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EMISSION SCENARIO DOCUMENT ON THE USE OF METALWORKING FLUIDS

OECD Environment, Health and Safety Publications Series on Emission Scenario Documents Number 28

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Series on Emission Scenario Documents No. 28

EMISSION SCENARIO DOCUMENT ON THE USE OF METALWORKING FLUIDS



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Environment Directorate

ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

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The Inter-Organisation Programme for the Sound Management of Chemicals (IOMC) was established in 1995 following recommendations made by the 1992 UN Conference on Environment and Development to strengthen co-operation and increase international co-ordination in the field of chemical safety. The Participating Organisations are FAO, ILO, UNEP, UNIDO, UNITAR, WHO, World Bank and OECD. UNDP is an observer. The purpose of the IOMC is to promote co-ordination of the policies and activities pursued by the Participating Organisations, jointly or separately, to achieve the sound management of chemicals in relation to human health and the environment.

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EXPLANATORY NOTES

Purpose and background

This OECD Emission Scenario Document (ESD) is intended to provide information on the sources, use patterns, and potential release pathways of chemicals to be used in metalworking fluids. The document presents standard approaches for estimating the environmental releases of and occupational exposures to chemicals used in metalworking fluids. These approaches may be used to provide conservative, screening-level estimates of environmental releases of and occupational exposures to chemicals used in these types of operations. Such estimates might result in release and exposure amounts that are likely to be higher, or at least higher than average, than amounts that might actually occur in real-world settings.

This ESD may be periodically updated to reflect changes in the industry, if new information becomes available, or if the ESD is extended to cover the industry area in countries other than the lead (the United States). Users of the document are encouraged to submit comments, corrections, updates, and new information to the OECD Environment, Health and Safety Division (env.riskassessment@oecd.org) and U.S. Environmental Protection Agency (EPA) (EPA contact: Nhan Nguyen, nguyen.nhan@epa.gov). The OECD Task Force on Exposure Assessment (TFEA) will forward the comments to the lead country, which updates the document as necessary. Submitted information will also be made available to users by way of the OECD web site (www.oecd.org/env/riskassessment).

How to use this document

This document may be used to provide conservative, screening-level estimates of environmental releases of and occupational exposures to chemicals used in metalworking operations. Such estimates might result in release and exposure amounts that are likely to be higher, or at least higher than average, than amounts that might actually occur in real world practice.

The users of this ESD should consider how the information contained in the document applies to the specific scenario being assessed. Where specific information is available, it should be used in lieu of the defaults presented in this document, as appropriate. All input values (default or industry-specific) and the estimated results should be critically reviewed to assure their validity and appropriateness.

Coverage and Methodology

EPA developed this document using relevant data¹ on the industrial use of metalworking fluids, including process descriptions, operating information, chemicals used, wastes generated, waste treatment, worker activities, and exposure information. EPA also discussed with the Independent Lubricant Manufacturers Association (ILMA), a leading trade association for manufacturers of metalworking fluids. ILMA reviewed the document and provided extensive comments. EPA supplemented the data collected with standard models² to develop the environmental release and occupational exposure estimating approaches presented in this ESD.

¹ Please refer to Section 8 for a list of the specific references used in developing this ESD.

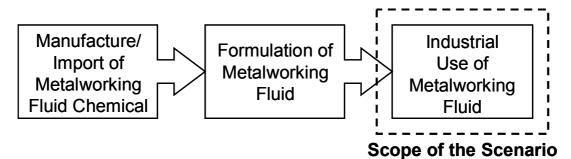
² EPA has developed a series of "standard" models for use in performing conservative release and exposure assessments in the absence of chemical- or industry-specific data. Several of these standard models are described in Appendix B to this ESD.

The primary sources of information cited in this document include environmental data collected by EPA during the proposal development phase of the Metal Products and Machinery (MP&M) industry effluent limitation guidelines, occupational exposure data collected by NIOSH, and information provided by ILMA in response to requests for technical input. The effluent guidelines data were collected from actual field surveys and are specific to the use of metalworking fluids. The occupational exposure data were obtained through personal monitoring studies at 79 metalworking shops in the U.S. Additional specific sources of current information include the Organisation for Economic Co-operation and Development (OECD), Annals of Occupational Hygiene, and the AIHA Journal. Additional information on the sources investigated and the references cited in this document are presented in Section 0.

The information in this document is based on U.S. data. Certain aspects of the chemicals used in metalworking fluids may differ in other regions and/or countries; therefore, alternate assumptions and parameters may be necessary in some applications of this emission scenario.

This ESD presents methods for estimating potential occupational exposures and environmental releases from the industrial use of metalworking fluids. Metalworking fluids provide lubrication and cooling during the manufacture of metal parts. Metalworking fluids may include emulsifiers, lubricity agents, oiliness agents, corrosion inhibitors, coupling agents, extreme-pressure additives, wetting agents, biocides, mineral oil, synthetic lubricants, and water. Chemicals used in metalworking fluids are generally non-volatile. This document addresses both water-based and straight oil metalworking fluids.

Releases and exposures from the manufacture of component chemicals and the formulation of the chemicals into metalworking fluids, other than dilution with water at the use site, are beyond the scope of this ESD, and therefore not addressed. The following life-cycle diagram demonstrates the applicability of this scenario.



This ESD presents methods that can be used to estimate the following releases of and exposures to chemicals during the use of the metalworking fluids:

- Releases from transport container residue (via container cleaning or direct disposal of empty containers);
- Releases from dragout of metalworking fluid coating metal parts;
- Releases from filter media disposal and other recycling wastes;
- Releases from spent metalworking fluid disposal;
- Dermal exposures to liquids during transport container unloading;
- Dermal exposures to liquids during transport container cleaning;
- Dermal exposures to liquids during mixing and transfer of diluted metalworking fluid;
- Inhalation exposure from mists generated during metal shaping operations and dermal exposure from rinsing, wiping, and/or transferring the shaped part;
- Dermal exposures to liquids during filtering and other recycling operations;
- Dermal exposures to liquids during transfer of spent metalworking fluid and cleaning of machine and trough; and
- Dermal exposures to liquids during on-site waste treatment operations.

How this document was developed

EPA with support from Eastern Research Group, Inc. (ERG) has developed this draft ESD on the chemicals used in metalworking fluids. The scope of the ESD is designed to serve the needs of both EPA and OECD programs. The Chemical Engineering Branch (CEB) of EPA's Office of Pollution Prevention and Toxics (OPPT) is responsible for preparing occupational exposure and environmental release assessments of chemicals for a variety of programs under the Toxic Substances Control Act (TSCA), including Premanufacture Notice (PMN) review. While OECD ESDs traditionally focus on the potential releases of chemicals from industrial processes, this document also describes approaches for estimating the potential occupational exposures to metalworking fluids. The occupational exposure estimation methods are included so that the ESD may be used to fully support EPA's chemical review programs.

A proposal to develop this document as an OECD ESD was approved at the 15th meeting of the Task Force on Environmental Exposure Assessment (then TFEEA, to be re-organised to TFEA in 2009) in December 2007. The first draft ESD was forwarded to the TFEEA for comments in August 2008. Comments were received from the United Kingdom and Canada on the first draft. The draft is also circulated to the Task Force on Biocides (TFB) for their review and comments were received from a member of the TFB from the Joint Research Centre, the European Commission. These comments were included in the revised draft submitted to the TFEA in October 2009. Additional comments on the revised draft were received in February 2010 from the UK and were incorporated by EPA. The final draft ESD was then circulated to the TFEA in July 2010 and approved at the final commenting round by the end of January 2011.

Note: Summary of Changes Since the first draft

EPA revised the first draft to include information from the European Commission document, *Harmonisation of Environmental Emission Scenarios for biocides used as metalworking fluid preservatives (Product type 13).* EPA also incorporated minor editorial comments and further refined the text of the document.

This document is published on the responsibility of the Joint Meeting of the Chemicals Committee and the Working party on Chemicals, Pesticides and Biotechnology of the OECD.

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Industry Summary and Background

Metalworking fluids are typically used in metal shaping operations. Metal shaping operations are one type of unit operation in the Metal Products and Machinery (MP&M) industry. This section presents an overview of the MP&M industry, followed by a more detailed description of metal shaping operations and the use of metalworking fluids.

MP&M Industry

EPA's Office of Water collected data on the MP&M industry during the development of the MP&M effluent limitation guidelines and pretreatment standards. The Office of Water's data collection included both surveys and on-site sampling. The Office of Water divides the MP&M industry into 18 industrial sectors and collected data in two phases:

Phase I	Phase II
Aerospace Aircraft Electronic Equipment Hardware Mobile Industrial Equipment Ordnance Stationary Industrial Equipment	Bus and Truck Household Equipment Instruments Motor Vehicle Office Machine Precious Metals and Jewelry Railroad Ships and Boats Printed Wiring Boards
	Job Shops Miscellaneous Metal Products

EPA proposed effluent limitation guidelines for Phase I facilities in May 1995; however, EPA decided to combine the Phase I and Phase II sectors and proposed effluent limitation guidelines covering all 18 industrial sectors in December 2000. This ESD was developed using data collected for the proposed Phase I effluent guidelines, as well as data from 15 to 20 additional MP&M Phase II sites.

The MP&M industry includes facilities performing the following operations within the previously mentioned 18 industrial sectors:

- **Manufacturing** The series of unit operations necessary to produce metal products. These operations normally take place within production facilities.
- **Rebuilding** Unit operations needed to disassemble used metal products into components, replace or restore the components to their original function, and reassemble the metal product. Like manufacturing, rebuilding operations also take place predominantly in production environments.
- **Maintenance** Operations required to keep metal products in operating condition. Maintenance is generally performed in a non-production environment. (USEPA, 2003)

The operations in the 18 MP&M industrial sectors span over 200 different Standard Industrial Classification (SIC) codes.

According to MP&M detailed survey data, approximately 89,000 MP&M sites operate in the Unites States (USEPA, 2003). Because the survey's primary purpose was to obtain data and information for use in the development of effluent guidelines, much of the industry-specific data focuses on sites that discharge process wastewater. Based on the detailed survey results, 63,000 MP&M sites discharge process wastewater (USEPA, 2003). The remaining sites fall into three categories: zero dischargers, non-water-users, and sites using contract haulers to remove wastewater. MP&M sites that discharge process wastewater were found to range in size from less than 10 employees per site to tens of thousands of employees per site. Approximately 92 percent of MP&M sites have 500 or fewer employees and approximately 78 percent have 100 or fewer employees (USEPA, 2003).

MP&M sites perform a variety of process unit operations on metal parts. At a given MP&M site, the specific unit operations performed and the sequence of operations depends on many factors such as the activity performed, industrial sector, and the type of product processed. The MP&M effluent guidelines development effort focused on 47 unit operations performed at MP&M sites including machining and grinding. While each of the 47 operations performs a specific function, each can be characterized as belonging to one or more of the following types of unit operations:

- Metal Shaping Transforms raw material (bar stock, sheet stock, metal plate) into intermediate forms for further processing using impact or pressure deformation, machining, or grinding.
- Metal/Organic Deposition Typically occurs after metal shaping and surface preparation activities. Deposition operations apply either a metal or an organic material to the part by chemical or physical means. The operations are often performed to alter the appearance of the surface, to modify the electrical properties of the surface, or to prevent the surface from wearing or corroding.
- Surface Finishing Normally takes place after shaping and surface preparation operation. Some surface finishing operations take place after metal deposition while others take place prior to organic coating operations. These operations protect the surface from wear or corrosion by chemical means.
- Assembly and Disassembly May take place during many steps of the manufacturing and rebuilding process. Disassembling operations are usually performed as the first step in the rebuilding process. Assembly operations may occur during different unit operations to prepare the final product. Assembly may also involve some final shaping operations (e.g., drilling and grinding) and surface preparation operations (e.g., alkaline cleaning). Final assembly operations are typically the last operations performed prior to shipment to the customer. (USEPA, 2003)

This ESD focuses on methods used to estimate releases of and exposures to chemicals in metalworking fluids used in metal shaping operations. A detailed description of these operations is included later in Section 0 and Section \cdot .

Metal Shaping Operations

Sites in the MP&M industry perform metal shaping operations to alter the physical form of raw metal materials to make intermediate or final products. These types of operations include machining, grinding, impact deformation, pressure deformation, abrasive blasting, burnishing, and heat treatment operations. Metal

shaping operations can be performed with or without the use of metalworking fluids such as oil-water emulsions or oil-based lubricants. Metalworking fluids provide cooling and lubrication in metal shaping operations, and are designed to physically assist in the metal shaping process and physically protect the shaped part from oxidation (USEPA, 2003). Typical metal shaping unit operations include:

- Abrasive Jet Machining;
- Electrical Discharge Machining;
- Electrochemical Machining;
- Electron Beam Machining;
- Grinding;
- Heat Treating;
- Impact Deformation;
- Machining;
- Plasma Arc Machining;
- Pressure Deformation;
- Thermal Cutting; and
- Ultrasonic Machining. (USEPA, 2003)

PROCESS DESCRIPTION

This section presents a detailed description of metal shaping operations performed in the MP&M industry along with the types and compositions of metalworking fluids used in these operations. Water-based metalworking fluids include conventional soluble, semi-synthetic, and synthetic fluids, and are diluted prior to use. Straight oils are mineral or synthetic oil based fluids that are not diluted prior to use. Additional information on the types and composition of metalworking fluids is found in Section 2.2.

Metalworking fluids provide cooling and lubrication in metal shaping operations, and are designed to physically assist in the metal shaping process by removing metal chips or fines and protecting the shaped part from oxidation (USEPA, 2003). Metal shaping operations include:

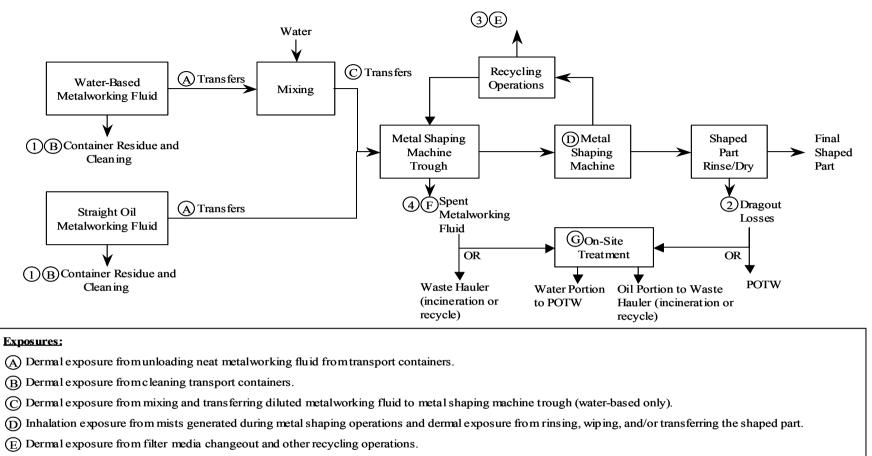
- **Machining** A cutting tool is forced against a part to remove stock (as chips). Machining processes include turning, milling, drilling, boring, tapping, planing, broaching, sawing, shaving, shearing, threading, reaming, shaping, slotting, hobbing, and chamfering. A variety of metalworking fluids cool and lubricate the part during the shaping operation, and help to protect the part from oxidation (USEPA, 2003).
- **Grinding** Abrasive grains held by a rigid or semirigid binder remove stock from the part. Grinding shapes or deburrs the part. The grinding tool usually is a disk (the basic shape of grinding wheels), but can also be a cylinder, ring, cup, stick, strip, or belt. The most commonly used abrasives are aluminum oxide, silicon carbide, and diamond. Metalworking fluids cool the part and remove debris or metal fines (USEPA, 2003).
- **Impact Deformation** To permanently deform or shape it, a part is subjected to an impact force such as hammer forging, shot peening, peening, coining, high-energy-rate forming, heading, or stamping. These operations typically do not use water-based metalworking fluids; however, natural and synthetic oils, light greases, and pigmented lubricants are occasionally used (USEPA, 2003).
- **Pressure Deformation** A part is permanently deformed or shaped when a force (other than impact force) is applied. Pressure deformation may include rolling, drawing, bending, embossing, sizing, extruding, squeezing, spinning, necking, forming, crimping or flaring. These operations typically do not use water-based metalworking fluids; however, natural and synthetic oils, light greases, and pigmented lubricants are occasionally used (USEPA, 2003).
- Abrasive Blasting Abrasives directed at high velocity against the part remove surface film. Abrasive blasting may be performed either dry or with water using bead, grit, shot, and sand blasting. Abrasive blasting is used to remove burrs on precision parts, produce satin or matte finishes, remove fine tool marks, and remove light mill scale, surface oxide, or welding scale. In abrasive blasting, the water and abrasive typically are reused until the particle size diminishes due to impacting and fracture (USEPA, 2003). Metalworking fluids are not used in abrasive blasting.

