



National Pollutant Inventory

Emission Estimation Technique Manual

for

**The Electronics and
Computer Industry**

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**EMISSION ESTIMATION TECHNIQUES
FOR
THE ELECTRONICS AND COMPUTER INDUSTRY**

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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 electronics and computer manufacturing.

EET MANUAL : The Electronics & Computer Industry

HANDBOOK : Computers and Electronic Equipment Manufacturing

ANZSIC CODE : 2841, 2849

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

2.0 Process Description and Emission Sources

The electronics and computer industry is comprised of five major groups: telecommunications, computers, industrial electronics, consumer electronics, and semiconductors. Many segments of the electronics and computer industry are interdependent and share common manufacturing processes. Products produced by the electronics and computer industry are shown in Table 1.

Table 1 - Sectors of the Electronics and Computer Industry

Industry	Industry
Transformers	Motors and Generators
Communication Equipment	Printed Circuit Boards & Semiconductors
Integrated Circuits	Cathode Ray Tubes

Source: Queensland Department of Environment and Heritage, 1998.

Due to the vast variety of equipment manufactured by the electronics and computer industries, this Section focuses on the distinct equipment and products that raise environmental issues and which are most likely to be included by manufacturing facilities reporting to the NPI. This equipment includes:

- Semiconductors and Related Devices;
- Printed Circuit Boards (also called printed wiring boards); and
- Cathode Ray Tubes.

The Section focuses on semiconductors and not integrated circuits because integrated circuits are used to produce semiconductors and most electronic devices manufactured today are multiple devices/circuit chips. Semiconductors, although accounting for only a tiny portion of industry sales, are crucial to electronic products and pose numerous environmental concerns. Printed circuit boards and cathode ray tubes also raise environmental concerns from their manufacturing processes and facilities producing any of these products are likely to trigger NPI reporting obligations.

2.1 Semiconductors

Semiconductors can serve one of two purposes:

- (1) they act as a conductor by guiding or moving an electrical current; or
- (2) as an insulator by preventing the passage of heat or electricity.

Semiconductors are used in computers, consumer electronic products, telecommunication equipment, industrial machinery, transportation equipment, and military hardware. Typical functions of semiconductors in these products include information processing, display purposes, power handling, data storage, signal conditioning, and conversion between light and electrical energy sources. Computers, however, remain the principal end-use of semiconductors, constituting around 40 percent of the market.

Semiconductors are made of solid crystalline material, usually silicon, formed into a simple diode or many integrated circuits. A simple diode is an individual circuit that performs a single function

affecting the flow of electrical current. Integrated circuits combine two or more diodes. Up to several thousand integrated circuits can be formed on the wafer, although 200 to 300 integrated circuits are usually formed. The area on the wafer occupied by integrated circuits is called a chip or die.

The semiconductor manufacturing process is complex and may require that several of the steps be repeated to complete the process. To simplify this description, the process has been broken down into five steps:

- design;
- crystal processing;
- wafer fabrication;
- final layering and cleaning; and
- assembly.

The primary reason that semiconductors fail is contamination, particularly the presence of any microscopic residue (including chemicals and particulates) on the surface of the base material, or circuit path. Therefore, a clean environment is essential to the manufacture of semiconductors. Cleaning operations occur before and after many of the manufacturing process steps. Wet processing, during which semiconductor devices are repeatedly dipped, immersed, or sprayed with solutions, is commonly used to minimise the risk of contamination.

Step One: Design

As with any manufacturing process, the need for a particular type of product must be identified and process specifications must be developed to address that need. In the case of semiconductors, the circuit is designed using computer modelling techniques. Computer simulation is used to develop and test layouts of the circuit path. Then, patterning *masks*, which are like stencils, are fabricated, manufacturing equipment is selected, and operating conditions are set. All of these steps occur prior to actually producing a semiconductor.

Step Two: Crystal Processing

Wafers, which consist of thin sheets of crystalline material, are the starting phase of semiconductor production. Silicon, in the form of ingots, is the primary crystalline material used in the production of 99 percent of semiconductors. Silicon crystals are actually *grown* using controlled techniques to ensure a uniform crystalline structure. Because crystals of pure silicon are poor electrical conductors, controlled amounts of chemical impurities or **dopants** are added during the development of silicon ingots to enhance their semiconducting properties. Dopants are typically applied using **diffusion** or **ion implantation** processes. Dopants eventually form the circuits that carry the flow of current.

- **Diffusion** is a chemical process, which exposes the regions of the silicon surface to vapours of the metal additive (dopant) while maintaining high temperatures. The process ends when the additives migrate to the proper depth and reach the appropriate concentration in the silicon wafer.
- **Ion Implantation** is a process that allows for greater control of the location and concentration of dopants added to the wafer. Metal dopants are ionised and accelerated to a high speed.

Either doping process can be used in semiconductor manufacturing. The NPI-listed substances: antimony, arsenic, phosphorus, and boron compounds are the dopant materials most commonly used for silicon-based semiconductors. Other dopants include aluminium, gallium, gold, germanium, silicon, tin, tellurium, and the NPI-listed metals beryllium and magnesium. Emissions and solid wastes containing the listed substances: antimony, arsenic, phosphorus, and boron may be generated in the wastewater as a result of ion implantation or diffusion. Excess dopant gases, contaminated carrier gases, and out-gassed dopant gases from semiconductor materials may also be generated.

Most semiconductor manufacturers obtain single crystal silicon ingots from other manufacturing firms. Ingots are sliced into round wafers approximately 0.76mm thick and then *rinsed*. The wafers are further prepared by mechanical or chemical means. A wafer's surface may be *mechanically ground, smoothed, and polished*, as well as *chemically etched* so that the surface is smooth and free of oxides and contaminants. Chemical etching removes organic contaminants using cleaning solvents and removes damaged surfaces using acid solutions. Chemical etching is usually followed by a *deionised water* rinse and *drying* with compressed air or nitrogen. In some cases, bare silicon wafers are cleaned using ultrasound techniques, which involve potassium chromate or other mildly alkaline solutions.

Etching is a method of cutting into, or imprinting on, the surface of a material. Several etching processes can be used on semiconductors, as well as integrated circuits and printed circuit boards. Wet etching uses acid solutions to cut patterns into the metal. Dry etching involves reactive gases and is rapidly becoming the method of choice for high resolution. Dry etching processes use various halogenated or non-halogenated gaseous compounds.

In the semiconductor industry, dry plasma etching, reactive ion etching, and ion milling processes are being developed to overcome the limitations of wet chemical etching. Dry plasma etching, the most advanced technique, allows for etching of fine lines and features without the loss of definition. This process forms a plasma layer above the surface to be etched by combining large amounts of energy with low-pressure gases. The gases usually contain halogens.

Materials used during the wet etching process may include the following NPI-listed substances: sulfuric, phosphoric, nitric, hydrofluoric, and hydrochloric acids; ethylene glycol; and solutions of ammonium. Other etching materials used include hydrogen peroxide and other hydroxide solutions and ferric or potassium compounds. Materials used during the dry etching process may include chlorine, hydrogen bromide, carbon tetrafluoride, sulfur hexafluoride, trifluoromethane, fluorine, fluorocarbons, boron trichloride, hydrogen, oxygen, helium, and argon. Typical solvents and cleaning agents include the NPI-listed substances acetone, xylenes, glycol ethers, together with deionised water and isopropyl alcohol. The most commonly used cleaning solution in semiconductor manufacturing includes a variety of proprietary products containing a combination of hydrogen peroxide and sulfuric acid.

Emissions generated include acid fumes and organic solvent vapours from cleaning, etching, resist drying, developing, and resist stripping operations. Hydrogen chloride vapours may also be emitted during the etching process.

Step Three: Wafer Fabrication

Wafers are usually fabricated in batches of 25 to 40. Wafer preparation begins with an *oxidation* step.

- **Oxidation** is a process in which a film of silicon dioxide is formed on the exterior surface of the silicon wafer. Thermal oxidation takes place in a tube furnace with controlled, high temperatures

and a controlled atmosphere. Oxidation is a reaction between the silicon wafer surface and an oxidant gas, such as oxygen or steam. This process may be needed as a preliminary step before diffusion or ion implantation (doping). This layer protects the wafer during further processing. Following oxidation, the wafer surface is thoroughly cleaned and dried.

Materials used during oxidation include silicon dioxide, acids (hydrofluoric), and solvents. Materials such as oxygen, hydrogen chloride, nitrogen, trichloroethane, and trichloroethylene (perchloroethylene) may also be used.

Emissions generated from this process include spent solvents (non-halogenated) including xylenes, acetone, ethyl acetate, styrene, methyl isobutyl ketone, and methanol as well as spent acids and solvents in the wastewater.

Next, patterns are imprinted onto the substrate using *photolithography* (also referred to as lithography) and *etching* processes. Photolithography is the most crucial step in semiconductor manufacturing because it sets a device's dimensions - incorrect patterns affect the electrical functions of the semiconductor.

- **Photolithography** is a process similar to photoprocessing techniques and other etching processes. The silicon wafer is coated uniformly with a thin film of resist. A glass plate or mask is created with the circuit pattern, and the pattern is imprinted in one of several ways. One type of optical photolithography is the projection of x-rays through a special mask close to the silicon slice. Another type of optical photolithography, one that does not need a mask, is electron-beam direct patterning, which uses a controllable electron beam and an electron sensitive resist. Once the pattern is developed, some areas of the wafer are clear and the rest are covered with resist.

Two types of photoresists can be used during semiconductor production:

- **Positive photoresists** are chemicals that are made more soluble, after exposure to radiation. During development, the developer removes the resist that was exposed to radiation.
- **Negative photoresists** are chemicals that polymerise and stabilise upon exposure to radiation. During development, the developer removes the resist that was protected from radiation.

After photolithography, chemical *developers* are used to remove the unnecessary coatings or the resist material that remain on the substrate. Development can be conducted by liquid methods (dip, manual immersion, or spray coating) or dry methods (plasma). The wafer is then *etched* in an acid solution to remove selected portions of the oxide layer to create depressions or patterns. The patterns are areas in which dopants will be applied. The wafer is generally *rinsed* by immersion in a stripping solution to remove unwanted photoresist, and then dried. Table 2 provides a list of material used during the photolithography process and highlights those pollutants listed on the NPI.

