



National Pollutant Inventory

Emission Estimation Technique Manual

for

Galvanizing

First published in July 1999

EMISSION ESTIMATION TECHNIQUES

FOR GALVANIZING

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GALVANIZING

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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 galvanizing activities.

The galvanizing activities covered in this Manual apply to facilities primarily engaged in the hot dip coating of a metallic workpiece with another metal to provide a protective film by immersion into a molten bath. Galvanizing (hot dip zinc) is the predominant form of hot dip coating in Australian industry.

EET MANUAL : Galvanizing

HANDBOOK : Metal Coating and Finishing

ANZSIC CODE : 2764

This Manual was drafted by the Queensland Department of Environment and Heritage on behalf of the Commonwealth Government. The Manual 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.

2.0 Process Description

Galvanizing is a process undertaken to coat metals and metal products in a layer of zinc to prolong their life. The metal to be coated requires pre-treatment prior to being immersed into the zinc bath in order to remove rust, grease and other materials, and therefore to promote the galvanizing process. Pre-treatment can include treatment of the metal with an alkaline degreasing solution, an acid pickling solution, water rinse, and a preflux solution. The preflux solution is usually comprised of zinc ammonium chloride ($ZnCl_2 \cdot 3NH_4Cl$), and is used to promote the zinc-metal bond. After pre-treatment, the metal is immersed in molten zinc followed by a quench bath.

Figure 1 shows a basic galvanizing flow diagram and some expected emission points. As each galvanizing facility in Australia is unique, you are encouraged to develop flow diagrams for your operation that detail the input of materials and NPI-listed substances, and the emissions resulting from the operation of each process.

