

National Pollutant Inventory

Emission Estimation Technique Manual

for

Fibreglass Product Manufacturing

First published in September 1999

EMISSION ESTIMATION TECHNIQUES FOR FIBREGLASS PRODUCT MANUFACTURING

TABLE OF CONTENTS

1.0	INTRODUCTION	1
2.0	PROCESSES AND EMISSIONS	3
	2.1 Process Description	3
	2.1.1 Custom Operation	5
	2.1.2 Large Operation	7
	2.2 Emission Sources and Control Technologies	8
	2.2.1 Emissions to Air	8
	2.2.2 Emissions to Water	9
	2.2.3 Emissions to Land	9
3.0	EMISSION ESTIMATION TECHNIQUES	10
	3.1 Direct Measurement	11
	3.1.1 Sampling Data	11
	3.1.2 Continuous Emission Monitoring System (CEMS) Data	13
	3.1.3 Mass Balance	13
	3.1.4 Emission Factors	13
	3.2 Estimating Emissions	14
	3.2.1 Emissions to Air	14
	3.2.2 Emissions to Water	22
	3.2.3 Emissions to Land	22
4.0	EMISSION ESTIMATION TECHNIQUES: ACCEPTABLE RELIABILITY	
	AND UNCERTAINTY	24
	4.1 Direct Measurement	24
	4.2 Mass Balance	24
	4.3 Engineering Calculations	25
	4.4 Emission Factors	25
5.0	REFERENCES	26

FIBREGLASS PRODUCT MANUFACTURING

LIST OF FIGURES, TABLES AND EXAMPLES

Figure	1 - Small Custom Operation Production Area	4
	2 - Large Operation Production Area	6
Table	1 - Typical Fibreglass Manufacturing Processes, Materials Used and Emissions	8
	2 - List of Variables and Symbols	12
	3 - Styrene Emission Factors for Open Moulding Operations	15
	4 - Emission Rate in kg of Methyl Methylacrylate Emitted per tonne of Gel Coat Processed	15
	5 - Solvent Emission Factors	18
Examp	le 1 - Estimating Styrene Emissions	16
	2 - Calculating Parts Cleaning Emissions using Equation 3 and Equation 5	19
	3 - Calculating Parts Cleaning Emissions using Equation 4	19
	4 - Estimating Styrene Emissions to Air	21

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 fibreglass product manufacturing activities.

EET MANUAL:	Fibreglass Product Manufacturing
HANDBOOK:	Plastic Product Rigid Fibre Reinforced Manufacturing
ANZSIC CODE:	2564

The Queensland Environmental Protection Agency drafted this Manual on behalf of the Commonwealth Government. It has been developed through a process of national consultation involving State and Territory environmental authorities and key stakeholders, and has been considered by independent reviewers.

Context and use of this Manual

This Manual provides a "how to" guide for the application of various methods to estimate emissions as required by the NPI. It is recognised that the data that is generated in this process will have varying degrees of accuracy with respect to the actual emissions from fibreglass manufacturing facilities. In some cases there will necessarily be a large potential error due to inherent assumptions in the various emissions estimation techniques (EETs) and/or a lack of available information of chemical processes.

EETs should be considered as 'points of reference'

The EETs and generic emission factors presented in this Manual should be seen as 'points of reference' for guidance purposes only. Each has associated error bands that are potentially quite large (eg. based on generic emission factors only); uncertainties of 100% are considered likely. Chapter 4 discusses the general reliability associated with the various methods. The potential errors associated with the different EET options should be considered on a case-by-case basis as to their suitability for a particular facility. Facilities may use EETs that are not outlined in this document. They must, however, seek the consent of their relevant environmental authority to determine whether any 'in house' EETs are suitable for meeting their NPI reporting requirements.

Hierarchical approach recommended in applying EETs

This Manual presents a number of different EETs, each of which could be applied to the estimation of NPI substances. The range of available methods should be viewed as a hierarchy of available techniques in terms of the error associated with the estimate. Each

substance needs to be considered in terms of the level of error that is acceptable or appropriate with the use of the various estimation techniques. Also the availability of preexisting data and the effort required to decrease the error associated with the estimate will need to be considered. For example, if emissions of a substance are clearly very small no matter which EET is applied, then there would be little gained by applying an EET which required significant additional sampling.

The steps in meeting the reporting requirements of the NPI can be summarised as follows:

- for Category 1 and 1a substances, identify which reportable NPI substances are used (or handled by way of their incidental presence in ore or materials, or exceeds the bulk storage capacity for 1a), and determine whether the amounts used or handled are above the "threshold" values and therefore trigger reporting requirements;
- for Category 2a and 2b substances determine the amount and rate of fuel (or waste) burnt each year, the annual power consumption and the maximum potential power consumption, and assess whether the threshold limits are exceeded;
- for Category 3 substances determine the annual emissions to water and assess whether the threshold limits are exceeded; and
- for those substances above the threshold values, examine the available range of EETs and determine emission estimates using the most appropriate EET.

Generally it will be appropriate to consider various EETs as alternative options whose suitability should be evaluated in terms of:

- the associated reliability or error bands; and
- the cost/benefit of using a more reliable method.

The accuracy of particular EETs is discussed in Section 4.4 Emission Factors.

NPI emissions in the environmental context

It should be noted that the NPI reporting process generates emission estimates only. It does not attempt to relate emissions to potential environmental impacts, bioavailability of emissions, natural background levels etc.

Facilities may undertake 'Ancillary Activities', such as the production of substances, either as a process input or through processing of waste streams. When estimating emissions a facility should ensure that emissions are not 'double accounted' and process maps should be used to minimise the potential for this.

This Manual is structured to allow facilities to work through it and address issues in a structured and coherent manner.

This approach has been adopted in order to demonstrate how an EET may be applied to estimating emissions of a substance and supported by other EETs. For example facilities may choose to use a mass balance approach to their estimation of styrene emissions. However the mass balance EET is likely to be supported by direct monitoring data and emission factors.