Table 2 - Substances Used in Photolithography for Semiconductors

Photoresists	Developer	Solvents and Cleaning Agents
Positive: Ortho-diazonketone ^c Polymethacrylate ^c Polyfluoroalkylmethacrylate ^b Polyalkylaldehyde ^c Polycyanoethylacrylate ^{b c} Polymethylmethacrylate ^{a c}	Positive: Sodium hydroxide Potassium hydroxide Silicates Ethylene glycol ^{a c} Ethanolamine ^c Isopropyl alcohol ^c	Deionised water Detergents ^b Isopropyl alcohol ^c Acetone ^{a c} Ethanol ^{a c} Hydrofluoric acid ^a Sulfuric acid ^a

Poly(hexafluorobutylmethacrylate) ^{b c} Negative: Isoprene ^c Ethyl acrylate ^c Glycidylmethacrylate ^c Copolymer-ethylacrylate ^c	Tetramethyl-ammonium hydroxide ^b Phosphates ^a Alkyl amine ^c Ethyl acetate ^{a c} Methyl isobutyl ketone ^{a c} Negative: Xylenes ^{a c} Aliphatic hydrocarbons ^{b c} <i>n</i> -Butyl acetate ^c Cellosolve acetate ^c Isopropyl alcohol ^c Stoddard solvent ^{b c} Glycol ethers ^{a c}	Hydrogen peroxide Hydrochloric acid ^a Nitric acid ^a Chromic acid ^b Ammonium hydroxide ^b Hexamethyldisilazane ^c Xylenes ^{a c} Cellosolve acetate ^c <i>n</i> -Butyl acetate ^c Styrene ^{a c} Chlorotoluene ^c Glycol ethers ^{a c}
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Adapted from: USEPA *Office of Compliance Sector Notebook Project*, September 1995.

^a NPI-listed substance.

^b Compound or mixture containing one or more NPI-listed substance.

^c Volatile organic compound (VOC).

During the next step, *dopants* are applied to the patterned wafer surface typically using diffusion or ion implantation. See Step two for a list of materials used and emitted during the doping process.

Additional layers of silicon may also be applied to the wafer using *deposition* techniques, typical epitaxial growth or chemical vapour deposition.

- **Epitaxyl** allows the growth of another layer of silicon on top of the wafer. A silicon layer is grown using high temperatures and dopant compounds. This top layer of silicon is where the final device will be formed. Not all semiconductors need this layer.
- **Chemical vapour deposition** deposits a thin coating on materials by a chemical process. Vapour deposition is a low-pressure process that combines appropriate gases in a reactant chamber at elevated temperatures to produce a uniform film thickness.

Emissions generated from these processes include:

- acid fumes from etching operations;
- organic solvent vapours from cleaning resist drying, developing, and resist stripping; hydrogen chloride vapours from etching;
- rinsewaters containing acids and organic solvents from cleaning, developing, etching, and resist stripping processes;
- rinsewaters from aqueous developing systems; and
- spent etchant solutions; spent solvents and spent acid baths.

Many products require steps two and three to be repeated several times in order to create the specified structure.

Step Four: Final Layering and Cleaning

Once the wafer is patterned, the wafer surface is coated with thin layers of metal by a process called **metallisation**. These metal layers perform circuit functions within the finished semiconductor.

External connections to the silicon wafer are provided by evaporation of thin metal films onto areas of the semiconductor chip surface in a vacuum. Almost every metal can be used to make this electrical connection to the silicon; aluminium, platinum, titanium, nickel, chromium, silver, copper, tungsten, gold, germanium, and tantalum are the most common. Argon gas is also used in some operations. *Sputtering* and *high vacuum evaporation* are two types of metallisation.

- **Sputtering** (also called partial vacuum evaporation) is a physical, rather than chemical process. This process occurs in a vacuum chamber which contains a target (solid slab of the film material) and the wafers. Argon gas is introduced in the chamber and ionised to a positive charge. The positively charged argon atoms accelerate toward and strike the target, dislodging the target atoms. The dislodged atoms are deposited onto the wafer surface. A uniform thickness of the coating is produced over the silicon slice.
- **High vacuum evaporation** is a process that uses an electron beam, a ceramic bar heated by thermal resistance, or a wire heated by electrical resistance. This method coats the surface of the wafer with metal.

Photolithography and etching are also used to remove any unnecessary metal using chlorinated solvents or acid solutions. Emissions generated include: acid fumes and organic solvent vapours from cleaning, etching, resist drying, developing, and resist stripping; liquid organic wastes; aqueous metals; and wastewater contaminated with spent cleaning solutions.

In the next step, **passivation** is used to apply a final layer of oxide over the wafer surface to provide a protective seal over the circuit. This coating protects the semiconductor from exterior influences and may range in thickness from a single layer of silicon dioxide to a relatively thick deposit of special glass. It also insulates the chip from unwanted contact with other external metal contacts. Materials used to form the passivation layer are silicon dioxide or silicon nitride.

After all layers have been applied to the wafer, the wafer is typically rinsed in deionised water. The back of the wafer is then mechanically ground (also called lapping or backgrinding) to remove unnecessary material. A film of gold may be applied to the back of the wafer by an evaporation process to aid the connection of leads to the bonding pads during a later process step.

Testing with alcohol compounds is conducted to ensure that each chip is performing the operations for which it was designed. Chips that do not meet specifications are marked with an ink droplet for discard during assembly operations. The wafer is cleaned again after testing, using solvents such as deionised water, isopropyl alcohol, acetone, and methanol.

Emissions generated from these processes include:

- spent solvents and acids in the wastewater and rinsewater from cleaning, developing, etching, resist stripping, and rinsing processes;
- acid fumes and organic solvent vapours from cleaning, rinsing, resist drying, developing, and resist stripping;
- spent silicon dioxide or nitride;
- hydrogen chloride vapours from etching;
- rinsewaters from aqueous developing systems;
- spent etchant solutions;
- spent acid baths; and
- spent solvents.

Step Five: Assembly

Semiconductors are assembled by mounting chips onto a metal frame, connecting the chips to metal strips (leads), and enclosing the device to protect against mechanical shock and the external environment. There are many types of packaging such as plastic or ceramic.

Each package contains five parts:

1. the die (ie. the chip);
2. the lead frame of the package;
3. the die-attach pad;
4. the wire bond; and
5. the moulded encapsulant (ie. the plastic housing).

This section describes how plastic packages are assembled. All semiconductor packages whether plastic or ceramic share the same basic parts and are assembled using the same general processes.

The lead frame and leads provide the connections for the electronic components.

- The **punching** process consists of an array of small mechanical punches that remove sections of the metal sheet until the lead frame is complete. The leads are cleaned with water-based cleaning systems. Historically, manufacturers used chlorinated fluoro-carbons (CFCs) or other solvents to remove cutting fluids. The use of CFCs in Australia has been phased out during the last decade, due to their role in the depletion of the stratospheric ozone, and the manufacture and import of these chemicals has not been undertaken since early in 1996. Since this time, the use of CFCs in the semiconductor industry has been replaced by other solvents. The lead frame is coated with a layer of photoresist, exposed, and developed. The manufacturer etches the lead frame, removes the photoresist, and cleans the lead frame again with water-based cleaning systems.
- If the lead frames are **etched**, the process is similar to that used during the manufacturing of printed circuit boards. Acids or metal chlorides are usually used during etching. Sometimes ammonia is used to stabilise the metal chloride. The photoresist contain solvents (such as trichloroethylene or TCE) that are baked out and generate VOC emissions. Developers that are typically used include either an amine or metal hydroxide. Once the photoresist is removed, it is cleaned with solvents such as a mild hydrochloric acid (HCl) solution with a brightener that contains sulfuric acid (H₂SO₄).

Emissions generated during punching or etching may include:

- spent organic vapours generated from cleaning, resist drying, developing, and resist stripping;
- spent cleaning solutions;
- rinsewaters contaminated with organic solvents; and
- spent aqueous developing solutions.

Scrap copper or copper alloy may be recycled during the punching process.

The chip is then **attached** to an *attach pad*, with a substance such as an epoxy material (thermoset plastic). Once mounted, the chips are inspected. The chip parts are bonded to the leads of the package with tiny gold or aluminium wires. A package may have between two and 48 wire bonds. The assembly is cleaned and inspected again. The combined components are then placed into a moulding press, which encases the chip, wire bonds, and portions of the leads in plastic. After the moulding compound cures and cools around the package, the package is heated again to ensure that

the plastic is completely cured. Excess material is removed using a chemical or mechanical deflash process. M-Pyrol is one organic solvent used during the **deflash** process. The final steps in package fabrication include **trimming** and **forming** the leads.

Emissions generated during these steps include excess epoxy/thermoset plastic; antimony trioxide (from the moulding process); and spent organic solvents.

Table 3 summarises the emissions from all semiconductor manufacturing processes.

Table 3 - Emissions from Semiconductor Manufacturing

Process	Air Emissions	Water Emissions	Solid-Waste Emissions
Crystal Preparation	Acid fumes, VOCs, dopant gases	Spent deionised water, spent solvents, spent alkaline cleaning solutions, spent acids, spent resist material	
Wafer Fabrication	VOCs and dopant gases	Spent solvents, spent acids, aqueous metals, spent etchant solution, and spent aqueous developing solutions	Spent non-halogenated solvents: xylene, acetone, ethyl acetate, ethyl ether, ethyl benzene, methyl isobutyl ketone, methanol, cyclohexanone, and n-butyl alcohol in still bottoms
Final Layering and Cleaning	Acid fumes and VOCs	Spent deionised water, spent solvents, spent acids, spent etchants, spent aqueous developing solutions, spent cleaning solutions, aqueous metals, and chromium	Spent solvents
Assembly	VOCs	Spent cleaning solutions, spent solvents, and aqueous developing solutions	Spent epoxy material and spent solvents

Adapted from: USEPA Office of Compliance Sector Notebook Project, September 1995.

2.2 Printed Circuit Boards

Computers are also the largest Australian market for printed circuit boards (PCBs), with communications being the second largest application market. PCBs and assemblies are used in many electronic products such as electronic toys, radios, television sets, electrical wiring in cars, avionics, computers, biotechnology, medical devices, digital imaging technology, and industrial control equipment.

PCBs are the physical structures on which electronic components such as semiconductors and capacitors are mounted. The combination of PCBs and electronic components is an electronic assembly or printed circuit assembly (PCA). The manufacture of PCBs is the most chemical-intensive process in the building of a computer workstation.

PCBs are subdivided into single-sided, double-sided, multilayer, and flexible boards. Multilayer boards are manufactured in the same way as single and double-sided boards, except that conducting circuits are etched on both the external and internal layers. Multilayer boards allow for increased complexity and density. PCBs are produced using three methods: additive, subtractive, or semi-additive technology. The subtractive process accounts for a significant majority, perhaps 80 percent or more, of PCB manufacturing.

The conventional **subtractive** manufacturing process begins with a board, consisting of epoxy resin and fiberglass, onto which patterns are imaged. In most operations, conducting material, usually copper, is bonded onto the substrate surface to form copper-clad laminate. After drilling holes through the laminate and making those holes conductive, unwanted copper is etched off, leaving copper patterns. The patterns on the board form the electric circuits that conduct electricity. Multilayer boards typically use metals such as platinum, palladium, and copper to form electric circuits. Specialised PCBs may use nickel, silver, or gold.

