

National Pollutant Inventory

Emission Estimation Technique Manual

for

Shipbuilding Repair and Maintenance

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EMISSION ESTIMATION TECHNIQUES FOR

SHIPBUILDING REPAIR AND MAINTENANCE

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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 shipbuilding and repair.

The activities covered by this Manual include facilities primarily engaged in the building, repair and maintenance of ships, barges and other large vessels as well as smaller nonocean going vessels primarily used for recreation, fishing and transport.

EET MANUAL:	Shipbuilding Repair and Maintenance
HANDBOOK:	Shipbuilding
ANZSIC CODE:	2821, 2822

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

The scope of this Manual is presented diagrammatically in Figure 1.



Figure 1 - Scope of the Shipbuilding Repair and Maintenance Manual

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 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 to 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. Section 5.4 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 Manual. 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 pre-existing data and the effort required to decrease the error associated with the estimate will need to be considered. For example, there would be little gained by applying an EET that required significant additional sampling, if emissions of a substance are clearly very small no matter which EET is applied.

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 5.4 - 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, bio-availability of emissions or natural background levels.

Facilities may undertake 'Ancillary Activities', such as the production of a substance, either as a process input or through processing of waste steams. 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 the Manual addressing issues in a structured and coherent manner.

Likely emissions from facilities are discussed as are the approach to emissions estimation and those elements of the environment where emissions may result.

2.0 **Processes and Emissions**

2.1 **Process Description**

This section describes common production processes used in the shipbuilding and repair industry and the likely emissions of NPI-listed substances. The Australian shipbuilding and repair industry produces a wide range of products including ships, barges, submarines and other large vessels as well as smaller vessels primarily used for recreation, fishing and transport. This industry has characteristics of both manufacturing and construction. Numerous processes are involved depending on construction materials and shipyard layout. This Manual covers building, re-fitting, and overhauls including dry dock operations such as hull cleaning and re-painting.

Significant production processes include those used in foundry operations, metal working, construction, solvent cleaning and degreasing, surface preparation and painting. More detailed descriptions of other processes carried out at shipyards and their emissions are contained in the *Ferrous Foundries*, *Combustion Engines*, *Combustion in Boilers*, *Non-Ferrous Foundries*, *Electroplating and Anodising*, *Fuel and Organic Liquid Storage*, *and The Electronics and Computer Industry EET Manuals*. Users of this Manual may also need to consult these Manuals for more details on emission estimation techniques for particular processes.

The structural framework of most large ships is constructed of various grades of mild and high strength steel. Smaller ships are usually constructed of aluminium, wood or composite materials such as fibreglass. Other metals such as stainless steel, galvanised steel, and copper and nickel alloys are used in shipbuilding in areas requiring specific corrosion resistance.

Shipyards are generally made up of specific facilities laid out to facilitate the flow of materials and assemblies. Some shipyards build only large ships and also have repair and dry dock facilities. Other shipyards have facilities for building small and medium sized vessels such as patrol boats, fire and rescue boats, water taxis, ferries, tug boats, fishing boats and shallow drafted barges.

A shipyard consists of a number of major production facilities with supporting workshops and services. The steps involved in building a ship include:

- handling raw materials and fabricating basic parts;
- joining fabricated parts into assembled parts;
- joining fabricated and assembled parts into sub-block assemblies which are in turn fitted together to form blocks;
- fitting and welding blocks together to erect the ship; and,
- outfitting the ship with fabricated parts that are not structural in nature.

Ship repair includes conversions, overhauls and maintenance as well as major and minor damage repairs. Maintenance includes cleaning and blasting and re-painting the hull.

2.2 Metal Working and Assembly

Cutting oils and lubricants are used to cool high-speed tools used in cutting, pressing, boring, milling, and grinding metals. Solvents are frequently used to clean parts and tools prior to and after machining.

2.3 Surface Preparation

Surface preparation is a very important step in the shipbuilding industry. Without proper surface preparation, subsequent surface coatings will prematurely fail due to poor adhesion. Surface preparation is also typically one of the most significant sources of shipyard wastes and pollutant outputs. Surface preparation techniques are used to remove surface contaminants such as mill scale, rust, dirt, dust, salts, old paint, grease, and flux. Contaminants that remain on the surface are the primary causes of premature failure of coating systems. Depending on the surface location, contaminants, and materials, a number of different surface preparation techniques are used in the shipbuilding and repair industry.

2.3.1 Solvent, Detergent and Steam Cleaning

The surfaces of metals used in shipbuilding are often cleaned and degreased with organic solvents. Solvent cleaning involves wiping, scrubbing, immersion in solvent, spraying, vapour degreasing, and emulsion cleaning the surface with rags or brushes until the surface is cleaned. Cold cleaning refers to operations in which the solvent is used at room temperature. The surfaces or parts are soaked in a tank of solvent, or sprayed, brushed, wiped, or flushed with solvent. Diphase cleaning is sometimes used to combine a water rinse before and after the solvent cleaning into a single step. In diphase cleaning, water insoluble halogenated solvents and water are placed in a single tank where they separate with the solvent on the bottom. Parts are lowered through the water bath before reaching the solvent and are then rinsed through the water level as they are removed from the tank. In vapour degreasing, parts and surfaces are cleaned with a hot solvent vapour. Solvent in a specially designed tank is boiled, creating a solvent vapour in the upper portion of the tank. The parts are held in the vapour zone where solvent vapour condenses on the surface, removing dirt and oil as it drips back into the liquid solvent.

In this way, only clean solvent vapours come in contact with the part. A condensing coil at the top of the tank reduces the amounts of solvent escaping to the atmosphere.

Inorganic compounds such as chlorides, sulfates, weld flux, rust and mill scale cannot be removed with organic solvents. In many cases steam cleaning is a better alternative to solvent wipe down. Steam cleaning or high-pressure washing is used to remove dirt and grime that is present on top of the existing paint, and bare steel. Many hot steam cleaners with detergents will remove most petroleum products and sometimes, old chipping paint. Further surface preparation may be required before painting.

2.3.2 Abrasive Blasting

Abrasive blasting is the most common method for paint removal and surface preparation. Copper slag, coal slag, steel grit, steel shot, glass and garnet are common blasting abrasives that provide a range of particle size and hardness.

Centrifugal blasting machines also called roto-blasting or automatic blasting, are one of the more popular methods of blasting steel surfaces. In centrifugal blasting, metallic shot or grit is propelled to the surface to be prepared by a spinning wheel. Parts to be prepared must be brought to the machine and passed through on a conveyor or rotary table. The process allows easy recovery of abrasive materials for reuse and recycling which can result in significant savings in materials and disposal costs.

In air nozzle blasting (or dry abrasive blasting), abrasive is conveyed to the surface to be prepared in a medium of high pressure air (approximately 689.5 kPa) through a nozzle at velocities approaching 500 km/hr. Traditionally, sand was used as the abrasive, but it is being replaced by metallic grit due to the adverse health and environmental effects of silica dust associated with sand blasting. Air nozzle blasting is generally carried out manually by shipyard workers either within a building or in the open air, depending on the application. If the application allows, blast booths can be used for containing abrasives.