- **Burnishing** A previously machined or ground part is finish sized or smooth finished by displacing, rather than removing, minute surface irregularities with smooth point or line-contact, fixed or rotating tools. Lubricants or soap solutions can be used to cool the tools used in burnishing operations; however, metalworking fluids are not typically used (USEPA, 2003).
- Heat Treatment The physical properties of a part are modified by applying controlled heating and cooling cycles. This operation includes tempering, carburizing, cyaniding, nitriding, annealing, aging, normalizing, austenitizing, austempering, siliconizing, martempering, and malleablizing. Aqueous quenching solutions may be used to cool the part; however, metalworking fluids are not typically used in heat treatment operations (USEPA, 2003).

While impact deformation and pressure deformation may use some straight oils, most metalworking fluids are used in machining and grinding operations. Therefore, this ESD focuses on these two operations. Some components of metalworking fluids used in these operations may be consumed in the metal shaping process, either due to a reactive function (e.g., corrosion inhibitors), by thermal degradation, or by biodegradation (ILMA, 2005a; ILMA, 2006a). Quantitative data on these losses were not available; therefore, this ESD assumes that the components in metalworking fluids do not react chemically or degrade during the shaping process, or during the treatment of the spent metalworking fluids. A flow diagram for a typical metal shaping operation that utilizes metalworking fluids is presented as Figure 0-1.

Use of Metalworking Fluids

As shown in Figure 0-1, metalworking fluid is received in transport containers at a metal shaping site. A literature search did not find information on typical shipping containers and container residue handling for metalworking fluids (Release 1, Exposure B). A search of recent PMN submissions found that transport containers range in size from 5-gallon pails to bulk containers (CEB, 2003). Water-based metalworking fluids are unloaded (Exposure A), diluted on site with water, and then transferred to the trough (Exposure C), usually located inside a metal shaping machine. Straight oils are not diluted with water and are directly transferred to the trough (Exposure A). Metalworking fluids are typically pumped from the trough and applied as needed to the parts during metal shaping operations (Exposure D). Most frequently a metalworking fluid is sprayed over the part for lubrication and cooling. Fluid remains on the shaped part and inhibits corrosion of the metal surfaces. Information collected during MP&M guideline development indicated the parts are allowed to drip dry, and the fluids are collected and treated with other contaminated process fluids (USEPA, 2003). The part may then be rinsed or wiped off using shop towels (USEPA, 2003). Any residual metalworking fluid on the part is likely removed during an alkaline cleaning or degreasing operation prior to metal/organic deposition or surface finishing operations. Recent information from industry indicates both water-based and straight oil metalworking fluids are expected to be rinsed off of shaped parts (Release 2) (ILMA, 2006b).



 (\mathbf{F}) Dermal exposure from transferring spent metalworking fluid and cleaning of shaping machine and trough.

 \bigcirc Dermal exposure from on-site waste treatment operations.

<u>Releases</u>:

(1) Release of container residue (unknown media).

(2) Release of dragout losses (on-site treatment (default, oil/water separation) or POTW).

(3) Release of filter and other recycling wastes (water-based: water, incineration or landfill; straight oils: incineration or landfill).

(4) Release of spent metal working fluid (water-based: on-site treatment (default, oil/water separation); straight oils: incineration).

Figure 0-1. Process Flow Diagram for Metal Shaping Operations

During use, the metalworking fluid becomes contaminated with tramp oils and metal fines. The bulk of the fines are filtered from the fluid and the tramp oil is often skimmed prior to the reuse of the fluids. The metalworking fluid in the sludge and on the metal fines is then disposed of (Release 3, Exposure E). Eventually, the fluid becomes unusable, and may be removed from the trough and sent through either a centrifugation or pasteurization unit to extend its life. These units thoroughly remove metal fines and tramp oils and help to destroy any microbes (bacteria and fungi) growing in the fluid (USEPA, 2003). Regenerated metalworking fluids are then recycled to the trough.

Metalworking fluids are typically used and recycled until the fluid is degraded to the point of uselessness or "spoiled" by microbial growth. In general, straight oils are less susceptible to microbial growth and biodegradation than water-based metalworking fluids. At this point the metalworking fluid is disposed, the equipment is cleaned, and fresh metalworking fluid replaces the old (Exposure F). Because the microbes consume the organic components (oil and other additives) present in the metalworking fluid, equipment must be thoroughly cleaned; otherwise, if the accumulated microbes were to come into contact with fresh metalworking fluid they would have a fresh source of food. They would rapidly multiply and, within a short period of time, the new fluid would become unusable (OSHA, 2001). This ESD does not provide an estimate for potential equipment cleaning releases, but instead assesses a spent metalworking fluid release that accounts for the balance of the metalworking fluid not remaining in the transport containers, dragged out on parts, or lost during filtering and recycling operations.

When they can no longer be recycled on site, metalworking fluids are hauled off site for disposal, oil recycling, or fuel blending; or sent to an on-site wastewater treatment area prior to discharge (Releases 4, Exposure G). Spent straight oils are not expected to be included in process wastewater. Based on the detailed survey results, 63,000 MP&M sites (71 percent of all MP&M sites) discharge process wastewater (USEPA, 2003). Facilities may treat or dispose of their process wastewater using a variety of methods. The most common methods are on-site wastewater treatment (65.18 percent) prior to discharge or discharge directly to a POTW (15.3 percent) (USEPA, 2000a). However, facilities no longer typically discharge wastewater directly to POTW due to stringent discharge limits (ILMA, 2005b; ILMA, 2006b; Byers, 2006) required by 40 CFR 403.5(b)(6). On-site wastewater treatment usually consists of either oil/water separation or ultrafiltration, typically followed by chemical precipitation and sedimentation (USEPA, 2003). During the original data gathering effort for the MP&M Phase I effluent guidelines (1989 to 1993) oil/water separation followed by chemical precipitation was the most frequently used method of treatment. However, during later data collection for the combined guidelines (1995 to 2000) more facilities employed ultrafiltration either as a stand-alone treatment operation or followed by chemical precipitation and sedimentation. Ultrafiltration is more effective at removing oils (including emulsions) and organic constituents that are present in metalworking fluids. Other methods of treatment are on-site reuse/recycle/recovery (11.86 percent of facilities), evaporative treatment (3.4 percent of facilities), incineration (3.05 percent of facilities), and hazardous disposal (1.21 percent of facilities) (USEPA, 2003).

Composition of Metalworking Fluids

Metalworking fluids used in metal shaping operations can be separated into four main groups: conventional soluble, micro-emulsion (semi-synthetic), synthetic, and straight oils. Conventional soluble, semi-synthetic, and synthetic fluids are typically referred to as water-based metalworking fluids because they are diluted with water prior to use. This ESD uses the term "neat" to refer to undiluted, water-based metalworking fluids, as used by OSHA in its "Metalworking Fluids: Safety and Health Best Practices Manual" (OSHA, 2001). The composition data presented in this section are for neat metalworking fluids (i.e., as received by a user). Straight oils generally do not contain any water and are not diluted prior to use. This ESD covers chemical components of both water-based metalworking fluids and straight oils.

Conventional Soluble Oils

Because of its high specific heat, good thermal conductivity, and high latent heat of evaporation, water is an excellent coolant. However, because water is a poor lubricant, emulsions of soluble oils in water are commonly used as metalworking fluids. A typical conventional soluble cutting oil formulation contains mineral oil, emulsifiers, corrosion inhibitors, and defoamers (OECD, 2004). Biocides are added to prevent biological growth and extend the fluid's working life. These oils are typically used for lower duty general machining operations. Table 0-1 presents the typical composition of these fluids.

Table 0-1. Typical Composition of Undiluted Conventional Soluble Cutting Oils

Component	Percentage
Emulsifiers	< 30
Corrosion inhibitors	< 10
Oiliness agents	< 10
Coupling agents	< 5
Extreme-pressure additives	< 30
Water (from neutralization reaction)	< 5
Biocides	<2
Mineral oil	40-85

Source: ILMA, 2005a.

Before use, these fluids are mixed with water to produce an emulsion containing typically between 2 and 5 percent of the cutting oil, although concentrations above 10 percent can be used for heavy cutting operations (OECD, 2004).

Table 0-2 shows examples of additives that could be used in emulsifiable cutting oils. These additives may also be found in the semi-synthetic and synthetic fluids described below.

Table 0-2.	Examples of	Typical Additiv	ves for Emulsifiable	Cutting Oils
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Type of Additive	Function	Examples
Corrosion inhibitors	Form a non-metallic protective layer to prevent water and oxygen from contacting the metal part	Triethanolamine Alcohol amines Amine borates Amine dicarboxylate Aryl sulfamido carboxylic acid Alkyl amido carboxylic acid Calcium sulfonate
Emulsifiers	Assist in the formation and stabilization of oil-in-water and water-in-oil emulsions	Petroleum sulfonates Synthetic sulfonates Sulfonate base Alkyl sulfamido carboxylic salt Octyl phenol ethoxylate Nonyl phenol ethoxylate Alkali fatty acid soap 2:1 Diethanolamine fatty acid amide 2:1 Diethanolamine fatty amide Glyceryl mono-oleate Sorbitan mono-oleate
Oiliness agents	Base stock for metalworking fluids	Inverse soluble ester Complexed polymeric fatty acid Sulfated castor oil Block copolymer ethylene diamine Block copolymer Reverse block copolymer Poly alkylene glycol Triethanolamine/acid polyglycol Phosphate ester - low phenol Phosphate ester - alcohol Phosphate ester - phenol Amphoteric carboxylic salt Imidazoline
Coupling agents	Maintain the homogeneity of products	Butyl glycol Hexylene glycol
Extreme-pressure additives	Provide lubrication of metal parts at high pressures	Sulfurised oil/fats/esters Chlorinated paraffins Neat sulfur Polysulfides

Type of Additive	Function	Examples
Type of Additive Biocides	Function Destroys living organisms	ExamplesHexahydro-1,3,5-tri (2-hydroxy ethyl)-5-triazine4,4-dimethyloxazolidine3,4,4-trimethyloxazolidine2-bromo-2-nitro-1,3-propanediol4-(2-nitrobutyl)-morpholine4,4'-(2-ethyl-2-nitro-methylene)dimorpholine2-hydroxymethyl-2-nitro-1,3-propanediolPoly{oxyethylene(dimethyl imino)ethylene}dichloridePotassium dimethyldithiocarbamate2-(triocyanomethylthio)-benzothiazoleHexahydro-1,3,5-tris-(2-hydroxyethyl)-s-triazine
		1-(3-chloroallyl)-3,4,7-triaza-1- azoniaadamantane chloride o-phenylphenol Sodium o-phenylphenate 1,2-benzisothiazolin-3-one Hexahydro-1,3,5-tris(2-hydroxyethyl)-s-triazine Sodium 2-pyridinethiol-1-oxide 5-chloro-2-methyl-4-isothiazoline-3-one 2-methyl-4-isothiazoline-3-one 2-n-octyl-4-isothiazoline-3-one Hexahydro-1,3,5-tris (2-hydroxy ethyl)-s- triazine

Source: OECD, 2004.

Semi-Synthetic Soluble Oils

Semi-synthetic soluble oils have better cooling and wetting properties than conventional soluble oils and permit the use of higher speeds and feed rates in machining operations. Table 0-3 presents the typical composition of semi-synthetic soluble oils. The additives listed inTable 0-2 may also be found in the semi-synthetic soluble oils.

Component	Percentage
Emulsifiers	< 35
Oiliness agents	< 20
Corrosion inhibitors	< 5
Coupling agents	< 8
Extreme-pressure additives	< 10
Water	< 60
Biocides	< 2
Mineral oil ^a	< 40

Source: ILMA, 2005a.

a – Portions of this mineral oil may be substituted by a synthetic lube.

Synthetic Fluids

Synthetic fluids are used in a variety of machining operations including relatively heavy duty machining and grinding. Synthetic fluids are distinct from other metalworking fluids in that they do not contain mineral oil. Some synthetic fluids replace mineral oil with synthetic lubricants, but are otherwise similar to conventional soluble and semi-synthetic fluids and form emulsions in water. Other synthetic fluids receive their lubricant properties from soluble organic and/or inorganic compounds that form true solutions with water. Although synthetic fluids are formulated in numerous ways, Table 0-4 and Table 0-5 present typical compositions for emulsion and solution-synthetic fluids, respectively. The additives listed in Table 0-2 may also be found in the synthetic soluble oils.

Table 0-4. Typical Composition of Undiluted Synthetic Emulsion Cutting Fluids

Component	Percentage
Emulsifiers	< 30
Corrosion inhibitors	< 10
Oiliness agents	< 10
Coupling agents	< 5
Extreme-pressure additives	< 45
Water (from neutralization reaction)	< 5
Biocides	<2
Synthetic lube	40-80

Source: ILMA, 2005a.

Component	Percentage
Lubricity agents	< 25
Corrosion inhibitors	< 10
Fatty acid	< 5
Biocides	< 2
Extreme-pressure additives	< 5
Water	< 60

Table 0-5. Typical Composition of Undiluted Solution-Synthetic Cutting Fluids

Source: ILMA, 2005a.

Water-based metalworking fluids may also contain additives such as wetting agents (or surfactants) and defoamers. Wetting agents or surfactants may be present at concentrations up to 10 percent (ILMA, 2005a). Defoamers are typically used at concentrations less than 1 percent (Whodeck, 1997).

Regardless of fluid type, water-based metalworking fluids are diluted with water at the use site. Dilution ratios may vary significantly depending on the type of fluid and operation; however, dilution ratios generally depend on the metal shaping operation. Table 0-6 presents typical dilution percentages of metalworking fluid in water based on the shaping operation. Table 2-7 presents the range of dilutions factors found in literature.

Table 0-6. Typical Dilution of Metalworking Fluids in Water

Shaping Operation	Percentage of Metalworking Fluid in Water
Machining	5
Grinding	3
Pressure/Impact Deformation	10

Source: Whodeck, 1997.

Table 0-7. Water-Based Metalworking Fluid Dilution Factors in Literature

Study	Percentage of Metalworking Fluid in Water
Abrams et al. (AOEH, 2000)	2.4 - 9
Dasch et al. (JOEH, 2005)	5 – 10
Johnson and Phillips (AIHAJ, 2002)	2.5 - 5
Simpson et al. (Ann. Occup. Hyg., 2003)	5
Virji et al. (AIHAJ, 2000)	2 - 20

Straight Oils

Straight cutting oils consist mainly of mineral oils fortified with other additives to meet necessary performance requirements for a variety of applications. Animal- or vegetable-derived oils add lubricity to the mineral oil. Oil-soluble esters of these fatty oils may also be used as lubricants because they have higher resistance to biodegradation than the original oil. Straight oils can also contain sulfurized, chlorinated, and phosphate compounds to enhance lubrication in extreme-temperature, extreme-pressure applications (Byers, 2006; OECD, 2004). Straight oils are not diluted prior to use in metal shaping operations. Table 0-8 presents typical compositions of straight oils.

Component	Percentage
Mineral oil	60-90
Lubricity agents	< 40
Extreme-pressure additives	< 15
Antioxidants	<1
Anti-mist agents	<1
Metal passivators	<1
Dyes	<1
Odorants	<1

Table 0-8. Typical Composition of Straight Oils

Source: Byers, 2006; ILMA, 2005a; OECD, 2004.

