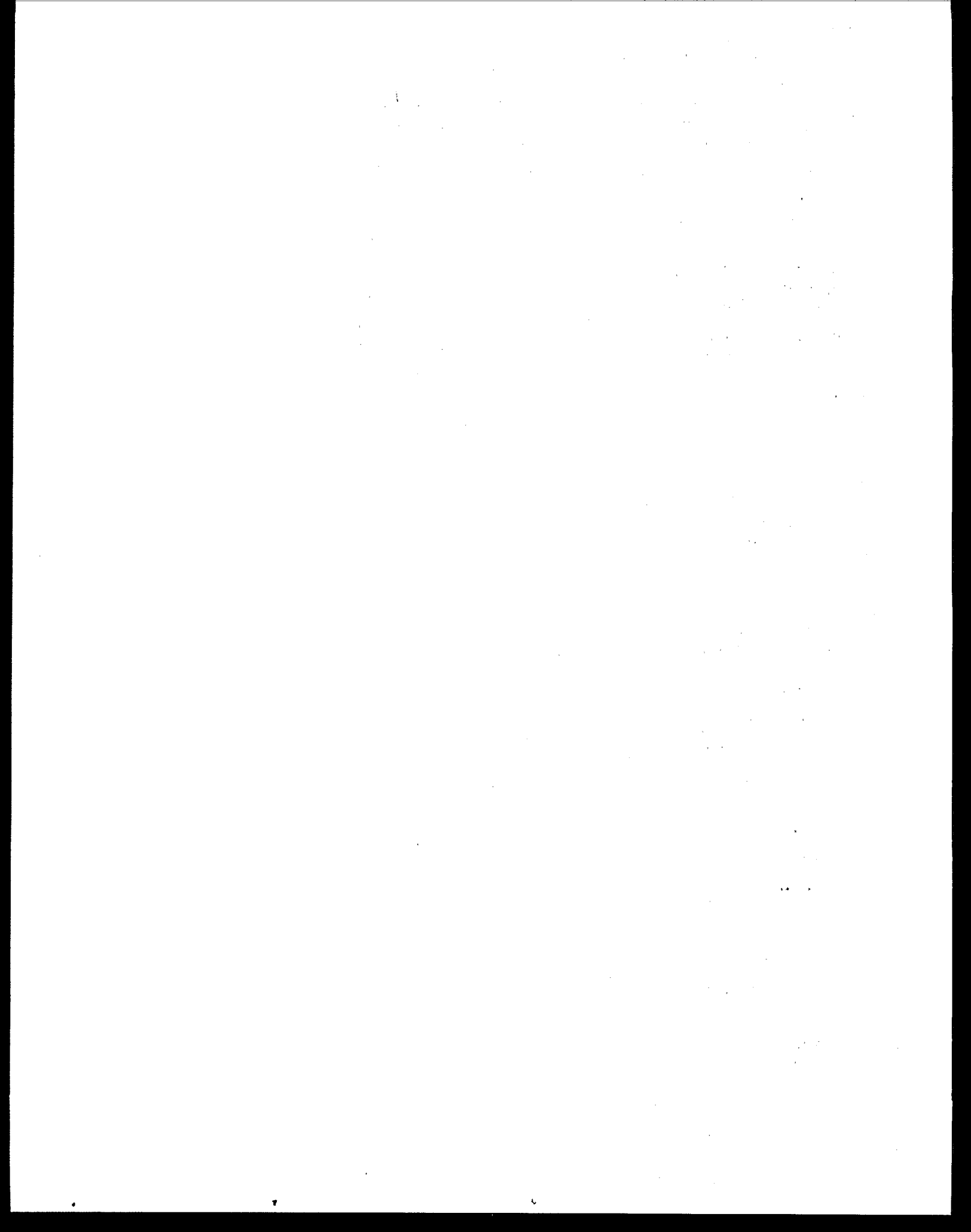




Title III Section 313 Release Reporting Guidance

*Estimating Chemical Releases From
Semiconductor Manufacturing*



Estimating Chemical Releases From Semiconductor Manufacturing

Manufacturers of semiconductors may be required to report annually any releases to the environment of certain chemicals regulated under Section 313, Title III, of the Superfund Amendments and Reauthorization Act (SARA) of 1986. If your facility is classified under SIC codes 20 through 39 (semiconductor manufacturers generally fall under SIC code 3674) and has 10 or more full-time employees, for calendar year 1987 you must report all environmental releases of any Section 313-listed chemical or chemical category manufactured or processed by your facility in an amount exceeding 75,000 pounds per year or otherwise used in an amount exceeding 10,000 pounds per year. For calendar years 1988 and 1989 (and beyond), the threshold reporting quantity for manufactured or processed chemicals drops to 50,000 and 25,000 pounds per year, respectively.

