Depending on the tank type, these openings or pathways include breather vents, rim seals, deck fittings, and deck seams.

Table 2 - Pathways for VOC Emissions to Atmosphere from Solvent Storage Tanks

Tank Type	Standing Storage Emissions	Working Emissions
Fixed Roof	Breathing Emissions: Changes in temperature or pressure cause an imbalance between internal and external vapour pressures. Breather valves are opened to equalise pressure, allowing emission of evaporated VOCs.	Displacement Emissions: During tank filling, liquid displaces gas inside the tank, forcing it to be expelled through the breather valve. Air Saturation Emissions: During solvent removal, air drawn into the tank becomes saturated with VOCs and expands, thus causing an imbalance of vapour pressure with the atmosphere. This imbalance is relieved by venting to the atmosphere.
External Floating Roof	Rim Seal, Roof Fitting Emissions: Emissions occur from rim seals and roof fittings due to slight imbalances in internal and external vapour pressure. Exposure of the floating roof to the wind increases emission rates.	Clingage Emissions: As the roof is lowered during withdrawal, solvent clings to the tank walls and evaporates when exposed to the atmosphere. Evaporation rate increases with wind speed.
Internal Floating Roof	Rim Seal, Deck Fitting, Deck Seam Emissions: Emissions occur from rim seal, deck fitting, and deck seam due to slight imbalances in internal and external pressures. Lower emissions occur because the roof is protected from the wind.	Clingage Emissions: As the roof is lowered during withdrawal, solvent clings to the tank wall and evaporates. Wind does not increase the evaporation rate.

Adapted from: Energy and Environmental Analysis Inc., 1995.

The EET for calculating storage tank VOC emissions may be expressed by Equation 1.

Equation 1

$$E_{kpy,VOC} = E_S + E_W$$

where:

$$E_{kpy,VOC} = \text{total VOC emissions from a single tank, kg/yr}$$

$$E_S = \text{standing storage emissions from the tank, kg/yr}$$

$$E_W = \text{working emissions from the tank, kg/yr}$$

The techniques for estimating E_S and E_W are different for each tank type. These techniques are described in the *Fuel and Organic Liquid Storage EET Manual*.

Storage Tank Emissions - Data Inputs

A number of data sources are required for an accurate assessment of standing storage and working emissions from solvent storage tanks. These include the type of tank, physical dimensions of the tank, solvent type, climatic data, rate of solvent throughput, and other tank-specific characteristics. Detailed information on data requirements is given in the *Fuel and Organic Liquid Storage* EET Manual, and an overview of these requirements and the likely sources of this information is given in the following paragraphs:

- **Type of Storage Tank** - The three most common types of solvent storage tanks are fixed roof, external floating roof, and internal floating roof tanks. Descriptions of the different tank types are given in the *Fuel and Organic Liquid Storage* EET Manual.
- **Solvent Type** - Solvent vapour pressure and density for each storage tank are required to calculate emission losses. Specification of the type of solvent stored in the tank allows for the use of default values for vapour pressure and density in the *Fuel and Organic Liquid Storage* EET Manual.
- **Climatic Data** - Average wind speed, average daily ambient temperature range, average daily solar insolation, and average atmospheric pressure values are each required for the emission calculations. The *Fuel and Organic Liquid Storage* EET Manual contains the necessary climatic data for most Australian cities and towns where solvent recyclers are located. If a reporting facility is located in a city or town where climatic data is not specified, the closest nearby city, or city with similar climatic conditions, needs to be specified by the user.
- **Solvent Throughput** - An estimate of annual throughput of solvent for each tank needs to be obtained for the July to June reporting year.
- **Tank-Specific Characteristics** - Tank-specific characteristics used in calculating emission losses include one or more of the following: physical dimensions of the tank, type of seals, breather vent settings, tank paint colour, number of vacuum breakers, number of columns, effective column diameter, deck fitting types, and deck seam length. This information can be obtained from the tank manufacturer or distributor or by visual inspection of the tank. In many cases, default values are given in the *Fuel and Organic Liquid Storage* EET Manual.

4.2 Emissions from Solvent Handling

VOC emissions resulting from the addition of solvents to vessels, mixers, and storage tanks may be calculated using a loading loss equation. Equation 2, shown below, is related to tank loading but can be applied to any tank or vessel loading (NPCA, 1995). This equation may also be applied to estimate solvent end-product filling losses.