Physical Properties of Metalworking Fluid Chemicals

In general, metalworking fluid components are non-volatile liquids. Table 2-9 presents the physical properties of a chemical compound from each additive category. The chemicals were chosen to be representative of the category; however, physical properties may vary across the category. The physical property data are only provided for a general estimate of the properties of the category.

Table 0-9. Physical Properties of Representative Metalworking Fluid Chemicals

Additive Category	Chemical (CAS)	Neat Physical State	Molecular Weight	Vapor Pressure (torr at 25°C)	Boiling Point (°C)	Melting Point (°C)	Water Solubility (g/L)	Other (Specific Gravity, Oct/H ₂ O)
Emulsifier	Sodium dodecylbenzenesulfonate (25155-30-0)	Solid ^e	348.48ª	2.29e-15 ^b	N/A	N/A	0.8 ^b	log K _{OW} 1.96 ^b
Lubricity agent	Methyl oleate (112-62-9)	Liquid ^e	296.50 ^b	6.29e-6 ^b	218.5 (@ 20 torr) ^e	-19.9°	Insoluble ^c	<i>sg</i> 0.88 ^a log K _{OW} 7.45 ^b
Oiliness agent	1-Decanol (112-30-1)	Liquid ^a	158.28 ^a	0.00851 ^b	232.9 ^a	6 ^a	0.037 ^b	<i>sg</i> 0.83 ^a log K _{OW} 4.57 ^b
Corrosion inhibitor	Triethanolamine (102-71-6)	Liquid ^a	149.19 ^a	3.59e-6 ^b	335.4ª	21.57 ^a	Miscible ^a	<i>sg</i> 1.12 ^a log K _{OW} -1.00 ^b
Coupling agent	Hexylene glycol (107-41-5)	Liquid ^a	118.18 ^a	0.013 ^b	198 ^a	-50 ^b	Miscible ^a	<i>sg</i> 0.92 ^a log K _{OW} 0.58 ^b
Extreme- pressure additive	Tricresyl phosphate (1330-78-5)	Liquid ^a	368.37 ^a	6e-7 ^b	265ª	-33 ^b	3.6e-4 ^b	<i>sg</i> 1.16 ^a log K _{OW} 5.11 ^b
Biocide	Tris(hydroxymethyl)nitrom ethane (126-11-4)	Solid ^a	151.12 ^a	1.54e-6 ^b	Decomp ^c	175°	2,200 ^b	log K _{OW} -1.66 ^b
Wetting agent/ surfactant	2-ethylhexanol (104-76-7)	Liquid ^a	130.23 ^a	0.136 ^b	185 ^a	-70 ^b	0.88 ^b	<i>sg</i> 0.83 ^a log K _{OW} 2.73 ^b
Defoamer	(<i>p</i> -Nonylphenoxy)acetic acid (3115-49-9)	Liquid ^a	278.39 ^a	9.82e-6 ^b	N/A	N/A	2.2e-3 ^b	<i>sg</i> 1.01 ^a log K _{OW} 5.80 ^b

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Additive	Chemical (CAS)	Neat Physical	Molecular	Vapor Pressure	Boiling	Melting Point	Water Solubility	Other (Specific
Category		State	Weight	(torr at 25°C)	Point (°C)	(°C)	(g/L)	Gravity, Oct/H ₂ O)
Mineral Oil	Petrolatum, Liquid (8042- 47-5, 8012-95-1)	Liquid ^a	N/A	N/A	330-930°	N/A	Insoluble ^c	sg 0.83-0.860 (light); sg 0.975- 0.905 (heavy) ^a

N/A – Not Available

a – Merck, 1996 b – SRC, 2006 c – Hawley, 1997

OVERALL APPROACH AND GENERAL FACILITY ESTIMATES

This document presents EPA's standard approach for estimating environmental releases of and worker exposures to chemical components of metalworking fluids (MWF), including both water-based fluids and straight oils. The estimation methods described in this document utilize available industry-specific information and data to the greatest extent possible; however, EPA acknowledges several areas in which additional chemical and process information would benefit the ESD. These data needs are summarized in Section 7. EPA intends that the default values cited throughout this ESD only be used when appropriate site-specific or industry-specific information is not available.

Because this ESD presents several alternative default assumptions or values for some estimation parameters, selecting different defaults will affect the final assessment results differently. For example, conservative or high-end daily use rates will result in more conservative release estimates³. Alternatively, average or median use rates will result in release estimates that are more "typical" of the industry. This ESD presents available data that support alternative input values.

This section of this ESD presents general facility calculations, which estimates the operating days, concentration of the chemical of interest in both the neat metalworking fluid (i.e., as received) and the trough metalworking fluid (i.e., as used), throughput of the metalworking fluid containing the chemical of interest, number of facilities that use the chemical, and the number of containers used per facility.

Section 4 of this document presents the environmental release assessment, which uses the general facility estimates to estimate of the quantity of metalworking fluid chemical released from various points in the metal shaping process and the most likely media of release for each release source.

Section 5 of this document presents the occupational exposure assessment, which uses the general facility estimates to estimate the number of workers potentially exposed while performing various process activities and the corresponding potential level (quantity) of both inhalation and dermal exposure.

Section 6 of this document presents sample calculations using all of the equations introduced in Sections 3, 4, and 5 of this ESD. The hypothetical operating ESD presented in this section demonstrates how the equations might be used to estimate releases of and exposures to an additive chemical used in metalworking fluids.

Introduction to the General Facility Estimates

The estimates presented in this section are based on data collected by EPA's Office of Water during the effort to develop effluent limitation guidelines and pretreatment standards for the MP&M industry and information collected by NIOSH during their assessments of inhalation exposure to metalworking fluids.

Table 0-1 summarizes the general facility parameters developed in this section with their corresponding section number. In addition, Table A-4 in Appendix A presents a detailed summary of the default values used as inputs to each of the general facility estimates, accompanied by their references.

³ Note: When evaluating environmental releases, EPA typically assumes the highest daily release is the most conservative, because it will result in the highest aquatic stream concentrations. Therefore, EPA typically uses high-end daily use rates to generate conservative environmental release estimates. Conversely, for conservative occupational exposure assessments, EPA typically utilizes lower daily use rates, which will result in a greater number of use sites, longer use duration, and a greater number of workers exposed.

Parameter	Description	Section
$TIME_{working_days}$	Operating days (days/yr)	0
$Q_{neat_site_yr}$	Annual use rate of neat metalworking fluid (kg/site-yr)	3.3
F _{chem_neat}	Weight fraction of the chemical of interest in the neat metalworking fluid (kg chemical/kg neat MWF)	3.4
F_{neat_trough}	Weight fraction of the neat metalworking fluid in the trough (kg neat MWF/kg trough MWF)	3.4
F_{chem_trough}	Weight fraction of the chemical of interest in the trough (kg chemical/kg trough MWF)	3.4
$Q_{chem_site_yr}$	Annual use rate of chemical of interest, per site (kg chemical/site-yr)	0
$Q_{chem_site_day}$	Daily use rate of chemical of interest, per site (kg chemical/site-day)	0
N _{sites}	Number of sites using a metalworking fluid containing the chemical of interest (sites)	0
N _{cont_site_yr}	Annual number of containers of neat metalworking fluid, per site (containers/site-yr)	0

Table 0-1. Summary of General Facility Parameters

The general facility estimates presented in this section are primarily based on three parameters, for which alternate defaults are presented. The selection of the default value for each of these parameters will affect the final assessment, as discussed below:

- Type of metalworking fluid (straight oil or water-based) Straight oils are not diluted prior to use; therefore, their use concentration would be the highest, resulting in more conservative occupational exposure estimates. However, spent straight oil baths are typically not discharged to water, unlike water-based fluids. Therefore, water-based fluids may result in more conservative environmental release assessments.
- Annual volume of neat metalworking fluid used per site $(V_{neat_site_yr})$ Geometric mean and 90th percentile use rate information is available from the NIOSH study of 79 sites using metalworking fluids. Using the 90th percentile use rate will result in higher daily releases (more conservative for environmental releases) but a lower number of use sites, and thus a lower number of potentially exposed workers (less conservative for occupational exposures).
- Number of metalworking fluids used per site (N_{mwf_site_total}) In general, not all metalworking fluids used at a facility will contain the chemical of interest. Facilities may use multiple metalworking fluids for particular operations (e.g., one fluid for machining copper and another for machining steel). Selecting a lower number of metalworking fluids provides a larger throughput of the chemical of interest (more conservative for environmental releases). Selecting a higher number of metalworking fluids provides a smaller throughput and results in a greater number of sites using metalworking fluids and a greater number of workers potentially exposed (more conservative for occupational exposures). Selecting a typical number of metalworking fluids provides a balance between throughput and number of sites, and a consequent balance between environmental releases and occupational exposures.

Therefore, based on the considerations presented above, Figure 3-1 should be utilized when selecting default parameters.

Operating Days (TIME_{working_days})

During the development of the MP&M effluent guidelines, EPA collected industrial data for metal shaping activities. These data were analyzed for different metal shaping operations, including machining and grinding. Table 0-2 shows averages of the data for each metal shaping operation that can be used in the calculations (presented in the following sections) to estimate the releases and exposures. Appendix C presents the ranges and number of data points for each of the values in Table 0-2. The average number of shifts of operation per day was assumed based on the hours of operation per day. These ranges may be used to compare any site-specific information with the defaults presented in the ESD.

Table 0-2. Information for Metal Shaping Release and Exposure Calculations

Average NumbMetal ShapingOperationper Day (Nsh		Average Hours of Operation per Day	Average Days of Operation per Year (TIME _{working days})	Average Number of Machines per Facility (N _{machines}) ^a
Grinding	2	12.7	249	17
Machining	2	13.3	246	93
General Average for Metal Shaping Operations	2	13.0	247	48

Source: U.S. EPA, 2000a.

a – These values have been rounded.

The operating days for specific metal shaping operations are provided in Table 0-2. If the metal shaping operation is not known, use the general average value. This information should be used only when site-specific information is not available.

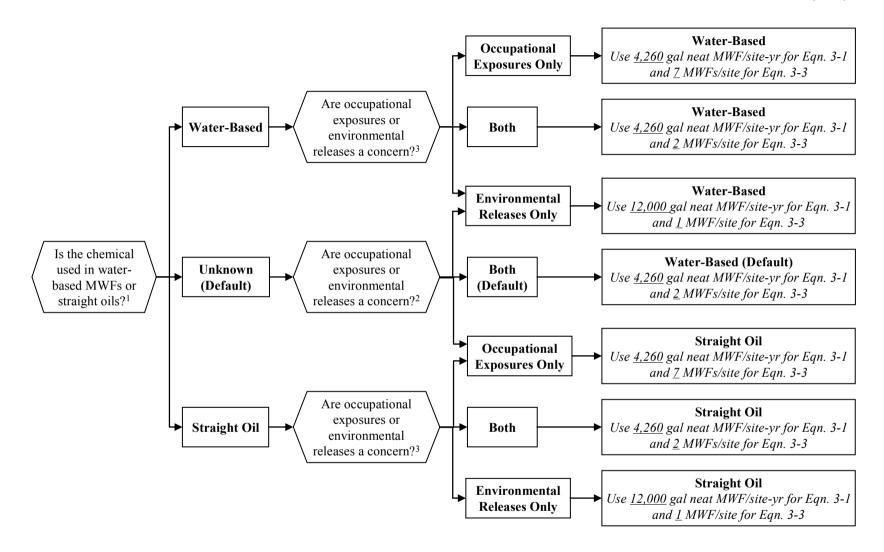


Figure 0-1. Decision Logic Diagram for Determining the Use Rate

Notes for Figure 0-1 are presented on the following page.

Notes for Figure 0-1:

- 1. Water-based metalworking fluids are more widely used because of their better cooling properties, while straight oils are typically limited to use in lower speed machines. Certain additive types found in water-based metalworking fluids are not used in straight oils. If the chemical of interest is an emulsifier or coupling agent, the fluid is water-based.
- 2. If the type of metalworking fluid is unknown, the concerns of the screening-level assessment should be considered. If occupational exposures are the only concern, *straight oils* may be selected because they have higher mist concentrations during metal shaping operations than *water-based* metalworking fluids. Using the geometric mean volume of metalworking fluids (4,260 gal MWF/site-yr) and the high-end number of metalworking fluids (7 MWF/site) will result in a smaller use rate, maximizing the number of sites and total number of workers potentially exposed. If environmental releases are the only concern, selecting *water-based* metalworking fluids will result in greater potential releases to water (on-site treatment or POTW) than for *straight oils*. The <u>90th-percentile</u> use volume of metalworking fluid (12,000 gal MWF/site-yr) and <u>low-end</u> number of metalworking fluids (1 MWF/site) will result in a higher use rate, maximizing daily releases per site. If both exposures and releases are a concern, selecting *water-based* metalworking fluids and the geometric mean volume (4,260 gal MWF/site-yr) and <u>typical</u> number of metalworking fluids (2 MWF/site) will provide a typical use rate suitable for balancing exposures and releases.
- 3. If the metalworking fluid is known to be either water-based or straight oil, the concerns of the screening-level assessment are also considered. The methodology for selecting the appropriate volume of metalworking fluid and number of metalworking fluid is based on similar logic to Note 2. If occupational exposures are the only concern, the values resulting in a lower daily use rate are selected to maximize the number of workers that may be exposed. If the environmental releases are the only concern, the values resulting in a higher daily use rate are selected to maximize the daily release. If both releases and exposures are a concern, typical defaults are utilized to provide a use rate that balances both release and exposure concerns.

Annual Facility Metalworking Fluid Use Rate (Qneat_site_yr)

NIOSH conducted a study of 79 small metalworking shops⁴ in 1997 and 1998 (Piacitelli, 2001). The geometric mean annual volume of neat metalworking fluid purchased per site was 4,260 gallons, and the 90th percentile was 12,000 gallons. When site-specific information is not available, the steps outlined in Figure 0-1 should be followed to determine the value for the annual volume of neat metalworking fluid per site that should be utilized. Figure 0-1 includes notes providing further explanation of the outlined steps.

If the density of the neat metalworking fluid is unknown, a default of 1 kg/L may be assumed based on the density of water. The density of metalworking fluids may range between 0.9 and 1 kg/L depending on the concentration of mineral oil versus water in the neat fluid. The annual use rate of metalworking fluid can then be estimated using the following equation:

$$Q_{\text{neat_site_yr}} = V_{\text{neat_site_yr}} \times \text{RHO}_{\text{neat}} \times 3.785 \frac{\text{L}}{\text{gal}}$$
(3-1)

Where:

Qneat site yr	=	Annual use rate of neat metalworking fluid (kg/site-yr)
V _{neat site yr}	=	Annual volume of neat metalworking fluid used per site
/		(gallons/site-yr) (See Figure 3-1; Defaults: 4,260 gallons neat
		MWF/site-yr (geometric mean); 12,000 gallons neat MWF/site- yr (90 th percentile))
		yr (90° percentric))
$RHO_{neat} =$	Density	y of neat metalworking fluid (kg/L) (Default: 1 kg/L, assumed
		similar to water)

Concentration of Chemical of Interest (F_{chem trough})

If the concentration of the chemical of interest in the neat metalworking fluid (as received by the site) or in the trough (as used in the metal shaping operations) is unknown, the following section may be used to determine the concentrations.

Fraction of the Chemical of Interest in the Neat Metalworking Fluid (F_{chem neat})

If the weight fraction of the chemical in the metalworking fluid is unknown, use the following guidelines to help determine the value.

- If the submitter provides enough information to determine the type of metalworking fluid (conventional, semi-synthetic, synthetic, or straight oil) and the type of additive, use data from Table 0-1, Table 0-3, Table 0-4, Table 0-5, or Table 0-8 to determine the neat metalworking fluid composition (F_{chem_neat}).
- If the type of additive is known but the type of metalworking fluid is unknown, use Table 0-3 to determine the fraction of the chemical in the neat metalworking fluid (F_{chem_neat}). This table combines the concentration data in Section · for all types of metalworking fluids.