Additive technology is used less often than subtractive technology because it is a more difficult and costly production process. This capital-intensive technology is used primarily for small interconnection components used in multi-chip devices. The production process begins with a base plate upon which a dielectric material is deposited. An interconnecting layer of copper is plated onto the dielectric layer, which connects the layers of dielectric material and copper. Copper posts are plated-up and another layer of dielectric material is deposited exposing the posts. The next interconnecting layer is plated and makes contact with the posts. Layers of dielectric material, copper, and copper posts are added to complete the chip. A lithographic process, similar to the one used in semiconductor manufacturing, diminishes the spaces and widths of the PCB.

This section provides a simplified discussion of the steps commonly performed during conventional subtractive manufacturing. The actual steps and materials used by a PCB manufacturer vary depending on customer requirements and the products being manufactured. This feature of the PCB industry ensures it is both complex and difficult to characterise the industry for NPI reporting obligations and to provide guidance in estimating emissions from PCB manufacture. Nevertheless, the following discussion attempts to provide the reader with information on the likely emissions of NPI substances expected to arise from PCB manufacture. PCB manufacturing can be grouped into five distinct steps:

- Board preparation;
- Application of conductive coatings (plating);
- Soldering;
- Fabrication; and
- Assembly.

Step One: *Board Preparation*

Board preparation begins with a **lamination** process. Two-side etched copper dielectric boards (consisting usually of fiberglass and epoxy resin) are separated by an insulating layer and laminated or bonded together, usually by heat and pressure. Photographic tools are used to transfer the circuit pattern to the PCB, and computer control programs are used to control the drilling, routing, and testing equipment. Preparing the copper-clad board involves drilling holes to establish an electrical path between the layers and to mount components. The boards are then mechanically cleaned to remove drilling wastes (that is, fine particulate contaminants, such as copper).

Vapour degreasing, abrasive cleaning, chemical cleaning with alkaline solutions, acid dips, and water rinses are techniques used to clean the boards and prepare them for the next process, namely electroless plating. Table 4 shows a list of materials used during the lamination, drilling, and cleaning processes.

Table 4 - Chemicals Used in Lamination, Drilling, and Cleaning

Lamination	Drilling	Cleaning
Epoxies ^b	Sulfuric acid ^a Potassium permanganate ^b Ammonium bifluoride ^a Oxygen Fluorocarbon gas ^{b c}	Acetone ^{a c} 1,1,1-Trichloroethane ^{a c} Silica (and other abrasives) Sulfuric acid ^a Ammonium hydroxide ^a Hydrochloric acid ^a

Source: Queensland Department of Environment and Heritage, 1998.

^a NPI-listed substance.

^b Compound or mixture containing one or more NPI-listed substance.

^c Volatile organic compound (VOC).

Emissions generated include:

- airborne particulates including PM₁₀ (particulate matter with an aerodynamic diameter of less than or equal to 10µm), acid fumes, and organic vapours from cleaning, surface preparation, and drilling;
- spent acid and alkaline solutions;
- spent developing solutions, spent etchants and waste rinsewaters in the wastewater; and
- scrap board materials and sludges from wastewater treatment.

Drilling and routing dusts (including copper) are collected and recycled.

Step Two: Electroless Plating

The first process in this step is to prepare the surfaces of the drilled holes. The holes are prepared by an etchback process to remove smeared epoxy resin and other contaminants using one of the following: sulfuric or hydrochloric acid; potassium permanganate; or carbon tetrachloride, oxygen, and nitrogen. The holes are then coated with a material such as copper or graphite carbon by a chemical process called **electroless plating**.

Electroless plating coats a uniform conducting layer of copper or other material on the entire surface including the barrels of the holes of the prepared board without outside power sources. According to *Printed Circuit Board Basics*, this coating of copper is not thick enough to carry an electrical current, but provides a base upon which additional copper can be deposited electrolytically. Copper is the industry standard, but many are switching to direct metallisation processes. Chemical deposition is the technique used to coat the board. After the electroless plating, the boards are dried to prevent the board from oxidation, or rusting. The board may also be cleaned to prepare for a following electroplating process. See Table 6 for a list of materials used.

Emissions generated include:

- spent electroless copper baths;
- spent catalyst solutions;
- spent acid solutions;

-
- spent electroless copper baths;
 - spent catalyst solutions;
 - spent acid solutions;
 - waste rinsewaters; and
 - sludges from wastewater treatment.

Step Three: Imaging

During imaging, circuit patterns are transferred onto the boards through photolithography or a stencil printing process. Photoresist (ie. a light sensitive chemical) is applied to the board in areas where the circuit pattern will not be set. The board is exposed to a radiation source and developed to remove the unwanted areas of the resist layer. Stencil printing uses a printing process, such as silk screening, to apply a protective film that forms the circuit pattern.

After photolithography, the boards are subjected to a light etching process, typically using ammoniacal etchants, to remove rust inhibitor (applied by the company that produced the material from which the board is made) or other metals (usually copper). After the stencil printing process, the protective film is dried, and the exposed copper is etched away. Sulfuric acid and hydrogen peroxide are common etchants used during imaging. After plating or etching, the photoresist is removed with a photoresist stripper.

Table 5 and Table 6 detail the materials used during photolithography and etching processes.

Table 5 - Chemicals Used in Printed Circuit Board Photolithography

Resists	Photopolymer Developers	Photopolymer Strippers
Mylar (DuPont) or Melinex (Orica) polyester film Vinyl Photoresists	Isopropyl alcohol ^c Potassium bicarbonate Sodium bicarbonate 1,1,1-Trichloroethane ^c Amines ^{b c} Glycol ethers ^c	Sodium hydroxide Potassium hydroxide Dichloromethane ^c (methylene chloride)

Source: Queensland Department of Environment and Heritage, 1998.

^a NPI-listed substance.

^b Compound or mixture containing one or more NPI-listed substance.

^c Volatile organic compound (VOC).

Emissions generated during the cleaning and etching processes include a wide range of solvents, many of which are NPI-listed. The solvents emitted depend on the concentration of the spent solvents and the mixture of spent halogenated and non-halogenated solvents; spent resist material; and wastewater containing metals (copper). Other emissions generated include organic vapours and acid fumes, spent developing solutions, spent resist material, spent etchant, spent acid solutions, and sludges from wastewater treatment.

Table 6 - Substances Used During Etching

Ammonia ^a Ammonium chloride ^a Ammonium hydroxide ^a Ammonium persulfate ^a Ammonium sulfate ^a Boric acid ^a Carbon tetrachloride ^c Chlorine ^a Cupric chloride ^a Hydrochloric acid ^a	Hydrofluoric acid ^a Hydrogen peroxide Lead ^a Nickel ^a Nickel chloride ^a Nickel sulfamate ^a Nitrate ^a Nitric acid ^a Nitrogen Orthophosphate ^a	Oxygen Peptone Permanganates ^b Sodium citrate Sodium hydroxide Stannous chloride Sulfuric acid ^a Tin
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Source: Queensland Department of Environment and Heritage, 1998.

^a NPI-listed substance.

^b Compound or mixture containing one or more NPI-listed substance.

Step Four: Electroplating

Electroplating is a process in which a metal is deposited on a substrate through electrochemical reactions. Electroplating is required to build up the thickness and strength of the conducting layers to provide reliable electrical conductivity between inner layers or from one side of the PCB to the other. Electroplating can also protect against corrosion, wear, and erosion. This process involves immersing the article to be coated or plated into a bath containing acids, bases, or salts. The industry standard for this process is copper, although many are switching to direct metallisation techniques.

The electroplating process for PCBs usually begins with the copper laminate which is coated with a plating resist (photolithography) by stencilling, leaving the area exposed to form the circuit pattern. The resist prevents the conductive material from adhering to other areas of the board and forms the circuit pattern.

The PCB plating process generally uses copper and tin-lead as plating materials, although silver, nickel, or gold, can also be used. Copper in a plating bath solution is deposited to a sufficient thickness, and a solvent or aqueous solution is applied to remove the plating resist. The copper coating forms inter-connections between the layers and provides electrical contact for electronic parts mounted or assembled on the PCB surface. PCB manufacturers then typically electroplate a tin or tin-lead solder on the board to protect the circuit pattern during the following etching or stripping processes. An acid etch solution (ammoniacal, peroxide solutions, sodium persulfate, cupric chloride, or ferric chloride) removes the exposed copper foil, leaving the thicker copper plating to form the circuit pattern. Ammoniacal and cupric chloride are the primary etchants used by PCB manufacturers. Fluoroboric acid is used in the tin-lead plating process to keep the metals dissolved in the solution and to ensure a consistent deposition of the tin-lead alloy onto the circuit board.

After the plating bath, the board is rinsed with water, scrubbed, and then dried to remove the copper, spray etch solutions, and other materials. Rinsing ends the chemical reactions during plating and prevents contamination or dragout from being released in the next bath or rinse water (dragout is the plating solution that sticks to parts after the board has been taken out of the plating bath). Dragout can occur in any bath step, not just in one plating bath. The tin-lead layer is generally removed and the panel is electrically tested for irregularities in the electrical pathway and shorts. Table 7 lists materials used during electroplating processes and highlights those listed on the NPI.

Table 7 - Materials Used in Copper and Tin-Lead Electro and Electroless Plating Processes

Type of Plating	Electroplating Chemicals	Electroless Chemicals
Copper	Copper pyrophosphate ^b Orthophosphate ^b Nitrates ^a Ammonia ^a Acid copper ^a Copper sulfate ^a Sulfuric acid ^a	Hydrochloric acid ^a Palladium chloride Stannous chloride Metallic tin pellets Sodium hydroxide Copper sulfate ^a Formaldehyde ^a
Tin-Lead	Tin-Lead ^a Fluoroboric acid ^b Boric acid ^a Peptone	Tin chloride Sodium hypophosphate ^b Sodium citrate

Source: Queensland Department of Environment and Heritage, 1998.

^a NPI-listed substance.

^b Compound or mixture containing one or more NPI-listed substance.

Emissions generated, including wastes containing NPI-listed substances, generated during plating include:

- photoresist skins;
- sludges from wastewater treatment (containing metals and acids, lead compounds, spent cyanide plating bath solutions, and plating bath residues from the bottom of plating baths from plating and etching operations where cyanides are used in the process);
- spent acid solutions, waste rinsewaters, spent developing solutions, spent etchant, and spent plating baths in the wastewater;
- organic vapours from spent developing solution and spent resist removal solution; and
- acid and ammonia fumes.