Equation 2

$$E_{\text{kpy,VOC}} = 0.1203 * (S * P * MW * Q) / T$$

where:

$E_{\text{kpy,VOC}}$ = total VOC loading emissions, kg/yr
 S = saturation factor (dimensionless); see Table 3.
 P = vapour pressure of the material loaded at temperature T,
kPa
 MW = vapour molecular weight, kg/kg-mole
 Q = volume of material loaded, 1000L/yr
 T = temperature, K
0.1203 = constant, {(kg-mole * K) / (kPa * 1000L)}

Calculation of VOC emissions from solvent loading using Equation 2 is based on the following assumptions:

- the vapours displaced from the process vessel are identical to the vapours from the materials being loaded;
- the volume of the vapour being displaced is equal to the volume of material being loaded into the vessel;
- the vapour within the headspace of the vessel is saturated at room temperature and remains at room temperature during loading; and
- all solvent additions are coincident at a constant temperature (in reality, solvent is generally added in stages).

Table 3 - Saturation (S) Factors for calculating Organic Liquid Loading Emissions

Transport Carrier	Mode of Operation	S Factor
Road and Rail	Submerged loading of a clean cargo tank	0.50
Tankers	Submerged loading: normal service	0.60
	Submerged loading: vapour balance service	1.00
	Splash loading of a clean cargo tanker	1.45
	Splash loading : normal service	1.45
	Splash loading: vapour balance service	1.0
Marine Vessels	Submerged loading: ships	0.2
	Submerged loading: barges	0.5

Source: USEPA AP-42 Section 5.2, 1995.

Most solvent recycling operations will be using solutions containing multiple NPI-listed solvents. In these cases, the vapour pressure (P) will need to be calculated using Equation 3.

Equation 3

$$P = \sum P_i$$

where:

P = vapour pressure of material loaded, kPa
 P_i = partial pressure of VOC species i, kPa

P_i may be calculated using Raoult's Law (for ideal solutions) or Henry's Law constants (when sparingly soluble gases are dissolved at low concentrations in water). Raoult's Law is given in Equation 4.

Equation 4

$$P_i = m_i * VP_i$$

where:

$$\begin{aligned} P_i &= \text{partial vapour pressure of VOC species } i, \text{ kPa} \\ m_i &= \text{liquid mole fraction of VOC species } i, \text{ mole/mole} \\ VP_i &= \text{true vapour pressure of VOC species } i, \text{ kPa} \end{aligned}$$

P_i may be calculated using Henry's Law constants and Equation 5.

Equation 5

$$P_i = m_i * H_i$$

where:

$$\begin{aligned} P_i &= \text{partial vapour pressure of VOC species } i, \text{ kPa} \\ m_i &= \text{liquid mole fraction of VOC species } i, \text{ mole/mole} \\ H_i &= \text{Henry's Law constant for VOC species } i, \text{ kPa} \end{aligned}$$

The liquid mole fraction of VOC species i (m_i) may be calculated if the liquid weight fractions of all species are known using Equation 6.

Equation 6

$$m_i = (z_i / MW_i) / \sum (z_i / MW_i)$$

where:

$$\begin{aligned} m_i &= \text{liquid mole fraction of VOC species } i, \text{ mole/mole} \\ z_i &= \text{liquid mass fraction of VOC species } i, \text{ kg/kg} \\ MW_i &= \text{molecular weight of VOC species } i, \text{ kg/kg-mole} \end{aligned}$$

The vapour molecular weight (MW) will also need to be calculated if multiple solvents are used for a single cleaning event. Equation 7 shows this calculation.

Equation 7

$$MW = \sum (y_i * MW_i)$$

where:

$$\begin{aligned} MW &= \text{vapour molecular weight, kg/kg-mole} \\ y_i &= \text{vapour mole fraction of VOC species } i, \text{ mole/mole} \\ MW_i &= \text{molecular weight of VOC species } i, \text{ kg/kg-mole} \end{aligned}$$

The vapour mole fraction is calculated using Equation 8.

Equation 8

$$y_i = P_i / P$$

y_i = vapour mole fraction of VOC species i, mole/mole

P_i = partial pressure of VOC species i (calculated using Equation 4 or Equation 5, kPa)

P = vapour pressure of the material loaded (calculated using Equation 3)

Speciated VOC emissions are calculated using Equation 9.