This document has been developed to assist semiconductor manufacturers in the completion of Part III (Chemical Specific Information) of the Toxic Chemical Release Inventory Reporting Form. Included herein is general information on toxic chemicals used and process wastes generated, along with several examples to demonstrate the types of data needed and various methodologies available for estimating releases. If your facility performs other operations in addition to semiconductor manufacturing, you must also include any releases of toxic chemicals from these operations.

Step One

Determine if your facility processes or uses any of the chemicals subject to reporting under Section 313.

A suggested approach for determination of the chemicals your facility uses that could be subject to reporting requirements is to make a detailed review of the chemicals and materials you have purchased. If you do not know the specific ingredients of a chemical formulation, consult your suppliers for this information. If they will not provide this information, you must follow the steps outlined to handle this eventuality in the instructions provided with the Toxic Chemical Release Inventory Reporting Form.

The list presented here includes chemicals typically used in the manufacture of semiconductors that are subject to reporting under Section 313. This list does not necessarily include all of the chemicals your facility uses that are subject to reporting, and it may include many chemicals that you do not use. You should also determine whether any of the listed chemicals are created during processing at your facility.

Solvents: Acetone, aniline, chlorinated fluorocarbons, chlorobenzene, chloroform, chloromethane, methanol, methyl ethyl ketone, methyl isobutyl ketone, tetrachloroethylene, 1,2,4-trichlorobenzene, 1,1,1-trichloroethane

Dopants: Antimony, arsenic, cadmium, phosphorus, selenium, zinc

Electroless solutions: Formaldehyde

Etch components: Chlorine, hydrochloric acid, hydrogen fluoride, nitric acid, phosphoric acid, sodium hydroxide, sulfuric acid

Carrier gas: Ammonia

Solder components: Lead, silver

Metallization components: Beryllium, chromium, copper, nickel, vanadium

Photoresist chemicals: Ethylene glycol, toluene, xylene

part of the marketed finished product. Degreasing solvents, cleaning agents, and other chemicals that do not become part of the finished product would be considered "otherwise used."

The amount of a chemical processed or otherwise used at your facility represents the amount purchased during the year, adjusted for beginning and ending inventories. To ascertain the amount of chemical in a mixed formulation, multiply the amount of the mixture (in pounds) by the concentration of the chemical (weight percent) to obtain the amount of chemical processed.

Example: Calculating annual use of acetone through purchases and inventory changes.

Opening stock	5,000lb
Plus purchases during year	12,000 lb
	<hr/>
	17,000 lb
Less closing stock	6,000 lb
	<hr/>
Total use	11,000 lb

A listed chemical may be a component of several formulations you purchase, so you may need to ask your supplier for information on the concentration (percentage) of the chemical in each. For chemical categories, your reporting obligations are determined by the total amounts of all chemicals in the category.

You must complete a report for each chemical for which a threshold is exceeded. The thresholds apply separately; therefore, if you both process and use a chemical and either threshold is exceeded, you must report for both activities. If neither threshold is exceeded, no report is needed.

Step Two

Determine if your facility surpassed the threshold quantities established for reporting of listed chemicals last year.

You must submit a separate Toxic Chemical Release Inventory Reporting Form for each listed chemical that is "manufactured," "processed," or "otherwise used" at your facility in excess of the threshold quantities presented earlier. Manufacture includes materials produced as byproducts or impurities. Toxic compounds that are incorporated into your products (for example, a dopant applied to a metal) would be considered "processed" because they become

Step Three

Identify points of release for the chemical(s) subject to reporting.