2.0 **Processes and Emissions**

The following section presents a brief description of the fibreglass product manufacturing industry and identifies some likely sources of emissions.

2.1 **Process Description**

Fibreglass reinforced plastic (FRP) is used in the manufacture of a diverse range of products including boats, motor vehicle and truck components and accessories, bathroom fixtures, (eg. shower stalls, baths, vanities, and spas), swimming pools, cast furniture, fuel and organic liquid storage tanks and piping, simulated marble products, buttons, surfboards, and bowling balls.

FRP is comprised of unsaturated polyester resins and can be used in reinforced or nonreinforced applications. Eighty per cent of unsaturated polyester resin is used in reinforced applications, usually with glass fibres, and extended with various inorganic fillers such as calcium carbonate, talc, mica, or small glass spheres. Advanced reinforced fibreglass products are now formulated with fibres other than glass, such as carbon, aramid, and aramid/carbon hybrids.

While the composition, shape, and size of the FRP products manufacturing industry vary significantly from one production line to the next, the mould-based manufacturing process is very similar. Most FRP facilities use the following unit processes:

- mould preparation;
- gel-coating and laminating;
- tool and equipment clean-up;
- operation of secondary systems (eg. air filtration and ventilation, resin/gel coat transfer and storage); and
- operation of finish lines (eg. upholstery, painting, etc).

Along with these central processes and techniques, some facilities also have pipe fitting and lining systems, and/or use closed-mould systems and centrifugal moulding systems. Fibreglass product manufacturing activities generate emissions of styrene, methyl methacrylate, particulate matter (PM_{10}), and total volatile organic compounds (VOCs) - all NPI-listed substances.

The styrene content of the resin is from 23 to 35 per cent by weight, and 45 to 55 per cent of the gel coat. Gel coat also contains methyl methacrylate in varying weight percentages. Material safety and data sheets or product suppliers can provide information on the content of listed substances in the resins and gel coats. This information can be used for threshold determination and reporting requirements. For example, 28.6 tonnes of resin containing 35 per cent by weight styrene would have to be consumed during the reporting year for a 10 tonne annual threshold to be tripped and styrene emissions reported. The *NPI Guide* provides a detailed explanation of reporting thresholds for all listed substances.

The following paragraphs provide process descriptions for a small custom FPR operation manufacturing such products as surfboards, shower stalls, and windowsills and for a larger production facility manufacturing products such as spa baths or recreational boats. This characterisation of processes by custom operation and large production operation is necessary as techniques for estimating emissions of NPI-listed substances are determined largely according to the size of normal production activities at each facility. Facility operators preparing an emissions report for the NPI should select the emission factors which best represent their manufacturing processes or choose other emissions estimation techniques from those provided in Section 3.0.

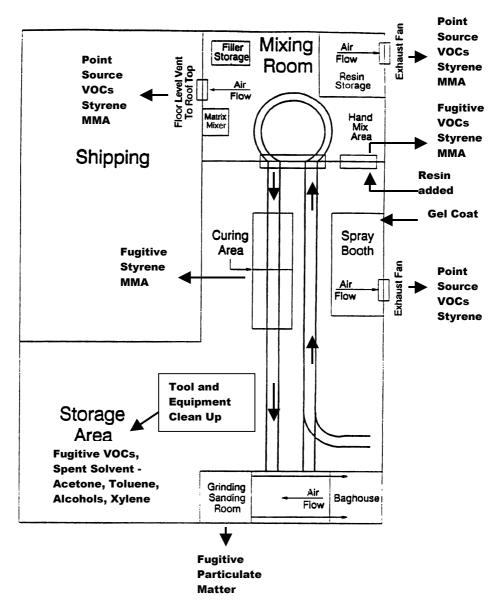


Figure 1 - Small Custom Operation Production Area

2.1.1 Custom Operation

This section describes the production process and emissions at a small, custom fibreglass manufacturing facility. Figure 1 illustrates a schematic of the facility production area and highlights likely emission sources of NPI pollutants - styrene, methyl methacrylate, particulate matter (PM_{10}), and total volatile organic compounds (VOCs). Fibreglass resin and gel coat are usually purchased from distributors in bulk liquid form in 200 litre drums with no vapour suppressors added.

Several steps are taken to complete the product. The first step involves mould preparation. Moulds are hand-made, often using standard patterns. After a mould is formed it is cleaned, waxed, and transported to a spray booth where a thin layer of gel coat is applied. After gel-coating, moulds proceed to the casting process, which takes place in the mixing room. Resin, crushed marble filler, and catalyst are mixed in a closed process and applied to the moulds, which are then mechanically vibrated to remove bubbles and allow the resin to settle. The filled open moulds are allowed to cure and harden in the curing area. After the resin has hardened, the moulds are polished and sanded in the grinding room. Lastly, the finished product is taken to the warehouse for packaging and shipment.

The entire production operation is contained in a large single room with the exception of the grinding and sanding area. This segment of the process is contained in a separate, enclosed area within a large manufacturing room. Workplace health and safety regulations require that air is vented to the outside through a series of exhaust fans. One fan usually exhausts air from the spray booth. A second exhaust fan and a floor level vent connected to a rooftop fan remove air from the resin mixing and casting area. A high efficiency filtration system controls particulate matter generated during the grinding and polishing area. Filtered air from this system is returned to the work place and not vented to the outside of the building. The only control devices used are the grinding room filtration system and a bank of filters at the spray booth.

Emissions of listed substances may originate from several points located within the building as illustrated in Figure 1. Vapour emissions are primarily generated in the spray booth during gel-coating. Vapours are also generated from the automatic resin/catalyst/filler mixer and emissions to wastewater may originate from tool and equipment clean-up and finish line activities.

