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Title III Section 313 Release Reporting Guidance

Estimating Chemical Releases From Formulation of Aqueous Solutions

Emergency Planning and
Community Right-to-Know Act of 1986

Estimating Chemical Releases From Formulation of Aqueous Solutions

Formulators of aqueous solutions 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 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 formulators of aqueous solutions, emulsions, and slurries 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 formulation of aqueous solutions, emulsions, and slurries, 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.

Many chemicals typically used in the formulation of aqueous solutions, emulsions, and slurries are subject to reporting under Section 313. You should also determine whether process operations at your facility actually create any of the listed chemicals.

The list presented here includes many of the water-soluble Section 313 chemicals that may be used in aqueous-based formulations. It 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.

Acids: Sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid, hydrofluoric acid

Bases: Sodium hydroxide, ammonia, hydrazine

Co-solvents: Methanol, acetone, n-butanol, acetonitrile, sec-butyl alcohol, tert-butyl alcohol, methylene chloride, ethylene glycol, 2-methoxyethanol, methylene bromide, methyl ethyl ketone, methyl isobutyl ketone, glycol ethers, 2-ethoxyethanol

Dyes: C.I. Acid Blue 9 (diammonium salt), C.I. Acid Blue 9 (disodium salt), C.I. Acid Green 3, C.I. Basic Green 4, C.I. Basic Red 1, C.I. Disperse Yellow 3, C.I. Food Red 5, C.I. Direct Black 38, C.I. Direct Blue 9, C.I. Direct Brown 95

Textile chemicals: Acetamide, bis (2-chloroethyl) ether, 2,4-diamino anisole, 2,4-diaminoanisole sulfate, urethane (ethyl carbamate), sodium sulfate, ethyleneimine, 2-phenylphenol, diepoxybutane, peracetic acid, phenylenediamine, acetamide

Metal chelating agents, corrosion inhibitors, metal treatment chemicals: Cupferron, quinoline, thiourea, hydrogen cyanide, calcium cyanamide, nitriloacetic acid, cyanide compounds

Preservatives, disinfectants, biocides: Chlorothalonil, cresols (mixed isomers), o-cresol, 2,4-dimethylphenol, 2-phenylphenol, 2,4,5-trichlorophenol, formaldehyde, phenol, mercury compounds, zinc oxide (zinc compounds)

Fertilizers: Ammonium nitrate, ammonium sulfate, calcium cyanamide, metal compounds

Detergent additive: Sodium sulfate

Many non-water-soluble Section 313 chemicals also may be emulsified or dispersed into water. These include:

Pesticides, herbicides, fungicides: Too numerous to list here; consult the Section 313 list.

Metal-containing pigments: Titanium dioxide and compounds containing zinc, lead, chromium, barium, cadmium, nickel, molybdenum, antimony, and copper

Metal-containing paint driers: See the metal compound categories in the Section 313 list.

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 products, byproducts, and impurities. Toxic compounds that are incorporated into your products would be considered "processed" because they become part of the marketed finished product. Degreasing solvents, cleaning agents, and other chemicals that are used in processing but 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.

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.

Example: Calculating annual processing of sodium hydroxide.

In 1987, a plant processed from inventory 75,000 pounds of a solution containing sodium hydroxide (NaOH) at 50 percent by weight. It also purchased 50,000 pounds of solid sodium hydroxide at 100 percent by weight, which was processed into aqueous solutions at the facility.

Amount of NaOH processed =

(75,000 lb x 0.50) (used from inventory) +

(50,000 lb x 1.00) (purchased)

= 87,500 lb

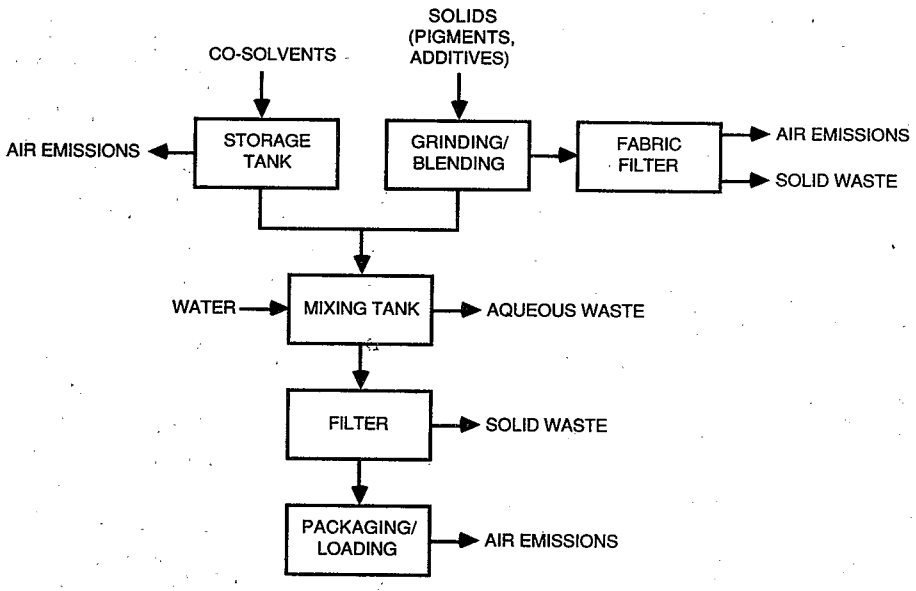
You must complete a report for each chemical for which a threshold is exceeded. The thresholds apply separately; therefore, if you both process and use a chemical and either threshold is exceeded, you must report for both activities. If neither threshold is exceeded, no report is needed.