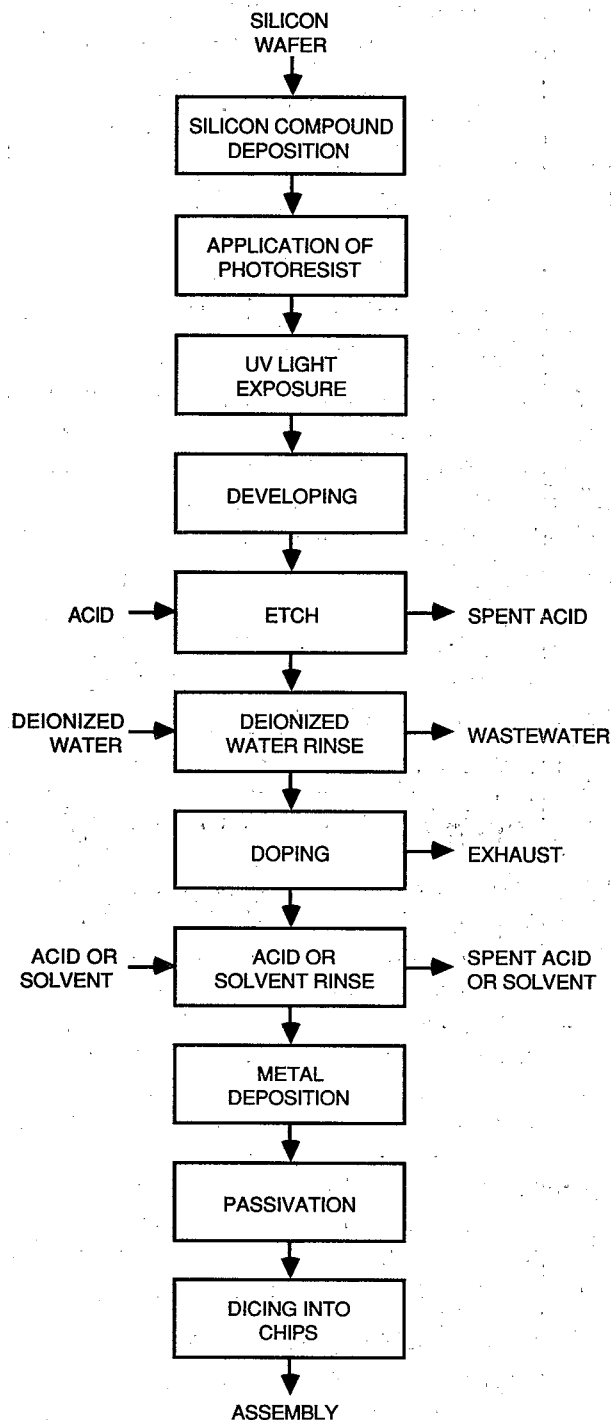
An effective means of evaluating points of release for listed toxic chemicals is to draw a process flow diagram identifying the operations performed at your facility. The figure on the right is an example flow diagram for semiconductor manufacturing. Because each facility is unique, you are strongly urged to develop a flow diagram for your particular operations that details the input of materials and chemicals and the waste sources resulting from the operation of each unit.

Wastewater and "solid" wastes are likely to be the primary releases to consider. If water is treated on site, you may also have a sludge or other waste containing the chemical. Other releases may come from discarded containers or samples, vessel washings, or (for some substances) volatilization to the air. All releases must be accounted for when reporting.

Step Four

Estimate releases of toxic chemicals.

After all of the toxic chemicals and waste sources have been identified, you can estimate the releases of the individual chemicals. Section 313 requires that releases to air, water, and land and transfers to offsite facilities be reported for each toxic chemical meeting the threshold reporting values. The usual approach entails first estimating releases from waste sources at your facility (that is, wastewater, air release points, and



Example Flow Diagram of Semiconductor Manufacturing

solid waste) and then, based on the disposal method used, determining whether releases from a particular waste source are to air, water, land, or an offsite disposal facility.

In general, there are four types of release estimation techniques:

- **Direct measurement**
- **Mass balance**
- **Engineering calculations**
- **Emission factors**

Descriptions of these techniques are provided in the EPA general Section 313 guidance document, Estimating Releases and Waste-Treatment Efficiencies for the Toxic Chemical Release Inventory Form.

Provisions of the Clean Air Act, Clean Water Act, Resource Conservation and Recovery Act, and other regulations require monitoring of certain waste streams. If available, data gathered for these purposes can be used to estimate releases. When only a small amount of direct measurement data is available, you must decide if another estimation technique would give a more accurate estimate. Mass balance techniques and engineering assumptions and calculations can be used in a variety of situations to estimate toxic releases. These methods of estimation rely heavily on process operating parameters; thus, the techniques developed are very site-specific. Emission factors are available for some industries in publications referenced in the general Section 313 guidance document. Also, emission factors for your particular facility can be developed in-house by performing detailed measurements of wastes at different production levels.