2.3.3 Wet Abrasive blasting and Hydro-blasting

Wet abrasive blasting and hydro-blasting are generally performed on ships to remove chipping paint, marine growth including organisms, mud, and salt water from the ship's hull while it is in a floating dry-dock, graving dock, or other building or repair positions. Wet abrasive blasting involves blasting with a mixture of water, air and solid abrasives. Hydro-blasting is a widely used wet blasting technique which uses only high pressure water. Hydro-blasting is often followed by air nozzle blasting for final surface preparation.

2.3.4 Metal Plating

Metal plating and surface treatment are used in shipyards to alter the surface properties of the metal in order to increase corrosion or abrasion resistance, and to improve electrical conductivity. Metal plating and surface treatment includes chemical and electrochemical conversion, case hardening, metallic coating, and electroplating. Descriptions of these processes and their associated wastes are contained in the *Emission Estimation Manual for Electroplating and Anodising*.

2.3.5 Chemical Surface Preparation

Chemical surface preparations consist of paint removers, alkaline cleaning solutions, chlorinated solvents, and pickling acids.

Alkaline cleaners can be brushed or sprayed on, and applied in a dip tank. Alkaline dip tanks of caustic soda solution are frequently used for cleaning parts and preparing them for painting. After the surface is cleaned, it is thoroughly rinsed before a coating system is applied. Many solvents and alkaline cleaners cannot be used for nonferrous materials, (eg. bronze, aluminium, and galvanised steel) which are frequently found on ships.

Pickling is a process of chemical abrasion/etching that prepares surfaces for good paint adhesion. The pickling process is used in shipyards mainly for preparing pipe systems and small parts for paint. The process involves a system of dip tanks and is illustrated in Figure 2. Caustic soda is used to remove oil, grease, flux, and other contaminants from the surface of steel parts, which are then rinsed and dipped in sulfuric acid and phosphoric acid. Copper-nickel alloy or copper parts are dipped in hot dilute nitric acid and rinsed. Once the part is dry, the final coating can be applied.



Source: USEPA, November 1997

Figure 2 - Typical Pickling Tank Arrangement

2.4 Surface Coating

Surface coating systems are essential in the shipbuilding and repair industry to prevent corrosion and deterioration of the structure and component parts of ships. Painting is performed at many stages from the initial priming of the steel, to the final paint detailing of the ship. The nature of shipbuilding and repair requires several types of paints to be

used for a variety of applications. Paint types range from water-based coatings to high performance epoxy coatings. The type of paint needed for a certain application depends on the environment to which the coating will be exposed. Many factors are considered when choosing a particular application.

In general there are six areas where shipboard paint requirements exist:

- Underwater (Hull Bottom);
- Waterline;
- Topside Superstructures;
- Internal Spaces and Tanks;
- Weather Decks; and
- Loose Equipment

2.4.1 Paint Coating Systems

Paints are made up of three main ingredients: pigment, binder, and a solvent vehicle. Pigments are small particles that generally determine the colour as well as many other properties associated with the coating. Examples of pigments include: zinc oxide, talc, carbon, coal tar, lead, mica, aluminium, and zinc dust. The binder can be thought of as the glue that holds the paint pigments together. Many paints are referred to by their binder type, (ie. epoxy, alkyd, urethane, vinyl, phenolic, etc.). The binder is also very important for determining a coating's performance characteristics (eg. flexibility, chemical resistance, durability, finish, etc.). The solvent is added to thin the paint so that it will flow to the surface and then dry. The solvent portion of the paint evaporates when the paint dries. Some typical solvents include acetone, mineral spirits, xylene, methyl ethyl ketone, and water. Anticorrosive and antifouling paints are typically used on ship hulls and are the main two types of paint used in the shipbuilding industry.

Antifouling paints are used to prevent the growth of marine organisms. Copper-based and tributyl-tin (TBT) -based paints are widely used as antifouling paints, though TBT may only be used on vessels longer than 25 metres and with regulatory authority approval. These paints release small quantities of toxins, which discourage the marine life from growing on the hull. Anticorrosive paints are vinyl, lacquer, urethane, or newer epoxybased coating systems.

The first coating system applied to raw steel sheets and parts is generally pre-construction primer. This pre-construction primer is sometimes referred to as shop primer. This coat of primer is important for maintaining the condition of the part throughout the construction process. Pre-construction priming is performed on steel plates, shapes, sections of piping, and ventilation ducting. Most pre-construction primers are zinc-rich with organic or inorganic binders. Zinc silicates are predominant among the inorganic zinc primers. Zinc coating systems protect coatings in much the same manner as galvanising. If zinc is coated on steel, oxygen will react with the zinc to form zinc oxide, which forms a tight layer that does not allow water or air to come into contact with the steel.

2.4.2 Paint Application Equipment

There are many types of paint application equipment used in the shipbuilding industry. The most widely used form of paint application in the shipbuilding industry is the airless sprayer.

The airless sprayer is a system that simply compresses paint in an hydraulic line and has a spray nozzle at the end. Airless sprayers can have up to 90% transfer efficiency and are much cleaner to operate than compressed air systems.

Thermal spray is the application of aluminium or zinc coatings to steel for long term corrosion protection. Thermal spray is significantly different to conventional coating practices due to its specialised equipment and relatively slow production rates. There are two basic types of thermal coating machines: combustion wire and electric arc spray. The combustion wire type consists of combustible gases and flame system with a wire feed controller. The combustible gases melt the material to be sprayed onto the parts. The electric arc spray machine uses a power supply arc to melt the flame sprayed material.

2.5 Fibreglass

Many of the medium and small shipyards manufacture and repair fibreglass ships and boats, or construct fibreglass parts for steel ships. The process involves combining polymerising resin with fibreglass reinforcing material. The resin is polymerised with a catalyst or curing agent.

Typical resins used include polyesters, epoxies, polyamides, and phenolics. The type of resin to be used in a particular process depends on the specific properties required for the end product. The resin is supplied in liquid form and may contain a solvent. Resin preparation involves mixing with solvents, catalysts, pigments, and other additives. The fibreglass content of the reinforced product ranges from 25 to 60 percent. Acetone, methanol, methyl ethyl ketone, and styrene are commonly used as solvents. Various amines, anhydrides, aldehyde condensation products, and Lewis acid products are used as catalysts. Gelcoat is a pigmented polyester resin or a polyester resin-based paint, containing approximately 35 percent styrene that is applied to the mould or surface with an air atomiser or airless spray gun. A catalyst is injected into the resin in a separate line or by hand mixing in order to thermoset the polyester resin.

A number of different processes are used, but the mould-based process is the most common for this industry. Mould-based fibreglass reinforced construction typically involves either the hand application or spray application of fibreglass reinforcing. In the hand application method, the reinforcing material is manually applied to a mould wetted with catalysed resin mix or gelcoat and then sprayed or brushed with more resin or gelcoat. In the sprayup method, catalysed resin and fibreglass reinforcement are mechanically sprayed onto the mould surface. Most moulds are made of wood with a plastic finish.

2.6 Emission Source Categories and Control Technologies

2.6.1 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 and the 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 ducting 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.

2.6.2 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. However, leakage and other emissions (including dust) from a tailings storage facility are reportable. (See also Section Three of the *NPI Guide*).

2.6.3 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;
- unintentional leaks and spills; and
- emissions to groundwater.