⁴ The NIOSH study investigated occupational exposures to metalworking fluids at sites across a variety of SIC codes and geographic regions. The study focused on "job shops", which machine a variety of products according to changing customer orders, rather than sites that manufacture a large quantity of the same part (e.g., automobile part manufacturing). Many "job shops" are smaller than part manufacturers; however, sites included in the study had up to 850 workers and the 90th percentile annual volume is expected to encompass large shops. These types of shops represent 70-80% of the workers potentially exposed to metalworking fluids in the United States (Piacitelli, 2001).

• If both the type of metalworking fluid and type of additive are unknown, determine if the metalworking fluid will be assessed as water-based or straight oil according to Figure 0-1. Assume the chemical is an emulsifier if the metalworking fluid is water-based or a lubricity agent if the fluid is a straight oil. This results in more conservative estimates (higher concentration than other chemical components for all operations).

Component	Percentage
Emulsifiers (default component for water-based)	< 35
Lubricity agents (default component for straight oils)	< 25 (water-based) < 40 (straight oil)
Oiliness agents	< 10
Corrosion inhibitors	< 10
Coupling agents	< 5
Extreme-pressure additives	< 30
Biocides	< 2
Wetting agents/surfactants	< 10
Defoamers	< 1
Mineral oil	< 80
Water	< 60

Source: Byers, 2006; ILMA, 2005a; OECD, 2004.

Fraction of the Neat Metalworking Fluid in the Trough (Fneat_trough)

Water-based metalworking fluids are diluted with water before use. Dilution ratios generally depend on the metal shaping operation. Table 0-6 presents typical dilution percentages of metalworking fluid in water based on the shaping operation (F_{neat_trough}). Alternate ranges of dilution factors are presented in Table 2-7; however, the data presented in Table 2-6 should be used as default. Because water-based metalworking fluids are most commonly used in machining and grinding operations, if the metal shaping operation is unknown, machining and a weight fraction of 0.1 kg of neat metalworking fluid/kg of metalworking fluid in the trough should be assumed as a conservative estimate. In contrast, straight oils are not diluted. The concentration of the chemical of interest in the neat oil received at the facility is the same concentration as the chemical is used in metal shaping operations.

Fraction of the Chemical of Interest in the Trough (F_{chem trough})

Using the fraction of the chemical of interest in the neat metalworking fluid and the fraction of the neat metalworking fluid in the trough, the fraction of the chemical of interest in the trough can be estimated using the following equation:

$$F_{chem_trough} = F_{chem_neat} \times F_{neat_trough}$$
(3-2)

Where:

F_{chem} trough

= Weight fraction of the chemical of interest in the trough (kg

chemical/kg trough MWF)

F _{chem_neat}	=	Weight fraction of the chemical of interest in the neat metalworking fluid (kg chemical/kg neat MWF) (See Table 0-3; Defaults: 0.35 kg chemical/kg neat MWF (water-based
		MWF); 0.4 kg chemical/kg neat MWF (straight oil))
F _{neat_trough}	=	Weight fraction of the neat metalworking fluid in the trough
		(kg neat MWF/kg trough MWF) (See Table 0-6; Defaults: 0.1
		kg neat MWF/kg trough MWF (water-based MWF); 1 kg neat
		MWF/kg trough MWF (straight oil))

Annual Use Rate of the Chemical of Interest (Q_{chem site vr})

In general, not all metalworking fluids used at a facility will contain the chemical of interest. Facilities may use multiple metalworking fluids for particular operations (e.g., one fluid for machining copper and another for machining steel). In NIOSH's study of small metalworking shops, 79 percent used at least two different metalworking fluids (Piacitelli, 2001). Based on a literature search by industry, larger sites may use up to seven different metalworking fluids (ILMA, 2005a). Assuming a facility only uses one metalworking fluid containing the chemical of interest, the annual use rate of chemical can be determined based on the annual use rate of metalworking fluids, the concentration of chemical of interest in the metalworking fluid, and the total number of metalworking fluids used by the site. Use the decision logic presented in Figure 3-1 to determine the number of metalworking fluids used per site (N_{mwf site total}) that should be used to estimate the throughput of the chemical of interest. Selecting a lower number of metalworking fluids provides a larger throughput of the chemical of interest and results in a more conservative estimate of the releases to the environment. Selecting a higher number of metalworking fluids provides a smaller throughput and results in a greater number of sites using metalworking fluids containing the chemical of interest and a greater number of workers potentially exposed to the chemical of interest. The following equation may be used to estimate the annual throughput of the chemical of interest:

 \cap

$$Q_{chem_site_yr} = \frac{Q_{neat_site_yr} \times F_{chem_neat} \times N_{mwf_site_chem}}{N_{mwf_site_total}}$$
(3-3)
Where:

$$Q_{chem_site_yr} = Annual use rate of chemical of interest, per site (kg
chemical/site-yr)
Q_{neat_site_yr} = Annual use rate of neat metalworking fluid (kg neat MWF/site-
yr)(See Section 3.3)
F_{chem_neat} = Weight fraction of the chemical of interest in the neat
metalworking fluid (kg chemical/kg neat MWF) (See Section
3.4)
N_{mwf_site_chem} = Number of metalworking fluids containing the chemical of
interest used per site (Default: 1 MWF/site)
N_{mwf_site_total} = Number of different metalworking fluids used per site (See$$

 $\cdots \mathbf{E}$

N_{mwf site total}

Figure 3-1; Defaults: 1 MWF/site; 2 MWFs/site; 7 MWFs/site)

Daily Use Rate of the Chemical of Interest (Q_{chem_site_day})

=

Although the addition of fresh metalworking fluid to the trough may occur periodically, the daily use rate is an average of all trough changes at a facility over the total number of working days at the facility (TIME_{working days}). The following equation can be used to estimate the daily throughput at a facility.

$$Q_{\text{chem_site_day}} = \frac{Q_{\text{chem_site_yr}}}{\text{TIME}_{\text{working days}}}$$
(3-4)

Where:

=	Daily use rate of chemical of interest, per site (kg
	chemical/site-day)
=	Annual use rate of chemical of interest, per site (kg
	chemical/site-yr)(See Section 3.4)
=	Operating days (See Table 0-2; Default: 247 days/yr) (USEPA,
	2000a)
	=

Number of Sites (N_{sites})

The number of sites using metalworking fluids containing the chemical of interest can be estimated by using the daily use rate calculated above (Section 0), the operating days per year, and the annual production volume of the chemical of interest. The following equation can be used to estimate the number of sites. This equation does not account for any pre-process losses (i.e., losses during the manufacturing and formulation operations). The number of sites should not exceed 89,000 sites (USEPA, 2003).

$$N_{sites} = \frac{Q_{chem_yr}}{Q_{chem_site_day} \times TIME_{working_days}}$$
(3-5)

Where:

Nsites=Number of sites using a metalworking fluid contr chemical of interest (sites)Qchem_yr=Annual production volume of the chemical of interest (sites)	
Q_{chem_yr} = Annual production volume of the chemical of int	taining the
chemical/yr)	terest (kg
Q _{chem_site_day} = Daily use rate of chemical of interest, per site (kg chemical/site-day) (See Section 0)	g
TIME _{working_days} = Operating days (See Table 0-2; Default: 247 day 2000a)	ys/yr) (USEPA,

Annual Number of Metalworking Fluid Containers (N_{cont site yr})

The number of transport containers can be estimated based on the daily use rate, container size, density of the neat metalworking fluid, and concentration of the chemical of interest in the fluid. A search of recent PMN submissions found that transport containers range in size from 5-gallon drums to bulk containers (CEB, 2003); therefore, a default transport container size of 208 L may be assumed based on a 55-gallon drum if chemical-specific information is not available. If the fluid density is not known, a density of 1 kg/L (water) can be used as a default. The number of containers can be estimated through the following equation.

$$Q_{\text{chem_site_day}} = \frac{Q_{\text{chem_yr}}}{\text{TIME}_{\text{working days}} \times N_{\text{sites}}}$$

 $^{^{5}}$ The value for N_{sites}, calculated using Equation 3-6, should be rounded up. Q_{chem_site_day} should be adjusted after N_{sites} is calculated to account for any rounding errors:

	$N_{cont_site_yr} = \frac{Q_{chem_site_day} \times TIME_{working_days}}{V_{container} \times RHO_{neat} \times F_{chem_neat}} $ (3-6)	6)
Where:		
$N_{cont_site_yr}$	 Annual number of containers of neat metalworking fluid, per site (containers/site-yr) 	
$Q_{chem_site_day}$	 Daily use rate of chemical of interest (kg chemical/site-day) (See Section 0) 	
$TIME_{working_days}$	 Operating days (See Table 0-2; Default: 247 days/year) (USEPA, 2000a) 	
V _{container}	 Volume of container (Default: 208 L/container (55-gallon drum)) 	
RHO _{neat}	 Density of neat metalworking fluid (Default: 1 kg/L; consister with Equation 3-1) 	ıt
F_{chem_neat}	 Weight fraction of the chemical of interest in the neat metalworking fluid (kg chemical/kg neat MWF)(see Section 3.4) 	

Summary of the Relationship of Section 0 Parameters

The values for chemical of interest throughput ($Q_{chem_site_day}$), number of sites (N_{sites}), and production volume of the chemical of interest (Q_{chem_yr}) are all related. This ESD presents an equation to calculate the parameter for the chemical of interest throughput ($Q_{chem_site_day}$) from US EPA and NIOSH data. The chemical of interest throughput and supplied production volume are then used to determine the number of sites.

If the number of sites is known, the chemical of interest throughput can be calculated directly without the use of Equation 3-2. This alternate calculation is:

$$Q_{chem_site_day} = \frac{Q_{chem_yr}}{TIME_{working days} \times N_{sites}}$$

If N_{sites} is known and TIME_{working_days} is unknown, the default assumption that facilities operate 247 days per year is recommended (see Section 0), and $Q_{chem_site_day}$ should be calculated using the equation above.

It is recommended to calculate the chemical of interest throughput based on the methodology presented in Section 0 and compare it to the throughput based on the number of sites and operating days, as calculated above.

ENVIRONMENTAL RELEASE ASSESSMENTS

This section presents approaches for calculating the amount of chemical of interest released for each release source during metal shaping operations. The release sources are discussed in the order that they occur in the process (please refer to flow diagram in Figure 0-1). An indication of the most likely receiving media (i.e., air, water, landfill, incineration) is also provided. Key default values used for the release estimates, accompanied by their respective references, are provided in Table A-4 of Appendix A.

All release equations below estimate daily rates for a given site. To estimate annual releases for all sites for a given source, the release rates must be multiplied by the number of days of release (TIME_{working_days}) and by the number of sites using metalworking fluid containing the chemical of interest (N_{sites}) (See Section 0).

For most release sources, this ESD assumes that the number of days of release is the same as the days of operation. Some of these releases are expected to go to the same medium of release on the same days; therefore, daily and annual releases to a given medium may be summed to yield total amounts released per site per day and per year, respectively.

One of the environmental release estimates presented in this document is based on standard EPA/OPPT release models. The remaining estimates are based on data collected by EPA during the development of the MP&M effluent limitation guidelines and pretreatment standards, and on the assumption that the entire volume of metalworking fluid loaded into metal shaping machines is discharged to the environment. As stated in Section ·, some chemicals may be consumed in the metal shaping process (ILMA, 2005a; ILMA, 2006a). Data were not available to quantify such losses. Therefore, this ESD assumes that chemicals do not react or degrade in order to provide conservative release estimates. Note that this ESD does not assess any releases from equipment cleaning because the spent metalworking fluid release accounts for the balance of the production volume not already released from other sources.

Table 0-1 summarizes the release estimation methods used in this ESD. Refer to Section 0 for a description of the sources reviewed and full citations for those specifically used in these calculations.

Note that the standard model default values cited are current as of the date of this document; however, EPA may update these models as additional data become available. EPA recommends using the most current version of the models in these calculations.

EPA has developed a software package (ChemSTEER) containing these models as well as all current EPA defaults. Appendix B provides additional information on ChemSTEER, including instructions for obtaining the program, as well as background information, model equations, and default values for several parameters for all standard EPA/OPPT models.

To estimate environmental releases, this ESD assumes chemicals in metalworking fluids are nonvolatile. EPA often assumes chemicals with a vapor pressure less than 0.001 torr are nonvolatile, resulting in negligible releases to air and negligible associated inhalation exposures (CEB, 1991). Each ESD user will have to decide the definition of what constitutes *volatile* based on the specific objectives of the assessment. Although not used in this ESD, Appendix B provides standard EPA/OPPT models for assessing releases of and exposures to volatile chemicals.

Table 0-1. Summary of Metalworking Fluids ESD Release Models

Release Source #	Description	Model Name or Description	Standard EPA Model (✔)
1	Container Residue released to uncertain media (water, incineration, or landfill)	EPA/OPPT Bulk Transport Residual Model EPA/OPPT Drum Residual Model(Default) EPA/OPPT Small Container Residual Model EPA/OPPT Solid Residuals in Transport Containers Model	~
2	Dragout Losses released to water (on-site treatment or POTW)	Loss rate is based on available industry-specific data	
3	Filter Media and Other Recycling Wastes released to uncertain media (water-based: water, incineration, or landfill; straight oil: incineration or landfill)	Loss rate is based on available industry- specific data	
4	Spent Metalworking Fluid released to water (water-based: on-site treatment or POTW) or incineration (straight oil)	Release rate is based on mass balance	

OPPT - Office of Pollution Prevention and Toxics.

Control Technologies

Development of the MP&M Phase I guidelines determined that facilities that perform *metal shaping operations* and send their wastewater to on-site treatment will typically use oil/water separation followed by chemical precipitation as treatment. Since the initial Phase I effort, facilities have dramatically shifted towards treatment by ultrafiltration. Thus ultrafiltration, oil/water separation, and chemical precipitation are control technologies expected to be used in metal shaping operations. The following subsections briefly describe these control technologies. Currently, facilities do not typically discharge wastewater directly to POTW due to stringent discharge limits (ILMA, 2005b; ILMA, 2006b; Byers, 2006) required by 40 CFR 403.5(b)(6). Facilities without wastewater treatment typically contract waste haulers to periodically haul wastewater off site for treatment. The effect of on-site wastewater treatment on the releases presented in this document is discussed in Section 4.7.

Chemical Precipitation and Sedimentation

The common process used to remove dissolved metals from wastewater is chemical precipitation followed by sedimentation. During this process, the dissolved metals are converted to an insoluble form, and then the separated metals are removed from the wastewater. Facilities generally used one of four methods: hydroxide precipitation (the most common), sulfide precipitation, carbonate precipitation, and sodium borohydride precipitation, although variations of these methods are sometimes used. These treatments are not designed to remove oil and grease or organic compounds; when MP&M wastewater is treated in this manner any oil and grease or organics removal is incidental.

The types of equipment used for chemical precipitation and sedimentation vary widely. Small batch operations can be performed in a single tank, usually having a conical bottom that permits removal of settled solids. Continuous processes are usually performed in a series of tanks, including a rapid mix tank for mixing the precipitating chemicals, a slow mix tank for addition of coagulants and flocculants and floc formation, and a settling tank or clarifier for separation of the solids from the wastewater. An alternative method of separating precipitated solids from wastewater is filtration, during which the entire wastewater flow is passed through either a filter press or a microfiltration unit.

Chemical Emulsion Breaking with Oil/Water Separation

Chemical emulsion breaking is used to break stable oil/water emulsions (oil dispersed in water and stabilized by electrical charges and emulsifying agents). Treatment of spent oil/water emulsions involves adding chemicals to break the emulsion followed by oil/water separation. The major equipment required for chemical emulsion breaking includes reaction chambers with agitators, chemical storage tanks, chemical feed systems, pumps, and piping. Factors to be considered for destroying emulsions are type of chemicals, dosage and sequence of addition, pH, mixing, heating requirements, and retention time.