Step Five: *Soldering Coating*

Solder coating is used to add solder to PCB copper component before component assembly. Manufacturers use several methods of solder coating, but all of them involve dipping the panel into molten solder. The solder, an alloy consisting of 60 percent tin and 40 percent lead, coats the pads and holes not covered by solder mask. The excess solder is removed with a blast of hot oil or hot air. However, the hot oil or hot air does not remove the solder that has formed a chemical (intermetallic) bond with the copper. The removal of the excess solder is called *solder levelling*. The most common process is hot-air levelling. According to *Printed Circuit Board Basics: Quick and Easy Guide*, a final solder coating thickness of 1.25µm to 30.50µm can be achieved with most solder-levelling processes. Solder is only applied to desired areas so there is no metal or *objectionable fluid* emitted to the wastestream.

Step Six: *Electrical and Mechanical Testing*

A cross-section is cut from a sample panel from each lot using a grinding process called **routing**, and the plated holes are examined with a photomicrograph. Individual circuit boards are cut out of panels that pass quality control. Routing generates particulate emissions that may contain copper, lead, or other NPI-listed metals plated to the panel. However, in most instances, the particulate is recycled. Electrical tests, dimensional and visual inspections, and quality audits are performed to ensure compliance with customer expectations. Finally, the finished PCBs are packaged, labelled, and shipped to the customer which in most cases is the original equipment manufacturer (OEM) or contract electronic assembly company.

Step Seven: *Printed Circuit Board Assembly and Soldering*

After the PCBs are manufactured, the electrical components are attached during **assembly**. Adhesives are applied to the boards, and then the components are attached and soldered to the boards. Components are attached to the PCB by a process called **soldering**. There are several different kinds of soldering processes, including wave, dip, and drag. In wave soldering, the PCB is passed over the crest of a wave of molten solder, thereby permanently attaching the components to the board. A type of chemical known as *flux* is used before soldering to facilitate the production of the solder connection. Not only does flux clean the surface and remove oxidised material, it prevents oxidation from occurring during the solder process. After the solder has been applied, flux residue may be removed from the board.

Traditionally, CFCs (such as Freon 113) and 1,1,1-trichloroethane have been used to remove flux, however the manufacture and import of these materials in Australia has been banned since January 1996 due to their ozone depleting characteristics and the industry has been forced to find alternative chemicals. Many facilities have turned to deionised water. Although the residue may not affect the

PCB's performance, it may lower the board's cosmetic quality. After soldering, the board may be cleaned and dried. Many assemblies, however, are now looking at no-clean soldering operations.

Emissions generated during assembly include:

- solder dross;
- post-solder scrap boards;
- filters; and
- spent gaseous or semi-gaseous solvents from cleaning processes.

The emissions that may be generated during soldering, flux application, and cleaning include: organic vapours; copper, lead, spent solvents, and spent deionised water into the wastewater; solder dross; and wastewater treatment sludge. Solder dross is primarily oxidised solder skin that forms on any molten solder exposed to oxygen and can be transferred to be recycled off-site.

Table 8 summarises emissions from all of the PCB manufacturing processes.

Table 8 - Emissions from Printed Circuit Board Manufacture

Process	Air Emissions	Water Emissions	Solid-Waste Emissions
Board Preparation	Particulates, acid fumes, and VOCs	Spent acids and spent alkaline solutions	Sludges containing organic solvents and scrap board material (metals)
Electroless Plating		Spent electroless copper baths, spent catalyst solutions, spent acids	Waste rinse water and sludges from wastewater treatment
Imaging	Organic vapours and acid fumes	Spent developing solutions, spent resist material, spent etchants, spent acid solutions, aqueous metals	Range of spent solvents, depending on concentration and mixture of solvents. Sludges from wastewaters
Electro-plating	Acid fumes, ammonia fumes, and VOCs	Spent etchants, spent acid solutions, spent developing solutions, spent plating baths, lead compounds	Wastewater treatment sludges, spent cyanide plating bath solutions and residues
Soldering	VOCs		
PCB Assembly and Wiring	VOCs	Metals (lead, nickel, silver, and copper compounds), flux residues, spent deionised water, spent solvents	Solder dross, scrap boards, wastewater treatment sludges and residues

Adapted from: USEPA Office of Compliance Sector Notebook Project, September 1995.

2.3 Cathode Ray Tubes

The cathode ray tube (CRT) industry produces tube glass, colour picture tubes and single phosphor tubes, television sets, and computer displays. There is virtually no television tube and computer display manufacturers or CRT glass manufacturers located in Australia and, therefore, the CRT profile of this Manual focuses on the production of colour picture tubes, single phosphor tubes, and rebuilt tubes (collectively called CRTs). These products are the video display components of televisions, computer displays, military and commercial radar, and other display devices.

Cathode ray tubes (CRTs) have four major components: the glass panel (faceplate), shadow mask (aperture), electron gun (mount), and glass funnel. The glass funnel protects the electron gun and

forms the back-end of the CRT. In response to electrical signals, the electron gun emits electrons that excite the screen. The shadow mask forms a pattern on the screen. The shadow mask itself is a steel panel with a mask pattern applied through one of several kinds of photolithography.

This Section summarises the manufacturing process for colour CRTs. This description groups CRT manufacturing into six steps:

1. preparation of the glass panel and shadow mask;
2. application of the coating on the glass panel interior;
3. installation of the electron shield;
4. preparation of the funnel and joining to the glass panel/shadow mask assembly;
5. installation of the electron gun; and finishing.

Colour CRTs

The names of CRT operations may vary depending on the manufacturer, but the basic processing sequence is identical in all colour CRT manufacturing facilities. Lead in CRT display components and end-of-life concerns have been the most significant environmental issues in CRT manufacturing.

Step One: Preparation of the Panel and Shadow Mask

The shadow mask is constructed from a thin layer of aluminium steel (referred to as a flat mask) which is etched with many small slits or holes, and a metal frame that supports the flat mask. The shadow mask serves as a template for preparing a pattern on the glass panel surface. Shadow masks are commonly manufactured off shore, particularly in China and the ASEAN countries, and shipped to CRT manufacturers in Australia. The shadow mask is then **moulded** to match the contour of the glass panel's interior surface and *blackened* in an oven to provide corrosion resistance. Finally, the shadow mask is **welded** to a blackened metal frame, usually steel, which provides support. Degreasing solvents and caustics are frequently used for **cleaning** the shadow mask assembly and production equipment. Oils are used for lubricating the press and other production equipment.

The front-end glass panel is purchased from a glass manufacturer and shipped to the CRT manufacturer. Metal *pins*, provided as part of the glass panel, are attached to the inside of the glass to serve as connection points for the shadow mask.

The shadow mask is carefully positioned inside the glass panel. Steel springs are then placed over the pins in the glass panel and attached to *hook-plates* or *clips* located on the mask assembly frame. With the glass panel and shadow mask assembly positions fixed in relation to each other, the springs are **welded** to the hook-plates. The glass panel and mask must remain as a matched pair through the remaining processes. The glass panel and shadow mask preparation operation frequently uses organic solvents or caustic cleaners for degreasing, oil for equipment maintenance, and oxidisers, such as hydrogen peroxide, for cleaning reclaimed masks.

Emissions generated during this step include spent organic solvents emitted to wastewater and vapours from degreasing tanks.

Step Two: Application of Coating to Panel Interior

For the panel-mask to create images, a special coating is applied to the interior surface through a process called screening. Screening, the most complex part of the manufacturing process, is comparable to a photographic development process.

The glass panel undergoes the **carbon stripe** process, which uses organic photoresist, chromate, deionised water, dilute acids and oxidisers, carbon slurry with binding agents, and surfactants to produce the black and clear striped pattern called *black matrix*. The clear areas will eventually be filled with colour-producing phosphors. The glass panels are coated with a photoresist, which contains chromate as a catalyser. The panel is spun to even out the photoresist and then dried.

The shadow mask is re-inserted in the glass panel and a series of exposures are made on the panel surface using ultraviolet (UV) light in a **photolithography** process. The light passes through the mask openings to imprint the mask pattern on the photoresist. The mask also shadows the areas of the photoresist that will not be exposed. When UV light contacts the photoresist, polymerisation occurs, and the exposed areas become less soluble in water than in the non-exposed areas.

After the exposure, the shadow mask is removed and the glass panel is sprayed with water to remove the non-polymerised material. The imprinted pattern of exposed photoresist remains on the glass panel. The glass panel is then coated and developed again. The resulting image is essentially a *negative image* of the original photoresist exposure pattern.

During the **phosphor stripe** process, three phosphor colours (green, blue, and red) are used to make a colour CRT and are applied using the same steps as the carbon stripe process. The phosphor stripe process uses various chemicals and NPI-listed substances, including phosphor slurries containing metals (such as zinc compounds) and organic photoresists, chromate, deionised water, dilute oxidisers, and surfactants. The phosphor materials that are spun off the panels and removed in the developers are recovered and reclaimed either on-site or by a phosphor recycler. The reclaiming process involves the use of acids and caustics, chelating agents, and surfactants.

Two **coatings** are then added to the glass panel, which now has the black matrix and the three phosphor colours on it: lacquer (a wax-like layer) to smooth and seal the inside surface of the screen, and aluminium to enhance brightness. The panel is then ready to be joined to the back end of the CRT, known as the funnel. In preparation for joining, the panel edges must be **cleaned** to remove all traces of contaminants. A clean edge is critical to ensuring a good panel-to-seal connection in the finished CRT. The shadow mask and glass panel, are then reattached. Chemicals used in these processes include organic solvents and ethanol, caustics, silica-based coatings, aluminium, acids, ammonia, and deionised water. The material removed in the cleaning process is often transferred off-site to a smelter to recover metals and sulfites.

Emissions generated from this step include:

- vapours from the lacquer area;
- wastewater containing deionised water, acids, oxidisers, carbon slurry, surfactants, chromate, phosphor solutions, chelating agents, caustics, organic solvents, alcohols, silica-based coatings, ammonia, zinc, and aluminium;
- process cooling waters, liquid wastes from precipitation, washing, filtration, and scrubber blowdown;
- lacquer wastes from spun off and over-sprayed lacquer; and
- lacquer remaining in lacquer containers.

Step Three: Installation of the Electron Shield

Most CRT manufacturers employ an internal **electron shield** to prevent stray electrons from reaching outside the screen area. Computer monitor CRTs often use external shielding, which is installed on the outside of the CRT's glass bulb. Before installation, the shields are cleaned with degreasing solvents or caustic cleaners. The internal-type electron shield is made of thin aluminium and is typically **welded** to the shadow mask assembly before the panel and shadow mask are connected with the funnel. Metal (steel) springs are welded to the mask frame at this time. The springs provide an electrical connection between the mask and the funnel interior surface.

Emissions generated from these processes include electron shield degrease wastewaters containing solvents and metals from the welding.