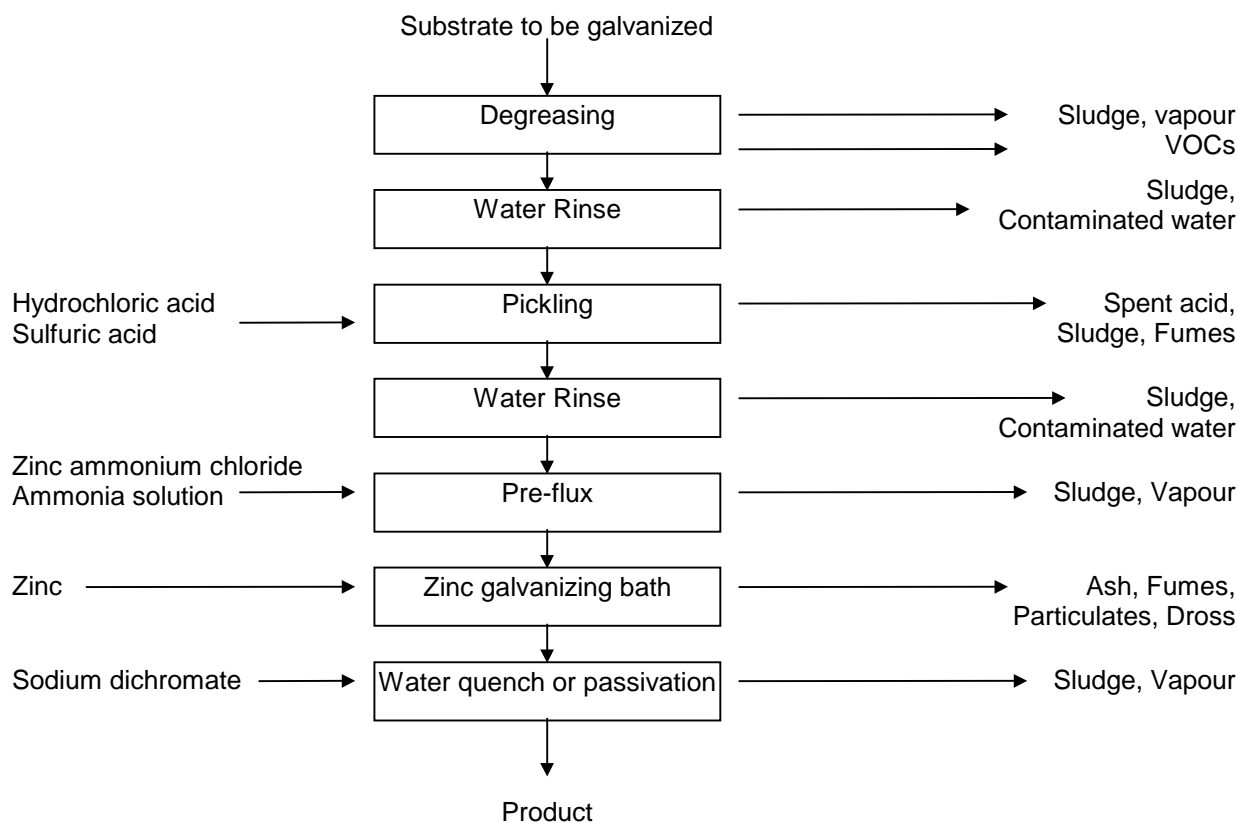


Figure 1 - The Basic Galvanizing Process Steps and Likely Emission Points

Source: Queensland Department of Environment and Heritage, 1998.

3.0 Emissions from Galvanizing Operations

This Section describes the raw material inputs, the equipment used, and the processes employed that result in emissions of NPI-listed substances in the galvanizing process. This section also provides a concise description of the potential fate (to air, land, and water) of these emissions.

Galvanizing generally produces atmospheric emissions, contaminated wastewaters, and solid waste emissions. Hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) fumes may be emitted from baths, while ammonia and ammonium chloride emissions to atmosphere occur from pre-flux, and during the galvanizing bath stage. Zinc and PM_{10} emissions (particulate matter with an equivalent aerodynamic diameter of 10 micrometres or less ie. $\leq 10\mu m$) may result from hot dip metal coating activities.

Water emissions occur from spent rinse water following pre-cleaning, and sometimes from quenching activities after coating. Other sources of wastewater emissions occur through rinsing and batch dumping of process baths. The process baths usually contain metal salts, acids, bases, and dissolved base materials.

Galvanizing and hot dip coatings also generate solid wastes. Solid wastes include an oxide dross that is periodically skimmed off the heated tank, as well as spent solutions and wastewater treatment sludges. Characterisation of these wastes may be required where emissions estimation is required using the mass balance approach (see Section 5.0).

Table 1 summarises the raw material inputs and the emissions of NPI-listed substances that could be generated during the galvanizing process.

Table 1 - Material Inputs and Emissions from Galvanizing Processes

Process	Material Input	Emissions to Air	Emissions to Water	Solid Waste Emissions
Degreasing	Substrate to be galvanized, alkaline degreasing solution	VOCs	Dissolved solution in water	Process sludges
Pickling	Acid pickling solution, Hydrochloric Acid Sulfuric Acid	fumes	Spent acids in water	Process sludges
Water Rinses	Rinse Water and substrate to be galvanized		Metal salts, acids, bases, dissolved base materials	Zinc and other metal sludges
Pre-flux	Zinc ammonium chloride ammonia solution	Ammonia, ammonium chloride		Zinc and other metal sludges
Galvanizing bath and kettle	Zinc, metal salts, acids	Hydrochloric acid, sulfuric acid, ammonia, ammonium chloride, zinc oxide, particulate matter, lead, copper, chlorine	Metal and acid wastes, zinc, chromium (VI)	Oxide dross, zinc and other metal sludges
Water Quench	Sodium dichromate	zinc oxide	metal and acid wastes, zinc, chromium (VI)	zinc and other metal sludges
Heating of zinc bath	Fuel	VOCs, oxides of nitrogen, particulate matter, sulfur dioxide		

Source: Queensland Department of Environment and Heritage, 1998.

Galvanizing may involve the use and handling of a number of NPI-listed substances. These substances commonly include zinc and compounds (eg. zinc ammonium chloride), chromium (VI) and compounds, hydrochloric and sulfuric acids, chlorine, and ammonia.

A galvanizer will be required to report all VOC emissions (Volatile Organic Compounds) if they trip the thresholds, therefore emissions from possible sources such as boilers or solvents need to be included. Emissions from combustion will need to be evaluated in circumstances where boilers are used, for example to heat a zinc bath. The *Combustion in Boilers* EET Manual can be used to calculate these emissions from boilers. Surface coating emissions that may occur can be evaluated using the *Surface Coating* EET Manual.

4.0 Emission Estimation Techniques

This Section provides guidance for estimating emissions of metals and inorganic compounds, (eg. mineral acids and ammonia), from galvanizing, and hot dip metal coating activities. Examples of the application of the various emission estimation techniques are provided to illustrate practical application.