Chemicals (e.g. polymers, alum, ferric chloride, and organic emulsion breakers) break emulsions by neutralizing repulsive charges between particles, precipitating or salting out emulsifying agents, or weakening the interfacial film between the oil and water so it is readily broken. Once the charges have been neutralized or the interfacial film broken, the small oil droplets and suspended solids either adsorb on the surface of the floc that is formed, or break out and float to the top. The oil floats to the surface of the water because of the difference in specific gravities between the oil and the water. Solids usually form a layer between the oil and water, since some solids become suspended in the oil. Oils and solids are typically skimmed from the surface of the water in a subsequent step after chemical emulsion breaking.

To separate oil from process solutions, oil skimming devices are typically mounted onto the side of a tank and operated on a continuous basis. Common separation devices include belts, rotating drums, disks, and weir oil skimmers and coalescers. Belt and drum skimmers operate in a similar manner, with either a

continuous belt or drum rotating partially submerged in a tank. As the surface of the belt or drum emerges from the liquid, the oil that adheres to the surface is scraped off (drum) or squeezed off (belt) and diverted to a collection vessel. Gravity separators use overflow and underflow weirs to skim a floating oil layer from the surface of the wastewater. A weir allows the oil layer to flow over the weir into a trough for disposal or reuse while most of the water flows underneath the weir.

A skimmer's removal efficiency depends on the composition of the waste stream and the retention time of the water in the tank. Gravity-type separators tend to be more effective for wastewater streams with consistently large amounts of floating oil. Drum and belt type skimmers are more applicable to waste streams containing smaller amounts of floating oil. Oil separation not only removes oil but also removes organics that are more soluble in oil than in water. Subsequent clarification removes organic solids directly and probably removes dissolved organics by adsorption on inorganic solids.

Solid wastes generated by chemical emulsion breaking include surface oil and oily sludge, which are usually contract hauled for disposal by a licensed contractor. If the recovered oil contains a low enough percentage of water, it may be burned for its fuel value or processed and reused.

Ultrafiltration

Ultrafiltration uses a pressure-driven membrane process to separate solution components based on molecular size and shape. Using an applied pressure difference across a membrane, solvent and small solute species pass through the membrane and are collected as permeate while larger compounds are retained by the membrane and recovered as concentrate.

Filtration configurations can be either "dead-end" flow configurations, where the fluid flow is directed at a right angle to the membrane surface, or tangential-flow configurations, where the fluid flow is parallel to the membrane surface. Based on information from site visits and surveys, tangential-flow configurations are more common at MP&M facilities. Several types of tangential-flow configurations are available, including plate and frame, hollow fiber, tubular, and spiral-wound. The systems typically operate in batch or semibatch mode, where a batch of wastewater is recirculated from a holding tank through the filter. The concentrate is returned to the holding tank while a continuous stream of permeate is discharged. The concentrate remaining in the holding tank is typically batch discharged.

MP&M Release Data

During the development of the MP&M effluent guidelines, EPA collected discharge data for metal shaping operations, including machining and grinding. Table 0-2 presents data on the releases of metalworking fluids during metal shaping operations. Trough discharges and other aqueous releases include dilute metalworking fluid released during trough discharges of spent fluids and equipment cleaning losses. Dragout releases include residual metalworking fluid remaining on the part. Sludge and filtration releases include metalworking fluids lost during skimming, metal fines filtering, and other losses from recycling the fluid. Note that since facilities reported the percent solids of sludge discharges, the solids fraction has been removed from the data presented in Table 0-2. Appendix C presents the ranges and number of data points for each of the values in Table 0-2. These ranges may be used to compare any site-specific information with the defaults presented in the ESD.

	Trough Discharges		Dragout Re	eases	Sludge and Filtrati	Total Release of Dilute MWF	
Metal Shaping Operation	kg dilute MWF/machine-yr	% of Total Releases	kg dilute MWF/machine-yr	% of Total Releases	kg dilute MWF/machine-yr	% of Total Releases	kg dilute MWF/machine-yr
Grinding	2,022	38	1,375	26	1,954	37	5,350
Machining	1,269	66	230	12	422	22	1,921
General Average for Metal Shaping Operations	1,535	53	315	11	1,048	36	2,898

Table 0-2. Releases of Dilute Metalworking Fluid from Metal Shaping Operations

Source: U.S. EPA, 2000a

Note: Sludge and filtration releases included metal fines and other solid materials. When reporting in response to the MP&M survey, facilities estimated the percent solids of the sludge waste streams. The solids fraction was removed from the data presented above (see Appendix C for additional details); however, these data still appear to be a greater percentage of losses than expected. Note, however, for water-based metalworking fluids, the default media of release for all release sources is water.

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In determining metalworking fluid throughput, EPA judged the NIOSH data presented in Section 3.3 to be more reliable than the MP&M discharge data, as the NIOSH data measured consumption rather than releases⁶. However, EPA also judged the MP&M discharge data to be reliable within themselves for determining relative loss fractions for different release sources.

Container Residue Release (Release 1)

The amount of metalworking fluid remaining in the transportation containers depends on the size of the transport container. Metalworking fluids can be transported in containers of various sizes; recent PMN submissions show that containers range from 5-gallon pails to bulk containers (CEB, 2003). The default transportation container size of a 55-gallon drum should be used in the absence of site-specific information. In the absence of industry-specific data, the following standard EPA/OPPT models may be used to estimate container residue releases. The rationale, defaults, and limitations of these models are further explained in Appendix B.

- *EPA/OPPT Bulk Transport Residual Model* may be used for large containers (e.g., totes, tank trucks, rail cars) containing greater than or equal to 100 gallons of liquid;
- *EPA/OPPT Drum Residual Model* may be used for drums containing between 20 and 100 gallons of liquid;
- *EPA/OPPT Small Container Residual Model* may be used for liquid containers containing less than 20 gallons; and

The media of release for container residues from metal shaping operations is not known; therefore, the entire release from container residue is assessed to each of water, incineration, or landfill by default. If containers are rinsed on site with water and the water is sent to on-site wastewater treatment, Section 0 presents wastewater treatment data for metal shaping facilities.

To estimate releases from container residue, first determine $N_{cont_site_yr}$, the number of transport containers containing the chemical of interest that are used per site per year (see Section 0). If $N_{cont_site_yr}$ is fewer than the days of operation (TIME_{working_days}), the days of release equal $N_{cont_site_yr}$ and the daily release is calculated based on the following equation:

$$Elocal_{container_residue_disp} = V_{container} \times RHO_{neat} \times F_{chem_neat} \times F_{container_residue} \times 1\frac{container}{site-day}$$
(4-1)

This release will occur over $[N_{cont_site_yt}]$ days/year from $[N_{sites}]$ sites Where:

$Elocal_{container_residue_disp}$	=	Daily release of chemical of interest to water, incineration, or landfill from container residue (kg chemical/site-day)
V _{container}	=	Volume of container (Default: 208 L/container (55-gallon
		drum); consistent with Equation 3-6)
RHO _{neat}	=	Density of neat metalworking fluid (Default: 1 kg/L; consistent
		with Equation 3-6)
F _{chem_neat}	=	Weight fraction of the chemical of interest in the neat
		metalworking fluid (kg chemical/kg neat MWF) (See Section
		3.4)

⁶ Note: The NIOSH and MP&M data are on the same order of magnitude when compared on a consistent basis. For example, the NIOSH value of 4,260 gallons neat MWF/site-yr is equivalent to 322,000 kg dilute MWF/site-yr for a 20:1 dilution and a density of 1 kg/L (see Sections 2.2 and 3.3), while the MP&M value of 2,898 kg dilute MWF/machine-yr is equivalent to 139,000 kg dilute MWF/site-yr for 48 machines/site (USEPA, 2000a).

F _{container} residue	=	Fraction of neat metalworking fluid remaining in the container
_		as residue (Default: 0.03 kg neat MWF remaining/kg neat
		MWF shipped for drums (CEB, 2002); See Appendix B for
		defaults used for other container types)

If $N_{cont_site_yr}$ is greater than $TIME_{working_days}$, the days of release equal $TIME_{working_days}$ and the average daily release is calculated based on the following equation (note most sites should use less than one container per day):

El	ocal	$_{\text{ontainer_residue_disp}} = Q_{\text{chem_site_day}} \times F_{\text{container_residue}}$	(4-2)
This release v	vill o	ccur over $[TIME_{working_days}]$ days/year from $[N_{sites}]$ sites	
Where:			
$Elocal_{container_residue_disp}$	=	Daily release of chemical of interest from container residue chemical/site-day) (Default media: water, incineration, or landfill)	e (kg
$Q_{chem_site_day}$	=	Daily use rate of chemical of interest (kg chemical/site-day (See Section 0)	1)
$F_{container_residue}$	=	Fraction of neat metalworking fluid remaining in the conta as residue (Default: 0.03 kg neat MWF remaining/kg neat MWF shipped for drums (CEB, 2002); See Appendix B for defaults used for other container types)	

Dragout Losses (Release 2)

Metalworking fluid remains on the part after shaping. This coating of fluid inhibits corrosion of the metal surfaces of the part. The residual metalworking fluid on the part is likely removed during an alkaline cleaning or degreasing operation prior to metal/organic deposition or surface finishing operations. Recent industry information indicates both straight oils and water-based metalworking fluids are typically removed during an intermediate washing step (ILMA, 2006b). Table 0-2 presents the percent of total process releases associated with dragout losses. Because residual water-based metalworking fluids and straight oils are expected to be rinsed from shaped parts, this industry-average percent release is applicable to both categories of metalworking fluids.

The average daily amount of chemical of interest released to water from dragout losses can be estimated using the following equation, which accounts for the amount of chemical released from container residue. However, if site-specific information indicates on-site wastewater treatment of dragout losses, refer to Section 0 to obtain wastewater treatment data for metal shaping facilities.

This relea	e =	$s_{es} = Q_{chem_site_day} \times (1 - F_{container_residue}) \times F_{dragout_losses}$ cur over [TIME _{working_days}] days/year from [N _{sites}] sites	(4-3)
Where:			
$Elocal_{dragout_losses}$	=	Daily release of chemical of interest from dragout losses (k chemical/site-day) (Default medium: water)	g
$Q_{chem_site_day}$	=	Daily use rate of chemical of interest (kg chemical/site-day (See Section 0)	')
$F_{container_residue}$	=	Fraction of neat metalworking fluid remaining in the contait as residue (Default: 0.03 kg neat MWF remaining/kg neat MWF shipped for drums; consistent with Section 4.3)	iner

F _{dragout} losses	=	Fraction of chemical of interest lost from dragout (See
		Table 0-2; Default: 0.11 kg trough MWF lost/kg trough MWF
		used)

Filter Media and Other Recycling Wastes (Release 3)

During use the metalworking fluid becomes contaminated with tramp oils and metal fines. The bulk of the fines are filtered from the fluid and the tramp oil is often skimmed prior to the reuse of the fluids. Eventually, the fluid becomes unusable in its present state, and may be sent through either a centrifugation or pasteurization unit to extend its life. These units thoroughly remove metal fines and tramp oils and help to destroy any bacteria or fungi growing in the fluid. Regenerated metalworking fluids are then recycled to the trough. During these recycling operations a percentage of the metalworking fluid will be lost. Because replacing the entire fluid bath can be expensive, filtering and recycling operations can be extensive to extend the fluid life. Table 0-2 presents the percent of total process releases associated with filtration, sludge, and other recycling wastes.

Based on the MP&M effluent guidelines database, the average machining and grinding operation discharges filter wastes and other recycling sludge 114 times per year (USEPA, 2000a). At a default facility this release would occur at least 5,472 times a year (48 machines/site \times 114 discharges/year). Therefore, assume that this release occurs over the days of operation (default is 247 days per year).

The media of release for these wastes varies by site. In the MP&M effluent guidelines database, facilities reported that these wastes are discharged directly to POTW, or sent to on-site wastewater treatment, landfill, or incineration. Filtration and recycling systems for straight oils are not expected to use water or produce process wastewater. Therefore, the default media of release for filtration and recycling wastes should be water, incineration, or landfill for water-based metalworking fluids and incineration or landfill for straight oils.

The average daily amount of chemical of interest released to an unknown media from filtration and other recycling operations can be estimated using the following equation, which accounts for the amount of chemical released from container residue. However, if site-specific information indicates on-site wastewater treatment, refer to Section 0 to obtain wastewater treatment data for metal shaping facilities.

$\text{Elocal}_{\text{recycle}_{\text{wastes}}} = \text{Q}_{\text{chem}_{\text{site}_{\text{day}}}} \times (1)$	$1 - F_{\text{container_residue}}$	$\times F_{\text{recycle}_{\text{wastes}}}$	(4-4)
This release will occur over [TIMEworki	ng_days] days/year	from [N _{sites}] sites	

Where:

nere:		
Elocal _{recycle_wastes}	 Daily release of chemical of interest from filtration and other recycling operations (kg chemical of interest/site-day) (Defau media: water, incineration, or landfill (water-based MWF); incineration or landfill (straight oil)) 	
$Q_{chem_site_day}$	 Daily use rate of chemical of interest (kg chemical/site-day) (See Section 0) 	
$F_{container_residue}$	 Fraction of neat metalworking fluid remaining in the contain as residue (Default: 0.03 kg neat MWF remaining/kg neat MWF shipped for drums; consistent with Section 4.3) 	er
$F_{recycle_wastes}$	 Fraction of chemical of interest lost during filtration and other recycling operations (See Table 0-2; Default: 0.36 kg trough MWF lost/kg trough MWF used) 	

Spent Metalworking Fluid Release (Release 4)

Regardless of the type of operation, the metalworking fluid will eventually degrade or "spoil" and be disposed. Straight oils typically last longer than water-based metalworking fluids because of limited biodegradation and evaporation, but are still expected to be susceptible to degradation over time. Fluid troughs and equipment must be flushed and cleaned. Spent water-based metalworking fluid may first be sent to on-site treatment or hauled off site for treatment. Spent straight oils that can no longer be recycled on site are expected to be hauled off site for oil recycling or fuel blending. The default media of release for spent metalworking fluids is discharge to POTW for water-based metalworking fluids and incineration for straight oils. However, if site-specific information indicates on-site wastewater treatment of spent metalworking fluid, refer to Section 0 to obtain wastewater treatment data for metal shaping facilities.

Based on the MP&M effluent guidelines database, the average machining and grinding operation trough is changed and cleaned eight times per year (USEPA, 2000a). Therefore, at the default facility this release occurs at least 384 times a year (48 machines/site \times 8 changes/year). All machines may be cleaned on the same day or at random intervals throughout the year. Also, the database indicates that both on-site treatment with discharge to a POTW and direct discharge to a POTW without treatment occur at a frequency equal to or greater than the number of operating days. Therefore, the default frequency of this release is equal to the number of operating days (default is 247 days per year).

The average daily amount of chemical of interest released to water from spent troughs can be estimated through the following equation.