Step Four: *Preparation of the Funnel and Joining to Panel-Mask Assembly*

The back end of the CRT (funnel) is purchased from a glass vendor and washed prior to use. The funnel is made of high lead content glass and the resulting wash water contains elevated lead levels. After the funnel is **washed**, the interior surface is **coated** with a black graphite coating which is a good electrical conductor and a non-reflective coating. The seal edge of the funnel is **cleaned** to facilitate bonding with the panel, and **frit** or **solder** glass is applied in a bead along the entire surface of the seal edge. The frit, approximately 70 percent lead, has the consistency of toothpaste or caulking. The viscosity of the frit is controlled by the addition of organic solvents. The frit serves as an adhesive to join the panel-mask assembly to the funnel.

After the frit is applied, the panel-mask assembly is connected to the funnel, and the whole glass package is placed in a positioning clamp to hold the two parts in place. The connected panel-mask and funnel assembly is then exposed to high temperatures in an oven to fuse the frit joint between the panel and funnel at the seal edges. The frit forms a strong bond between the two pieces of glass. During the **frit-seal fusion** process, the organic chemicals from the screening operation and in the frit are *burned out* of the CRT. The organic materials must *burn* cleanly to minimise any remaining residue.

Emissions generated include wastewaters contaminated with spent black graphic, lead, and chemicals associated with the funnel wash, frit application, and seal surface cleaning, including organic solvents.

Step Five: *Installation of the Electron Gun*

Each CRT contains three guns: one dedicated to each of the phosphor colours used in the screen (red, green, and blue). To produce an electron gun, several metal components are **assembled** and loaded onto spindles to align the various elements. Glass parts are placed into fixture blocks and **heated**. When the glass reaches the proper temperature, the metal parts are embedded in the glass. The combination of metal parts and glass make up the gun. The guns are **cleaned** with organic solvents or caustic cleaners before they are mounted in the neck of the CRT funnel. Materials commonly found in the gun assemblies include metals, high lead glass stem (for electrical connection feed-through and exhaust purposes), ribbon connectors, and other manufacturer-specific parts.

The gun assembly is then inserted in the neck of the CRT funnel. The gun is aligned and the CRT funnel neck is **fused** to the gun by rotating the parts in front of open flame burners. An additional component is **welded** to the gun assembly to allow for removal of gases from the electron gun in subsequent steps.

Emissions generated from this step include waste lead glass from breakages and wastewaters contaminated with spent organic solvents and caustic cleaners from mount cleaning.

Step Six: *Finishing*

The CRT *bulb* is still open to the atmosphere after the gun mount is sealed in the neck of the funnel. To complete the tube, the gases are removed by applying a vacuum to the bulb. Organic solvents are used to clean and maintain the vacuum pumps.

The bulb is *aged* by an electronic treatment applied to the gun or mount. The CRT is then coated with an external carbon black paint, and a metal band is placed around the outside of the panel with adhesives for implosion protection and safety. The band also provides mounting brackets for installing the CRT. The finished tube is tested in a high voltage testing station, and the CRT tested thoroughly to ensure that it meets all specifications before shipment. Each tube is packaged prior to shipment to the customer.

Emissions generated from finishing processes include spent solvents and VOC emissions.

In some cases where the bulb face needs a special application, such as reference lines for an oscilloscope, a separate panel and funnel are used. A photoresist and mask are used to apply the reference lines on the panel. The single phosphor is applied in the same way as for a one-piece bulb, using a settling solution that contains potassium silicate and, usually, an electrolyte.

Tube Salvage

Cathode ray tubes may or may not be salvaged. Picture tube salvage operations reclaim spent or rejected picture tubes and return them to production. Salvage operation processes include a panel-funnel acid defrit, acid cleaning of panels and funnels (usually with nitric acid), and cleaning of the shadow mask. These reclaimed components are returned to the process for reuse or are returned to the glass manufacturer for recycling. A product with knocks, scratches, or chips is repaired. New necks are spliced onto funnels. Electron guns are usually discarded. Glass that cannot be used because of serious defects is recycled back to a glass plant directly or is transferred off-site for cleaning and segregation before going to a glass plant.

CRT technology is a mature and efficient process; however, the use of a new technology called Flat Panel Displays (FPD) is becoming more common. FPDs offer certain environmental advantages over CRTs because of the tenfold reduction in the glass required with associated substantial energy savings. Existing performance deficiencies, such as poorer screen brightness and substantially higher prices, are currently hampering the widespread incorporation of FPDs into electronic products.

Table 9 summarises the likely emissions from all CRT manufacturing processes.

Table 9 - Emissions Generated from Cathode Ray Tube Manufacture

Process	Air Emissions	Water Emissions	Land Emissions
Panel and Shadow Mask	Solvent vapours	Spent solvents	Glass (lead) from breakages
Application of Coating to Panel Interior	Vapours from lacquer area	Spent photoresists, deionised water, acids, oxidisers, carbon slurry, surfactants, chromate, phosphor solution, chelating agents, caustics, solvents, alcohols, ammonia	Lacquer wastes containing organic solvents
Installation of Electron Shield		Electron shield degrease and cleaners and metals	
Preparation of Funnel & Joining to Panel-Mask Assembly		Funnel wash, seal surface cleaning, and frit application wastewaters	Frit contaminated clothing, instruments, utensils, unusable frit glass (lead), glass (lead) from breakage and off-spec product
Installation of Electron Gun		Spent solvents and caustic cleaners	Glass (lead) from breakages
Finishing	VOCs	Spent solvents	

Adapted from: USEPA *Office of Compliance Sector Notebook Project*, September 1995.

3.0 Emission Estimation Techniques: Acceptable Reliability and Uncertainty

Several techniques are available for calculating emissions of NPI-listed substances from electronics and computer manufacturing operations. The best emission estimation technique (EET) to use

depends on the emission source being evaluated, available data, available resources, and the degree of accuracy required by the facility in conducting the estimate.

In general, there are four types of emission estimation techniques from calculating emissions from electronic and computer manufacturing processes:

- mass balance;
- emission factors;
- source tests; and
- engineering calculations.

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

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

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

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

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

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

3.1 Mass Balance

A mass balance approach may be used to estimate emissions when the quantities of a material used, recycled, emitted, and disposed of are known. For liquid applications, such as wet chemical stations or coating/solvent application stations, usage figures would generally be in litres. The difference (by mass) of the amount of a liquid used and the amount of the liquid recovered, either through product recovery or disposal, is assumed to equal emissions to atmosphere.

Similarly, estimating emissions for gaseous operations would require knowledge of gas usage containing NPI-listed substances. Annual usage may be based on gross purchase amount (in cubic

metres). When operations have several formulas for different batches, a conservative emissions estimate for each listed substance may be based on the formula with the highest listed substance usage. This approach is suitable for these types of listed pollutants (xylenes, ethylbenzene, toluene, etc) because they are not involved in chemical reactions. Also, their usage and emission rates may already be tracked for purchasing reasons.

For other listed substances emitted at electronic and computer manufacturing facilities, a mass balance may not be appropriate due to the uncertainty in the extent of the chemical reactions occurring. For example, while hydrofluoric acid is used in baths and spray tools, it is also formed from the use of PFCs, such as hexafluoroethane, sulfur hexafluoride, and nitrogen trifluoride, in dry etching and chemical vapour deposition processes.

3.2 Emission Factors

Emission factors are used to estimate emissions based on known relationships between process rates and emission rates. The use of emission factors to estimate emissions from electronics and computer manufacturing facilities is an appropriate approach for NPI reporting. Development of an accurate emission factor would require detailed knowledge of the process conditions and chemical usage rates during the time period for which emissions are known. Emission factors should be applied to similar type processes utilising similar or identical chemical recipes.

Emission factors are available both for wastewater emissions and from semiconductor manufacturing activities for a wide range of NPI-listed substances and are based on the results of source tests performed on individual facilities. The reader should be aware that, in most cases, emission factors adopted for the NPI are averages of available industry-wide data, usually US or European and seldom Australian, with varying degrees of quality. Emission factors are, however, an acceptable technique for estimating emissions for the NPI where estimations of emissions are required to quantify medium to long-term emission trends.

Basically, an emission factor is the pollutant emission rate relative to the level of source activity and is usually expressed as the weight of a substance emitted multiplied by the unit weight, volume, distance, or duration of the activity emitting the substance. For example, milligrams of dichloromethane emitted per litre of wastewater discharged.

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

When using emission factors, the reader 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

3.3 Direct Measurement or Sampling Data

While technologies such as gas chromatography, mass spectrometry, and infrared spectroscopy may be available for use at electronics and computer manufacturing facilities, Australian data is not currently available to evaluate their actual use in the industry. Test methods (from the US Environmental Protection Agency) may also be used to obtain emission estimates from semiconductor, PCB, and CRT manufacturing processes for specific classes of compounds. The reader should contact their relevant State or Territory environment authority to obtain information on these test methods.

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

3.4 Engineering Calculations

In the absence of other data, engineering calculations may be used to estimate emissions from some electronic and computer manufacturing processes. For example, for any process that involves the transfer of a chemical species from the liquid phase to the vapour phase, the saturation (equilibrium) vapour pressure and exhaust flow rate from the process can be used to establish the upper limit of emissions from that process. This is a conservative approach because of the assumption that the airflow is saturated.

Table 10 summarises the most reliable EETs to use for specific NPI-listed substances from electronic and computer manufacturing processes.

Table 10 - Summary of EET Reliability for Electronic and Computer Manufacturing Processes

NPI-Listed Substance	Most Reliable EET	Alternative EETs Available
VOCs (both total and speciated)	Mass Balance	Source Testing Engineering Calculations Emission Factors
Inorganic compounds (including acids and fluoride compounds)	Source Testing	Mass Balance Engineering Calculations Emission Factors

Source: Queensland Department of Environment and Heritage, 1998.

4.0 Estimating Emissions

The first step in undertaking emission estimations at an electronics and computer manufacturing facility is generally to identify the emission points. An effective means of evaluating points of emission for NPI-listed substances is to draw a process flow diagram identifying the operations performed at a reporting facility. Figure 1 below is an example flow diagram for a semiconductor manufacturing facility.