3.0 Emission Estimation Techniques

Numerous processes are employed in the shipbuilding and repair industry. Many of these processes are common to other manufacturing and construction sectors. Other EET Manuals in this series that are available to assist in estimating emissions from the shipbuilding and repair industry include:

- Combustion Engines;
- Combustion in Boilers;
- Ferrous Foundries;
- Non-Ferrous Foundries;
- Fuel and Organic Liquid Storage;
- Electroplating and Anodising; and
- The Electronics and Computer Industry.

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. 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^a 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.

 \underline{PM}_{10} is a category 2a substance. You should report your facility's emissions of category 2a substances if your facility: burns 400 tonnes or more of fuel or waste in a year; or burns 1 tonne or more of fuel or waste in an hour at any time during the reporting year.

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 licence 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.

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 emissions estimations.

3.1.3 **Predictive Emission Monitoring (PEM)**

Predictive emission monitoring is based on developing a correlation between pollutant emission rates and process parameters. PEM allows facilities to develop site-specific emission factors, or emission factors more relevant to their particular process.

Based on test data, a mathematical correlation can be developed that predicts emissions using various parameters.

3.2 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.

Mass balance calculations for estimating emissions to air of NPI-listed substances can be represented conceptually by Equation 1.

Equation 1

 $E_{kpy,i} = Amount in_i - Amount out_i$

where:

E _{kpv.i}	=	emissions of pollutant i, kg/yr
Amount in _i	=	amount of pollutant i entering the
		process, kg/yr
Amount out _i	=	amount of pollutant i leaving the
		process as a waste stream, article or
		product, kg/yr

"Amount out_i" could include the amount recovered or recycled, the amount leaving the process in the manufactured product, the amount leaving the process in wastewater, the amount emitted to the atmosphere, or the amount of material transferred off-site as hazardous waste or to landfill. A thorough knowledge of the different destinations for the pollutant of interest including possible chemical conversion of pollutant i in the process is necessary for an accurate emission estimate to be made using the mass balance approach.

3.3 Engineering Calculations

An engineering calculation is an estimation method based on physical/chemical properties (eg. vapour pressure) of the substance and mathematical relationships (eg. ideal gas law).

3.4 Emission Factors

An emission factor is a tool that is used to estimate emissions to the environment. In this Manual, it relates the quantity of substances emitted from a source to a common activity associated with those emissions. Emission factors are obtained from US, European, and Australian sources and are usually expressed as the weight of a substance emitted, divided by the unit weight, volume, distance, or duration of the activity emitting the substance.

Very few emission factors have been developed specifically for the shipbuilding and repair industry. Many of the processes are common to other industries and emission factors can be obtained from the EET Manuals listed at the beginning of this section.

Table 3 gives emission factors for solvents that may be used for cleaning and surface degreasing in the shipbuilding and repair industry.

4.0 Inputs and Emissions of NPI-Listed Substances

4.1 Introduction

This section identifies the by-products and wastes that may be emitted from processes used in the shipbuilding and repair industry. The many different production processes employed in shipbuilding and repair require a vast amount of material inputs and generate large amounts of waste and considerable emissions. The outputs resulting from the various stages of production range from air emissions from foundry operations, to spent solvents from surface painting and finishing. Many of the material inputs and emissions are of NPI-listed substances.

Raw material inputs to the shipbuilding and repair industry are primarily steel and other metals, paints and solvents, blasting abrasives, and machine and cutting oils. In addition, a variety of chemicals are used for surface preparation and finishing such as solvent degreasers, acid and alkaline cleaners, and plating solutions containing heavy metal and cyanide ions. Pollutants and wastes generated include volatile organic compounds (VOCs), particulates (PM_{10}), waste solvents, oils and resins, metal bearing sludges and wastewater, waste paint, waste paint chips, and spent abrasives. The major shipyard activities that generate wastes and pollutant outputs are summarised in Table 1 and discussed below.

Industrial Process	Material Inputs	Air Emissions	Wastewater	Residual Wastes
Surface Preparation	Abrasives (steel shot, lead shot, steel grit, garnet, copper slag, and coal slag), detergents, VOCs from solvent paint strippers and cleaners, and caustic solutions	Particulates (metal, paint, and abrasives) and VOCs from solvent cleaners and paint strippers	Wastewater contaminated with paint chips, cleaning and paint stripping solvents, surface contaminants, and oil residues from bilges and cargo tanks.	Paint chips (potentially containing metals, tributyl-tin), spent abrasives, surface contaminants, organic matter from marine growth and cargo tank residues.
Metal Plating and Surface Finishing	Plating metals, cyanide solutions cleaning solvents, rinse water, acid and caustic solutions and rust inhibitors.	Metal mists and fumes, and VOCs from solvents.	Rinse and quench water contaminated with metals, cyanides, acids, alkalies, organics, and solvents.	Sludge from wastewater treatment, spent plating solutions and cyanide solutions, bath cleaning residues.
Painting	Paints (containing lead, zinc, chromium, copper and tin compounds), solvents, and water.	VOCs from paint solvents and equipment cleaning solvents, and metal pigments in overspray where relevant.	Waste equipment- cleaning water and water wash spray paint booth sump water contaminated with paints and solvents.	Leftover paint (containing lead, zinc and tin compounds) and solvents, waste paint and solvent containers, spent paint booth filters, and spent equipment.
Fibreglass Reinforced Construction	Fibreglass, resin, solvents, curing catalysts, and wood and plastic reinforcing materials.	VOC emissions released during construction operations and curing (eg. styrene) and during cleaning with solvents (eg. acetone and methylene chloride).	Little or no wastewater generated.	Waste fibreglass, gelcoat, resin, unused resin that has exceeded its shelf life, spent solvents, and used containers.
Machining and Metal Working	Cutting oils, lube oils, and solvents.	VOC emissions from the use of cleaning and degreasing solvents.	Wastewater containing solvents, emulsified lubricating and cutting oils and coolants.	Waste cutting oils, lube oils, and metal chips and shavings.

 Table 1 - Material Inputs and Potential Pollutant Outputs for the Shipbuilding Repair and Maintenance Industry

Source: USEPA Sector Handbook 1997

4.2 Maintenance Operations

Maintenance operations encompass a variety of applications from surface coating of hulls and ancillary equipment to the degreasing of bearings or other weathered components both on vessels and on shore plant and equipment. Table 2 illustrates some of the inputs and possible emissions of NPI-listed substances that can be anticipated from port maintenance operations. The operations listed in Table 2 are not exhaustive and serve as a guide to assist facility operators to identify possible uses and emissions of NPI-listed substances.

Process	Material Inputs	Possible Emissions of NPI-Listed Substances
Engineering operations	Degreasing agents, solvents, acids	spent solvents, VOCs, waste acids
Rust removal	Acids, abrasive blasting materials	waste acids, PM ₁₀
Paint preparation	Solvents (thinners), white spirits, enamel reducers	spent solvents, VOCs
Surface coating and finishing	Enamels, paints, electroplating substances, galvanising metals, acids	spent solvents, VOCs, metals, waste acids
Engine Repairs	Degreasing agents, solvents, acids	spent solvents, VOCs, waste acids

 Table 2 - Inputs and Emission Sources of Maintenance Operations

Source: Queensland Department of Environment and Heritage, 1998.