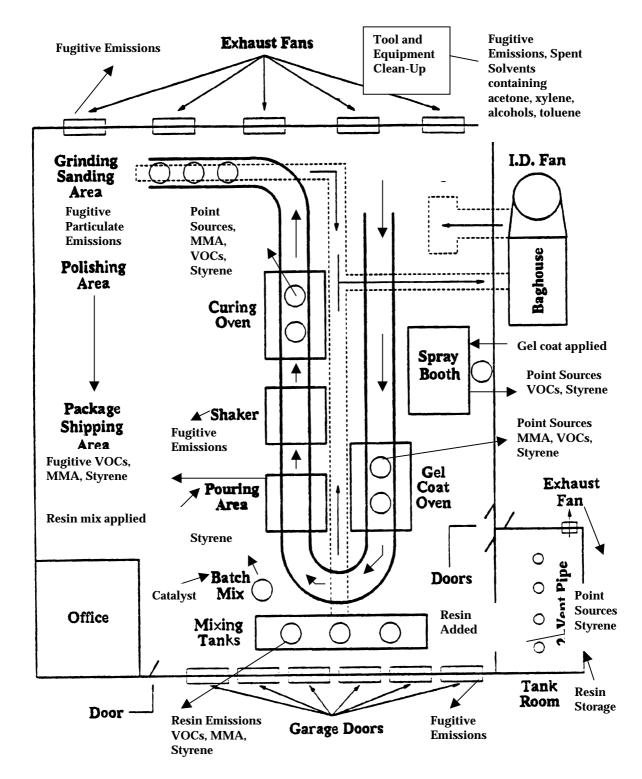


Figure 2 - Large Operation Production Area

2.1.2 Large Operation

Figure 2 illustrates the production area of a large fibreglass product manufacturing operation. Facilities of this nature purchase resin and gel coat in bulk liquid form. The resin is stored on site in large tanks (around 10 000 litres) which are housed in a separate room attached to the manufacturing area. The gel coat is purchased in 200 litre drums. With the exception of the resin storage tanks, which are contained in a separate room, the entire manufacturing operation is housed in a single room. Each day, resin is mixed with crushed filler in large open top mixing vats. Each vat holds upwards of 500 kilograms of mix of which 23 per cent by weight is resin. From these large vats, smaller 50 kilogram working batches are removed as needed. Catalyst is then added to the working batch before the mixture is poured into moulds.

The manufacturing process begins with the cleaning and waxing of moulds. These moulds then proceed to the spray booth, where a thin layer of gel coat resin is applied. A conveyor takes the gel-coated moulds through a gel coat-drying oven. After drying, a pre-mixed composition of resin, filler, and catalyst is manually applied to the moulds using hand held trowels. The back of the mould is then clamped into place and the assembly is mechanically vibrated in the shaker to remove bubbles and allow the resin to settle. The moulds remain on the conveyor and pass through a curing oven before proceeding to the grinding, sanding, and polishing area. Lastly, finished products are taken to the warehouse for packaging and shipment.

Various exhaust fans are used to vent workplace air to the outside of the building. Both the gel coat oven and the curing oven have two ducts each that extend through the roof. The spray booth has a single duct extending through the roof. The tank room has a floor level intake vent that exhausts through a louvred fan mounted on an outside wall. Each of the storage tanks is equipped with a static vent pipe that extends through an outside wall. A high efficiency filtration system controls particulate from the grinding and sanding operations as shown in the dashed lines in Figure 2. Filtered air is returned to the work place and not vented to the outside of the building. Louvred exhaust fans mounted close to the ceiling on the back of the outside wall provide general building exhaust.

Styrene and VOC emissions to atmosphere originate from several points within the building housing the entire operation. The adjacent tank room is also a source of styrene vapours. Styrene is emitted from the spray booth during gel coal application, the gel coat curing oven, and the curing oven. The mixing vats and working batches are also sources of styrene vapours. Emissions to wastewater may originate from tool and equipment clean-up and finish line activities. Table 1 highlights the material inputs and likely emissions of listed substances.

Process	Process and Primary	Primary Emissions of
	Products Used	NPI-Listed Substances
Mould Preparation	Release agents	Air Emissions - styrene and other
	_	volatile organic compounds (VOCs)
Gel-coating and	Resins - containing styrene	such as methyl methacrylate
Laminating	monomer	(MMA), xylene, toluene, acetone,
		alcohols
	Initiators and Catalysts	
		Water Emissions and Emissions to
Equipment and Tool	Reinforcements	Land - spent solvents and still
Clean-up	Solvents- acetone and	bottoms may contain styrene and
_	various alcohols, xylene	alcohols and are often managed
	and toluene	through local sewers. Spilled
Finish Lines (mould	Paints & Stains, Thinners,	materials, spent filters, residual
making, painting,	Adhesives, and Foaming	resin, and out-of-date materials.
Upholstery and foam	Agents - halogenated	
manufacturing lines)	solvents and metals	

 Table 1 - Typical Fibreglass Manufacturing Processes, Materials Used and Emissions

Source: Queensland Environmental Protection Authority, 1999.

2.2 Emission Sources and Control Technologies

2.2.1 Emissions to Air

Air emissions may be categorised as:

Fugitive Emissions

These are emissions that are not released through a vent or stack. Examples of fugitive emissions include dust from stockpiles, volatilisation of vapour from vats, open vessels, or spills and materials handling. Emissions emanating from ridgeline roof-vents, louvres, and open doors of a building as well as equipment leaks, and leaks from valves and flanges are also examples of fugitive emissions. Emission factor EETs are the usual method for determining losses through fugitive emissions.

Point Source Emissions

These emissions are exhausted into a vent (excluding roof vents) or stack and emitted through a single point source into the atmosphere.

Air emission control technologies, such as electrostatic precipitators, fabric filters or baghouses, and wet scrubbers, are commonly installed to reduce the concentration of substances in venting air streams prior to emission.

Where such emission abatement equipment has been installed, and where emission factors from uncontrolled sources have been used in emission estimation, the collection efficiency of the abatement equipment needs to be considered. Guidance on applying collection efficiencies to emission factor equations is provided in later sections.

With regards to emission controls for PM_{10} , in the absence of measured data or knowledge of the collection efficiency for a particular piece of equipment, an efficiency of 90% should be used in the emission factor equation to calculate actual mass emissions. This default should only be used if there is no other available control efficiency.