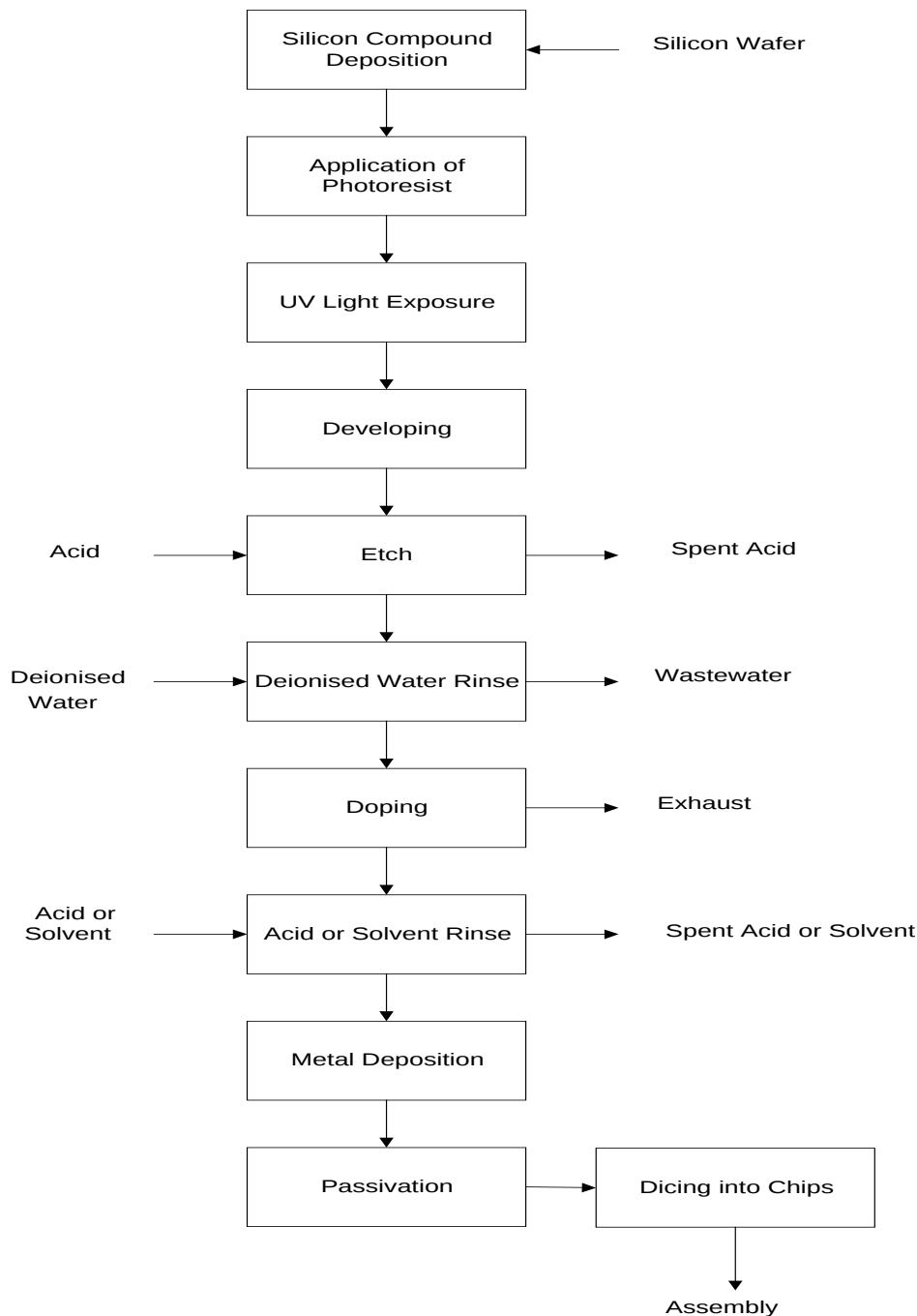


Figure 1 - Process Flow Diagram of a Semiconductor Manufacturer

Source: Queensland Department of Environment and Heritage, 1998.

Because each facility is unique, reporting facilities are strongly urged to develop flow diagrams for their own particular operations that detail the input of materials and chemicals and the emissions sources resulting from the operation of each unit.

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

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

Table 11 lists the variables and symbols used in the equations and examples throughout this section.

Table 11 - List of Variables and Symbols

Variable	Symbol	Units
Concentration of pollutant i entering the process	C_{in}	parts per million volume dry in Q_{in} , ppmvd
Concentration of pollutant i leaving the process as a product	C_{pr}	parts per million volume dry in Q_{pr} , ppmvd
Concentration of pollutant i leaving the process as waste or recycled off site	C_{rec}	parts per million volume dry in Q_{rec} , ppmvd
Molecular weight	MW	kg/kg-mole
Hourly volume of wastewater	V	litres per hour, L/hr
Molar volume	M	cubic metres (m ³)/kg-mole
Emission factor for pollutant i	EF_i	kg/units
Emissions per hour of pollutant i	E_i	kg/hr
Annual emissions of pollutant i	$E_{kpy,i}$	kg/yr
Material entering the process	Q_{in}	litres per hour, L/hr
Material leaving the process as a product (or amount of product)	Q_{pr}	litres per hour, L/hr
Material leaving the process as waste or recycled off site	Q_{rec}	litres per hour, L/hr
Volumetric flow rate of stack gas	Q_a	actual cubic metres per second (m ³ /s)
Volumetric flow rate of stack gas	Q_d	dry cubic metres per second (m ³ /s)
Average concentration of pollutant i	$C_{a,i}$	ppmvd
VOC content of material	C_{VOC}	kg/L

Table 11 - List of Variables and Symbols (cont')

Variable	Symbol	Units
Percentage by weight of pollutant i in material	wt%	%
Temperature correction for differences in temperature during test	K_t	dimensionless
Pressure correction for differences in pressure during test	K_p	dimensionless
Activity rate	A	units/hr
Saturation vapour pressure of pollutant i	$P_{sat,i}$	kilopascals, kPa
Total pressure	P_t	kPa
Density of pollutant i (or vapour density of pollutant i)	ρ_i	kg/m ³
Density of material	ρ_m	kg/L
Evaporation rate of pollutant i	$W_{kpy,i}$	kg/yr
Gas-phase mass transfer coefficient for VOC species i	K_i	m/sec
Surface area	area	m ²
Vapour pressure of pollutant i	$P_{vap,i}$	kPa
Universal gas constant	R	8.314 kPa * m ³ /(kgmol * K)
Metered volume at standard temperature and pressure	$V_{m, STP}$	m ³
Wind speed	U	km/hr
Temperature	T	°Celsius, specify °C (or if necessary Kelvin, ie. absolute temperature, K) in each equation
Annual operating hours	OpHrs	hours/year

Source: Queensland Department of Environment and Heritage, 1998.

4.1 Using Mass Balance

4.1.1 Estimating Emissions to Air

Mass balance is the recommended EET for estimating emissions of total VOCs and speciated organics in solvents, etchants, and cleaners. Total VOC emissions from electronic and computer manufacturing facilities may be estimated by application of Equation 1 where the pollutant concentration is constant throughout the process.

Equation 1

$$E_i = (Q_{in} - Q_{out}) * C_i$$

where:

$$\begin{aligned}
 E_i &= \text{total emissions of pollutant i, kg/hr} \\
 Q_{in} &= \text{material entering the process, L/hr} \\
 Q_{out} &= \text{material leaving the process as waste, recycled,} \\
 &\quad \text{or in product, L/hr} \\
 C_i &= \text{concentration of pollutant i, kg/L}
 \end{aligned}$$

Example 1 illustrates the application of Equation 1.

Example 1 - Using a Mass Balance to Estimate VOC Emissions

This example shows how VOC emissions may be calculated using Equation 1 for a cleaning process given the following data:

$$\begin{aligned}
 Q_{in} &= 6 \text{ L/hr} \\
 Q_{out} &= 4 \text{ L/hr} \\
 C_{VOC} &= 0.85 \text{ kg VOC/L} \\
 E_{VOC} &= (Q_{in} - Q_{out}) * C_{VOC} \\
 &= (6 \text{ L/hr} - 4 \text{ L/hr}) * 0.85 \text{ kg VOC/L} \\
 &= 1.7 \text{ kg/hr}
 \end{aligned}$$

The term Q_{out} may actually cover several different fates for an individual listed substance. This could include the amount recovered or recycled, the amount leaving the process in the manufactured product, the amount leaving the process in wastewater, or the amount of material transferred off-site as hazardous waste or to landfill. A thorough knowledge of the different fates for the pollutant of interest is necessary for an accurate emission estimate to be made using the mass balance approach. Where the pollutant concentrations are different in the process and waste materials to the stream entering the process Equation 2 can be used.

Equation 2

$$E_i = Q_{in} * C_{in} - Q_{pr} * C_{pr} - Q_{rec} * C_{rec}$$

where:

$$\begin{aligned}
 E_i &= \text{total emissions of pollutant i, kg/hr} \\
 Q_{in} &= \text{material entering the process, L/hr} \\
 Q_{pr} &= \text{amount of material leaving the process as a product (or amount of product), L/hr} \\
 Q_{rec} &= \text{material leaving the process as waste or recycled off-site, L/hr} \\
 C_{in} &= \text{concentration of pollutant i in } Q_{in}, \text{ kg/L} \\
 C_{pr} &= \text{concentration of pollutant i in } Q_{pr}, \text{ kg/L} \\
 C_{rec} &= \text{concentration of pollutant i in } Q_{rec}, \text{ kg/L}
 \end{aligned}$$

Speciated VOC emissions may be estimated by a mass balance approach using Equation 3.

Equation 3

$$E_i = (Q_{in} - Q_{out}) * \rho_m * (wt\%_i) / 100$$

where:

E_i	=	total emissions of pollutant i, kg/hr
Q_{in}	=	material entering the process, L/hr
Q_{out}	=	material leaving the process as a transfer, or as an article or product, L/hr
ρ_m	=	density of material, kg/L
$wt\%_i$	=	percentage by weight of pollutant i in material, %

The use of Equation 3 should provide a reasonably accurate estimate in most cases, especially if other emissions are small compared with air emission losses. Individual emissions of organic chemicals from storage tanks should be estimated using the methods and procedures outlined in the *Fuel and Organic Liquid Storage EET Manual*.

Example 2 illustrates the application of Equation 3.

Example 2 - Using a Mass Balance to Speciate VOC Emissions

This example shows how toluene emissions may be calculated using Equation 3 for a cleaning process using toluene-containing solvent given the following data:

Q_{in}	=	6 L/hr
Q_{out}	=	4 L/hr
$\rho_{solvent}$	=	0.87 kg /L
$wt\%_{toluene}$	=	25%
$E_{toluene}$	=	$(Q_{in} - Q_{out}) * \rho_{solvent} * (wt\%_{toluene} / 100)$
	=	$(6 \text{ L/hr} - 4 \text{ L/hr}) * 0.87 \text{ kg /L} * (25/100)$
	=	0.435 kg/hr

4.1.2 Estimating Emissions to Water

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

Equation 4

$$E_{kpy,i} = (Q_{in} - Q_{out})$$

where:

$E_{kpy,i}$	=	emissions of pollutant i, kg/yr
Q_{in}	=	amount of pollutant i used, kg/yr
Q_{out}	=	amount of pollutant i incorporated into product + treated on-site + transferred off-site in the reporting year, kg/yr

Where a facility uses a listed mineral acid or base, with this acid or base being effectively neutralised in use or during wastewater treatment (to a pH of 6 to 8, as required by most State and

Territory effluent standards), no emission quantities should be reported. If the acid or base is itself transformed into another listed substance, however, the quantity of this substance coincidentally produced must be determined to assess if a threshold value has been reached. For example, sulfuric acid often yields hydrogen sulfide (an NPI-listed substance) in effluent streams.