• <u>=</u>	0	$ \sum_{\text{em_site_day}} \times (1 - F_{\text{container_residue}}) \times (1 - F_{\text{dragout_losses}} - F_{\text{recycle_wastes}}) $ (4-5) cur over [TIME _{working days}] days/year from [N _{sites}] sites
Where:		
$Elocal_{trough_discharge}$	=	Daily release of chemical of interest to water from trough discharge and cleanout (kg chemical/site-day) (Default media: POTW (water-based MWF); incineration (straight oils))
$Q_{chem_site_day}$	=	Daily use rate of chemical of interest (kg chemical/site-day) (See Section 0)
$F_{container_residue}$	=	Fraction of neat metalworking fluid remaining in the container as residue (Default: 0.03 kg neat MWF remaining/kg neat MWF shipped for drums; consistent with Section 4.3)
$F_{dragout_losses}$	=	Fraction of chemical of interest lost from dragout (See Table 0-2; Default: 0.11 kg trough MWF lost/kg trough MWF used)
$F_{recycle_wastes}$	=	Fraction of chemical of interest lost during filtration and other recycling operations (See Table 0-2; Default: 0.36 kg trough MWF lost/kg trough MWF used)

Effect of On-Site Waste Treatment

The MP&M database indicates 65 percent of sites use on-site wastewater treatment prior to discharge, while 15 percent discharge directly to a POTW (USEPA, 2000a). The remaining 20 percent of facilities do not discharge to a POTW, and employ treatment or disposal methods including reuse/recycle/recovery (11.86 percent of facilities), evaporative treatment (3.4 percent of facilities), incineration (3.05 percent of facilities), and hazardous disposal (1.21 percent of facilities) (USEPA, 2003). However, much of these data were collected in the 1980's and early 1990's. Recent industry information suggests that the number of sites that discharge directly to POTW has significantly decreased due to more stringent discharge limits (ILMA, 2005b; ILMA, 2006b; Byers, 2006) required by the national

pretreatment standards found in 40 CFR 403.5(b)(6). Therefore, this ESD presents information concerning on-site wastewater treatment. Wastewater containing the chemical of interest may be produced by Releases 1 through 4 for water-based metalworking fluids and by Release 2 for straight oils. The MP&M effluent guidelines database indicates that both on-site treatment with discharge to a POTW and discharge to a POTW without on-site treatment occur at a frequency equal to or greater than the number of operating days. Therefore, the default frequency of this release is equal to the number of operating days (default is 247 days per year).

On-site wastewater treatment is typically performed by either oil/water separation (by chemical methods, reverse osmosis, or evaporation); oil phase separation by physical (ultrafiltration and adsorption) and chemical (salt or acid addition) processes, typically followed by chemical precipitation and sedimentation (USEPA, 2003; EC, 2003). While onsite treatment may be used, the effectiveness of the treatment technology at removing the chemical of interest is uncertain. For example, the effectiveness of oil/water separation at removing a chemical will depend on the chemical's water solubility and octanol/water partition coefficient. Similarly, the effectiveness of ultrafiltration will depend on the size of the chemical species. While chemical-specific data may not be available, total organic carbon (TOC) removal data were collected during the data gathering phase of the MP&M Phase II effluent guidelines proposal process. TOC removal may be used in this ESD to estimate the removal of organic chemicals in metal shaping operation wastewater (USEPA, 2000b). Based on a survey of recently submitted PMN cases, new chemicals in metalworking fluids are expected to be organic in nature (CEB, 2003). However, the physical properties of the chemical should be critically reviewed before utilizing the default TOC removal efficiencies presented in Table 4-3.

Two waste streams are created if spent metalworking fluid is treated on site: aqueous waste (containing a low concentration of chemical of interest) and concentrate/sludge waste. Typically, the treated aqueous waste is sent to a POTW, while the concentrate waste is either sent to a waste oil recycler or incinerated. TOC removal data from the MP&M database indicate default efficiencies for oil/water separation (default: 50 percent) and ultrafiltration (default: 70 percent). Chemical precipitation is not designed to remove organic compounds, and any organic compound removal from this process is incidental. Therefore, a conservative estimate of zero percent removal should be assumed for chemical precipitation. Appendix D presents additional information on the data used to determine TOC removal. Table 0-3 summarizes these treatment options.

On-Site Treatment	Organic Removal Efficiency (F _{eff WWT})
Chemical precipitation (default)	0
Oil/Water separation	0.5
Ultrafiltration	0.7

Source: U.S. EPA, 2000a. See Appendix D.

If the type of on-site treatment is unknown, assume chemical precipitation as a conservative estimate due to uncertainty. On-site treatment creates two waste streams: treated aqueous waste containing a low concentration of chemical of interest and the concentrated waste removed from the wastewater. The treated aqueous waste is usually discharged to a POTW, while the concentrated waste will be incinerated or reclaimed as waste oil (USEPA, 2003). If site-specific information indicates on-site wastewater treatment, releases may be partitioned between water and incineration. Equations 4-6 and 4-7 show the

partition of Release 2 between water and incineration respectively. Similar equations may be used to partition Releases 1, 3, and 4 if water releases are assessed.⁷

	Elocal	$_{\text{vater}_{WWT}} = \text{Elocal}_{\text{dragout}_{losses}} \times (1 - F_{\text{eff}_{WWT}})$	(4-6)	
This release will occur over [TIME _{working days}] days/year from [N _{sites}] sites				
Where:				
Elocal _{water_WWT}	=	Daily release of chemical of interest to POTW after WW	Γ (kg	
		chemical/site-day) (Default medium: POTW)		
Elocal _{dragout} losses ⁸	=	Daily release of chemical of interest from dragout losses	(kg	
		chemical/site-day) (See Section 0)		
Feff WWT	=	Wastewater treatment efficiency (See Table 0-3; Default:	0.	
-		(chemical precipitation))		

 $Elocal_{concentrate} = Elocal_{dragout_losses} \times F_{eff_WWT}$ (4-7)

This release will occur over [TIMEworking_days] days/year from [Nsites] sites

Where:

nere:		
Elocal _{concentrate}	=	Daily release of chemical of interest in concentrated treatment
		waste (kg chemical/site-day) (Default medium: incineration)
Elocal _{dragout_losses} ⁸	=	Daily release of chemical of interest from dragout losses (kg
		chemical/site-day) (See Section 0)
F _{eff_WWT}	=	Wastewater treatment efficiency (See Table 0-3; Default: 0
_		(chemical precipitation))

The EU Environmental Emission Scenario on biocides used as metalworking fluids states that the major emissions from the use of metalworking fluids are due to emissions from wastewater treatment. The EU scenario focuses on releases to wastewater treatment from dragout losses and spent metalworking fluids. The release formulas presented by the EU incorporate the octanol/water partition coefficient, as well as factors for chemical degradation during use (F_{deg}) and elimination of the chemical during physical chemical treatment (F_{elim}) to determine the portion of the chemical in the water phase after oil/water separation (EC, 2003). These formulas are presented in Appendix E.

Air Releases

Volatile releases of metalworking fluids to air during the metal shaping process are expected to be negligible. This ESD assumes that the chemical of interest is not volatile, which is supported by a search of past metalworking fluid related PMN submissions (PMN, 2003).

Metalworking fluids sprayed onto the parts during metal shaping operations may result in occupational exposure to a mist of the metalworking fluid; however, releases of these mists to air are not expected. The two options found in the literature to control mist generation from metal shaping operations are increased use of metal shaping machine enclosures and the use of air cleaners to filter the air (Heitbrink, 2000; Yacher, 2000). As described in the literature, air cleaners exhaust filtered air to the workplace and drain the filtered metalworking fluid back to the metalworking fluid filter. Since neither enclosure nor filtration exhaust the mist outside the facility, the assumption of negligible air releases is supported.

⁷ To partition Releases 1, 3, and 4, replace Elocal_{dragout_losses} with Elocal_{container_residue_disp} for Release 1, Elocal_{recycle_wastes} for Release 3, and Elocal_{trough_discharge} for Release 4.

⁸ To partition Releases 1, 3, and 4, replace Elocal_{dragout_losses} with Elocal_{container_residue_disp} for Release 1, Elocal_{recycle} wastes for Release 3, and Elocal_{trough} discharge for Release 4.

Mass Balance

The following equation provides a balance for the use of metalworking fluids at metal shaping sites.

$Q_{chem_yr} = \left(Q_{chem_site_day} \times F_{container_residue} + Elocal_{dragout_losses} + Elocal_{recycle_wastes} + Elocal_{trough_discharge}\right)$	(4-8)
$ imes$ N _{sites} $ imes$ TIME _{working_days}	(+-0)

Where:

nore.		
Q _{chem_yr}	=	Annual production volume of the chemical of interest (kg chemical/yr)
$Q_{chem_site_day}$	=	Daily use rate of chemical of interest (kg chemical/site-day) (See Section 0)
$F_{container_residue}$	=	Fraction of neat metalworking fluid remaining in the container as residue (Default: 0.03 kg neat MWF remaining/kg neat MWF shipped for drums; consistent with Section 4.3)
$Elocal_{dragout_losses}$	=	Daily release of chemical of interest from dragout losses (kg chemical/site-day)
$Elocal_{recycle_wastes}$	=	Daily release of chemical of interest from filtration and other recycling operations (kg chemical of interest/site-day)
$Elocal_{trough_discharge}$	=	Daily release of chemical of interest to water from trough discharge and cleanout (kg chemical/site-day)
N _{sites}	=	Number of sites using a metalworking fluid containing the chemical of interest (sites) (See Section 0)
$TIME_{working_days}$	=	Operating days (See Table 0-2; Default: 247 days/yr)

Summary of Relationship Between Release Estimates of Section 0

Chemical of interest release estimates (Releases 1 through 4) are all related. If less than one container is used per site per day (typically true), the release from container residue will not occur over the number of operating days, while other releases will occur over the number of operating days. Equations 4-3, 4-4, 4-5, and 4-8 rely on the alternate method for calculating the release from container residue shown in Equation 4-2, because the release of dragout losses, filtration and recycling wastes, spent metalworking fluid discharge, and the mass balance are based on daily releases occurring over the number of operating days. Due to rounding errors when determining the number of containers per site per year, Elocal_{container_residue_disp} may not be equal to the terms used in Equation 4-4 (e.g., calculating the release based on five full containers per site per year, when only four and a half will be used). However, this rounding error is automatically corrected when using standard EPA/OPPT container residual models in ChemSTEER.

OCCUPATIONAL EXPOSURE ASSESSMENTS

The following section presents estimation methods for worker exposures to the chemical of interest. Figure 2-1 illustrates the occupational activities that have the greatest potential for worker exposure to the chemical.

Industry-specific occupational exposure monitoring data for both inhalation and dermal exposures during metal shaping operations were found in the references reviewed for the development of this ESD (refer to Section 8 for a description of the sources reviewed and full citations for those specifically used in these calculations). The occupational exposure estimates presented in this document for all other activities are based on standard EPA/OPPT exposure models. Table 0-1 summarizes the exposure estimation methods used in this ESD.

Note that the standard model default values cited are current as of the date of this ESD; however, EPA may update these models as additional data become available and recommends that the most current version of the models be used in these calculations.

EPA has developed a software package (ChemSTEER) containing these models as well as all current defaults. Appendix B provides additional information on ChemSTEER, including information on obtaining the program, as well as background information, model equations, and default values for several parameters for all standard EPA/OPPT models.

Exposure Activity	Description	Route of Exposure / Physical Form	Model Name or Description	Standard EPA Model (✓)
A		Dermal exposure to liquid chemical	EPA/OPPT 2-Hand Dermal Contact with Liquid Model	~
В		Dermal exposure to liquid chemical	<i>EPA/OPPT 2-Hand Dermal Contact</i> <i>with Liquid Model</i>	~
С	Exposure to liquid chemical during mixing and transfer of dilute metalworking fluid (water-based only)	Dermal exposure to liquid chemical	EPA/OPPT 2-Hand Dermal Contact with Liquid Model	~
D		Inhalation of liquid chemical particles (mist)	Mist concentration data from industry-specific monitoring study	
	including rinsing,	Dermal exposure to liquid chemical	Surface loading rate data from industry-specific monitoring study	
Е		Dermal exposure to liquid chemical	EPA/OPPT 2-Hand Dermal Contact with Liquid Model	~
F	Exposure to liquid chemical during transfer of spent metalworking fluid and cleaning of shaping machine and trough	1	EPA/OPPT 2-Hand Dermal Contact with Liquid Model	~
G	Exposure to liquid chemical during on-site treatment operations	Dermal exposure to liquid chemical	Assumed to be negligible due to process automation	

Table 0-1. Summary of Metalworking Fluids ESD Exposure Models

Engineering Controls and Personal Protective Equipment (PPE)

The OSHA Best Practices Manual states that engineering controls, work practice controls, and a metalworking fluid management program are the preferred methods for reducing employee exposure to metalworking fluid (OSHA, 2001). Ventilation, including general, dilutional, and local exhaust, is the most common category of engineering controls used in metal shaping facilities (ILMA, 2005a). Mist collectors, which are series of filters, may also be used in combination with ventilation systems to capture metalworking fluid aerosols.

Machine enclosures are the most effective control to reduce exposure to metalworking fluid mists. Enclosures can range from full enclosures to splash guards. A full enclosure surrounds the machine and is only opened when the metal shaping has ceased and the mists have been evacuated (ILMA, 2005a). Due to the isolation of the machine, full enclosures can only be used for automated processes. Splash

guards are one- or two-sided shields in between the machinist and the cutting zone of the machine (Piacitelli, 2001).

In NIOSH's study of 79 small machine shops, 24 percent of all machines studied had full enclosures, 22 percent had "partial" enclosures (three or four sides), 38 percent had splash guards, and 16 percent had no such controls. 91 percent of machines less than 10 years old had one of these types of enclosures, while 82 percent of machines 30 or more years old had an enclosure. In the same study, 18 percent of machines had local exhaust ventilation (Piacitelli, 2001).

Antimisting polymer additives for metalworking fluids can reduce mist concentrations by 30 to 70 percent. These additives are high molecular weight polymers (500,000 to 2,000,000) that increase the elogational viscosity of metalworking fluids so that the fluid stretches rather than forming droplets (Byers, 2006).

During site visits for the MP&M guidelines study, workers were typically observed wearing safety glasses and hearing protection⁹. Most facilities also required steel-toed boots and gloves. Machinists do not generally wear respirators (ILMA, 2005a). Workers may wear protective gloves when handling neat metalworking fluids due to the high concentrations of potentially irritating chemicals in the fluid (ILMA, 2005b). Machinists also may wear protective gloves when performing activities other than metal shaping, such as removing swarf or other debris from their machines (ILMA, 2005b). In general, machinists do not wear gloves during metal shaping operations due to dexterity concerns (ILMA, 2005a; Roff, 2004). Machinists' use of gloves may increase in the future because of new glove designs that do not inhibit manual dexterity (ILMA, 2005b).

Number of Workers

Worker activities at metal shaping sites involving the metalworking fluid include transferring and diluting the neat metalworking fluid from the receiving containers to the metal shaping equipment, supervising of the metal shaping equipment, and removing the shaped parts. In NIOSH's study of 79 small machine shops, there was an average of 46 machinists per site (Piacitelli, 2001). Based on site visits during MP&M effluent limitation guidelines development, it is estimated that one worker per shift would be responsible for the transfer and dilution of the neat metalworking fluids⁹. Either these workers or the machinists could be responsible for disposing of spent metalworking fluids can be estimated with the following equation.

 $N_{workers} = N_{machinist} + (N_{worker shift} \times N_{shift})$ (5-1)

Where:

liele.		
N _{workers}	=	Total number of workers potentially exposed to the chemical of interest per site (workers/site)
N _{machinist}	=	Number of machinists per site (machinists/site) (Default: 46 machinists/site)
N_{worker_shift}	=	Number of workers supervising per shift (worker/shift-site) (Default: 1 worker/shift-site ¹)
N _{shift}	=	Number of shifts (shifts) (See Table 0-2; Default: 2 shifts)

⁹ This information was gathered from individuals with extensive experience with the MP&M industry. It is intended to be anecdotal in nature and may not be accurate for every metal shaping operation. This information is based on first hand observations of individuals during MP&M industry site visits.

Based on the default values, 48 workers per site may potentially be exposed to the chemical of interest. Some facilities may also have assembly workers and on-site waste treatment operators, although they would not typically be exposed to metalworking fluids. Large shops may have many more exposed employees. For example, a study at an automotive engine plant found 800 workers exposed to metalworking fluids (Zacharisen, 1998).

Transfer of Neat Metalworking Fluid (Exposure A)

Metalworking fluids are received in neat (concentrated) form. Water-based metalworking fluids are diluted with water to the working concentration, and transferred to the trough for the metal shaping machine. Straight oils are not diluted and are used at the neat concentration. New metalworking fluid is added to the trough either to make up fluid lost during operations or after spent metalworking fluid for the machine/trough is discharged and the machine is cleaned. Based on the MP&M effluent guidelines database, the average machining and grinding operation trough is changed eight times per year (USEPA, 2000a). Therefore, at the default facility this activity occurs at least 384 times a year (48 machines/site × 8 changes/year). All machines may be cleaned on the same day or cleaned at random intervals throughout the year. As a conservative estimate, assume this activity occurs over TIME_{working_days} (default: 247 days per year); however, if no makeup fluid is added and all machines are cleaned on the same day, this activity may occur as infrequently as 8 days per year. At most sites, a limited number of workers are responsible for handling the neat metalworking fluid; however, at some small sites the individual machine operators may add neat metalworking fluid to their machines. The number of workers for this activity ranges from 2 shift workers (typical) to 46 machinists (high-end).