2.2.2 Emissions to Water

Emissions of substances to water can be categorised as discharges to:

- Surface waters (eg. lakes, rivers, dams, and estuaries);
- Coastal or marine waters; and
- Stormwater.

Because of the significant environmental hazards posed by emitting toxic substances to water, most facilities emitting NPI-listed substances to waterways are required by their relevant State or Territory environment agency to closely monitor and measure these emissions. This existing sampling data can be used to calculate annual emissions.

If no wastewater monitoring data exists, emissions to water can be calculated based on a mass balance or using emission factors.

The discharge of listed substances to a sewer or tailings dam does not require you to report to the NPI (See also Section Three of *The NPI Guide*).

2.2.3 Emissions to Land

Emissions of substances to land on-site include solid wastes, slurries, sediments, spills and leaks, storage and distribution of liquids, and such emissions may contain listed substances. These emission sources can be broadly categorised as:

- surface impoundments of liquids and slurries; and
- unintentional leaks and spills.

3.0 Emission Estimation Techniques

Estimates of emissions of NPI-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.

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

Although the NPI does not recommend the use of one emission estimation technique over other techniques, this section does attempt to evaluate the available emission estimation techniques with regards to accuracy.

Several techniques are available for calculating emissions from fibreglass product manufacturing facilities. The technique chosen is dependent on available data, available resources, and the degree of accuracy sought by the facility in undertaking the estimate. In general, site-specific data that is representative of normal operations is more accurate than industry averaged data, such as the emission factors presented in Section 3.0 of this Manual.

This section discusses the techniques available for estimating emissions from fibreglass product manufacturing and identifies the different techniques of calculation available on a pollutant basis. These emission estimation techniques are listed in no particular order and the reader should not infer a preference based on the order they are listed in this section.

3.1 Direct Measurement

You may wish to undertake direct measurement in order to report to the NPI, particularly if you already do so in order to meet other regulatory requirements. However, the NPI does not require you to undertake additional sampling and measurement. For the sampling data to be adequate and able to be used for NPI reporting purposes, it would need to be collected over a period of time, and to be representative of operations for the whole year.

3.1.1 Sampling Data

Stack sampling test reports often provide emissions data in terms of kg per hour or grams per cubic metre (dry). Annual emissions for NPI reporting can be calculated from this data. Stack tests for NPI reporting should be performed under representative (ie. normal) operating conditions. You should be aware that some tests undertaken for a State or Territory license condition may require the test be taken under maximum emissions rating, where emissions are likely to be higher than when operating under normal operating conditions.

Table 2 lists the variables and symbols used throughout this Manual and indicates the level of information required in estimating emissions of NPI-listed substances from fibreglass manufacturing using the emission estimation techniques illustrated.

Table 2 - List of Variables and Symbols	C 1 1	TT •/
Variable	Symbol	Units
Annual emissions of pollutant i	E _{kpv.i}	kg/yr
Emission factor of pollutant i	\mathbf{EF}_{i}	%, kg/tonne, kg/hr/m²,
		t/yr/unit
Total emissions of pollutant i per hour	\mathbf{E}_{i}	kg/hr
Emissions per tonne of pollutant i	E _{kpt.i}	kg/tonne of resin consumed
Overall Control efficiency for pollutant i,	CE _i	% reduction in emissions
(ie. Emission reduction control factor)		
Number of units in use	NU	units
Concentration of pollutant i	C_{i}	ppm _{v.d} , mass%, mg/L
Amount of pollutant i in sludge	AS _{kpy'i}	kg/yr
"Particles which have an aerodynamic	PM_{10}	
diameter equal to or less than 10		
micrometers"		
Process losses of pollutant i	PL_{i}	kg/yr
Losses in wastewater of pollutant I	WL_i	kg/yr
Molecular weight of pollutant i	MW _i	kg/kg-mole
Stack gas volumetric flow rate	Q	m ³ /sec
Hourly volume of wastewater	Vol	L/hr
Molar volume	V	m ³ /kg-mole
Operating hours	OpHrs	hr/yr
Activity rate	А	kg/yr, t/yr, t/hr
Surface area	area	m ²
Temperature	Т	Celsius

Table 2 - List of Variables and Symbols

Source: modified from Queensland Department of Environment and Heritage, 1998.

At fibreglass manufacturing plants, workplace health and safety data (concentrations) can be used in conjunction with exhaust system flow rates to estimate fugitive emissions of styrene or other pollutants from a room, floor, or building. Direct-reading instruments that may be used to obtain an instantaneous reading of vapour concentrations include photoionisation detectors, portable infrared spectrophotometers, and portable gas chromatographs.

Emissions of volatile organic compounds (VOCs) from some operations, such as hand or spray lay-up or casting and lamination operations, can also be measured by performing a gravimetric analysis.

Use of stack and/or workplace health and safety sampling data is likely to be a relatively accurate method of estimating air emissions from fibreglass manufacturing facilities. However, collection and analysis of air samples from facilities can be expensive and especially complicated where a variety of VOCs are emitted and where most of these emissions are fugitive in nature. Sampling data from a specific process may not be representative of the entire manufacturing operation and may provide only one example of the facility's emissions.

Due to the variable nature of most fibreglass fabrication shops, source testing may not provide an emission estimate or factor that can be used year round with any degree of

confidence. To be representative, sampling data used for NPI reporting purposes needs to be collected over a period of time, and to cover all aspects of production the fibreglass products.

3.1.2 Continuous Emission Monitoring System (CEMS) Data

A continuous emission monitoring system provides a continuous record of emissions over time, usually by reporting pollutant concentration.

Once the pollutant concentration is known, emission rates are obtained by multiplying the pollutant concentration by the volumetric gas or liquid flow rate of that pollutant.

It is important to note that prior to using CEMS to estimate emissions, you should develop a protocol for collecting and averaging the data in order that the estimate satisfies your relevant environmental authority's requirement for NPI emission estimations. Section 3.2.1.2 illustrates how monitoring data can be used to estimate emissions.