Step 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 below is an example flow diagram for formulation of aqueous solutions. 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.

Releases of the chemicals processed in your industry may emanate from the following sources: equipment cleaning, filter solids, volatilization, discarded containers and samples, or airborne particulates. Releases also may result from wastewater treatment or occur from other wastes containing the chemical. Your reporting must account for all releases.



Example Flow Diagram for Formulation of Aqueous Solutions

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 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 to Air

As a formulator of aqueous solutions, your primary solvent will be water. Many volatile organic compounds are also used as co-solvents in significant quantities, however, and VOC emissions to air will result from the processing and storage of these compounds. Particulate emissions of reportable solid chemicals (for example metal-containing pigments) also may occur. Processing emissions can be estimated by one or more of the following methods.

1) Use of mass balance

Release of particulates to the air from grinding/blending operations may best be estimated by using a mass balance of the processing operation.

Amount of particulate chemical released to air =

Amount of solid chemical processed per year –

Amount of solids dissolved or suspended in final product –

Amount of solids in filter cake –

Amount of solids in wastewater sludge

For metal compounds, the amounts reported as releases should represent the amount of parent metal, not the amount of metal compound.

If you use fabric filter systems in the weighing/blending/mixing areas, you can estimate the particulate emissions based on the weight of the filtered particulates and an assumed efficiency of 98 to 99 percent. In the absence of measured efficiency data, you could use design efficiencies from the fabric filter manufacturer, if available.

Amount of particulate air emissions =

Amount of particulates in filter x

[(1 – filter efficiency) ÷ filter efficiency]

Example: Estimating releases of a particulate through a filter.

A facility grinds and blends chromium (III) oxide (Cr_2O_3) for use as a pigment in a water-based paint. The air around the grinding operation is exhausted to a filter with a particulate collection efficiency of 99 percent. According to facility measurements, the annual amount of chromium (III) oxide solids collected from the filter is 2,000 pounds.

Amount of Cr_2O_3 released to air =

2,000 pounds x

[(1 – 0.99) ÷ 0.99]

= 20 lb

To report as a release of parent metal (Cr), adjust as follows:

Amount of metal released =

Amount of metal compound released x

Molecular weight of parent metal portion ÷

Molecular weight of metal compound

Molecular weight of Cr = 52

Molecular weight of Cr_2O_3 = 152

Amount of Cr released to air =

20 lb Cr_2O_3 x

(52 x 2) ÷ 152

= 14 lb

2) Use of empirical equations for volatile emissions

a) Emissions from storage

Breathing and working loss emissions for volatile compounds such as co-solvents can be estimated for different storage tanks (fixed-roof, internal and external floating-roof) by using equations from EPA's Compilation of Air Pollutant Emission Factors (AP-42). The molecular weight and vapor pressure of the chemical, tank design parameters, and operating conditions are used in these empirical equations. The equations and how to use them can be found in Chapter 3 and Appendix C of the general Section 313 guidance document. Storage tank emissions should be reported as stack emissions on the reporting form.

b) Emissions from loading

Losses due to vapors generated from loading of products, from evaporation of products, and from evaporation of residual product in returned cargo carriers can be estimated by the following equation:

$$L = 12.46 \times S \times P \times M \div T$$

where L = *vapor loss, lb/1,000 gal of liquids loaded*

P = *liquid vapor pressure, psia*

M = *molecular weight*

T = *liquid temperature, °R (°F + 460)*

S = *saturation factor (see below)*

Mode of operation	*S factor*
Submerged loading:	
Clean cargo vessel	*0.50*
Normal dedicated service	*0.60*
Dedicated vapor balance service	*1.00*
Splash loading:	
Clean cargo vessel	*1.45*
Normal dedicated service	*1.45*
Dedicated vapor balance service	*1.00*

Uncontrolled/unrecovered loading emissions should be reported as fugitive emissions on the form. The cargo carriers may be drums, bins, trucks, or railcars.