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 Total Volatile Organic Compounds, VOCs) reporting threshold is exceeded. If the threshold is exceeded, **emissions** of these Category 1 and 1a substances must be reported for all operations/processes relating to the facility, even if the actual emissions of the substances are very low or zero.

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

4.1 Emissions to Air

Using Emission Factors

Table 2 provides uncontrolled emission factors for galvanizing emissions. The emission factors are based on total zinc input to the process, and are presented in units of kilograms of pollutant emitted per tonne of zinc used (kg/tonne). For controlled emissions from galvanizing operations, each of the add-on control devices used by the industry generally achieves a significant range of outlet concentrations of zinc oxide (ZnO) emissions. Therefore, the factors for galvanizing baths in Table 2 need to be applied using the uncontrolled emission factors provided, and typical control efficiencies of exhaust flow rates for the particular type of exhaust system in question. Example 1 illustrates the use of emission factors and control efficiencies in estimating emissions using Equation 1.

Equation 1

$$E_{kpy,i} = [A * OpHrs] * EF_i * [1 - (CE_i/100)]$$

where :

$E_{kpy,i}$	=	annual emissions of pollutant i, kg/yr
A	=	activity rate, t/hr
$OpHrs$	=	operating hours, hr/yr
EF_i	=	uncontrolled emission factor of pollutant i, kg/t
CE_i	=	overall control efficiency for pollutant i, %.

Example 1 illustrates the application of Equation 1.

Example 1 - Calculating Emissions Using Emission Factors^a

This example shows how total particulate matter emissions (kg per year of particulate matter $E_{kpy,PM}$ as zinc oxide (ZnO)) from a galvanizing hot dip bath may be calculated using Equation 1 and an emission factor (EF_i) from Table 2. The overall control efficiency for pollutant i is 80%. The following data is given:

$$\begin{aligned}
 EF_{PM} &= 2.5 \text{ kg particulate matter/tonne of zinc used} \\
 A &= 0.25 \text{ tonnes of zinc used/hr (based on 5 tonnes of steel} \\
 &\quad \text{dipped/hr, steel dipped has 5\% zinc)} \\
 CE_i &= 80 \% \\
 OpHrs &= 3\,000 \text{ hr/yr} \\
 \\
 E_{kpy,PM} &= A * OpHrs * EF_{PM} [1 - (CE_i/100)] \\
 &= 0.25 \text{ t/hr} * 3\,000 \text{ hr/yr} * 2.5 \text{ kg/t} * [1 - (80/100)] \\
 &= 375 \text{ kg particulate matter/yr}
 \end{aligned}$$

^a Total suspended particulates (TSP) are also referred to as total particulate matter (total PM). To determine PM_{10} from total PM emissions, a size analysis may need to be undertaken. The weight PM_{10} fraction can then be multiplied by the total PM emission rate to produce PM_{10} emissions. Alternatively, assume that 100% of PM emissions are PM_{10} .

Table 2 - Emission Factors for Galvanizing - Emissions to Air

Process	Emission	Uncontrolled Emission Factor EF (kg/tonne)	Emission Factor Rating
Galvanizing (zinc bath) ^{a,c}	Particulate matter ^c	2.5 kg of particulate matter/tonne of zinc used	C
Zinc galvanizing kettle ^{b,d}	Chlorine	0.1918246	U
	Chromium(VI)	0.0060749	U
	Cobalt	0.0001249	U
	Zinc	0.1431997	U
	Arsenic	0.0033499	U
	Cadmium	0.0019249	U
	Lead	0.1327247	U
	Magnesium	0.01355	U
	Oxides of nitrogen (NO _x)	0.0022499	U
	Manganese	0.032275	U
	Nickel	0.007775	U
	Copper	0.115225	U
	Selenium	0.00085	U
	Antimony	0.186	U
Mercury	0.0002	U	

^a Source: USEPA AP-42, 1985.

^b Source: USEPA *Speciate* computer program, 1993.

^c Units are kg of particulate matter emitted/tonne of zinc used. Particulate matter consists entirely of zinc oxide (ZnO). Factors are for uncontrolled sources.

^d Units are kg of substance emitted/tonne of zinc used. Factors are from uncontrolled sources.