Equation 9

$$E_{kpy,i} = E_{kpy,VOC} * x_i$$

where:

$E_{kpy,i}$ = loading emissions of VOC species i, kg/yr

$E_{kpy,VOC}$ = total VOC loading emissions (calculated using Equation 2), kg/yr

x_i = vapour mass fraction of VOC species i, kg/kg

The vapour mass fraction of VOC species i (x_i) is calculated using Equation 10.

Equation 10

$$x_i = y_i * MW_i / MW$$

where:

x_i = vapour mass fraction of VOC species i, kg/kg

y_i = vapour mole fraction of VOC species i (calculated using Equation 8), mole/mole

MW_i = molecular weight of VOC species i, kg/kg-mole

MW = vapour molecular weight (calculated using Equation 7), kg/kg-mole

Example 1 illustrates the use of Equation 2 through to Equation 10. Emissions are calculated by following Steps 1 through 8.

Example 1 - Calculating Solvent Loading Emissions

A solvent recycler is required to estimate emissions from a vessel for NPI reporting purposes. Using engineering equations, emission factor (S) and the following data the emission can be calculated:

- the yearly vessel throughput of the solvent mixture (Q) is 600 000 litres;
- the solvent is a 50/50 mixture (by weight) of toluene and *n*-heptane;
- the solvent mixture is splash loaded into the vessel (S = 1.45 from Table 3); and
- the temperature of the solvent is 298 K (25°C).

The following Steps 1 through 8 below calculate emissions.

Step 1: Apply Equation 6 - Calculation of Liquid Mole Fraction (m_i)

Component i	Liquid Mass Fraction, z_i (kg of i/kg of liquid)	Molecular Weight, MW_i (kg of i/kg- mole of i)	Liquid Mole Fraction, m_i (mole of i/mole of liquid)
Toluene	0.50	92	$(z_i / MW_i) / \Sigma (z_i / MW_i)$ $(0.5/92)/[(0.5/92) + (0.5/100)]$ = 0.52
<i>n</i> -Heptane	0.50	100	$(z_i / MW_i) / \Sigma (z_i / MW_i)$ $(0.5/100)/[(0.5/92) +(0.5/100)]$ = 0.48

Step 2: Apply Equation 4 - Calculation of Partial Vapour Pressure (P_i)

Component i	Liquid Mole Fraction, m_i (mole of i/mole of liquid)	True Vapour Pressure, VP_i (kPa)	Partial Vapour Pressure, P_i (kPa)
Toluene	0.52	4.0	$m_i * VP_i = 0.52 * 4.0$ = 2.08
<i>n</i> -Heptane	0.48	6.2	$m_i * VP_i = 0.48 * 6.2$ = 2.98

Step 3: Apply Equation 3 - Calculation of Vapour Pressure (P)

$$\begin{aligned} P &= \Sigma P_i \\ &= 2.08 + 2.98 \\ &= 5.06 \text{ kPa} \end{aligned}$$

Step 4: Apply Equation 8 - Calculation of Vapour Mole Fraction (y_i)

Component i	Partial Vapour Pressure, P _i (kPa)	Total Vapour Pressure, P (kPa)	Vapour Mole Fraction, y _i (mole of i/mole of vapour)
Toluene	2.08	5.06	$P_i / P = 2.08 / 5.06 = 0.41$
<i>n</i> -Heptane	2.98	5.06	$P_i / P = 2.98 / 5.06 = 0.59$

Step 5: Apply Equation 7 - Calculation of Vapour Molecular Weight (MW)

$$\begin{aligned}
 MW &= \Sigma (y_i * MW_i) \\
 &= (0.41 * 92) + (0.59 * 100) \\
 &= 97 \text{ kg/kg-mole}
 \end{aligned}$$

Step 6: Apply Equation 10 - Calculation of Vapour Mass Fraction (x_i)

Component i	Vapour Mole Fraction, y _i (mole of i/mole of vapour)	Molecular Weight, MW _i (kg of i/kg-mole of i)	Vapour Molecular Weight, MW (kg of vapour /kg mole of vapour)	Vapour Mass Fraction, x _i (kg of i/kg of vapour)
Toluene	0.41	92	97	$y_i * MW_i / MW = 0.41 * 92/97 = 0.39$
<i>n</i> -Heptane	0.59	100	97	$y_i * MW_i / MW = 0.59 * 100/97 = 0.61$