4.1.3 Estimating Emissions to Land

Wastewater treatment may transport the reportable substance to a sludge. Facilities are often required to obtain data on the concentration of metals and other substances in sludges as part of their licensing requirement and this data can be used to calculate the emissions as kilograms of sludge times concentrations of the substance in the sludge. Alternatively, the loss in the sludge can be estimated by application of Equation 5. Although listed substances in sludge transferred off-site for waste disposal/treatment do not require reporting, determining this loss may be a necessary step in the application of such a mass balance approach.

Equation 5

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

where:

$$\begin{aligned} AS_{kpy,i} &= \text{amount of pollutant i in sludge, kg/yr} \\ PL_i &= \text{process losses of pollutant i, kg/hr} \\ WL_i &= \text{losses of pollutant i in wastewater, kg/hr} \\ OpHrs &= \text{operational hours, hr/yr} \end{aligned}$$

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

4.2 Using Sampling Data

4.2.1 Estimating Emissions to Air

Sampling test methods can be used to estimate organic and inorganic pollutant emission rates from semiconductor and other electronic manufacturing processes. Airflow rates can be determined from flow rate metres or from pressure drops across a critical orifice (an opening).

Sampling test reports often provide chemical concentration data in parts per million by volume (ppmv). If the concentration is known, an hourly emission rate can be determined using Equation 6.

Equation 6

$$E_i = (C_i * MW_i * Q_d * 3600) / [22.4 * \{(T + 273)/273\} * 10^6]$$

where:

$$E_i = \text{total emissions of pollutant i, kg/hr}$$

C_i	=	concentration of pollutant i, ppmv (volume of pollutant gas/ 10^6 volumes of dry air)
MW_i	=	molecular weight of pollutant i, kg/kg-mole
Q_d	=	stack gas volumetric flow rate, m^3/s
22.4	=	volume occupied by 1 mole of ideal gas at standard temperature and pressure (0°C and 101.3 kPa), m^3/kg -mole
3 600	=	conversion factor, s/hr
T	=	temperature of gas sample, °C
10^6	=	conversion factor from ppmv to volume fraction

Emissions in kilograms per year can be calculated by multiplying the average hourly emission rate (kg/hr) from Equation 6 by the number of operating hours (shown in Equation 7 below) or by multiplying an average emission factor (kg/L) by the total annual amount of material used (L).

Equation 7

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

where:

$E_{kpy,i}$	=	annual emissions of pollutant i, kg/yr
E_i	=	total hourly emissions of pollutant i, kg/hr
OpHrs	=	annual operating hours, hr/yr

Concentration data obtained from source testing may come in a variety of units, including parts per million volume (ppmv), or grams per cubic metre (g/m^3), and in a variety of conditions, such as wet, dry, or excess O_2 . This may require conversion of concentration data to consistent units for compatibility with the equations given above.

Example 3 illustrates the use of Equation 6, and Equation 7.

Example 3 - Estimating Ammonia Emissions to Atmosphere

This example shows how annual ammonia (NH₃) emissions can be calculated using the data obtained from a stack or other point source emission points. Using a known ammonia concentration and an exhaust gas temperature of 25°C (298 K), annual emissions are calculated using Equation 6.

Given:

$$\begin{array}{llll} C_i & = & 15.4 \text{ ppmv} & MW_i & = & 17 \text{ kg/kg-mole of ammonia} \\ Q_d & = & 8.48 \text{ m}^3/\text{s} & \text{OpHrs} & = & 1760 \text{ hr/yr} \\ T & = & 25^\circ\text{C (298 K)} & & & \end{array}$$

Hourly emissions of NH₃ are calculated using Equation 6:

$$\begin{aligned} E_{\text{NH}_3} &= (C_i * MW_i * Q_d * 3600) / [22.4 * \{(T + 273)/273\} * 10^6] \\ &= (15.4 * 17 * 8.48 * 3600) / [22.4 * (298/273) * 10^6] \\ &= 3.269 * 10^{-1} \text{ kg/hr} \end{aligned}$$

Annual emissions of NH₃ are calculated using Equation 7:

$$\begin{aligned} E_{\text{kpy,NH}_3} &= E_{\text{NH}_3} * \text{OpHrs} \\ &= 3.269 * 10^{-1} * 1760 \\ &= 575.34 \text{ kg/yr} \end{aligned}$$

4.2.2 Estimating Emissions to Water

Because of the significant environmental hazards posed by emitting toxic substances to water, most facilities emitting NPI-listed substances to waterways are required by their relevant State or Territory environment authority to closely monitor and measure these emissions. This existing monitoring data can be used to calculate annual emissions by the use of Equation 8.

Equation 8

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

where:

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

In applying Equation 8 to water emission calculations, monitoring data should be averaged and only representative concentrations used in emission calculations.

4.3 Using Emission Factors

4.3.1 Estimating Emissions to Air

Emission factors may be used to estimate VOCs, speciated VOCs, and inorganic pollutant emissions from electronic and computer manufacturing processes using Equation 9.

Equation 9

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

where:

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

Example 4 illustrates the application of Equation 9. Currently there are no industry emissions factors available specific to electronic and computer manufacturing processes, and emission factors will need to be developed by facilities reporting to the NPI specific to the processes or operations of interest.

Example 4 - Using Emission Factors to Estimate Emissions to Air

This example^a shows how HF emissions may be calculated using emission factors and Equation 9 given the following data:

EF_{HF}	=	$6.0 * 10^{-3}$ kg HF/wafer
A	=	30 wafers/hr
$OpHrs$	=	1 750 hr/yr
CE_{HF}	=	0 (since EF_{HF} is a controlled figure)
$E_{kpy,HF}$	=	$[A * OpHrs] * EF_{HF} * [1 - CE_i/100]$
	=	$[30 \text{ wafers/hr} * 1\,750 \text{ hr/yr}] * 6.0 * 10^{-3} \text{ kg /wafer} * [1 - 0/100]$
	=	315 kg/yr

^a The emission factor used in this example was developed with site-specific data from a semiconductor manufacturing facility.

4.3.2 Estimating Emissions to Water

Table 12 gives minimum and maximum concentrations for many NPI-listed substances contained in untreated wastewaters from US semiconductor facilities. In the absence of site-specific monitoring data, this US data can be used as emission factors to estimate emissions to wastewater. Equation 10 shows this calculation.

Equation 10

$$E_{kpy,i} = C_i * V * OpHrs/10^6 * [1 - (CE_i/100)]$$

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
10^6	=	conversion factor, mg/kg
CE_i	=	overall emission control efficiency of the wastewater treatment operation for pollutant i, %

Where wastewaters are treated on-site, emissions must be adjusted to reflect the effectiveness of the treatment. Where available, data on the operation of the specific treatment facility should be used. Example 5 illustrates the application of Equation 10 showing how to adjust an emission factor equation to take account of the control efficiency of a wastewater treatment operation.

Example 5 - Using Emission Factors to Estimate Emissions to Water

Using published wastewater emission concentrations, annual wastewater emissions of chloroform can be calculated using Equation 10 and the maximum concentration reported from untreated wastewater (from Table 12). Assume the facility operates for 260 days during year, an average 4 000 000 litres of water is used daily, and the facility's wastewater treatment plant has an efficiency for chloroform of 87% following screening and trickling filter.

$$\begin{aligned} E_{kpy, \text{chloroform}} &= C_i * V * OpHrs/10^6 * [1 - (CE_i/100)] \\ E_{kpy, \text{chloroform}} &= 2.6 \text{ mg/L} * 4\,000\,000 \text{ L/day} * 260 \text{ day/yr} / \\ &\quad 10^6 \text{ mg/kg} * [1 - (87/100)] \\ &= 351.5 \text{ kg/yr} \end{aligned}$$

Table 12 - Concentration of NPI-Listed Substances in Untreated Wastewater from US Semiconductor Manufacturing Facilities

NPI-Listed Substance	Minimum Concentration (mg/L)	Maximum Concentration (mg/L)
Benzene	< 0.01	0.190
Chloroform	0.004	2.6
Dichloromethane (methylene chloride)	0.005	2.4
Phenol	0.0004	5.7
Bis(2-ethylhexyl)phthalate	0.002	0.750
Ethylbenzene	0.0002	0.107
Tetrachloroethylene (perchloroethylene)	0.0002	0.80
Toluene	0.0002	0.14
Trichloroethylene	0.0049	3.5
Antimony	< 0.0005	0.187
Arsenic	< 0.003	0.067
Beryllium	< 0.001	< 0.015
Cadmium	< 0.001	0.008
Chromium (total)	< 0.001	1.150
Cobalt	< 0.001	0.48
Copper	< 0.005	2.588
Cyanide	< 0.005	0.01
Lead	< 0.04	1.459
Manganese	< 0.001	0.209
Mercury	< 0.001	0.051
Nickel	0.005	4.964
Selenium	< 0.002	0.045
Zinc	0.001	0.289

Source: USEPA AP-42, 1988.

4.4 Using Engineering Calculations

Theoretical and complex equations or *models* can be used for estimating emissions from electronic and computer manufacturing processes. Inputs for theoretical equations generally fall into the following categories:

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

Engineering equations are suitable for estimating emissions from several chemical manufacturing processes. For example, for any process involving a transfer of a chemical species from the liquid phase to the vapour phase, the saturation or equilibrium vapour pressure and exhaust flow rate from the process can be used to establish the upper limit of emissions from that particular process. This is a conservative approach because of the assumption that the total airflow is saturated. An alternative technique based on mass transfer kinetics does not assume airflow saturation and results in a lower emission rate estimate than would be obtained assuming saturation.

4.4.1 Estimating Emissions Using Mass Transfer Kinetics

An EET based on mass transfer kinetics is shown by Equation 11.

Equation 11

$$E_{kpy,i} = (MW_i * K_i * area * P_{vap,i} * 3600 * OpHrs) / (R * T)$$

where:

$E_{kpy,i}$	=	emission (evaporation rate) of pollutant i, kg/yr
MW_i	=	molecular weight of pollutant i, kg/kg-mole
K_i	=	gas-phase mass transfer coefficient for VOC species i, m/sec
	=	$[0.00438 * (0.62138 * U)^{0.78} * (18/MW_i)^{1/3}] / 3.2808$
U	=	wind speed, km/hr
$area$	=	surface area, m^2
$P_{vap,i}$	=	vapour pressure of pollutant i, kPa
3600	=	conversion of 3600 sec/hr
$OpHrs$	=	hours of operation each year hr/yr
R	=	universal gas constant (8.314 kPa * m^3 / (kg-mol * K))
T	=	temperature, K

Example 6 illustrates the application of this equation.