Speciating PM₁₀ Emissions

PM₁₀ emissions (airborne particulate matter equal to or less than 10 microns in diameter) containing listed metals such as zinc, will require speciation into individual metal species where reporting thresholds for the metal have been triggered by the galvanizer. Example 1 illustrated the technique for estimating PM₁₀ emissions (as zinc oxide (ZnO)) using emission factors. Equation 2 illustrates the technique for speciating PM₁₀ emissions, and Example 2 below shows this application.

Equation 2

$$E_{kpy,i} = Q_{PM10} * C_i / 100$$

where:

$$\begin{aligned} E_{kpy,i} &= \text{total emissions of metal species } i, \text{ kg/yr} \\ Q_{PM10} &= \text{amount of PM}_{10} \text{ containing species } i \text{ emitted by the} \\ &\quad \text{facility, kg/yr} \\ C_i &= \text{concentration of species } i \text{ in PM}_{10}, \text{ mass } \% \end{aligned}$$

Example 2 - Speciating PM₁₀ Emissions

This example demonstrates how speciated PM₁₀ (zinc oxide) emissions from a galvanizing bath can be calculated using the total PM₁₀ emissions (calculated from Example 1), and Equation 2. It is assumed that all PM₁₀ is emitted as zinc oxide (ZnO) and that total PM₁₀ = total PM; see footnote in Example 1.

Elemental weight of zinc (Zn) is 65.38 grams, the elemental weight of oxygen (O) is 16 grams and the molecular weight of zinc oxide (ZnO) is 81.38 grams. From this information, the concentration of zinc in zinc oxide can be calculated.

$$\begin{aligned} C_{Zn} &= [\text{weight of zinc/weight of zinc oxide}] * 100\% \\ &= [65.38 / (65.38 + 16)] * 100\% \\ &= 0.8 * 100\% \\ &= 80\% \text{ zinc in zinc oxide} \end{aligned}$$

$$\begin{aligned} Q_{PM10} &= 375 \text{ kg ZnO/yr} \\ C_{Zn} &= 80\% \text{ zinc in ZnO} \end{aligned}$$

$$\begin{aligned} E_{kpy,Zn} &= Q_{PM10} * C_{Zn} / 100 \\ &= 375 * (80 / 100) \\ &= 300 \text{ kg zinc/yr} \end{aligned}$$

With regards to emission controls for PM₁₀, 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.

4.2 Emissions to Water

Using Emission Factors

In this Manual, emission factors for emissions to water from galvanizing activities relate the quantity in kilograms of pollutants emitted from a galvanizing activity to the amount of galvanized product produced per year (kg/yr).

Emission factors from Table 3 are used to estimate a facility's emissions to wastewater by Equation 1.

Example 3 further illustrates the application of Equation 1.

Example 3 - Estimating Zinc Emissions to Water

Table 3 shows that 0.007 kg of zinc is emitted to wastewater for each tonne of galvanized steel product produced in a hot dip bath. During the reporting year, the galvanizer estimates that 2.5 tonnes of product/hr has been shipped over 4 000 hours of operation. The galvanizer also estimates that 85 percent of zinc is recovered and recycled from on-site wastewater treatment. Emissions can be estimated using Equation 1.

$$EF_{Zn} = 0.007 \text{ kg of zinc/tonne of galvanized steel product}$$

Galvanizing production:

$$\begin{aligned} \text{Activity Rate} &= 2.5 \text{ tonne/hr} \\ \text{OpHrs} &= 4000 \text{ hr/yr} \\ CE_{Zn} &= 85 \% \end{aligned}$$

$$E_{kpy,i} = A * \text{OpHrs} * EF_i * [1 - (CE_i/100)]$$

$$\begin{aligned} \text{Zn emissions} &= 2.5 \text{ t/hr} * 4\,000 \text{ hr/yr} * 0.007 \text{ kg/t} * [1 - (85/100)] \\ &= 70 * 0.15 \\ &= 10.5 \text{ kg Zinc /yr} \end{aligned}$$

Table 3 - Emission Factors for Galvanizing - Emissions to Wastewater

Process	Pollutant	Emission Factor (kg/tonne of product)	Emission Factor Rating Code
Untreated wastewater ^a <i>Hot Dip</i>	Zinc	0.007	U
	Chromium (VI)	0.015	U
	Phosphorus	0.02	U
<i>Electrogalvanizing</i>	Zinc	0.405	U
Treated wastewater ^b	Zinc	0.009	U
	Chromium (VI)	0.004	U

Source: Economopoulos, 1993.