3.1.3 Mass Balance

A mass balance identifies the quantity of substance going in and out of an entire facility, process, or piece of equipment. Emissions can be calculated as the difference between input and output of each listed substance. Accumulation or depletion of the substance within the equipment should be accounted for in your calculation.

The mass balance approach requires the addition of all materials containing NPI pollutants received at the facility and then the subtraction of all the known losses or transfers of the material off-site, including finished product and waste materials. The difference is assumed to have been emitted to air, water, or land. The quantity received, and the quantity lost or used should be for the same time period, typically 1 July to 30 June (the NPI reporting year).

Mass balance techniques can be applied across individual unit operations, or across an entire facility. These techniques are best applied to systems with prescribed inputs, defined internal conditions, and known outputs.

It is essential to recognise that the estimates derived using mass balances are only as good as the values used in performing the calculations. For example, small errors in data or calculation parameters (eg. pressure, temperature, stream concentration, flow, and control efficiencies) can result in large errors in the final emissions estimates. Additionally, if sampling of input or output materials is conducted, failure to use representative samples will also contribute to the uncertainty of the result.

3.1.4 Emission Factors

Emission factors are available for several sources and processes for a fibreglass manufacturing facility, and are based on the results of tests performed at one or more facilities within the industry. An emission factor is the pollutant emission rate relative to the level of source activity. However, emission factors are an acceptable method for estimating emissions from all industry sectors and source categories for the NPI where estimations of emissions are required to quantify medium to long-term emission trends.

3.2 Estimating Emissions

This section provides guidance for estimating emissions of styrene, total VOCs, speciated VOCs (eg. methyl methacrylate), and particulate matter (PM_{10}) from fibreglass product manufacturing activities. Examples of the application of the various emission estimation techniques are provided to illustrate some of the calculation techniques available.

3.2.1 Emissions to Air

3.2.1.1 Using Emission Factors

The emission factors presented in this section have been produced by the US *Composites Fabricators Association (1998)*, and are the result of the most comprehensive investigation of styrene emissions conducted for the fibreglass industry. While the model is based on four emissions variable factors, it encompasses all of the influencing factors. These factors are taken into consideration by incorporating a range of testing parameters, which encapsulate a vast majority of conditions, materials and processing techniques found across the fibreglass product manufacturing industry. An MS Excel version of the model can be viewed and downloaded from the CFA website (http://www.cfa-hq.org/techsvcs.htm and downloading the CFA Emissions model. Alternatively, the table of emission factors derived from the model and example calculations below can be used to estimate emissions for NPI reporting.

To obtain a copy of the model from the web page: <u>http://www.cfa-hq.org</u>, click on **Technical Resources**, under **Styrene Emissions** click **on Overview of the CFA Emissions Model**, then choose either 'Open it' or 'Save it to Disk'.

The emission factors in Table 3 encapsulate, in the form of averages, a number of variables that influence styrene emissions in fibreglass manufacturing facilities. These variables include gel time, laminate thickness, ambient air temperature, and material flow rate. By including these variables, the emission factors produce accurate results for an overall estimation of emissions. Other variables that are not included in the emission factors are provided for in the model itself. These include resin styrene content and emission controls such as suppressants, controlled spray, and non-atomised application.

		nual pplication		Mec	hanical Res	in Applicati	Gel C Applica	Filament Winding				
Styrene Content	Bucket & Tool		Uncon Sp				Non-Ato Applic		Uncontrolled Spray	Controlled Spray		
	Α	В	Α	В	Α	В	Α	В	Α	В	Α	В
(% wt)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
33	4.1	2.8	5.6	3.4	4.3	2.7	2.8	1.8	14.7	10.7	6.1	4.0
34	4.4	2.8	6.3	3.9	4.8	3.0	3.2	2.0	15.7	11.5	6.4	4.1
35	4.7	2.9	7.0	4.3	5.4	3.3	3.6	2.2	16.8	12.2	6.6	4.3
36	5.0	2.9	7.7	4.8	5.9	3.7	3.9	2.4	17.8	13.0	6.9	4.5
37	5.3	2.9	8.4	5.2	6.5	4.0	4.3	2.7	18.8	13.7	7.2	4.7
38	5.6	3.0	9.1	5.7	7.0	4.4	4.7	2.9	19.9	14.5	7.5	4.8
39	5.9	3.0	9.8	6.1	7.6	4.7	5.0	3.1	20.9	15.3	7.7	5.0
40	6.2	3.1	10.6	6.5	8.1	5.0	5.4	3.3	21.9	16.0	8.0	5.2
41	6.4	3.1	11.3	7.0	8.7	5.4	5.7	3.6	23.0	16.8	8.3	5.4
42	6.7	3.2	12.0	7.4	9.2	5.7	6.1	3.8	24.0	17.5	8.6	5.6
43	7.0	3.2	12.7	7.9	9.8	6.1	6.5	4.0	25.0	18.3	8.8	5.7
44	7.3	3.3	13.4	8.3	10.3	6.4	6.8	4.2	26.1	19.0	9.1	5.9
45	7.6	3.3	14.1	8.8	10.9	6.7	7.2	4.5	27.1	19.8	9.4	6.1
46	7.9	3.3	14.8	9.2	11.4	7.1	7.6	4.7	28.2	20.6	9.7	6.3
47	8.2	3.4	15.6	9.6	12.0	7.4	7.9	4.9	29.2	21.3	9.9	6.5
48	8.4	3.4	16.3	10.1	12.5	7.8	8.3	5.1	30.2	22.1	10.2	6.6
49	8.7	3.5	17.0	10.5	13.1	8.1	8,7	5.4	31.3	22.8	10.5	6.8
50	9.0	3.5	17.7	11.0	13.6	8.4	9.0	5.6	32.3	23.6	10.8	7.0

Table 3 - Styrene Emission Factors for Open Moulding Operations^c

Source: Composites Fabricators' Association, 1998.