Step 7: Apply Equation 2 - Calculate Total VOC Emissions (E_{kpy,VOC})

$$\begin{aligned}
 E_{kpy,VOC} &= 0.1203 * (S * P * MW * Q) / T \\
 &= 0.1203 * (1.45 * 5.06 * 97 * 600) / 298 \\
 &= 172.4 \text{ kg VOC/yr}
 \end{aligned}$$

Step 8: Apply Equation 9 - Calculate Speciated VOC Emissions (E_{kpy,i})

Component i	VOC Emissions, E _{kpy,VOC} (kg VOCs/yr)	Vapour Mass Fraction, x _i (kg of i/kg of VOCs)	Speciated VOC Emissions, E _{kpy,i} (kg i)
Toluene	172.4	0.39	$E_{kpy,VOC} * x_i = 172.4 * 0.39 = 67.2$
<i>n</i> -Heptane	172.4	0.61	$E_{kpy,VOC} * x_i = 172.4 * 0.61 = 105.2$

$$E_{kpy,Toluene} = 67.2 \text{ kg Toluene /yr}$$

$$E_{kpy,n-Heptane} = 105.2 \text{ kg } n\text{-Heptane /yr}$$

4.3 Emissions from Solvent Distillation

VOC emissions from the loading and operation of a solvent distillation device may be calculated using the emission factors from Table 4 and the application of Equation 11.

Equation 11

$$E_{kpy,VOC} = EF_{VOC} * Q_{VOC}$$

where:

$$E_{kpy,VOC} = \text{VOC emissions from loading or operations of the distillation device, kg/yr}$$
$$EF_{VOC} = \text{VOC emission factor for loading of the distillation device or for the distillation column condenser vent, kg VOCs emitted/tonne solvent reclaimed}$$
$$Q_{VOC} = \text{amount of solvent reclaimed through the distillation device, tonne/yr}$$

Speciated VOC emissions are then calculated using Equation 12.

Equation 12

$$E_i = E_{kpy,VOC} * C_i / 100$$

where:

$$E_{kpy,i} = \text{emissions of VOC species i from loading or operation of the solvent distillation device, kg/yr}$$
$$E_{kpy,VOC} = \text{VOC emissions from loading or operation of the distillation device, calculated using Equation 11, kg/yr}$$
$$C_i = \text{concentration of VOC species i in the solvent processed through the distillation system, mass \%}$$

Table 4 - Emission Factors for Solvent Recycling

Emission Source	Pollutant	Emission Factor Average (kg/tonne)^a
Storage tank vent ^b	Volatile organic compounds	0.01 (0.002 - 0.04)
Condenser vent	Volatile organic compounds	1.65 (0.26 - 4.17)
Incinerator stack ^c	Volatile organic compounds	0.01
Incinerator stack	Particulates	0.72 (0.55 - 1.0)
Fugitive emissions		
Spillage ^c	Volatile organic compounds	0.10
Loading	Volatile organic compounds	0.36 (0.00012 - 0.71)
Leaks	Volatile organics	ND
Open sources	Volatile organics	ND

Source: USEPA, AP-42 Section 4.7, 1995.

^a All emission factors are for uncontrolled process equipment, except those for the incinerator stack. Average factors are derived from the range of data points available. Factors for these sources are given in terms of kg per tonne of reclaimed solvent. The ranges are in parentheses.

^b Storage tank is of fixed roof design.

^c Only one value available.

ND = no data.

Example 2 illustrates the use of Equation 11 and Equation 12.