4.3 Foundry Operations

Melting and casting metals generates both gaseous and particulate emissions (PM_{10}). The wastewaters generated during foundry operations may also contain NPI-listed substances. Wastewaters are generated primarily during slag quenching operations (ie. water is sprayed on the slag to cool it and pelletise it) and by the wet scrubbers employed as air pollution control devices connected to furnaces and sand and shakeout operations. Foundries may also use NPI-listed organics and mineral acids for cleaning which, when spent, may be collected and recycled on-site or transferred off-site to a recycle contractor.

4.4 Metal Working and Assembly

Cutting oils and lubricants are used to cool high-speed tools used in cutting, pressing, boring, milling, and grinding metals. Solvents are frequently used to clean parts and tools prior to and after machining.

Air Emissions

Fugitive air emissions arise from the use of solvents for cleaning and degreasing.

Residual Wastes

Waste cutting oils, lube oils, and degreasing solvents are the major residual wastes generated. Metal shavings and chips are also generated. If necessary, these are separated from coolants, and recycled along with scrap metal.

Waste-water

Wastewaters containing cleaning solvents and emulsified lubricants, coolants, and cutting oils may be produced if parts are cleaned or rinsed with water. In addition, some modern lubricating oils and grease are being formulated with limited or no mineral oil content. These lubricants are known as high water content fluids. When spent they can result in wastewater comprised of a maximum of 15 percent mineral oil emulsified in water.

Source: USEPA Sector Handbook 1997

4.5 **Surface Preparation**

The materials used and wastes generated during surface preparation depend on the specific methods used. The surface preparation method is chosen based on the condition of the metal surface (eg. coated with paint, rust, scale, dirt, grease, etc.), the type of coating to be applied, the size, shape, and location of the surface, and the type of metal. Material inputs used for preparing surfaces include: abrasive materials such as steel shot or grit, glass, garnet, copper or coal slag; cleaning water, detergents, and chemical paint strippers (eg. methylene chloride-based solutions, caustic solutions, and solvents). In the case of hydro blasting, only water and occasionally rust inhibitors are required.

4.5.1 Chemical Preparation

Chemical surface preparations consist of paint removers, alkaline cleaning solutions, chlorinated solvents, and pickling acids.

4.5.1.1 Solvent Cleaning

The type of solvent used in parts and surface cleaning and degreasing depends on the type of contaminants to be removed, degree of cleaning needed, properties of the surfaces to be cleaned, and properties of the various solvents (stability, toxicity, flammability, and cost). Both halogenated and non-halogenated solvents are used and mixtures of different solvents are common. Typical cleaning and degreasing solvents include mineral spirits, aromatic hydrocarbons (eg. xylenes, toluene, etc), aliphatic hydrocarbons, ketones, esters, alcohols, glycol ethers, phenols, turpentine, and various halogenated solvents, for example, trichloroethylene, 1,1,1-trichloroethane, and perchloroethylene.

Air Emissions

Solvent vapours comprised of VOCs are a significant pollutant output of cleaning and degreasing operations. Fugitive emissions arise from vapour degreasers, solvent tanks and containers, solvent stills, solvent soaked rags, and residual solvents on parts and surfaces.

Residual Wastes

Residual wastes may include contaminated or spent solvents, solvents that have become contaminated or deteriorated due to improper storage or handling, solvent residues and sludges from tank bottoms and still bottoms, solvent contaminated rags and filter cartridges, and solvent contaminated soil from solvent spills.

Wastewater

Wastewater containing solvents is generated when cleaning or rinsing parts or surfaces, and when cleaning equipment, tanks, and process lines with water. Wastewater contaminated with solvents is also generated when water from diphase parts cleaning operations is replaced.

Source: USEPA Sector Handbook 1997

Emissions from Equipment Cleaning

VOC emissions factors for parts cleaning in cold cleaners, open-top vapour degreasers, or conveyor degreasers are presented in Table 3. 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 2.

Equation 2

 $E_{kpy,VOC} = EF_{VOC} * area * OpHrs$

where:

E _{kpy,VOC}	=	VOC emissions from a cold cleaner or
10		open-top vapour degreaser, kg/yr
EF _{voc}	=	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
area OpHrs	=	open-top vapour degreasers, $kg/hr/m^2$ surface area of solvent exposed to the atmosphere, m^2 hours per year that the cold cleaner or vapour degreaser is in operation, hr/yr

Use Equation 3 if using emission factors based on the number of cleaning units.

Equation 3

$$\mathbf{E}_{_{\mathrm{kpy,VOC}}} = \mathbf{EF}_{_{\mathrm{VOC}}} * \mathbf{NU} * \mathbf{1000}$$

where:

E _{kpy,VOC}	=	VOC emissions from a cold cleaner,
		an open-top vapour degreaser, or a
		conveyor degreaser, kg/yr
EF _{voc}	=	VOC emission factor for cold cleaners,
		open-top vapour degreasers, or convey
		or degreasers, tonne/yr/unit
NU	=	number of cleaning units in use, units
1 000	=	conversion factor, 1000 kg/tonne
		•

Speciated VOC emissions from parts cleaning may be calculated using Equation 4.

Equation 4

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

where:

$E_{kpy,i}$	=	emissions of VOC species i from
15.		parts cleaning, kg/yr
E _{kpv.VOC}	=	VOC emissions, calculated using
15,		Equation 2 or Equation 3, kg/yr
C _i	=	concentration of VOC species i in the
		cleaning solvent, mass %

Example 1 and Example 2 illustrate the application of Equation 2, Equation 3 and Equation 4 and the emission factors from Table 3.

Type of Degreasing	Activity Measure	Uncontrolled Organic Emission Factor ª (kg/tonne)
All ^b	Solvent consumed	1000 kg/tonne
Cold cleaner		
Entire unit $^{\circ}$	Units in operation	0.30 tonne/yr/unit
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 kg/hr/m^2
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
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.
 All emission factors are rated E. See Section 5.0.

Example 1 - Calculating Emissions from Equipment Cleaning Using Equation 2 and Equation 4

This example shows how total and speciated VOC emissions from a cold cleaner may be calculated using an emission factor from Table 3 based on the surface area of the exposed solvent. First total VOC emissions are calculated using Equation 2 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))
1.5,****	=	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 %), in Equation 4

$\begin{array}{c} E_{_{kpy,VOC}} \\ C_{_i} \end{array}$	=	144 kg ' 99% trie	VOC/yr chloroethane i	n cleaning solvent
E _{trichloroeth}	ane	= = =	E _{VOC} * (C _{trichloroeth} 144 * (99/100) 142.6 kg trich	_{ane} /100)) loroethane/yr

Example 2 - Calculating Emissions from Equipment Cleaning Using Equation 3

This example shows how total VOC emissions can be calculated, from several cold cleaners using Equation 3. An emission factor of 0.3 tonnes/yr/unit from Table 3 can be used where information on surface area of the exposed solvents is not available.

EF _{voc} NU 1000	=	0.3 tonnes/yr/unit 5 units
E _{kpy,VOC}	=	EF _{voc} * NU * 1000
	=	0.3 * 5 * 1000 1500 kg VOC/yr

4.5.1 Abrasive Blasting

The materials used and wastes generated during surface preparation depend on the specific methods used. The surface preparation method is chosen based on the condition of the metal surface (eg. coated with paint, rust, scale, dirt, grease, etc.), the type of coating to be applied, the size, shape, and location of the surface, and the type of metal. Material inputs used for preparing surfaces include: abrasive materials such as steel shot or grit, glass, garnet, copper or coal slag, caustic solutions, and solvents). In the case of hydro blasting, only water and occasionally rust inhibitors are required.