Inhalation:

These activities are not expected to generate a mist. Since volatile chemicals of interest are not within the scope of this ESD, inhalation exposure is considered to be negligible for the transfer of nonvolatile liquids (ERG, 1999).

Dermal:

Dermal exposure is expected during transfer and dilution activities. No dermal monitoring data on the transfer of metalworking fluids were found. In the absence of data, the EPA/OPPT standard models for estimating dermal exposures from industrial activities can be used. The *EPA/OPPT 2-Hand Dermal Contact with Liquid Model* may be used to estimate dermal exposure to the chemical of interest during these activities. The rationale, defaults, and limitations of these models are further explained in Appendix B.

To estimate the potential worker exposure to the chemical of interest for this activity, use the following equation.

$$EXP_{dermal} = Q_{liquid_skin} \times AREA_{surface} \times N_{exp_incident} \times F_{chem_neat}$$
This exposure will occur over [8 to TIME_{working days}] days/year.
(5-3)

Where:

EXP_{dermal}

= Potential dermal exposure to the chemical of interest per day (mg chemical/day)

Q_{liquid_skin}	=	Quantity of liquid remaining on skin (Defaults = Transfer to mixing apparatus: 2.1 mg/cm ² -incident (high-end) and 0.7 mg/cm ² -incident (low-end)) (CEB, 2000)
	=	Surface area of contact (Default: 840 cm ² , 2 hands) (CEB, 2000)
$N_{exp_incident}^{10}$	=	Number of exposure incidents per day (Default:1 incident/day)
F _{chem_neat}	=	Weight fraction of the chemical of interest in the neat metalworking fluid (kg chemical/kg neat MWF) (See Section 3.4)

Cleaning of Transport Containers (Exposure B)

Metalworking fluid is received in concentrated form. Workers may be exposed to the chemical of interest during manual cleaning of transport containers. The number of exposure days for this activity should be the same as the number of release days for Release 1 (Section 0). Individual machine operators are not expected to clean transport containers; therefore, the number of workers for this activity is 2 shift workers per site.

Inhalation:

These activities are not expected to generate a mist. Since volatile chemicals of interest are not within the scope of this ESD, inhalation exposure is considered to be negligible for the cleaning of nonvolatile liquids from transport containers (ERG, 1999).

$$EXP_{inhalation} = Negligible$$
 (5-4)

Where:

EXP_{inhalation} = Inhalation exposure from the chemical of interest per day (mg chemical/day)

Dermal:

Dermal exposure is expected during manual shipping container cleaning activities. No dermal monitoring data on the manual cleaning of shipping containers containing residual metalworking fluids were found. In the absence of data, the EPA/OPPT standard models for estimating dermal exposures from industrial activities can be used. The *EPA/OPPT 2-Hand Dermal Contact with Liquid Model* may be used to estimate dermal exposure to the chemical of interest during these activities. The rationale, defaults, and limitations of these models are further explained in Appendix B.

To estimate the potential worker exposure to the chemical of interest for this activity, use the following equation.

 $EXP_{dermal} = Q_{liquid_skin} \times AREA_{surface} \times N_{exp_incident} \times F_{chem_neat}$ (5-5) This exposure will occur over [the lesser of $N_{cont_site_yr}$ or TIME_{working_days}, consistent with Section 0] days/year.

¹⁰ Only one contact per day ($N_{exp_incident} = 1$ event/worker-day) is assumed because Q_{liquid_skin} , with few exceptions, is not expected to be significantly affected either by wiping excess chemical material from skin or by repeated contacts with additional chemical material (i.e., wiping excess from the skin does not remove a significant fraction of the small layer of chemical material adhering to the skin and additional contacts with the chemical material do not add a significant fraction to the layer). Exceptions to this assumption may be considered for chemicals with high volatility and/or with very high rates of absorption into the skin.

Where:		
EXP _{dermal}	=	Potential dermal exposure to the chemical of interest per day (mg chemical/day)
Q_{liquid_skin}	=	Quantity of liquid remaining on skin (Defaults = Transfer to mixing apparatus: 2.1 mg/cm ² -incident (high-end) and 0.7 mg/cm ² -incident (low-end)) (CEB, 2000)
AREA _{surface}	=	Surface area of contact (Default: 840 cm ² , 2 hands) (CEB, 2000)
$N_{exp_incident}$	=	Number of exposure incidents per day (Default:1 incident/day) (See footnote to Equation 5-3)
F _{chem_neat}	=	Weight fraction of the chemical of interest in the neat metalworking fluid (kg chemical/kg of neat MWF) (See Section 3.4)

Mixing and Transfer of Diluted Metalworking Fluid (Exposure C)

Water-based metalworking fluids are diluted with water to the working concentration and transferred to the trough for the metal shaping machine. Straight oils are not diluted and are used at the neat concentration; therefore, this exposure activity only applies to water-based metalworking fluids. New metalworking fluid is added to the trough either to make up fluid lost during operations or after spent metalworking fluid for the machine/trough is discharged and the machine is cleaned. Based on the MP&M effluent guidelines database, the average machining and grinding operation trough is changed eight times per year (USEPA, 2000a). Therefore, at the default facility this activity occurs at least 384 times a year (48 machines/site × 8 changes/year). All machines may be cleaned on the same day or cleaned at random intervals throughout the year. As a conservative estimate, assume this activity occurs over TIME_{working_days} (default: 247 days per year); however, if no makeup fluid is added and all machines are cleaned on the same day, this activity may occur as infrequently as 8 days per year. The workers for this activity are usually the same workers who transfer the neat metalworking fluid from their shipping containers, discussed in Exposure B. Therefore, the number of workers for this activity ranges from 2 shift workers (typical) to 46 machinists (high-end).

Inhalation:

These activities are not expected to generate a mist. Since volatile chemicals of interest are not within the scope of this ESD, inhalation exposure is considered to be negligible for these activities (ERG, 1999).

$$EXP_{inhalation} = Negligible$$
 (5-6)

Where:

EXPinhalation

Inhalation exposure from the chemical of interest per day (mg chemical/day)

Dermal:

Dermal exposure is expected during transfer and dilution activities. No dermal monitoring data on the transfer of metalworking fluids were found. No dermal monitoring data on the transfer of metalworking fluids were found. In the absence of data, the EPA/OPPT standard models for estimating dermal exposures from industrial activities can be used. The *EPA/OPPT 2-Hand Dermal Contact with Liquid Model* may be used to estimate dermal exposure to the chemical of interest during these activities. The rationale, defaults, and limitations of these models are further explained in Appendix B.

To estimate the potential worker exposure to the chemical of interest for this activity, use the following equation.

		$\begin{array}{l} \label{eq:quid_skin} AREA_{surface} \times N_{exp_incident} \times F_{chem_trough} \\ \mbox{ire will occur over [TIME_{working days]} days/year.} \end{array} \tag{5-7}$
Where:		
EXP _{dermal}	=	Potential dermal exposure to the chemical of interest per day (mg chemical/day)
Q_{liquid_skin}	=	Quantity of liquid remaining on skin (Defaults = Transfer to mixing apparatus: 2.1 mg/cm ² -incident (high-end) and 0.7 mg/cm ² -incident (low-end)) (CEB, 2000)
AREA _{surface}	=	Surface area of contact (Default: 840 cm ² , 2 hands) (CEB, 2000)
$N_{exp_incident}$	=	Number of exposure incidents per day (Default: 1 incident/day) (See footnote to Equation 5-3)
$F_{\text{chem_trough}}$	=	Weight fraction of the chemical of interest in the trough (kg chemical/kg trough MWF) (See Section 3.4)

Metal Shaping Operations (Exposure D)

The workers operating metal shaping equipment are potentially exposed to the metalworking fluid by the mist that is generated from the shaping machine. Metal shaping machines typically spray the metalworking fluid on the part in the cutting zone, resulting in the generation of mist. Also, once the parts are machined they may be rinsed or wiped off using shop towels and collected in bins or baskets. Workers may be exposed to the metalworking fluid when cleaning and handling the machined/shaped parts.

During the development of the MP&M effluent guidelines, it was observed that some machines were well contained and the fluid dripped or sprayed over the parts was carefully collected. However, other machines sprayed the fluids in an uncontained manner, and the fluid was present throughout the work area or collected in a trough at the base of the machine¹¹. Although gloves should be worn when handling the machined/shaped products, more detailed information would be needed to develop an actual percentage of workers actually wearing them. Metal shaping operations occur over TIME_{working_days} (default: 247 days per year). The machine workers will perform this activity; therefore, the number of workers for this activity is 46 workers per site.

Inhalation:

Machine enclosures are sometimes used to fully or partially enclose the cutting zone of the machine, providing a physical barrier between the metal shaping machine and the work environment. Machine enclosures may eliminate the exposure to mist from spraying; however, as a conservative estimate mist exposure is expected.

NIOSH collected personal monitoring data at small machine shops to assess airborne exposures to metalworking fluids show that the NIOSH recommended exposure limit (REL) of 0.50 mg/m³ for total particulate is routinely exceeded (Piacitelli, 2001). Personal monitoring data were collected for 942

¹¹ This information was gathered from individuals with extensive experience with the MP&M industry. It is intended to be anecdotal in nature and may not be accurate for every metal shaping operation. This information is based on first hand observations of individuals during MP&M industry site visits.

machinists from 79 shops, from January 1997 to January 1998. Time-weighted average (TWA) exposure results ranged from 0.05 to 10.4 mg/m³ (total mass). A cumulative distribution of exposure shows that 99.8 percent were below the current OSHA permissible exposure limit (PEL) for total particulate mass of oil mist (5.0 mg/m³). Table 0-2 presents the geometric mean and 90th percentile concentrations of extractable particulate for the different types of metalworking fluids, which may be used to estimate typical and high-end worker exposures, respectively (Piacitelli, 2001; Piacitelli, 2006).

Table 0-2.	Typical and High-End N	1ist Concentrations	of Metalworking Fluids
------------	------------------------	---------------------	------------------------

Type of Metalworking Fluid	Typical Mist Concentration (mg of mist/m³)	High-End Mist Concentration (mg of mist/m³)
Conventional Soluble	0.19	0.87
Semi-synthetic	0.20	0.88
Synthetic (default if water-based fluid selected in Figure 3-1)	0.24	1.10
Straight Oil (default if straight oil selected in Figure 3-1)	0.39	1.42

Source: Piacitelli, 2001; Piacitelli, 2006.

The mass concentrations presented in Table 5-2 are for the solvent-extractable portion of collected total particulate and do not include contributions of water mist and other types of particulate (e.g., metal fines); therefore, the weight fraction of the chemical of interest in the non-water portion of the fluid should be used to calculate inhalation exposure as a conservative estimate. The weight fraction of the chemical of interest in the non-water portion of the chemical of interest in the non-water portion of the fluid is assumed equal to the weight fraction of the chemical of interest in the mist. Equation 5-8 estimates the weight fraction of the chemical of interest in the neat metalworking fluid by the total non-water portion of the neat fluid. Table 0-3 presents default values for the concentration of water in the neat metalworking fluid (F_{water_neat}). Note that regardless of dilution, the fraction of the chemical of interest in the non-water portion of the non-water portion of the metalworking fluid is constant.

Table 0-3. Default Values for F_{water_neat} by Type of Metalworking Fluid

Type of Metalworking Fluid ^a	F _{water neat}
Conventional Soluble	0.05
Semi-Synthetic	0.6
Solution-Synthetic (default if water-based fluid selected in Figure 3-1)	0.6
Synthetic Emulsion	0.05
Straight Oil (default if straight oil selected in Figure 3-1)	0

Source: ILMA, 2005a

a – See Figure 3-1 for the selection of the type of metalworking fluid.

$$F_{\text{chem_mist}} = \frac{F_{\text{chem_neat}}}{(1 - F_{\text{water neat}})}$$
(5-8)

Where:

F _{chem_mist}	=	Weight fraction of chemical of interest in the metalworking
		fluid mist (mg chemical/mg mist)
F _{chem_neat}	=	Weight fraction of the chemical of interest in the neat
		metalworking fluid (kg chemical/kg neat MWF) (See Section
		3.4)
Fwater neat	=	Weight fraction of water in the neat metalworking fluid (See
-		Table 0-3)

 F_{chem_mist} should never be greater than 1. However, a result greater than 1 may occur when using default values for F_{water_neat} and F_{chem_neat} , or if site-specific information indicates F_{chem_neat} is greater than 0.4 and F_{water_neat} is unknown. If F_{chem_mist} is greater than 1, assume the chemical of interest makes up the entire non-water portion of the metalworking fluid; therefore,

$$F_{\text{chem}_{mist}} = 1 \frac{\text{mg of chemical}}{\text{mg of mist}}$$
(5-9)

Where:

F_{chem_mist}

Weight fraction of chemical of interest in the metalworking fluid mist (mg chemical/mg mist)

According to information from ILMA, the typical exposure duration is expected to be 8 hours per day (ILMA, 2006a). Therefore, the following equation estimates the inhalation exposure from the chemical of interest in the mist formed during metal shaping operations:

$$EXP_{inhalation} = C_{shape_mist} \times RATE_{breathing} \times TIME_{exposure} \times F_{chem_mist}$$
This exposure will occur over [TIME_{working_days}] days/year. (5-10)

Where:

licic.	
EXP _{inhalation} =	 Inhalation exposure from the chemical of interest per day (mg chemical/day)
C _{shape_mist} =	 Metalworking fluid mist concentration in the air at workers breathing zone for shaping operations (See Table 5-1)
	(Piacitelli, 2001)
RATE _{breathing} =	 Typical worker breathing rate (Default: 1.25 m³/hr) (NIOSH, 1976)
TIME _{exposure} =	= Duration of exposure (Default: 8 hr/day) (ILMA, 2006a)
F _{chem_mist} =	 Weight fraction of chemical of interest in the metalworking fluid mist (mg chemical/mg mist) (See Equations 5-8 and 5-9)

Dermal:

Roff et al. conducted a study of dermal exposures to electroplating and metalworking fluids (Roff, 2004). Whole-body exposure data were collected for 25 machinists at three factories using oversuits, but only one machinist participated in underglove sampling. In the underglove sampling, the machinist wore sampling gloves underneath of protective gloves while conducting metal shaping operations. The sampling gloves were then analyzed to determine the exposure to metalworking fluid from the trough. Table 5-4 summarizes the additional statistics presented by Roff et al.

	Surface Loading Rate
Statistic	(µg/cm²-hr)
Median	3,200
Arithmetic Mean	3,300
Standard Deviation	1,500
Geometric Mean	2,900
Geometric Standard Deviation	1.67
Range	1,400–5,400
75 th Percentile	4,700
95 th Percentile	> 5,400

 Table 0-4. Dermal Surface Loading Rates during Metal Shaping Operations

Source: Roff, 2004.

Therefore, the geometric mean surface loading rate for hands of 2.9 mg metalworking fluid/cm²-hr can be used to estimate dermal exposure to metalworking fluids during metal shaping operations. The geometric mean value was selected because it suppresses the influence of outliers and was the primary result presented in Roff et al.

According to information from ILMA, the typical exposure duration is expected to be 8 hours per day (ILMA, 2006a). To estimate the potential worker exposure to the chemical of interest for this activity, the following equation can be used.

$$EXP_{dermal} = Q_{liquid_skin} \times AREA_{surface} \times TIME_{exposure} \times F_{chem_trough}$$
(5-11)
This exposure will occur over [TIME_working_days] days/year.