Example 2 - Calculating Solvent Distillation Emissions

First, total VOC emissions from operation of a distillation device may be calculated using an emission factor from Table 4 and Equation 11.

$$\begin{aligned}
 EF_{\text{VOC}} &= 1.65 \text{ kg VOCs/tonne of solvent processed} \\
 Q_{\text{VOC}} &= 4 \text{ tonnes of spent solvent processed/yr} \\
 E_{\text{kpy,VOC}} &= EF_{\text{VOC}} * Q_{\text{VOC}} \\
 &= 1.65 * 4 \\
 &= 6.6 \text{ kg VOCs/yr}
 \end{aligned}$$

Next, total VOC emissions are speciated using the concentration of VOC species *i*, mass %, and Equation 12.

$$\begin{aligned}
 E_{\text{kpy,VOC}} &= 6.6 \text{ kg VOCs/yr} \\
 C_i &= 99\% \text{ toluene in spent solvent} \\
 E_{\text{kpy,i}} &= E_{\text{kpy,VOC}} * C_i / 100 \\
 &= 6.6 * 99 / 100 \\
 &= 6.5 \text{ kg toluene/yr}
 \end{aligned}$$

If the species *i* concentration is provided on a volume basis from Material Safety Data Sheets (MSDS) or other sources, the volume percent will need to be converted to mass percent. If molecular weight of the total mixture is known, the volume percent of species *i* in the mixture can be converted to mass percent, using Equation 13.

Equation 13

$$X_i = 100 * Y_i * MW_i / MW$$

where:

X_i	=	mass percent of species <i>i</i> in mixture
Y_i	=	volume percent of species <i>i</i> in mixture
MW_i	=	molecular weight of species <i>i</i>
MW	=	molecular weight of mixture

If the molecular weight of the mixture is not known, it can be calculated using Equation 14.

Equation 14

$$MW = \sum_{i=1}^n \left(MW_i * Y_i / 100 \right)$$

where:

MW	=	molecular weight of mixture
n	=	number of species in mixture
Y_i	=	volume percent of species <i>i</i> in mixture
MW_i	=	molecular weight of species <i>i</i>

4.4 Emissions from Spills

A vaporisation equation can be used to estimate the evaporation rate of a liquid chemical spill if the size area of the spill is known or can be estimated. This is illustrated by Equation 15.

Equation 15

$$E_i = (MW_i * K_i * \text{area} * P_i * 3\,600 * HR) / (R * T)$$

where:

E_i	=	emissions of VOC species i from the spill, kg/event
MW_i	=	molecular weight of VOC species i, kg/kg-mole
K_i	=	gas-phase mass transfer coefficient for VOC species i, m/sec
area	=	surface area of spill, m ²
P_i	=	partial pressure of VOC species i (if a pure chemical is spilled) or the partial pressure of chemical i (if a mixture of VOCs is spilled) at temperature T, kPa; the partial pressure of VOC species i (P_i) may be calculated using Equation 4 or Equation 5
3 600	=	conversion factor, sec/hr
HR	=	duration of spill, hr/event
R	=	universal gas constant at 1 atmosphere of pressure, 8.314 kPa * m ³ /(kg-mole * K)
T	=	temperature of the liquid spilled, K

The gas-phase mass transfer coefficient (K_i) may be calculated using Equation 16.

Equation 16

$$K_i = [0.00438 * (0.62138 * U)^{0.78} * (D_i / 0.288)^{2/3}] / 3.2808$$

where:

K_i	=	gas-phase mass transfer coefficient for VOC species i, m/sec
U	=	wind speed, km/hr
D_i	=	diffusion coefficient for VOC species i in air, cm ² /sec

Diffusion coefficients (D_i) can be found in chemical handbooks and are usually expressed in units of square centimetres per second (cm²/sec). If a diffusion coefficient is not available for a particular NPI listed chemical, the gas-phase mass transfer coefficient (K_i) may be estimated using Equation 17.

Equation 17

$$K_i = (0.00438 * (0.62138 * U)^{0.78} * (18/MW_i)^{1/3}) / 3.2808$$

where:

K_i	=	gas-phase mass transfer coefficient for VOC species i, m/sec
U	=	wind speed, km/hr
MW_i	=	molecular weight of VOC species i, kg/kg-mole

Example 3 illustrates the use of Equation 15 through to Equation 17. Emissions are calculated by following Steps 1 and 2.