If your facility recovers these vapor losses, the losses should be adjusted by the vapor recovery efficiency to yield release amounts:

Release =

Losses x

(1 – vapor recovery efficiency)

3) Use of emission factors

You can use emission factors to estimate emissions from equipment leaks (valves, pumps, flanges). Such factors may be developed by your facility (from measurements) or by your industry (obtainable from published studies). If factors are not available from either of these sources, you can use the EPA SOCMI factors, which represent average fugitive equipment emissions of volatile organic compounds in the synthetic organic chemical manufacturing industry. These factors are available in Appendix D of the Section 313 general guidance document.

Example: Using fugitive emission factors to estimate equipment leak emissions.

A latex paint formulator uses three different volatile organic co-solvents. Each solvent is pumped from storage into a mix tank. For each solvent, the following equipment components must be considered for fugitive emission leaks: 12 flanges, 3 valves, 1 sample connection, and 1 pump seal. For light liquids with vapor pressure greater than 1 psia (5 mm Hg) at 100 °F, the following factors can be used to estimate fugitive emissions:

Number of equipment components		*Emission factor, lb/h*		*Emissions, lb/h*
12 flanges	*x*	*0.0018*	=	*0.0216*
3 valves	*x*	*0.016*	=	*0.048*
1 sample connection	*x*	*0.033*	=	*0.033*
1 pump seal	*x*	*0.11*	=	*0.11*
Total			=	*0.2126*

Annual fugitive emissions =

0.2126 lb/h x 8760 h/yr

= 1,862 lb

Fugitive equipment releases for each of the three chemicals is therefore approximately 1,900 pounds per year.

Toxic Releases Via Wastewater

If you have monitored your wastewater discharge for any of the listed chemicals, you can easily calculate the releases of such chemicals to water. If you have not monitored your waste streams, you must consider how much each individual source at your facility contributes to wastewater loading.

Potential sources of water release are equipment-cleaning water, drum-cleaning waste, and off-specification product or samples. If you do not have monitoring data for your wastewater and you wash out mixing vessels or empty drums with water, assume that up to 1 percent of the vessel content may be lost during each cleaning occurrence. You should base your estimates of the releases of off-specification product and samples on the method by which you dispose of them and on your knowledge of the process (for example, if 0.1 percent of the batches last year were off-spec but were not reworked; therefore, they were released to water).

If your facility treats wastewater on site, you should adjust the totals lost to water to yield the "release" values. If available, use actual plant operating data on removal efficiency. Primary treatment may filter out chemicals with low water solubility and allow water-soluble chemicals to pass through. You could estimate the amount released from primary filtering operations based on the water solubility of the chemical if the wastewater flow rate is known:

Amount of chemical passing through filter (lb/day) =

Water solubility (mg/liter) x

Wastewater flow rate (gal/day) ÷

453,600 mg/lb x

3.78 liter/gal

If secondary biological treatment is used, however, water-soluble chemicals may be biodegraded. Published treatment efficiency data may be used if such data exist for the biological wastewater treatment method used

for the chemical at your site. The adjusted releases to water may be estimated as follows:

Amount of chemical released after treatment =

amount lost in process water x

(1 - removal efficiency)

If no data are available, assume treatment does not remove the chemical.

Other Toxic Releases

Other wastes in the formulation of aqueous solutions, emulsions, and slurries from which toxic chemicals may be released include:

- **Residues from pollution control devices**
- **Spent filters**
- **Product rejects**
- **Treatment sludges**
- **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.

You can estimate the amounts of solids lost from the process by using data from waste generation/shipping records. Alternatively, if no data are available and if you discard (to landfill) "empty" drums that have not been cleaned, you can estimate the release as 1 percent of normal drum content. For mixtures, adjust the release for the concentrations of the chemical.

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 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, Emergency Planning and Community Right-to-Know Act, Section 313 Release Reporting Requirements (EPA 560/4-88-001) 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.

Additional Sources of Information on Releases From Formulation of Aqueous Solutions

U.S. Environmental Protection Agency. Compilation of Air Pollutant Emission Factors, AP-42, Fourth Edition. Research Triangle Park, North Carolina. September 1985.

U.S. Environmental Protection Agency. Emission Factors for Equipment Leaks of VOC and HAP. EPA 450/3-86-002. PB 86-171527. Research Triangle Park, North Carolina. January 1986.

*U.S. Government Printing Office : 1988 - 516-002/80168