Units are kg of pollutant emitted/tonne of galvanized steel product produced.

^a Emission factors calculated from 9.4 m³ of waste generated.

^b Emission factors calculated from 6.9 m³ of waste generated.

Using Sampling Data

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 using of Equation 3.

Equation 3

$$E_{kpy,i} = C_i * V * OpHrs / 10^6$$

where:

$E_{kpy,i}$	=	emissions of pollutant i, kg/yr
C_i	=	concentration of pollutant i in wastewater, mg/L
V	=	hourly volume of wastewater, L/hr
$OpHrs$	=	operating hours per year for which data apply, hr/yr
10^6	=	conversion factor, mg/kg

In applying Equation 3 to water emission calculations, monitoring data should be averaged, and only representative concentrations used in emission calculations.

Using Mass Balance

If no wastewater monitoring data exists, emissions to water can be calculated based on a mass balance of the galvanizing process, shown by Equation 4.

Equation 4

$$E_{kpy,i} = (AU_i - AI_i - AT_i)$$

where:

$E_{kpy,i}$	=	emissions of pollutant i, kg/yr
AU_i	=	amount of pollutant i used in the reporting year, kg/yr
AI_i	=	amount of pollutant i incorporated into product in the reporting year, kg/yr
AT_i	=	total amount of pollutant i treated on-site, emitted to air, and transferred off-site in the reporting year, kg/yr

Where a galvanizer uses an NPI-listed mineral acid or base, and this acid or base is effectively neutralised in use or during wastewater treatment (ie. to a pH of 6 to 8, as required by most State and Territory effluent standards), no emission quantities should be reported. However, if the acid or base is itself transformed into another listed substance, the quantity of the substance coincidentally produced must be determined to assess if a threshold has been tripped. For example, sulfuric acid often yields hydrogen sulfide (an NPI-listed substance) in effluent streams.

4.3 Emissions to Land

Wastewater treatment may precipitate a reportable substance in a sludge. Galvanizers are often required to obtain data on the concentration of metals and other substances in sludges, as part of their State or Territory licensing requirements. This data can be used to calculate the emissions as kilograms of sludge, times the concentrations of the substance in the sludge. Alternatively, the loss in the sludge can be estimated by using Equation 5. Although NPI-listed substances in sludges transferred off-site do not require reporting, determining this loss can assist with estimating other process losses, or may require reporting if the sludge is stored or disposed of on-site.

Equation 5

$$AS_i = (PL_i - WL_i) * OpHrs$$

where:

AS_i	=	amount of pollutant i in sludge, kg/yr
PL_i	=	process losses of pollutant i, kg/hr
WL_i	=	losses from wastewater of pollutant i, kg/hr
$OpHrs$	=	operational hours, hr/yr

For many listed substances used by galvanizers, some degradation in treatment may occur so that not all the chemical is transferred to the sludge. Facilities can estimate the amount of listed substances in the sludge by using measured data, or by subtracting the amount biodegraded from the total amount removed in the treatment. The amount of removal can be determined from operating data, and the extent of biodegradation can be obtained from published studies. If the biodegradability of the substance cannot be measured, or is not known, reporting facilities should assume that all removal is due to absorption to sludge.

4.4 Estimating Emissions of Inorganic Compounds and Fugitive Losses

The emission factors, equations, and mass balance EETs presented in this Manual are intended to be applied to estimate operating, or point-source emissions. Other than emission factors for estimating emissions of zinc oxide (and other metal compounds), from galvanizing kettles and baths, there is little information currently available for estimating fugitive emissions of other inorganic compounds. However, in galvanizing processes, it may be necessary to estimate these fugitive emissions for NPI-reporting purposes. This is particularly the case for emissions of hydrochloric acid, sulfuric acid, ammonia, and chlorine in the gas/vapour phase.

Emission estimates of inorganic compounds can be obtained for galvanizing processes using the following methods:

- Develop correlations specific to particular galvanizing baths or processes;
- Use a portable monitoring instrument to obtain actual concentrations of the inorganic compounds, and then apply the screening values obtained (see paragraph below) into the applicable correlation equation shown in Table 4 and Equation 6; or
- Use the emission factors from Table 5.