Particulate matter is emitted from abrasive blasting. The particulate matter may contain NPI-listed metals such as lead, chromium, zinc and organo-tin which are present in materials used for abrasive blasting and as components of the paint. The USEPA (1994) emission estimation technique assumes that between 1 and 10 percent of the blast media and the abraded material paint are emitted to air.

Air Emissions

Air emissions from surface preparation operations include particulate emissions of blasting abrasives, and paint chips. Particulate emissions can also contain toxic metals, which are a concern both in the immediate area surrounding the work, and if they are blown off-site or into surrounding surface waters. Particulate emissions are typically controlled by preparing surfaces indoors when possible or by surrounding the work area with shrouding fences made of steel, plastic, or fabric. Other air emissions that could potentially arise during surface preparation operations are VOCs, arising from the use of solvent cleaners, paint strippers, and degreasers.

Residual Wastes

The primary residual waste generated is a mixture of paint chips and used abrasives. Paint chips containing lead or antifouling agents may be hazardous, but often in practice the concentration of toxic compounds is reduced, due to the presence of considerable amounts of spent blasting medium. Waste sludge containing paint chips and surface contaminants may also be generated in the case of hydro-blasting or wet abrasive blasting. Blasting abrasives and paint chips that collect in tank vessels, ship decks, or drydocks should be thoroughly cleaned up and collected after work is completed, or before the drydock is flooded or submerged. Particular attention should be paid to the cleanup of paint chips containing the antifouling tributyl-tin (TBT) compounds, which have been shown to be highly toxic to oysters and other marine life.

Wastewater

Significant quantities of wastewater can be generated when cleaning ship cargo tanks, ballast tanks, and bilges prior to surface preparation and painting. Such wastewater is often contaminated with cleaning solvents, and oil and fuel from bilges and cargo tanks. Wastewater contaminated with paint chips and surface contaminants is generated when hydro-blasting and wet abrasive blasting methods are used. Source: USEPA Sector Handbook 1997

Table 4 presents total PM, PM_{10} and $PM_{2.5}$ emission factors for abrasive blasting of mild steel surfaces. The factors will vary with the type of abrasive used and the targeted surface.

Source	Particle Size	Emission Factor kg/tonne of	Factor Rating
		abrasive material	
Sand blasting of mild	Total PM		
steel panels -	8 km/hr	27	E
uncontrolled	16 km/hr	55	E
	24 km/hr	91	E
	PM_{10}	13	Е
	$PM_{2.5}$	1.3	E
Abrasive blasting of unspecified metal parts using garnet and controlled with fabric filter	Total PM	0.69	Е

 Table 4 - Emission Factors for Abrasive Blasting

Source: USEPA AP-42 Section 13.2.6-1 (1997)

=

Total PM emissions are dependent on wind speed. Higher wind speeds increase emissions by enhanced ventilation of the process and by retardation of coarse particle deposition. Emissions of PM_{10} and $PM_{2.5}$ are not significantly dependent on wind speed.

Abrasive materials contain small amounts of NPI-listed metals. Table 5 gives typical metal content of some abrasives used in Australia. It is uncertain how much of the abrasive and the abraded surface coating materials actually become airborne during the abrasive blasting process. Conservative estimates are 10% for both abrasive material and abraded paint. Emissions of metal species which result from part of the abrasive material being discharged to air, may be estimated as follows:

Equation 5

 ${\rm E_{kpy,i}}$

A * OpHrs * $(C_1/10^6)$ * $(EF_{PM}/100)$

where:

$E_{_{kpy,i}} \\$	=	emissions of pollutant i, kg i/yr emitted as particulate matter
А	=	rate of usage of abrasive material, kg/hr
OpHrs	=	total annual hours of abrasive blasting
-		operations, hr/yr
C _i	=	content of metal species i in abrasive
1		material, ppm
10 ⁶	=	conversion for the proportion of species i
		in the abrasive material used, ppm by weight
EF_{PM}	=	assumed percentage of abrasive material
		emitted to air as particulate matter

Example 3 - Calculating Emissions from Abrasive Blasting

This example shows how Equation 5 can be used to calculate emissions of particulate lead from the copper slag while abrasive blasting activities are being carried out in a ventilated ship's compartment. The following data is given:

Copper slag from Port Kembla containing 2690 ppm of lead (from Table 5) is used at the rate of 10 kg/hr, for a total of 500 hours in a year. Approximately 10% of the abrasive material becomes airborne during the abrasive blasting process.

Lead emissions to atmosphere are then calculated as follows:

$E_{kpy,Pb}$	=	A * OpHrs * ($C_{Lead}/10^6$) * ($EF_{PM}/100$)
	=	$10 * 500 * (2690/10^6) * (10/100)$
	=	1.34 kg/yr of lead emitted as particulate matter

	Metal (ppm)						
Abrasive	Pb	As	Cr	Zn	Со	Ni	Cu
GMA Garnet	6	10	3	5	4	2	2
Steel Grit	68	62	1315	110	51	830	2750
Copper Slag	263	690	66	1480	715	1	6630
Ex Mt Isa							
Copper Slag	286	10	26	3600	635	210	5310
Ex Whyalla							
Copper Slag	2690	95	315	12 400	140	74	4880
Ex Pt Kembla							
Copper Slag	3680	1230	225	15 500	140	30	4070
Ex Newcastle							

Tuble 5 Micial Content of Common Mustianian Morasives

Source: Morris and Salome, 1996.

The metal emissions calculated using the concentration data from Table 5 only consider the metal contents of the abrasive materials used. The metal content of the paint being stripped must also be taken into account when estimating total metal emissions from abrasive blasting. Many older paints are high in lead content and priming paints are also high in zinc and other NPI-listed metals. The total amount of old paint removed by abrasive blasting can be estimated from the thickness of the coating (possibly in the range 0.1 to 0.6 mm) and the surface area treated. The amount of a metal species in the abraded material can be estimated from data on the composition of the original surface coating material according to Equation 6.

Equation 6

$$E_{kpy,i}$$
 = HS * (Th/1000) * (C_i/10⁶) * ρ * (EF_{PM}/100)

where:

E _{kpv.i}	=	emissions of species i, kg/yr
HS	=	total hull surface abraded, m²/yr
Th	=	average thickness of surface coating, mm
1000	=	conversion of 1000mm per m, mm/m
C _i	=	content of metal species, ppm by weight of
		dry surface coating
ρ	=	density of dry surface coating, kg/m^3
EF _{PM}	=	assumed % of abraded surface coating emitted
		to air as PM (100 kg per tonne of abraded surface coating).
10 ⁶	=	conversion for ppm

Example 4 shows how emissions of a metal species from abraded paint on a ship's hull can be calculated.

Example 4 - Calculating Emissions from Abraded Paints

This example shows how Equation 6 can be used to calculate emissions of particulate lead from abraded paint on a ship's hull. A ship's hull with surface area of 10 000 m² has a 0.4 mm coating of a paint of which the solids density is 1200 kg/m³, containing 790 ppm lead.