Example 6 - Using Mass Transfer Kinetics

This example shows how methanol emissions may be estimated using mass transfer kinetics and Equation 11 given the following data:

$MW_{methanol}$	=	32 kg/kg-mole
U	=	7.24 km/hr
$area$	=	0.6 m^2
$P_{vap,methanol}$	=	13.16 kPa
3600	=	3600 sec/hr
$OpHrs$	=	1000 hr/yr
T	=	296 K
R	=	8.314 kPa * m^3 / (kg-mol * K)

First, calculate the mass transfer coefficient, K_i :

$$\begin{aligned} K_i &= [0.00438 * (0.62138 * U)^{0.78} * (18/MW_i)^{1/3}] / 3.2808 \\ &= [0.00438 * (0.62138 * 7.24 \text{ km/hr})^{0.78} * (18/32 \text{ kg/kg-mole})^{1/3}] / 3.2808 \\ &= 0.0035 \text{ m/s} \end{aligned}$$

Then, calculate $E_{kpy,methanol}$:

$$\begin{aligned} E_{kpy,methanol} &= (MW_{methanol} * K_i * area * P_{vap,methanol} * 3600 * OpHrs) / (R * T) \\ &= (32 \text{ kg/kg-mole} * 0.0035 \text{ m/sec} * 0.6 \text{ m}^2 * 13.16 \text{ kPa} * 3600 \text{ sec/hr} * 1000 \text{ hr/yr}) / \{(8.314 \text{ kPa} * \text{m}^3 / (\text{kg-mol} * \text{K})) * (296 \text{ K})\} \\ &= 1294 \text{ kg/yr} \end{aligned}$$

4.4.2 Estimating Emissions from Spills

A vaporisation equation can be used to estimate the evaporation rate of a liquid chemical spill if the size area of the spill is known or can be estimated. This is illustrated by Equation 12.

Equation 12

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

where:

E_i	=	emissions of VOC species i from the spill, kg/event
MW_i	=	molecular weight of VOC species i, kg/kg-mole
K_i	=	gas-phase mass transfer coefficient for VOC species i, m/sec
area	=	surface area of spill, m ²
P_i	=	partial pressure of VOC species i (if a pure chemical is spilled) or the partial pressure of chemical i (if a mixture of VOCs is spilled) at temperature T, kPa; the partial pressure of VOC species i (P_i) may be calculated using Equation 13 or Equation 14
3 600	=	conversion factor, sec/hr
HR	=	duration of spill, hr/event
R	=	universal gas constant at 101.3 kPa of pressure, (8.314 kPa * m ³ / (kg-mol * K))
T	=	temperature of the liquid spilled, K

P_i may be calculated using Raoult's Law (for ideal solutions) or Henry's Law constants (when gases are dissolved at low concentrations in water). Raoult's Law is given in Equation 13.

Equation 13

$$P_i = m_i * VP_i$$

where:

P_i	=	partial vapour pressure of VOC species i, kPa
m_i	=	liquid mole fraction of VOC species i, mole/mole
VP_i	=	true vapour pressure of VOC species i, kPa

P_i may be calculated using Henry's Law constants and Equation 14.

Equation 14

$$P_i = m_i * H_i$$

where:

P_i	=	partial vapour pressure of VOC species i, kPa
m_i	=	liquid mole fraction of VOC species i, mole/mole
H_i	=	Henry's Law constant for VOC species i, kPa

The gas-phase mass transfer coefficient (K_i) may be calculated using Equation 15.

Equation 15

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

where:

K_i	=	gas-phase mass transfer coefficient for VOC species i, m/sec
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U = wind speed, km/hr
D_i = diffusion coefficient for VOC species i, in air, cm²/sec

Diffusion coefficients (D_i) can be found in chemical handbooks and are usually expressed in units of square centimetres per second (cm²/sec). If a diffusion coefficient is not available for a particular NPI-listed substance, the gas-phase mass transfer coefficient (K_i) may be estimated using Equation 16.

Equation 16

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

where:

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

Example 7 illustrates the use of Equation 12 through to Equation 16. Emissions are calculated by following Steps 1 and 2.

Example 7 - Calculating Emissions from Chemical Spills

Formaldehyde is spilled onto the ground outside a building. The following data is given:

- the spill is not detected for 1 hour; it takes an additional 2 hours to recover the remaining formaldehyde; the duration of the spill (hr), therefore, is 3 hours;
- the average wind speed (U) is 33.8 km/hr;
- the ambient temperature (T) is 298 K (25°C);
- the surface area of the spill (area) is 11 m²;
- the molecular weight of formaldehyde (MW_i) is 30 kg/kg-mole; and
- the vapour pressure of formaldehyde (P_i) at 298 K (25°C) is 29.6 kPa.

Step 1: Using Equation 16, Calculate the Gas-Phase Mass Transfer Coefficient ($K_{\text{formaldehyde}}$)

$$\begin{aligned} K_{\text{formaldehyde}} &= (0.00438 * (0.62138 * U)^{0.78} * (18/MW_i)^{1/3}) / 3.2808 \\ &= (0.00438 * (0.62138 * 33.8)^{0.78} * (18/30)^{1/3}) / 3.2808 \\ &= 0.0124 \text{ m/sec} \end{aligned}$$

Step 2: Using Equation 12, Calculate Emissions ($E_{\text{formaldehyde}}$)

$$\begin{aligned} E_{\text{formaldehyde}} &= (MW_i * K_i * \text{area} * P_i * 3600 * \text{HR}) / (R * T) \\ &= (30 * 0.0124 * 11 * 29.6 * 3600 * 3) / (8.314 * 298) \\ &= 528 \text{ kg/spill} \end{aligned}$$

4.4.3 Estimating Fugitive Emissions

Many of the engineering equations presented in this section are to be applied to estimate emissions of organic compounds. Other than using emission factors or applying the mass balance technique for estimating emissions, there is little information currently available for estimating fugitive emissions of inorganic compounds. However, in electronics and computer manufacturing, it may be necessary to estimate emissions of inorganic compounds for NPI-reporting purposes. This is particularly the case for mineral acids in the gas/vapour phase.

Emission estimates of inorganic compounds can be obtained for electronics and computer manufacturing processes by the following techniques:

- develop correlations specific to particular chemical manufacturing 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 13 and Equation 17; or
- Use the screening values obtained above and apply the emission factors, from Table 14, corresponding to the screening range obtained.

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).

Also, 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 process lines. Equation 17 illustrates an approach for estimating fugitive inorganic chemical emissions using data from Table 13.

Equation 17

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

where:

$$\begin{aligned}
 E_{kpy,i} &= \text{mass emissions of pollutant i calculated from} \\
 &\quad \text{either the screening values, correlation equation,} \\
 &\quad \text{or emission factors, kg/yr/source} \\
 ER_i &= \text{emission rate, kg/hr/source} \\
 C_i &= \text{concentration of pollutant i in the equipment, \%} \\
 OpHrs &= \text{operating hours, hr/yr/source}
 \end{aligned}$$

The application of Equation 17 is given at Example 8.

Table 13 - Correlation Equations, Default Zero Emission Rates, and Pegged^c Emission Rates for Estimating Fugitive Emissions

Equipment Type	Default Zero Emission Rate (kg/hr/source)	Pegged Emission Rates (kg/hr per source)		Correlation Equation (kg/hr per 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 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.

Example 8 - Estimating Fugitive Emissions

A electronics manufacturing facility operates a light-liquid pump on an 80 percent ammonia solution storage tank. The pump is run for 8760 hours during the year.

For a Screening Value of zero ppmv

$$\begin{aligned}\text{OpHrs} &= 8760 \text{ hr/yr} \\ \text{SV (screening value)} &= 0 \text{ ppmv} \\ \text{Default-zero emission rate} &= 7.5 * 10^{-6} \text{ kg/hr/source}\end{aligned}$$

Using Equation 17:

$$\begin{aligned}\text{NH}_3 \text{ emissions} &= \text{ER}_i * \text{C}_i/100 * \text{OpHrs} * \text{number of sources} \\ &= 7.5 * 10^{-6} \text{ kg/hr/source} * \\ &\quad (80/100) * 8760 \text{ hr/yr} \\ &= 5.26 * 10^{-2} \text{ kg/yr}\end{aligned}$$

For a Screening Value of 20 ppmv

$$\begin{aligned}\text{OpHrs} &= 8760 \text{ hr/yr} \\ \text{SV (screening value)} &= 20 \text{ ppmv} \\ \text{NH}_3 \text{ emissions (kg/hr)} &= 1.90 * 10^{-5} (\text{SV})^{0.824} \\ &= 1.90 * 10^{-5} (20)^{0.824} \\ &= 2.24 * 10^{-4} \text{ kg/hr} \\ \text{NH}_3 \text{ emissions (kg/yr)} &= 2.24 * 10^{-4} \text{ kg/hr} * 8760 \text{ hr/yr} * \\ &\quad (80/100) \\ &= 1.57 \text{ kg/yr}\end{aligned}$$

Table 14 - 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.

4.5 Other Emission Sources

As shown in earlier sections, electronic and computer manufacturing activities produce other emission sources for NPI-listed substances. These include:

- residues from pollution control devices;
- wash and rinse water from equipment cleaning;
- product rejects;
- used equipment; and
- empty chemical containers.

Emissions from these sources may already have been accounted for, depending on the emission estimation techniques used. These items (and others of a similar facility specific nature) should be included in the development of a process flow diagram.

The contribution of the above sources of emissions, such as cleaning out vessels or discarding containers, should be small when compared with process losses. If data is unavailable for these sources (or any monitoring data on overall water emissions), facility operators should assume up to 1 percent of total vessel content may be lost during each cleaning occurrence. For example, if a facility discards the *empty* drums that have not been cleaned, calculate the emission as 1 percent of normal drum content. If the drum is transferred off-site to a landfill or to a drum recycler, then the reportable substance is also transferred off-site and therefore does not require reporting. If however, the drums are washed before disposal, this may contribute 1 percent of the content to the facility's wastewater loading.

5.0 References

Flatt, Michael, 1992, *Printed Circuit Board Basics: Quick and Easy Guide*, 2nd Ed.

USEPA, January 1988, *Title II Section 313 Release Reporting Guidance: Estimating Chemical Releases from Semiconductor Manufacturing*. United States Environmental Protection Agency, Office of Pesticides and Toxic Substances, Washington, DC, USA.

USEPA, 1994, *Toxic Release Inventory (TRI) Public Data Release 1993*. United States Environmental Protection Agency, Office of Pollution Prevention and Toxics, (EPA/745-R94-001), 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, September 1995, *EPA Office of Compliance Sector Notebook Project. Profile of the Computer and Electronics Industry*, United States Environmental Protection Agency, Office of Enforcement and Compliance Assurance, Washington, DC, USA.

Van Zant, Peter, 1990, *Microchip Fabrication: A Practical Guide to Semiconductor Processing*, 2nd Ed. McGraw Hill, Inc.

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

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