A = Non-Vapour Suppressed

B = Vapour Suppressed

C Units of Table 3 are % of resin emitted as styrene.

Table 4 - Emission Rate in kg of Methyl Methacrylate Emitted per tonne of Gel Coat Processed

MMA content	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	<u>></u> 20
in Gel Coat, % ^ª																				
Kg MM emitted	6.75	13.5	20.25	27	33.75	40.5	47.25	54	60.75	67.5	74.25	81	87.75	94.5	101.25	108	114.75	121.5	128.25	0.75*
per tonne of Gel																				(%MMA)
Coat. ^b																				*2000*0.45

^a Including MMA monomer as supplied, plus any extra MMA monomer added by the molder, but before addition of other additives such as powders, fillers, glass,...etc.

^b Based on gel coat data from NMMA Emission Study

Emissions of styrene can be estimated by application of Equation 1 and the relevant emission factor from Table 3.

Equation 1

 $E_{kpy,i} = A * (EF_i / 100)$

where:

$E_{_{kpy,i}}$	=	emissions of pollutant i, (eg. styrene), kg/yr
A	=	amount of resin used, kg/yr
\mathbf{EF}_{i}	=	emission factor from Table 3, %

Example 1 illustrates the application of Equation 1 and the data from Table 3.

Example 1 - Estimating Styrene Emissions

The correct emission factor from Table 3 can be selected by following steps:

- 1. Select the resin styrene content (% by weight of styrene monomer);
- 2. Select application method;
- 3. Select Non-Vapour Suppressed or Vapour Suppressed; and
- 4. Find correct factor from the table.

A shower stall manufacturer uses a resin with 40% styrene content. The production line utilises mechanical application with controlled spray. The resin is purchased from the supplier in non-vapour suppressed form.

From Table 3, the correct emission factor to use is 8.1%. Purchasing records indicate that 30 tonnes of resin were used during the year. Equation 1 can be used to calculate emissions.

Emissions of Methyl Methacrylate can be calculated using Table 4 and Equation 2.

Equation 2

 $E_{kpy,MMA} = A * EF_{MMA}$

where:

$E_{kpy,MMA} =$	emissions of methyl methacrylate (MMA), kg/yr
A =	amount of gel coat processed, tonne/yr
$\mathrm{EF}_{\mathrm{MMA}}$ =	emission factor from Table 4,
	kg MMA/tonne gel coat processed

3.2.1.2 Emissions from Parts Cleaning

Styrene is soluble in ethanol, methanol, and acetone and these organic solvents are often used in the industry for tool and equipment clean-up and emissions may require reporting where thresholds have been tripped. The solvents used are emitted unless a recovery system is used. Total VOC emissions factors for parts cleaning in cold cleaners, open-top vapour degreasers, or conveyor degreasers are presented in Table 5. Emission factors for cold cleaners and vapour degreasers are in units of tonnes VOC/yr/unit or kg VOC/hr/m². Emission factors for vapour and non-boiling conveyor degreasers are presented only in units of tonnes VOC/yr/unit.

If using emission factors based on the surface area of the exposed solvent, use Equation 3.

Equation 3

 $E_{kpy,VOC} = EF_{VOC} * area * OpHrs * (1 - (CE_i/100))$

where:

$E_{kpy,VOC}$	=	VOC emissions from a cold cleaner or open-top
EF _{voc}		vapour degreaser, kg/yr uncontrolled VOC emission factor for cold cleaners
		or open-top vapour degreasers, kg/hr/m ²
area	=	surface area of solvent exposed to the
		atmosphere, m ²
OpHrs	=	hours per year that the cold cleaner or vapour
		degreaser is in operation, hr/yr
CE _i	=	overall control efficiency for pollutant i, %

Equation 4 can be applied where emission factors based on the number of cleaning units are used.

Equation 4

 $E_{kpy,VOC} = EF_{VOC} * NU * 1000$

where:

E _{kpy,VOC}	. =	VOC emissions from a cold cleaner, an open-top
		vapour degreaser, or a conveyor degreaser, kg/yr
$\mathbf{EF}_{\mathrm{voc}}$	=	VOC emission factor for cold cleaners, open-top
		vapour degreasers, or conveyor degreasers,
		tonne/yr/unit
NU	=	number of cleaning units in use, units
1000	=	conversion factor, kg/tonne

Speciated VOC emissions from parts cleaning may be calculated using Equation 5. The concentration of the VOC species in the cleaning solvent (C_i) can be obtained from a material and safety data sheet or from the manufacturer or supplier.

Equation 5

$$E_{kpy,i} = E_{kpy,VOC} * (C_i/100)$$

where:

E _{kpy,i} =	emissions of VOC species i from parts
13,	cleaning, kg/yr
$E_{kpy,VOC} =$	VOC emissions, calculated using Equation 3 or
1,577,577	Equation 4, kg/yr
$C_i =$	concentration of VOC species i in the cleaning
	solvent, mass %

Table 5 - Solvent Emission Factors

Type of	Activity	Uncontrolled VOC Emission Factors ^a
Degreasing	Measure	
All ^b	Solvent consumed	1000 kg/tonne
Cold cleaner		
Entire unit [°]	Units in operation	0.3 tonne/yr/unit ^f
Waste solvent loss		0.165 tonne/yr/unit
Solvent carryout		0.075 tonne/yr/unit
Bath spray evaporation		0.06 tonne/yr/unit
Entire unit	Surface area and duty	
	cycle ^d	$0.4 \text{ kg/hr/m}^{2 \text{ f}}$
Open top vapour		
Entire unit	Units in operation	9.5 tonne/yr/unit
Entire unit	Surface area and duty	-
	cycle ^e	0.7 kg/hr/m²
Conveyorised vapour		
Entire unit	Units in operation	24 tonne/yr/unit
	Ĩ	
Conveyorised non-boiling		
Entire unit	Units in operation	47 tonne/yr/unit

Source: USEPA, 1995.

^a 100% non-methane VOC.