Lead emissions to atmosphere are then calculated as follows:

$\mathrm{E}_{_{\mathrm{kpy,Lead}}}$	=	HS * (Th/1000) * ($C_{Lead}/100^{6}$) * $ ho$ * (EF $_{PM}/100$)
	=	$10\ 000 * (0.4/1000) * (790/10^6) * 1200 * (10/100)$
	=	0.38 kg/yr of lead emitted to air as particulate matter

Emissions of tri-butyl tin (TBT), which can be reported to the NPI as one of the organo-tin compounds, during hull scraping may be estimated roughly by a similar approach. Estimate the mass of the dry surface coating on the hull from knowledge of its average thickness, the surface area of the hull and concentration of tri-butyl tin in the dry surface coating. Then if it is possible to quantify the amount of surface coating lost (emitted to air and water) may be estimated and hence the emissions of tri-butyl tin. The facility should firstly estimate the total annual amount of paint that is removed from ship hulls and hence estimate the total annual amount of tri-butyl tin removed. If the total annual amount of tri-butyl tin handled is less than 10 tonnes, the facility would not be required to report TBT emissions as one of the organo-tin compound emissions to the NPI.

$$\mathbf{E}_{\rm kpy,TBT} = (\mathbf{M}_{\rm hull} - \mathbf{M}_{\rm recov}) * (\mathbf{C}_{\rm TBT} / 10^6)$$

where:

E _{kdv.tbt}	=	emissions of tri-butyl tin, kg/yr
M _{hull}	=	mass of surface coating on the hull, kg/yr
$\mathbf{M}_{\mathrm{hull}}$	=	HS * (Th/1000) * ρ, kg/yr
M_{recov}	=	mass of surface coating abraded and
		recovered for disposal, kg/yr
HS	=	total hull surface abraded, m²/yr
Th	=	average thickness of surface coating, mm
1000	=	conversion of 1000mm per m, mm/m
C _{TBT}	=	content of tributyl tin, ppm by weight,
-		in dry surface coating
ρ	=	density of dry surface coating, kg/m ³

 $\overline{\text{E}}$ xample 5 shows how emissions of a tri-butyl tin from hull cleaning may be estimated.

Example 5 - Calculating Emissions of Tri-butyl tin from Hull Cleaning

This example shows how Equation 7 can be used to calculate emissions of tri-butyl tin from abrading the paint from a ship's hull. A ship's hull with surface area of 10 000 m² has a 0.6 mm coating of a paint which has a density of 1200 kg/m³, containing 100 ppm by weight of tri-butyl tin. Approximately 4000 kg of abraded paint from the ship's hull is recovered.

TBT emissions are then calculated as follows:

$$\begin{split} M_{hull} &= 10\ 000\ ^*\ (0.6/1000)\ ^*\ 1200 \\ &= 7200 \mbox{kg/yr} \end{split} \\ E_{kpy,TBT} &= (7200\ -\ 4000)\ ^*\ (100/10^6) \\ &= 0.32\ \mbox{kg\ tri-butyl\ tin\ /yr} \end{split}$$

Therefore, the NPI threshold for organo-tin compounds has not been triggered.

Vent or other outlet testing is relatively uncommon for abrasive blasting activity at port facilities or on vessels in Australia. As a result, emissions test data for these facilities and vessels is generally only available in the form of monitoring results conducted by the port or shipping operator for compliance with Worksafe Australia Exposure Standards for Atmospheric Contaminants in the Workplace Environment. This data can be used in conjunction with exhaust system flow rates to calculate particulate metal emissions from a room, building, ship, or other vessel.

Abrasive	Lead Content of Abrasive (ppm)	Lead Exposure from Personal Air Samplers (µg/m³)	Lead Exposure from TSP High Volume Samplers (µg/m³)
GMA Garnet	< 6	< 480 [‡]	$< 27^{\dagger}$
Steel Grit	68	< 480 [‡]	175
Copper Slag Ex Mt. Isa	263	2720	NA
Copper Slag Ex SA	286	$< 480^{\ddagger}$	632
Copper Slag Ex Pt Kembla	2690	5880	NA
Zinc Slag Ex Newcastle	3680	9160	NA
Zinc Slag Ex Newcastle [§]	3680	3240	NA

Table 6 - Lead Content of Abrasives and Atmospheric Lead Exposures

† Detection limit using High Volume TSP sampler‡ Detection limit using Personal sampler.

§ The zinc-slag run was repeated with the blast room air extraction system turned on.

Equation 8 is used to calculate these emissions.

Equation 8

(FR * 3600 * OpHrs * C_i) / 10⁹ $\mathbf{E}_{k p v. i}$ =

where:

E _{kpy,i}	=	emissions of listed metal, or $PM_{_{10}}$	
		species i, kg/yr	
FR	=	flow rate through exhaust ventilation	
		system, m ³ /sec	
3600	=	conversion factor, sec/hr	
OpHrs	=	exhaust system operating hours, hr/yr	
C	=	concentration of metal, or PM_{10} species	
-		in µg/m ³	
10 ⁹	=	conversion factor, μg/kg	

Example 6 illustrates the application of Equation 8.

Example 6 - Calculating Emissions from Abrasive Blasting

This example shows how Equation 8 is used to calculate emissions of particulate lead from a ventilated ship's compartment where abrasive blasting activities are being conducted. The following data is given:

- the compartment exhaust flow rate (FR) is 5.1 m³/sec;
- the exhaust system operates for 500 hr/yr, OpHrs; and

• occupational hygiene data indicates that the concentration of lead in the compartment exhaust air is (C_i) is 5880 μ g/m³ (Personal air monitoring result taken while abrasive blasting using Copper Slag from Port Kembla containing 2690 ppm. Data taken from Table 6: Source - Morris and Salome, 1996).

Lead emissions to atmosphere are then calculated as follows:

 $\begin{array}{rcl} E_{kpy,Pb} & = & (FR * 3600 * OpHrs * C_i)/10^9 \\ & = & (5.1 * 3600 * 500 * 5880)/10^9 \\ & = & 54.0 \ kg \ Pb/yr \end{array}$

4.5.3 Metal Plating and Surface Treatment

Material inputs for metal plating and finishing include the solutions of plating metals such as chromium, aluminium, brass, bronze, cadmium, copper, iron, lead, nickel, zinc, gold, platinum, and silver. In addition, cyanide solutions, solvents, rinse water, and rust inhibitors are used. Many of the wastes generated from metal plating and surface finishing operations are considered hazardous resulting from their toxicity.

Air Emissions

Air emissions arise from metal mists, fumes, and gas bubbles from the surface of the liquid baths and the volatilisation of solvents used to clean surfaces prior to plating or surface finishing.

Residual Wastes

Solid wastes include wastewater treatment sludges, still bottoms, spent metal plating solutions, spent cyanide solutions, and residues from tank cleaning. Often, the solid waste generated contains significant concentrations of toxic metals, cyanides, acids, and alkalies.

Wastewater

Wastewaters are primarily rinse waters, quench water, and waste tank cleaning water contaminated with metals, cyanides, acids, alkalies, organics, and solvents. Wastewaters are typically either sent off-site for treatment or disposal, or are treated on-site by neutralisation and conventional hydroxide precipitation prior to discharging to a wastewater treatment plant.