Toxic Releases Via Wastewater

Because of the need to comply with EPA regulations for metals and Total Toxic Organics from semiconductor processing, you may have monitoring data specific to some of the chemicals you use. You can calculate annual

releases using this information in the following manner:

$$\begin{aligned} & \text{Amount of chemical released in} \\ & \text{wastewater} = \\ & \text{concentration in wastewater} \times \\ & \text{daily volume of wastewater} \times \\ & \text{days/year for which data apply} \end{aligned}$$

Review all monitoring data to determine average representative concentrations to use in this calculation. In the case of chromium, copper, cobalt, or any other metal-containing substances, releases should be reported only for the metal content.

The total releases of a chemical should equal the amount used during the year minus the amount incorporated into products minus the amount destroyed in onsite treatment. For the metals you use, it will be particularly helpful to estimate the amount incorporated into products before proceeding to individual release estimates, as this will provide a reference point.

If no monitoring data are available for wastewater, you can estimate the release in one of the following ways:

1) Use of mass balance

If no wastewater monitoring data exist, calculate releases to process water based on a mass balance of the process:

$$\begin{aligned} & \text{Amount of chemical released in} \\ & \text{wastewater} = \\ & \text{amount used} - \\ & \text{amount incorporated in product} - \\ & \text{amount accounted for in other wastes} \end{aligned}$$

If your facility uses a listed mineral acid or base, but this acid or base is effectively neutralized in use or during wastewater treatment (to pH 6 to 9, as required by most effluent standards), no release quantities should be reported. If the acid or base is transformed into a reportable substance,

however, you must estimate the quantity of this substance manufactured to determine if the "manufactured" threshold value has been reached. For example, sulfuric acid neutralized by sodium hydroxide yields sodium sulfate, which is a listed chemical.

2) Use of published data on the semiconductor industry

The table on the right gives minimum and maximum concentrations of approximately 50 of the listed chemicals in the untreated wastewater from semiconductor facilities. If you use one of these chemicals and do not have data on your waste stream, you can multiply maximum concentrations times your daily wastewater discharge flow to obtain daily and annual release estimates.

Example: Using published wastewater discharge concentrations to calculate annual use of 1,2-diphenylhydrazine.

During 1987 a plant used 1,2-diphenylhydrazine throughout the year. In the absence of monitoring data at the site,

Amount in untreated wastewater =

maximum concentration x

daily volume of wastewater x

days/year for which data apply

Using the maximum concentration reported for 1,2-diphenylhydrazine:

Amount of 1,2-diphenylhydrazine =

0.022 mg/liter x

40,000,000 liters/day x

1 lb/454,000 mg x

260 days/year

= 504 lb

Using this approach, the plant in this example could report releases to wastewater of 500 pounds of 1,2-diphenylhydrazine.

Measured Concentrations of Selected Section 313 Chemicals in Untreated Wastewater from Semiconductor Manufacturing Facilities^a

Parameter	Min. conc., mg/liter	Max. conc., mg/liter
Benzene	<0.01	0.190
Benzidine	<0.01	
Chlorobenzene	<0.01	
1,2,4-Trichlorobenzene	0.0029	27.1
1,1,1-Trichloroethane	0.0002	7.7
1,1-Dichloroethane	<0.01	0.01
Chloroform	0.004	2.6
1,2-Dichlorobenzene	0.001	186.0
1,3-Dichlorobenzene	0.0027	14.8
1,4-Dichlorobenzene	0.0011	14.8
1,1-Dichloroethylene	<0.01	0.071
1,2-Dichlorophenol	<0.01	
1,2-Diphenylhydrazine	<0.01	0.022
Ethylbenzene	0.0002	0.107
Fluoranthene	<0.01	
Methylene chloride	0.005	2.4
Chlorodibromomethane	0.005	
Naphthalene	<0.01	1.504
2-Nitrophenol	0.002	0.70
4-Nitrophenol	<0.01	3.10
Phenol	0.0004	5.7
Bis(2-ethylhexyl)phthalate	0.002	0.750
Butylbenzylphthalate	<0.01	0.013
n-Dibutyl phthalate	0.0009	0.280
n-Dioctyl phthalate	<0.01	0.01
Diethyl phthalate	<0.01	
Dimethyl phthalate	<0.01	
Tetrachloroethylene	0.0002	0.80
Toluene	0.002	0.14
2,4-Dichlorophenol	<0.01	0.071
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	<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
Silver	<0.001	0.013
Thallium	<0.001	0.012
Vanadium	<0.001	0.214
Zinc	0.001	0.289

^a Data obtained from Development Document for Effluent Limitations Guidelines and Standards for Electrical and Electronic Components.