Screening data is collected by using a portable monitoring instrument to sample air, from potential leak interfaces, on individual pieces of equipment. A screening value (SV) is a measure of the concentration of leaking compounds in the ambient air that provides an

indication of the leak rate from an equipment piece, and is measured in units of parts per million by volume (ppmv).

In addition, surrogate measurements can be used to estimate emissions of inorganic compounds. For example, potassium iodide (KI), or a similar salt solution, is an indicator for equipment leaks from acid (hydrochloric acid [HCl], hydrofluoric acid [HF]) process lines at galvanizing plants. Such leaks would then need to be quantified.

Equation 6 illustrates an approach for estimating fugitive inorganic chemical emissions using data from Table 4. An example of this estimation technique is given at Example 4.

Equation 6

$$E_{kpy,i} = EF_i * C_i / 100 * OpHrs * \text{number of sources}$$

where:

- $E_{kpy,i}$ = mass emissions of pollutant i calculated from either the screening values, correlation equation, or emission factors, kg/yr/source
- EF_i = emission factor (ie. emission rate), kg/hr/source
- C_i = concentration of inorganic pollutant i in the equipment, %
- $OpHrs$ = operating hours, hr/yr

Example 4 - Calculating Fugitive Chemical Leaks

A galvanizer operates a light liquid pump on an 11 percent hydrochloric acid (HCl) solution storage tank (ie. 110 g HCl/L). The pump is run for 500 hours during the year.

For a Screening Value of Zero ppmv

- OpHrs = 500 hr/yr
- SV (screening value) = 0 ppmv
- Default-zero emission rate = $7.5 * 10^{-6}$ kg/hr/source

Using the correlation Equation 6

$$\begin{aligned} \text{HCl emissions} &= EF_i * C_i / 100 * OpHrs * \text{number of sources} \\ &= 7.5 * 10^{-6} \text{ kg/hr/source} * \\ &\quad (11/100) * 500 \text{ hr/yr} \\ &= 4.13 * 10^{-4} \text{ kg hydrochloric acid/yr} \end{aligned}$$

For a Screening Value of 20 ppmv

- OpHrs = 500 hr/yr
- SV (screening value) = 20 ppmv
- HCl emissions (kg/hr) = $1.90 * 10^{-5} (SV)^{0.824} * C_i / 100$
- = $1.90 * 10^{-5} (20)^{0.824} * 11/100$
- = $2.47 * 10^{-5}$ kg hydrochloric acid/hr

Example 5 - Calculating Fugitive Chemical Leaks cont'

Using the correlation Equation 6

$$\begin{aligned} \text{HCl emissions (kg/yr)} &= 2.47 * 10^{-5} \text{ kg/hr} * 500 \text{ hr/yr} \\ &= 1.23 * 10^{-2} \text{ kg hydrochloric acid/yr} \end{aligned}$$

Note that when using the correlation equation, for the screening value of 20 ppmv, the HCl emissions calculated by the correlation equation results in the LR value being equal to the $(EF_i * C_i)$ terms. In the last step of this example, Equation 7 is used and $(EF_i * C_i)$ is multiplied by OpHrs to determine the emissions per year.

Table 4 - Correlation Equations, Default Zero Emission Rates, and Pegged Emission Rates for Estimating Fugitive Emissions

Equipment Type	Default Zero Emission Rate (kg/hr/source)	Pegged Emission Rates ^c (kg/hr/source)		Correlation Equation (kg/hr/source) ^a
		10 000 ppmv	100 000 ppmv	
Gas valves	$6.6 * 10^{-7}$	0.024	0.11	$LR = 1.87 * 10^{-6} * (SV)^{0.873}$
Light liquid valves	$4.9 * 10^{-7}$	0.036	0.15	$LR = 6.41 * 10^{-6} * (SV)^{0.797}$
Light liquid pumps ^b	$7.5 * 10^{-6}$	0.14	0.62	$LR = 1.90 * 10^{-5} * (SV)^{0.824}$
Connectors	$6.1 * 10^{-7}$	0.044	0.22	$LR = 3.05 * 10^{-6} * (SV)^{0.885}$

Source: Eastern Research Group, 1996.

LR = leak rate.