Source: USEPA Sector Handbook 1997

4.6 Painting

Material inputs for painting are primarily paints and solvents. Solvents are used in the paints to carry the pigment and binder to the surface, and for cleaning the painting equipment. VOCs from painting solvents are one of the most important sources of pollutant outputs for the industry. Paints may also contain toxic pigments such as chromium, titanium dioxide, lead, copper, and tributyl-tin compounds. Water is also used for equipment cleaning when water-based paints are used.

The organic solvents contained in marine paints and used for thinning and cleaning are also likely to contain the following NPI-listed substances:

- toluene;
- ethyl benzene;
- xylene;
- methyl ethyl ketone;
- ethylene glycol;
- n-hexane; and
- acetone.

For the purposes of the NPI, VOCs present in paints and thinners are assumed to be completely emitted to air. A high proportion of the solvents used for degreasing would either be recycled or transferred off-site for disposal.

Air Emissions

Painting can produce significant emissions of VOCs when the solvents in the paint volatilise while the paint dries. Other sources may occur of VOCs when solvents are used to clean painting equipment such as spray guns, brushes, containers, and rags. Sprayed paint, or overspray, that does not reach the surface being coated, is another source of painting air emissions. The solvents in overspray rapidly volatilise and the remaining dry paint particles that may contain metals in the pigment can drift off-site or into nearby surface waters.

Residual Wastes

Solid wastes associated with painting are believed to be the largest category of hazardous waste produced in shipyards. Typical wastes associated with painting include leftover paint, waste paint containers, spent equipment, rags and other materials contaminated with paint, spent solvents, still bottoms from recycled cleaning solvents, and sludges from the sumps of water wash paint spray booths. Wastes associated with antifouling bottom paints are sometimes collected separately from the typically less toxic topside and interior

paints. Antifouling paints contain toxic metal or organometallic biocides such as cuprous oxide, lead oxide, and tributyl-tin compounds.

Wastewater

Wastewater contaminated with paints and solvents may be generated during equipment cleaning operations; however, water is typically only used in cleaning water-based paints. Wastewater is also generated when water curtains (ie. water wash spray booths) are used during painting. Wastewater from painting water curtains commonly contains organic pollutants and certain metals. The wastewater can be treated at the source using filtration, activated carbon adsorption, or centrifugation and then reused instead of being discharged.

Source: USEPA Sector Handbook 1997

4.6.1 Emissions from Painting

Painting operations emit VOCs to the atmosphere through evaporation of the paint vehicle, thinner, or solvent used to facilitate the application of the coatings. The main factor affecting VOC emissions from painting operations is the volatile content of the coatings, which averages around 15 per cent for water-based coatings and over 50 per cent for solvent-based coatings. Most, if not all, of the volatile portion of the coating evaporates during or following application. To reduce these emissions, paint manufacturers have reduced the VOC content of coatings in recent years. In addition, air pollution control equipment, such as activated carbon adsorption of hydrocarbon emissions or destruction of hydrocarbons in an afterburner, is used in operations at larger Australian port facilities.

The technique for calculating VOC emissions from painting operations is quite straightforward. For each type of coating fluid used in painting, the quantity of coating used is multiplied by the VOC content of the coatings to obtain the total VOC emissions from the use of that coating. If any type of air pollution control equipment is in use, then the VOC emissions estimate is reduced to reflect the efficacy of the control device. To report speciated VOCs, such as toluene or xylenes, the same technique is used only the quantity of coating used is multiplied by the content of each individual species in the VOC being inventoried. The technique is expressed by Equation 9.

Equation 9

$$E_{kpy, \text{ coating type, species i}} = \left[Q_{coating} * VOC_{coating} * PC_{coating, species i} / 100 * (1 - CE / 100) \right]$$

where:

E _{kpy, coating type, s}	species i =	total emissions of VOC species i. from painting operations
15. 0.51		for a particular coating type, kg/yr
$Q_{coating}$	=	total quantity of the particular coating type used in the
		reporting year, L/yr
VOC	=	total VOC content for particular coating type, kg /L
CE	=	control efficiency, %
PC _{species i}	=	percentage by weight of species i in the VOC part of the
		particular coating type, %

The emissions of a particular VOC species can then be summed over various coating types (paint, varnish, shellac, lacquer, enamel, primer) used by the facility during a year.

Painting Emissions - Data Inputs

To estimate total and speciated VOC emissions from painting operations, four data inputs are required:

- (1) the type of coating used;
- (2) the quantity of coating used;
- (3) an uncontrolled emission factor; and
- (4) an air pollution control efficiency factor (if applicable).

Coatings include paint, varnish and shellac, lacquer, enamel, and primer. The port's paint shop operator and purchasing records should be able to provide information on the types of coatings used and the paint manufacturer details on the VOC content and VOC speciation profile of paint and other coating products used.

Air pollution emission control equipment, such as activated carbon adsorption or afterburner destruction of the vapours, is sometimes used in painting operations. Combustion products from these control devices may need to be considered for NPI reporting. Information on the demonstrated effectiveness of these control methods should be obtained from the equipment manufacturer, before calculating emissions for NPI reporting.

The quantities of each type of coating used are usually available in litres. Material and Safety Data Sheets (MSDS) or coating manufacturers and suppliers should be consulted to obtain the volatile content, expressed in terms of kilograms per litre of organic solvent or VOC. If this information is not available, the default values in Table 7 should be used to obtain total VOC content and Tables 8 through 11 to obtain the speciation profiles for various surface coatings.

Example 7 illustrates the application of Equation 9.

Example 7 - Estimating VOC Emissions from Painting

Purchasing records indicate that a vessel coating operation consumed 9 300 litres of one particular type of primer during the NPI reporting year. The MSDS for the primer shows that it contains 0.792 kg/L VOC (Table 7). The breakdown of the total VOC in percentages of species by weight (Table 9) is 44.31 per cent toluene, 3.68 percent xylenes and 52.01 per cent other VOCs. The facility estimates that 80 per cent of the primer was used in a paint booth with an afterburner fitted which typically destroys 98 per cent of VOCs. The remaining 20 per cent of primer was applied for retouching and other work outside the booth. Emissions of each VOC species in the primer can be estimated using Equation 9 by summing over the two processes with different control efficiencies.

$\mathbf{Q}_{\mathrm{primer}}$	=	9300 L/yr
VOC	=	0.792 kg/L
PC _{primer. toluene}	=	44.31 %
PC primer, xylenes	=	3.68%
PC _{primer, others}	=	52.01%
CE	=	98 %
E _{kpy, primer, toluene}	=	$\Sigma \left[Q_{\text{primer}} * \text{VOC}_{\text{primer}} * \text{PC}_{\text{primer,toluene}} / 100 * (1 - \text{CE} / 100) \right]$
	=	[(9300 * 0.792 * 80/100) * 44.31/100 * (1 - 98/100)] +
		[(9300 * 0.7920 * 20/100) * 44.31/100 * (1 - 0/100)]
	=	(9300 * 0.792 * 44.31/100) * [0.8 * (1 - 0.98) + 0.2 * (1 - 0)]
	=	3264 * 0.216
	=	705 kg toluene/yr
E _{kpy primer vylenes}	=	$\Sigma \left[Q_{\text{primer}} * \text{VOC}_{\text{primer}} * \text{PC}_{\text{primer}} / 100 * (1 - \text{CE} / 100) \right]$
kpy, princi, kyrenes	=	[(9300 * 0.7920 * 80/100) * 3.68/100 * (1 - 98/100)] +
		[(9300 * 0.7920 * 20/100) * 3.68/100 * (1 - 0/100)]
	=	(9300 * 0.792 * 3.68/100) * [0.8 * (1 - 0.98) + 0.2 * (1 - 0)]
	=	271.1 * 0.216
	=	58.5 kg xylenes/yr
E	=	$\Sigma [Q_{minus} * VOC_{minus} * PC_{minus} + chem/100 * (1 - CE/100)]$
kpy, primer, others	=	[(9300 * 0.7920 * 80/100) * 52.01/100 * (1 - 98/100)] +
		[(9300 * 0.7920 * 20/100) * 52.01/100 * (1 - 0/100)]
	=	(9300 * 0.792 * 52.01/100) * [0.8 * (1 - 0.98) + 0.2 * (1 - 0)]
	=	3831 * 0.216
	=	827 kg others/yr
Ekpy, primer total VOCs	=	$E_{\text{primer, toluene}} + E_{\text{primer, xylenes}} + E_{\text{primer, others}}$
	=	705 + 59 + 827
	=	1591 kg/yr