If wastewater is treated before release, you must adjust releases for the effectiveness of the treatment. If available, data on the operation of your treatment facility should be used. If not, consult the EPA publication, Development Document for Effluent Limitations Guidelines and Standards for Electrical and Electronic Components, for information on removal achieved by recommended treatment systems where available.

Toxic Releases Via Solid Waste

Wastewater treatment may transfer the chemical to sludge. You may have data on the concentration of metals in your sludge and can calculate release as pounds of sludge times concentrations of the chemical. Alternatively, the loss in the sludge can be estimated by:

$$\begin{aligned} \text{Amount of metal in sludge} = \\ \text{amount lost from process} - \\ \text{amount released in discharged water} \end{aligned}$$

or

$$\begin{aligned} \text{Amount of metal in sludge} = \\ \text{amount of metal in influent to} \\ \text{treatment} \times \\ \text{wastewater treatment efficiency} \end{aligned}$$

The latter approach would be appropriate if monitoring data for untreated wastewater and measured removal efficiencies were available (for example, in published sources).

For organic chemicals in general, some degradation in treatment may occur so all of the chemical is not transferred to the sludge. You can estimate the amount of organic compounds in the sludge by using measured data or by subtracting the amount biodegraded from the total amount removed in treatment. The amount of removal can be determined from operating data, and the

extent of biodegradation might be obtained from published studies. If the biodegradability of the chemical cannot be measured or is not known, you should assume that all removal is due to absorption to sludge.

Toxic Releases to Air

Your facility will release to air some volatile compounds, particularly solvents. The following is the simplest way to estimate this loss:

$$\begin{aligned} \text{Amount of solvent released to air} = \\ \text{solvent use} - \\ \text{solvent in wastewater} - \\ \text{solvent in "solid" wastes} - \\ \text{solvent destroyed by treatment} - \\ \text{solvent incorporated in products} \end{aligned}$$

This approach should provide a reasonably accurate estimate in most cases, especially if other releases are small compared with the air releases.

Individual contributions to air releases from storage tanks, valves, etc., can be calculated by using the approaches documented in Estimating Releases and Waste-Treatment Efficiency for the Toxic Chemical Release Inventory Form.

Other Toxic Releases

Semiconductor manufacturing produces other wastes from which toxic chemicals may be released. These include:

- **Residues from pollution control devices**
- **Wash water from equipment cleaning**
- **Product rejects**
- **Used equipment**
- **Empty chemical containers**

Releases from these sources may already have been accounted for, depending on the release estimation methods used. These items (and any other of a similar nature) should be included in your development of a process flow diagram.

The contribution of sources of wastes such as cleaning out vessels or discarding containers should be small compared with process losses. If you do not have data on such sources (or any monitoring data on overall water releases), assume up to 1 percent of vessel content may be lost during each cleaning occurrence. For example, if you discard (to landfill) "empty" drums that have not been cleaned, calculate the release as 1 percent of normal drum content. If the drums are washed before disposal, this may contribute 1 percent of the content to your wastewater loading.

Step Five

Complete the Toxic Chemical Release Inventory Reporting Form.

After estimating the quantity of each chemical released via wastewater, solid waste, and air emissions, you must determine the amount of each chemical released to water, land, or air or transferred to an offsite disposal facility. This determination will be based on the disposal method you use for each of your waste streams. Enter the release estimates for each chemical or chemical category in Part III of the Toxic Chemical Release Inventory Reporting Form. Also enter the code for each treatment method used, the weight percent by which the treatment reduces the chemical in the treated waste stream, and the concentration of the chemical in the influent to treatment (see instructions). Report treatment methods that do not affect the chemical by entering "0" for removal efficiency.

For More Information

**Emergency Planning
and Community
Right-to-Know
Hotline**

(800) 535-0202
or
(202) 479-2449
(in Washington, D.C.
and Alaska)

**Small Business
Ombudsman
Hotline**

(800) 368-5888
or
(703) 557-1938
(in Washington, D.C.
and Virginia)

The EPA brochure, Title III Section 313 Release Reporting Requirements (EPA 560/4-87-001) presents an overview of the new law. It identifies the types of facilities that come under the provisions of Section 313, the threshold chemical volumes that trigger reporting requirements, and what must be reported. It also contains a complete listing of the chemicals and chemical categories subject to Section 313 reporting. The EPA publication, Estimating Releases and Waste-Treatment Efficiencies for the Toxic Chemical Release Inventory Form (EPA 560/4-88-002), presents more detailed information on general release estimation techniques than is included in this document.