^a SV is the screening value (ppmv) measured by the monitoring device. To estimate emissions, use the default zero emission rates only when the screening value (adjusted for background) equals 0.0 ppmv. Otherwise use the correlation equations. If the monitoring device registers a pegged value, use the appropriate pegged emission rate.

^b The emission estimates for light liquid pump seals can be applied to compressor seals, pressure relief valves, agitator seals, and heavy liquid pumps.

^c When the monitoring device reads a pegged value; for example 10 000 ppmv for a gas valve, the pegged emission rate of 0.024 kg/hr per source would be used rather than determining the emission rate using a correlation equation, or a default zero emission rate.

The average emission factor approach is commonly used to calculate emissions when site-specific screening data is unavailable. To estimate emissions using the emission factors in Table 5, the concentration in weight percent of the pollutant of interest within the equipment is needed. This is important because equipment with higher pollutant concentrations tend to have higher emission leak rates. The pieces of equipment should be grouped into *streams*, such that all equipment within a *stream* has approximately the same pollutant weight percent.

This approach for estimating emissions allows the use of average emission factors in combination with unit-specific data that is relatively simple to obtain. This data includes:

- the number of each type of component in a unit (valve, connector, etc.);
- the service each component is in (gas, light liquid, or heavy liquid);
- the pollutant concentration of the stream; and
- the time period each component was in that service during the NPI reporting year.

Equation 7 can be used to estimate emissions from all of the equipment of a given type in a *stream* using the emission factors from Table 5.

Equation 7

$$E_{kpy,i} = EF_i * WF_i * OpHrs * N$$

where:

- $E_{kpy,i}$ = emission rate of pollutant i from all equipment in the *stream* of a given equipment type, kg/yr/source
- EF_i = applicable average emission factor for the equipment type, kg/hr/source
- WF_i = average weight fraction of pollutant i in the *stream*,
- $OpHrs$ = annual operation hours of equipment in the *stream*, hr/yr
- N = number of units of the applicable equipment type in the *stream*

Example 6 illustrates the emission factor approach for a stream. Note that the stream contains water (which is not an NPI-listed substance) and that this is accounted for when total emissions are estimated.

Example 6 - Average Emission Factor Technique

This example illustrates how annual emissions of 30% hydrochloric acid (HCl) can be calculated from pump seals using the emission factors from Table 5 and Equation 7. The following is given:

Number of Units (N)	Emission Factor (kg/hr/source)	Weight Fraction	OpHrs (hr/yr)
2	0.0199	0.30	500

$$E_{kpy, NH3} = EF_i * WF_{NH3} * OpHrs * N$$

$$= 0.0199 * 0.30 * 500 * 2$$

$$= 5.97 \text{ kg hydrochloric acid (HCl)/yr}$$

Table 5 - Emission Factors for Equipment Leaks

Equipment Type	Service	Emission Factor (kg/hr/source)
Valves	Gas	0.00597
	Light liquid	0.00403
	Heavy liquid	0.00023
Pump seals ^a	Light liquid	0.0199
	Heavy liquid	0.00862
Compressor seals	Gas	0.228
Pressure relief valves	Gas	0.104
Connectors	All	0.00183
Open-ended lines	All	0.0017
Sampling connections	All	0.0150

Source: Eastern Research Group, 1996.

^a The light liquid pump seal factor can be used to estimate the leak rate from agitator seals.

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 galvanizing activities. The technique chosen is dependent on available data, and 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 4.0 of this Manual.

5.1 Direct Measurement

5.1.1 Continuous Emission Monitoring System (CEMS)

A CEMS provides a continuous record of emissions over an extended and uninterrupted period of time. Various principles are employed to measure the concentration of pollutants in the gas stream, and are usually based on photometric measurements. Once the pollutant concentration is known, emission rates are obtained by multiplying the pollutant concentration, by the volumetric stack gas flow rate. The accuracy of this method can be problematic at low pollutant concentrations.

Instrument calibration drift can be problematic for CEMS and uncaptured data can create long-term incomplete data sets. However, it is 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).