- ^b Solvent consumption data will provide a more accurate emission estimate than any of the other factors presented here.
- ^c Emissions generally are higher for manufacturing units and lower for maintenance units.

^d For trichloroethane degreaser.

^e For trichloroethane degreaser. Does not include waste solvent losses.

^f Where units are tonne/yr/unit use Equation 4. Where units are kg/hr/m² use Equation 3. All emission factors are rated C.

Example 2 illustrates the use of Equation 3, Equation 4, and Equation 5.

Example 2 - Calculating Parts Cleaning Emissions Using Equation 3 and Equation 5.

This example shows how total and speciated VOC emissions from a cold cleaner may be calculated using an emission factor from Table 5 based on the surface area of the exposed solvent. First total VOC emissions are calculated using Equation 3 and the following data.

EF _{voc}	=	0.4 kg/hr/m^2
area	=	1.2 m ²
OpHrs	=	3000 hr/yr
ĊĒ	=	90% (assumed value)
E _{kpy,VOC}	=	EF _{voc} * area * OpHrs * (1 - (CE _i /100))
15,777	=	0.4 * 1.2 * 3000 * (1 - (90/100))
	=	144 kg VOC/yr

Next, total VOC emissions are speciated using the concentration of VOC species i (mass %), and Equation 5.

$\begin{array}{l} E_{_{kpy,VOC}} = \\ C_{_{i}} \end{array} = \end{array}$	144 kg VOC/yr 99% trichloroethane in cleaning solvent
E _{trichloroethane} =	${ m E_{_{VOC}}}*(C_{_{ m trichloroethane}}/100)$ 144 * (99/100)
=	142.6 kg trichloroethane/yr

Example 3 - Calculating Parts Cleaning Emissions Using Equation 4

This example shows how total VOC emissions can be calculated, from several cold cleaners using Equation 4. An emission factor of 0.3 tonnes/yr/unit from Table 5 can be used where information on surface area of the exposed solvents is not available.

 $\begin{array}{rcl} EF_{\rm VOC} &=& 0.3 \ tonnes/yr/unit\\ NU &=& 5 \ units\\ 1000 &=& 1000 \ kg/tonne\\ E_{\rm kpy,VOC} &=& EF_{\rm VOC} \ ^* \ NU \ ^* \ 1000\\ &=& 0.3 \ ^* \ 5 \ ^* \ 1000\\ &=& 1500 \ \ kg \ VOC/yr \end{array}$

3.2.1.3 Direct Measurement

Sampling test methods can also be used to estimate organic pollutant emission rates from fibreglass manufacturing processes. Variables which influence the accuracy of sampling

tests at fibreglass plants, include capture efficiency, background emissions, stack airflow fluctuations, and skill with instrument calibration. Airflow rates can be determined from flow rate metres or from pressure drops across a critical orifice (an opening).

Sampling test reports often provide chemical concentration data in parts per million by volume (ppmv). Equation 6 can be used to calculate hourly emissions of the substance based on the concentration measurements in the units parts per million (ie. volume of pollutant gas/ 10^6 volumes of dry air, ppm_{v,d}).

Equation 6

 \mathbf{E}_{i}

=

 $(C * MW * Q * 3600) / [22.4 * (T + 273/273) * 10^{6}]$

where:

E _i	=	emissions of pollutant i, kg/hr
С	=	pollutant concentration, ppm _{vd}
MW	=	molecular weight of the pollutant, kg/kg-mole
Q	=	stack gas volumetric flow rate, m^3/s
3600	=	conversion factor, s/hr
22.4	=	volume occupied by one mole of gas at standard temperature
		and pressure (0°C and 101.3 kPa), m ³ /kg-mole
Т	=	temperature of gas sample, degrees Celsius

Actual emissions in kilograms per year can be calculated by multiplying the emission rate in kilograms per hour, by the number of actual operating hours (OpHrs) as shown in Equation 7 and Example 4.

Equation 7

 $E_{kpy,i} = E_i * OpHrs$

where:

$E_{_{kpy,i}}$	=	annual emissions in kg per year of pollutant i
E	=	hourly emissions in kg per hour of pollutant i
OpHrs	s=	annual operating hours in hours per year

Emissions in kilograms of pollutant per tonne of resin consumed can be calculated by dividing the emission rate in kg per hour, by the resin consumption rate (tonnes per hour) during the same period (Equation 8) as shown below. It should be noted that the emission factor calculated below assumes that the selected time period (ie. hourly) is representative of annual operating conditions and longer time periods should be used for NPI reporting where they are available. Use of the calculation is shown in Example 4.

Equation 8

$$E_{kpt,i} = E_i / A$$

where:

${\rm E_{kpt,i}}$	=	emissions of pollutant i (of resin
r v		consumed), kg/t
E _i	=	hourly emissions of pollutant i, kg/hr
A	=	activity rate of resin consumption, t/hr

Example 4 - Estimating Styrene Emissions to Air

This example shows how annual styrene ($C_{s}H_{s}$) emissions can be calculated using the data obtained from stack testing.

С 15.4 ppmv $MW_i =$ 104 kg/kg-mole of styrene = 1500 hr/yr Q 8.58 m³/sec OpHrs = = Α 2 t/hr= = $(C * MW * Q * 3600) / (22.4 * ((T + 273)/273) * 10^{6})$ E_{stvrene} $(15.4 * 104 * 8.58 * 3600) / (22.4 * (298/273) * 10^{6})$ = 49 470 220/24 451 282 = 2.02 kg styrene/hr =

Emissions per year (based on a 1500 hour per year operating schedule) can then be calculated using Equation 7:

E _{kpy,styrene}	=	E _{styrene} * OpHrs
15. 5	=	2.02 kg/hr * 1 500 hr/yr
	=	3030 kg styrene/yr

Emissions in terms of kg per tonne of resin consumed are calculated using Equation 8:

E _{kpt, styrene}	=	styrene
	=	2.02 kg _{stvrene} /hr / 2 tonne resin/hr
	=	1.01 kg styrene emitted per tonne of resin consumed

You should note that mass balance is the preferred method to be used for estimating emissions from parts cleaning.