Surface Coating	VOC Content (kg/L)
Paint (solvent-based)	0.672
Paint (water-based)	0.156
Enamel	0.420
Lacquer	0.732
Primer	0.792
Varnish and Shellac	0.396
Thinner	0.883
Adhesive	0.528

 Table 7 - VOC Content of Common Surface Coatings

Source: Queensland Department of Environment and Heritage, 1998.

CASR	NPI-Listed	Weight %
No.	Substance	(total = 100%)
110-82-7	Cyclohexane	0.52
141-78-6	Ethyl acetate	2.04
67-64-1	Acetone	1.27
78-93-3	Methyl ethyl ketone	0.54
108-10-1	Methyl isobutyl ketone	0.36
1330-20-7	Isomers of xylene	8.17
108-88-3	Toluene	37.87
100-41-4	Ethylbenzene	0.54
	All other VOCs	48.69

Table 8 - VOC Speciation Profile for Solvent-Based Paints

Source: USEPA 1992. VOC / PM Speciation Data System - Version 1.50

Table 9 - VOC Speciation Profile for Primers

CASR	NPI-Listed	Weight %
No.	Substance	(total = 100%)
1330-20-7	Isomers of xylene	3.68
108-88-3	Toluene	44.31
	All Other VOCs	52.01

Source: USEPA 1992. VOC / PM Speciation Data System - Version 1.50

CASR	NPI-Listed	Weight %
No.	Substance	(total = 100%)
110-82-7	Cyclohexane	2.27
141-78-6	Ethyl acetate	8.96
67-64-1	Acetone	5.57
78-93-3	Methyl ethyl ketone	2.36
108-10-1	Methyl isobutyl ketone	1.57
1330-20-7	Isomers of xylene	23.09
108-88-3	Toluene	15.9
100-41-4	Ethylbenzene	2.36
	All Other VOCs	37.92

 Table 10 - VOC Speciation Profile for Enamels

Source: USEPA 1992. VOC / PM Speciation Data System - Version 1.50

Table 11 - VOC Speciation Profile for Water-Based Paints

CASR	NPI-Listed	Weight %
NO.	Substance	(total = 100%)
71-43-2	Benzene	5.52
75-09-2	Dichloromethane	0.36
	Other VOCs not listed	94.12

Source: USEPA 1992. VOC / PM Speciation Data System - Version 1.50

4.7 Fibreglass Reinforced Construction

Material inputs for fibreglass operations include fibreglass, mould or reinforcing materials (ie. wood and plastic), resins, solvents, and curing catalysts. Unsaturated polyester resins, (eg. orthophthalic polyester, isophthalic polyester, and bisphenol polyester) are the most commonly used resins. Other resins include epoxies, polyamides and phenolic compounds. In addition, some catalysts may be hazardous. Catalysts include amines (eg. diethylenetriamine and triethylenetetramine), anhydrides, aldehyde condensation products, and Lewis acid catalysts. Typical wastes include containers contaminated with residual chemicals, wash-down wastewater, spent cleaning solvents from equipment cleanup, scrap solvated resin left over in mix tanks, diluted resin and partially cured resin.

For more information on estimating emissions from fibreglass manufacturing, please refer to the *Emission Estimation Technique Manual for Fibreglass Product Manufacturing*.

Air Emissions

Organic vapours consisting of VOCs are emitted from fresh resin surfaces during the fabrication process and from the use of solvents for cleanup. The polyester resins used in gelcoating operations have a styrene content of approximately 35 percent. Emissions of styrene and other solvent VOCs during spraying, mixing, brushing, and curing can be significant. In addition, emissions of solvent vapours arise when acetone and methylene chloride, are used to clean fibre glassing equipment.

Residual Wastes

Residual wastes generated from fibreglass operations include, gelcoat and resin overspray, unused resins that have exceeded their shelf life, fibreglass boxes, gelcoat drums, waste solvents, and clean up rags.

Source: USEPA Sector Handbook 1997

5.0 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 shipbuilding and repair 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.

5.1 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 shipbuilding and repair 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 cover all aspects of production.

In the case of continuous emissions monitoring (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.

5.2 Mass Balance

Calculating emissions from a shipbuilding and repair facility using mass balance appears to be a straightforward approach to emission estimation. However, it is likely that few Australian facilities consistently track material usage and waste generation with 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.

5.3 Engineering Calculations

Theoretical and complex equations or *models* can be used for estimating emissions from a variety of shipbuilding and repair processes.

Use of emission equations to estimate emissions from 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.

5.4 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 Section 6 of this Manual. 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:

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

6.0 References

Morris and Salome, 1996, Occupational Exposures and Hazardous Wastes from Abrasive Blast Cleaning, 13th International Corrosion Congress, Melbourne.

USEPA. January 1990. Section 313 Reporting Issue Paper: Clarification and Guidance for the Metal Fabrication Industry, Office of Toxic Substances, EPA 560/4-90-012. Washington, DC, USA.

USEPA. October 1992. *VOC / PM Speciation Data System - Version 1.50.* United States Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC, USA.

USEPA. June 1994. Surface Coating Operations at Shipbuilding and Ship Repair Facilities--Background Information for Proposed Standards. United States Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC, USA.

USEPA. January 1995. *Compilation of Air Pollutant Emission Factors, Volume 1: Point and Area Sources, fifth edition, AP-42.* United States Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC, USA. <u>http://www.epa.gov/ttn/chief/ap42.html</u>

USEPA. November 1997. EPA Office of Compliance Sector Notebook Project. Profile of the Shipbuilding and Repair Industry. United States Environmental Protection Agency, Office of Enforcement and Compliance Assurance. Washington, DC, USA.

The following EET Manuals are available at the NPI Homepage (http://www.npi.gov.au), and from your local environmental protection agency:

- Emission Estimation Technique Manual for Combustion Engines;
- Emission Estimation Technique Manual for Combustion in Boilers;
- Emission Estimation Technique Manual for Ferrous Foundries;
- Emission Estimation Technique Manual for Non-Ferrous Foundries;
- Emission Estimation Technique Manual for Fuel and Organic Liquid Storage;
- Emission Estimation Technique Manual for Electroplating and Anodising; and
- *Emission Estimation Technique Manual for The Electronics and Computer Industry.*