Example 3 - Calculating Spill Emissions

Engineering equations can be used to calculate Methyl ethyl ketone (MEK) emissions when MEK is spilled onto the ground outside a building. The following data is given:

- the spill is not detected for 1 hour; it takes an additional 2 hours to recover the remaining MEK; the duration of the spill (HR), therefore, is 3 hours;
- the average wind speed (U) is 33.8 km/hr;
- the ambient temperature (T) is 298 K (25°C);
- the surface area of the spill (area) is 11 m²;
- the molecular weight of MEK (MW_i) is 72 kg/kg-mole
- the partial pressure of MEK (P_i) at 298 K (25°C) is approximately 13.31 kPa

Step 1: Using Equation 17, Calculate the Gas-Phase Mass Transfer Coefficient (K_i)

$$\begin{aligned}K_i &= (0.00438 * (0.62138 * U)^{0.78} * (18 / MW_i)^{1/3}) / 3.2808 \\ &= (0.00438 * (0.62138 * 33.8)^{0.78} * (18 / 72)^{1/3}) / 3.2808 \\ &= 0.0093 \text{ m/sec}\end{aligned}$$

Step 2: Using Equation 15, Calculate Emissions (E_i)

$$\begin{aligned}E_i &= (MW_i * K_i * area * P_i * 3\,600 * HR) / (R * T) \\ &= (72 * 0.0093 * 11 * 13.31 * 3\,600 * 3) / (8.314 * 298) \\ &= 427.35 \text{ kg MEK/spill}\end{aligned}$$

All emissions from spills in the reporting year should be added together for reporting to the NPI.

4.5 Emissions from Surface Evaporation

Emissions from surface evaporation from vessels during solvent recycling operations can be estimated using Equation 18.

Equation 18

$$E_{kpy,i} = [(MW_i * K_i * \text{area} * P_i * 3\,600 * H) / (R * T)] * B$$

where:

$E_{kpy,i}$	=	emissions of VOC species i, kg/yr
MW_i	=	molecular weight of VOC species i, kg/kg-mole
K_i	=	gas-phase mass transfer coefficient for VOC species i, m/sec
area	=	surface area of tank, m ²
P_i	=	vapour pressure of VOC i (if a pure chemical is used) or the partial pressure of chemical i (if a mixture of VOCs is used) at temperature T, kPa; the partial pressure of VOC species i (P_i) may be calculated using Equation 4 or Equation 5)
3 600	=	conversion factor, sec/hr
H	=	batch time, hr/batch
R	=	universal gas constant at 1 atmosphere of pressure, 8.314 kPa.m ³ /(kg-mole * K)
T	=	temperature of the liquid, K
B	=	number of batches per year, batches/yr

Equation 16 or Equation 17 can be used to estimate K_i . Total VOC emissions would equal the sum of all VOC species emissions.

Example 4 illustrates the use of Equation 17 and Equation 18. Emissions are calculated by following Steps 1 and 2.

Example 4 - Calculating Surface Evaporation Emissions

This example, using engineering equations, estimates toluene emissions from a solvent mixing operation due to surface evaporation. The following data is given:

- the batch time (H) is 4 hours;
- the number of batches per year (B) is 550;
- the average wind speed (U) is 1.28 km/hr;
- the ambient temperature (T) is 298 K (25°C);
- the surface area of the mixing tank (area) is 8.75 m²;
- the molecular weight of toluene (MW_i) is 92 kg/kg-mole; and
- the partial vapour pressure of toluene (P_i) at 298 K (25°C) is approximately 4 kPa

Step 1: Using Equation 17, Calculate the Gas-Phase Mass Transfer Coefficient (K_i)

$$\begin{aligned}K_i &= (0.00438 * (0.62138 * U)^{0.78} * (18 / MW_i)^{1/3}) / 3.2808 \\ &= (0.00438 * (0.62138 * 1.28)^{0.78} * (18 / 92)^{1/3}) / 3.2808 \\ &= 6.66 * 10^{-4} \text{ m/sec}\end{aligned}$$

Step 2: Using Equation 18, Calculate Emissions ($E_{kpy,i}$)

$$\begin{aligned}E_{kpy, \text{toluene}} &= [(MW_i * K_i * \text{area} * P_i * 3\,600 * H) / (R * T)] * B \\ &= [(92 * 6.66 * 10^{-4} * 8.75 * 4 * 3\,600 * 4) / (8.314 * 298)] * 550 \\ &= 6\,855 \text{ kg toluene/yr}\end{aligned}$$

5.0 References

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The following Emission Estimation Technique Manual referred to in this Manual is available at the NPI Homepage (<http://www.npi.gov.au>) and from your local environmental protection agency (see the front of the NPI Guide for details):

- Emission Estimation Technique Manual for Fuel & Organic Liquid Storage.