3.2.1.3 Liquid Storage Tank Emissions

The simplest method for estimating emissions from storage tanks of less than 30 tonnes capacity is to use the air displacement method outlined in the *Organic Chemical Processing Industries EET Manual.* For larger tanks, refer to the *Fuel and Organic Liquid Storage EET Manual.*

3.2.2 Emissions to Water

Because of the significant environmental hazards posed by emitting toxic substances to water, most facilities emitting NPI-listed substances to waterways are required by their relevant State or Territory environment authority to closely monitor and measure these emissions. This existing monitoring data can be used to calculate annual emissions by the use of Equation 9.

Equation 9

$$E_{kpv,i} = (C_i * Vol * OpHrs)/10^6$$

where:

$E_{kpy,i}$	=	emissions of pollutant i, kg/yr
${\displaystyle \mathop{E_{_{kpy,i}}}\limits_{i}}$	=	concentration of pollutant i in wastewater, mg/L
Vol	=	hourly volume of wastewater, L/hr
OpHrs	=	operating hours per year for which data
		applies, hr/yr
10^{6}	=	conversion factor, mg/kg

In applying Equation 9 to water emission calculations, monitoring data should be averaged and only representative concentrations used in emission calculations.

3.2.3 Emissions to Land

Wastewater treatment may transport the reportable substance to a sludge. Large fibreglass product manufacturing facilities are often required to obtain data on the concentration of styrene, and other substances in sludges, as part of their State or Territory licensing requirement. This data can be used to calculate the emissions as kilograms of sludge, multiplied by the concentrations of the substance in the sludge. Alternatively, the loss in the sludge can be estimated by Equation 10. Although listed substances in sludges transferred off-site do not require reporting, determining this loss can assist with determining other process losses or may require reporting if the sludge is stored or disposed of on-site.

Equation 10

$$AS_{kov,i} = (PL_i - WL_i) * OpHrs$$

where:

For organic chemicals in general, some degradation in treatment may occur so not all of the chemical is transferred to the sludge. Facilities can estimate the amount of organic compounds in the sludge by using measured data, or by subtracting the amount biodegraded from the total amount removed in treatment. The amount of removal can be determined from operating data, and the extent of biodegradation of most NPI-listed substances is contained in Appendix III of the *Sewage and Wastewater Treatment* EET Manual. If the biodegradability of the chemical cannot be measured or is not known, reporting facilities should assume that all removal is due to absorption to sludge. The biodegradation rate constant for styrene is $8.64 * 10^{-5}$ kg/kg of sludge biomass.

4.0 Emission Estimation Techniques: Acceptable Reliability and Uncertainty

This section is intended to give a general overview of some of the inaccuracies associated with each of the techniques. Although the National Pollutant Inventory does not favour one emission estimation technique over another, this section does attempt to evaluate the available emission estimation techniques with regards to accuracy.

Several techniques are available for calculating emissions from fibreglass product manufacturing facilities. The technique chosen is dependent on available data, available resources, and the degree of accuracy sought by the facility in undertaking the estimate. In general, site-specific data that is representative of normal operations is more accurate than industry-averaged data.

4.1 Direct Measurement

Use of stack and/or workplace health and safety sampling data is likely to be a relatively accurate method of estimating air emissions from fibreglass product manufacturing facilities. However, collection and analysis of samples from facilities can be very expensive and especially complicated where a variety of NPI-listed substances are emitted, and where most of these emissions are fugitive in nature. Sampling data from a specific process may not be representative of the entire manufacturing operation, and may provide only one example of the facility's emissions.

To be representative, sampling data used for NPI reporting purposes needs to be collected over a period of time, and to cover all aspects of production.

In the case of CEMS, instrument calibration drift can be problematic and uncaptured data can create long-term incomplete data sets. However, it may be misleading to assert that a snapshot (stack sampling) can better predict long-term emission characteristics. It is the responsibility of the facility operator to properly calibrate and maintain monitoring equipment and the corresponding emissions data.

4.2 Mass Balance

Calculating emissions from a fibreglass product manufacturing facility using mass balance appears to be a straightforward approach to emission estimation. However, it is likely that few Australian fibreglass product manufacturing facilities consistently track material usage and waste generation with the overall accuracy needed for application of this method. Inaccuracies associated with individual material tracking, or other activities inherent in each material handling stage, can result in large deviations for total facility emissions. Because emissions from specific materials are typically below 2 percent of gross consumption, an error of only \pm 5 percent in any one step of the operation can significantly skew emission estimations.

4.3 Engineering Calculations

Theoretical and complex equations, or *models* can be used for estimating emissions from fibreglass product manufacturing processes.

Use of emission equations to estimate emissions from fibreglass product manufacturing 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

4.4 Emission Factors

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 the reference section of this document. The emission factor ratings <u>will not</u> 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:

Α	-	Excellent
В	-	Above Average
С	-	Average
D	-	Below Average
E	-	Poor
U	-	Unrated

5.0 References

Composites Fabricators Association. May 1998. CA Open Moulding Emissions Model. Arlington, VA, USA.

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USEPA. April 1993. *Locating and Estimating Air Emissions From Sources of Styrene*. United States Environmental Protection Agency, Office of Air Quality Planning and Standards, EPA 454/R-93-011. Research Triangle Park, NC, USA.

USEPA, January 1995, *Compilation of Air Pollutant Emission Factors, Volume 1: Stationary Point and Area Sources, fifth edition, AP-42. Section 4.6 Solvent Degreasing,* United States Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC, USA.

http://www.epa.gov/ttn/chief/ap42.html

The following EET Manuals are available at the NPI Homepage <u>www.npi.gov.au</u> and from your local <u>E</u>nvironmental Protection Authority:

- Emission Estimation Technique Manual for Surface Coating;
- Emission Estimation Technique Manual for Sewage and Wastewater Treatment; and
- Emission Estimation Technique Manual for Organic Chemical Processing Industries.