5.1.2 Sampling Data

Sampling can be conducted to quantify point source, or fugitive emissions. With point source sampling, effluent gas samples are usually collected from the stack using probes inserted through a port or stack wall. Pollutants in the gas are collected in, or on, various media that are subsequently sent to a laboratory for analysis. Pollutant concentrations are obtained by dividing the amount of pollutant collected during the test, by the volume of gas sampled. Emission rates are then determined by multiplying the pollutant concentration by the volumetric stack gas flow rate. Because there are many steps in the stack sampling procedures where errors can occur, only experienced stack testers should conduct the sampling.

Workplace health and safety data (concentrations) can be used in conjunction with exhaust system flow rates to estimate fugitive emissions from a room, floor, or building at a galvanizing plant. Direct-reading instruments that can be used to obtain an instantaneous

reading of vapour concentrations include photoionisation detectors, portable infrared spectrophotometers, and portable gas chromatographs.

Use of stack and/or workplace health and safety sampling data can be a relatively accurate method of estimating air emissions from galvanizing facilities. However, the collection and analysis of air samples from facilities can be very expensive, and especially complicated where a variety of NPI-listed substances are emitted, and most of these emissions are fugitive in nature. Sampling data from one 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 production of all galvanizing bath formulations.

5.2 Engineering Calculations

Theoretical and complex equations or *models* can be used for estimating emissions from galvanizing and other metal surface coating processes. Emission estimation equations are available for the following types of emissions generated by galvanizing facilities:

- surface evaporation during bath mixing and blending operations;
- material storage;
- spills; and
- fugitive emissions and equipment leaks.

Inputs for theoretical equations can commonly be categorised as follows;

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

See Section 4.0 for examples of theoretical equations.

Using emission equations to estimate emissions from galvanizing, or other metal coating activities, 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.

5.3 Mass Balance

The mass balance approach to emissions estimation at a galvanizing or metal plating facility considers the facility as a *black box*, where the total quantities of NPI-listed substances in the raw materials consumed, and the quantities of listed substances leaving the facility as product and waste, are compared and analysed.

Calculating emissions from a galvanizing facility using a mass balance appears to be a straightforward approach to emissions estimations. However, it is likely that few

Australian galvanizers or metal platers consistently track material usage and waste generation with the overall accuracy needed for application of this method. Consequently, inaccuracies associated with individual material tracking, or other activities pertaining to each material handling stage can often result in large deviations of total facility emissions. Because emissions from specific materials are typically below 2 percent of gross consumption, an error of only ± 5 percent in any one step of the operation can significantly skew emission estimations.

5.4 Emission Factors

An emission factor is a tool used to estimate emissions to the environment. 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 6.0 of this Manual. The emission factor ratings will not form part of the public NPI database.

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

The EFR system is as follows:

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

6.0 References

ANZSIC: Australian and New Zealand Standard Industrial Classification
Australian Bureau of Statistics & NZ Dept of Statistics 1993
ABS Catalogue No 1292.0

Eastern Research Group. November 1996. *Final Report: Preferred and Alternative Methods for Estimating Fugitive Emissions From Equipment Leaks*. Morrisville, NC, USA.

Economopoulos A. P. 1993. *Assessment of Sources of Air, Water, and Land Pollution. A Guide to Rapid Source Inventory Techniques and their use in Formulating Environmental Control Strategies. Part One: Rapid Inventory Techniques in Environmental Pollution*. World Health Organisation, Geneva, Switzerland.

EMEP/ CORINAIR. (1996). *AIR - Atmospheric Emission Inventory Guidebook. Secondary Zinc Processing*. The European Environment Agency, Copenhagen, Denmark.

Noyes, Robert, Editor. 1993. *Pollution Prevention Technology Handbook*. Noyes Publications, Park Ridge, NJ, USA.

USEPA. January 1995. *Compilation of Air Pollutant Emission Factors, Volume 1: Stationary Point and Area Sources, fifth edition, AP-42. Section 12.14 Secondary Zinc Processing*. 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>

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.

The following Emission Estimation Technique Manuals can be downloaded from the NPI Homepage, (<http://www.environment.gov.au/epg/npi/home.html>) or obtained from your local environmental protection agency (see the front of the NPI Guide for details):

- Emission Estimation Technique Manual for Combustion in Boilers;
- Emission Estimation Technique Manual for Combustion Engines;
- Emission Estimation Technique Manual for Fuel & Organic Liquid Storage;
- Emission Estimation Technique Manual for Surface Coating; and
- Emission Estimation Technique Manual for Electroplating and Anodising.