Where:

nore.		
EXP _{dermal}	=	Potential dermal exposure to the chemical of interest per day
		(mg chemical /day)
Qliquid_skin	=	Quantity of liquid remaining on skin. (Default: 2.9 mg dilute
		$MWF/cm^2-hr)$ (Roff, 2004)
AREA _{surface}	=	Surface area of contact (Default: 840 cm ² , 2 hands) (CEB,
		2000)
TIME _{exposure}		Duration of exposure (Default: 8 hr/day) (ILMA, 2006a)
F _{chem_trough}	=	Weight fraction of the chemical of interest in the trough (kg
		chemical/kg trough MWF) (See Section 3.4)

Filtering and Other Recycling Operations (Exposure E)

Workers are potentially exposed to the metalworking fluid when changing or cleaning the filter media used to remove metal fines or when operating or transferring fluid to other fluid recycling operations. Based on the MP&M effluent guidelines database, the average machining and grinding operation discharges filter wastes and other recycling sludge 114 times per year (USEPA, 2000a). Therefore, at the default facility this activity occurs at least 5,472 times a year (48 machines/site × 114 discharges/year). As a conservative estimate, assume this activity occurs over TIME_{working_days} (default: 247 days per year). The individual machine operators typically perform this operation (ILMA, 2005b). Therefore, the number of workers for this activity is 46 workers per site.

Inhalation:

These activities are not expected to generate a mist. Since volatile chemicals of interest are not within the scope of this ESD, inhalation exposure is considered to be negligible for these activities (ERG, 1999).

$$EXP_{inhalation} = Negligible$$
(5-12)

Where:

EXP_{inhalation} = Inhalation exposure from the chemical of interest per day (mg chemical/day)

Dermal:

Dermal exposure is expected during transfer and cleaning activities. No dermal monitoring data on the filtering and recycling operations were found. In the absence of data, the EPA/OPPT standard models for estimating dermal exposures from industrial activities can be used. The *EPA/OPPT 2-Hand Dermal Contact with Liquid Model* may be used to estimate dermal exposure to the chemical of interest during these activities. The rationale, defaults, and limitations of these models are further explained in Appendix B. The concentration of the chemical of interest in the filter media or during other recycling operation may be greater than the concentration of the chemical of interest in the dilute metalworking fluid. As a conservative estimate, assume the concentration of the chemical of interest in the filter media or other during recycling operation is equal to the concentration of the chemical of interest in the neat metalworking fluid. To estimate the potential worker exposure to the chemical of interest for this activity, use the following equation.

$$EXP_{dermal} = Q_{liquid_skin} \times AREA_{surface} \times N_{exp_incident} \times F_{chem_neat}$$
This exposure will occur over [TIME_{working_days}] days/year.
(5-13)

here:	
EXP _{dermal}	 Potential dermal exposure to the chemical of interest per day (mg chemical/day)
Q_{liquid_skin}	 Quantity of liquid remaining on skin (Defaults = Transfer to mixing apparatus: 2.1 mg/cm²-incident (high-end) and 0.7 mg/cm²-incident (low-end)) (CEB, 2000)
AREA _{surface}	 Surface area of contact (Default: 840 cm², 2 hands) (CEB, 2000)
$N_{exp_incident}$	 Number of exposure incidents per day (Default: 1 incident/day) (See footnote to Equation 5-3)
F_{chem_neat}	 Weight fraction of the chemical of interest in the neat metalworking fluid (kg chemical/kg neat MWF) (See Section 3.4)

ansferring Spent Metalworking Fluid and Cleaning of Shaping Machine and Trough (Exposure F)

Transfer of spent metalworking fluid and subsequent cleaning of the shaping machine only occurs after the metalworking fluid for the machine/trough is discharged. Based on the MP&M effluent guidelines database, the average machining and grinding operation trough is changed eight times per year (USEPA, 2000a). Therefore, at the default facility this activity occurs at least 384 times a year (48 machines/site \times 8 changes/year). All machines may be cleaned on the same day or at random intervals throughout the year. As a conservative estimate, assume this activity occurs over TIME_{working_days} (default: 247 days per year); however, this activity may occur as infrequently as 8 days per year. The individual

machine operators or the additional shift worker may perform this operation. These workers are usually the same workers who transfer the neat metalworking fluid from their shipping containers, dilute the neat metalworking fluid, and fill the troughs with fresh fluids (discussed previously in Exposures A and C). Therefore, the number of workers for this activity ranges from 2 shift workers (typical) to 46 machinists (high-end).

Inhalation:

These activities are not expected to generate a mist, and since volatile chemicals of interest are not within the scope of this ESD, inhalation exposure is considered to be negligible for these activities (ERG, 1999).

$$EXP_{inhalation} = Negligible$$
(5-14)

Where:

Dermal:

Dermal exposure is expected during transferring and cleaning activities. No dermal monitoring data on the transfer of metalworking fluids were found. In the absence of data, the EPA/OPPT standard models for estimating dermal exposures from industrial activities can be used. The *EPA/OPPT 2-Hand Dermal Contact with Liquid Model* may be used to estimate dermal exposure to the chemical of interest during these activities. The rationale, defaults, and limitations of these models are further explained in Appendix B. To estimate the potential worker exposure to the chemical of interest for this activity, use the following equation.

	$EXP_{dermal} = C$	$Q_{\text{liquid_skin}} \times \text{AREA}_{\text{surface}} \times N_{\text{exp_incident}} \times F_{\text{chem_trough}} $ (5-15)
	This exposu	re will occur over [TIME _{working days}] days/year.
Where:		
EXP _{dermal}	=	Potential dermal exposure to the chemical of interest per day (mg chemical/day)
Q_{liquid_skin}	=	Quantity of liquid remaining on skin (Defaults = Transfers and cleaning: 2.1 mg/cm ² -incident (high-end) and 0.7 mg/cm ² -incident (low-end)) (CEB, 2000)
AREA _{surface}	=	Surface area of contact (Default: 840 cm ² , 2 hands) (CEB, 2000)
$N_{exp_incident}$	=	Number of exposure incidents per day (Default: 1 incident/day) (See footnote to Equation 5-3)
F_{chem_trough}	=	Weight fraction of the chemical of interest in the trough (kg chemical/kg trough MWF)

On-site Waste Treatment Operation (Exposure G)

Potential worker exposure to metalworking fluids from on-site waste treatment operations is applicable only to sites with treatment for their spent metalworking fluids. For these cases, the on-site treatment operator may come into contact with the metalworking fluid during the treatment of spent metalworking fluid. It is assumed that on-site treatment is automated and that exposures during this activity are insignificant when compared to other activities.

SAMPLE CALCULATIONS

This section presents an example using all of the equations introduced in Sections 3, 4, and 5 of this ESD. Table A-4 in Appendix A summarizes the parameters, default values if applicable, and the sources used throughout the ESD. The hypothetical operating ESD presented in this section demonstrates how the equations in Sections 3, 4, and 5 might be used to estimate releases of and exposures to an additive chemical used in metalworking fluids. The default values used in these calculations are presented in Sections 3, 4, and 5 and are appropriate only in the absence of site-specific information.

The following values are chemical-specific and should be provided by the manufacturer of the chemical. The following values were chosen to demonstrate the use of conservative estimates in the methodologies presented in this document:

The default values used in these calculations are presented in this document and should be used only in the absence of site-specific information. The following values and assumptions were chosen to demonstrate the use of conservative estimates in the methodologies presented in this document:

- The chemical of interest is an extreme-pressure additive for water-based metalworking fluids;
- The chemical of interest production volume (Q_{chem_yr}) is 7,000 kg/year;
- The type of metal shaping operation is unknown; and
- Occupational exposures are the primary concern.

General Facility Calculations

Operating Days (TIME_{working_days})

 $TIME_{working days} = 247 days/yr (default from Table 0-2)$

Concentration of the Chemical of Interest (Equations 3-1 and 3-2)

The chemical of interest is an extreme-pressure additive for water-based metalworking fluids; therefore, as presented in Table 0-3, the chemical concentration is 30 percent.

$$F_{\text{chem_neat}} = 0.3 \frac{\text{kg chemical}}{\text{kg neat MWF}}$$

The type of metal shaping operation is unknown; therefore, the neat metalworking fluid defaults to 0.1 kg neat MWF/kg trough MWF for water-based metalworking fluids (See Table 0-6 and Section 3.4).

$$F_{\text{neat_trough}} = 0.1 \frac{\text{kg neat MWF}}{\text{kg trough MWF}}$$

 $F_{chem_trough} = F_{chem_neat} \times F_{neat_trough}$

$$F_{\text{chem_trough}} = 0.3 \frac{\text{kg chemical}}{\text{kg neat MWF}} \times 0.1 \frac{\text{kg neat MWF}}{\text{kg trough MWF}}$$

 $F_{\text{chem_trough}} = 0.03 \frac{\text{kg chemical}}{\text{kg trough MWF}}$

Annual Facility Metalworking Fluid Use Rate (Equation 3-3)

Occupational exposures are the primary concern; therefore, use the typical volume of metalworking fluid per site (See Figure 0-1).

$$Q_{neat_site_yr} = V_{neat_site_yr} \times RHO_{neat} \times 3.785 \frac{L}{gal}$$

$$Q_{neat_site_yr} = 4,260 \frac{\text{gallons neat MWF}}{\text{site - yr}} \times 1 \frac{\text{kg}}{\text{L}} \times 3.785 \frac{\text{L}}{\text{gal}}$$

 $Q_{neat_site_yr} = 16,120 \frac{\text{kg neat MWF}}{\text{site - yr}}$

Annual Use Rate of the Chemical of Interest (Equation 3-4)

Occupational exposures are the primary concern; therefore, use the higher default number of metalworking fluid per site (See Figure 0-1).

$$Q_{\text{chem_site_yr}} = \frac{Q_{\text{neat_site_yr}} \times F_{\text{chem_neat}} \times N_{\text{mwf_site_chem}}}{N_{\text{mwf_site_total}}}$$
$$Q_{\text{chem_site_yr}} = \frac{16,120 \frac{\text{kg neat MWF}}{\text{site-yr}} \times 0.3 \frac{\text{kg chemical}}{\text{kg neat MWF}} \times 1 \frac{\text{MWF with chemical}}{\text{site}}}{7 \frac{\text{MWFs total}}{\text{site}}}$$

$$Q_{\text{chem_site_yr}} = 691 \frac{\text{kg chemical}}{\text{site - yr}}$$

Daily Use Rate of the Chemical of Interest (Equation 3-5)

yr

$$Q_{chem_site_day} = \frac{Q_{chem_site_yr}}{TIME_{working_days}}$$
$$Q_{chem_site_day} = \frac{691\frac{kg chemical}{site - yr}}{247\frac{days}{site}}$$

$$Q_{\text{chem_site_day}} = 2.8 \frac{\text{kg chemical}}{\text{site} - \text{day}}$$

Number of Sites (Equation 3-6)

$$N_{sites} = \frac{Q_{chem_yr}}{Q_{chem_site_yr}}$$

$$N_{sites} = \frac{7,000 \frac{\text{kg chemical}}{\text{yr}}}{691 \frac{\text{kg chemical}}{\text{site} - \text{yr}}}$$

 $N_{sites} = 10 sites$

Because N_{sites} is a rounded value, recalculated $Q_{chem_site_day}$.

$$Q_{chem_site_day} = \frac{Q_{chem_yr}}{TIME_{working_days} \times N_{sites}}$$
$$Q_{chem_site_day} = \frac{7,000 \frac{\text{kg chemical}}{\text{yr}}}{247 \frac{\text{days}}{\text{yr}} \times 10 \text{ sites}}$$

$$Q_{\text{chem_site_day}} = 2.8 \frac{\text{kg chemical}}{\text{site - day}}$$

Annual Number of Metalworking Fluid Containers (Equation 3-7)

 $N_{cont_site_yr} = \frac{Q_{chem_site_day} \times TIME_{working_days}}{V_{container} \times RHO_{neat} \times F_{chem_neat}}$

$$N_{cont_site_yr} = \frac{2.8 \frac{kg \text{ chemical}}{site - day} \times 247 \frac{days}{yr}}{208 \frac{L \text{ neat MWF}}{container} \times 1 \frac{kg}{L} \times 0.3 \frac{kg \text{ chemical}}{kg \text{ neat MWF}}}{kg \text{ neat MWF}}$$

 $N_{cont_site_yr} = 11 \frac{containers}{site - yr}$

Environmental Release Assessments

Container Residue Release (Release 1)

The number of containers per site-year ($N_{cont_site_yr} = 11$) is less than the number of operating days per year (TIME_{working_days} = 247); therefore, use Equation 4-1 rather than Equation 4-2. The default media of release is Uncertain: Water or Landfill or Incineration.

 $Elocal_{container_residue_disp} = V_{container} \times RHO_{neat} \times F_{chem_neat} \times F_{container_residue} \times 1 \frac{container}{site-day}$

$$Elocal_{container_residue_disp} = 208 \frac{L \text{ neat MWF}}{\text{container}} \times 1 \frac{\text{kg}}{\text{L}} \times 0.3 \frac{\text{kg chemical}}{\text{kg neat MWF}} \times 0.03 \times 1 \frac{\text{container}}{\text{site} - \text{day}}$$

 $\text{Elocal}_{\text{container}_{\text{residue}_{\text{disp}}}} = 1.9 \frac{\text{kg chemical}}{\text{site} - \text{day}} \text{ over } 11 \frac{\text{days}}{\text{yr}} \text{ from } 10 \text{ sites}$

Dragout Losses (Release 2)

The chemical of interest is used in water-based metalworking fluids; therefore, the default media of release is Water.

 $Elocal_{dragout_losses} = Q_{chem_site_day} \times (1 - F_{container_residue}) \times F_{dragout_losses}$

$$Elocal_{dragout_losses} = 2.8 \frac{\text{kg chemical}}{\text{site - day}} \times (1 - 0.03) \times 0.11$$

$$\text{Elocal}_{\text{dragout}_\text{losses}} = 0.30 \frac{\text{kg chemical}}{\text{site} - \text{day}} \text{ over } 247 \frac{\text{days}}{\text{yr}} \text{ from } 10 \text{ sites}$$

Filter Media and Other Recycling Wastes (Release 3)

The chemical of interest is used in water-based metalworking fluids; therefore, the default media of release is Uncertain: Water or Landfill or Incineration.

$$Elocal_{recycle_wastes} = Q_{chem_site_day} \times (1 - F_{container_residue}) \times F_{recycle_wastes}$$

$$Elocal_{recycle_wastes} = 2.8 \frac{kg \text{ chemical}}{site - day} \times (1 - 0.03) \times 0.36$$

$$\text{Elocal}_{\text{recycle}_{\text{wastes}}} = 0.99 \frac{\text{kg chemical}}{\text{site} - \text{day}} \text{ over } 247 \frac{\text{days}}{\text{yr}} \text{ from } 10 \text{ sites}$$

Spent Metalworking Fluid Release to Water (Release 4)

The chemical of interest is used in water-based metalworking fluids; therefore, the default media of release is Water.

$$Elocal_{trough_discharge} = Q_{chem_site_day} \times (1 - F_{container_residue}) \times (1 - F_{dragout_losses} - F_{recycle_wastes})$$

$$Elocal_{trough_discharge} = 2.8 \frac{kg \ chemical}{site - day} \times (1 - 0.03) \times (1 - 0.11 - 0.36)$$

 $\text{Elocal}_{\text{trough}_{\text{discharge}}} = 1.5 \frac{\text{kg chemical}}{\text{site} - \text{day}} \text{ over } 247 \frac{\text{days}}{\text{yr}} \text{ from } 10 \text{ sites}$

Mass Balance (Equation 4-8)

$$Q_{chem_yr} = (Q_{chem_site_day} \times F_{container_residue} + Elocal_{dragout_losses} + Elocal_{recycle_wastes} + Elocal_{trough_discharge}) \times N_{sites} \times TIME_{working_days}$$

 $Q_{chem_yr} = (2.8 \times 0.03 + 0.30 + 0.99 + 1.5) \frac{\text{kg chemical}}{\text{site} - \text{day}} \times 10 \text{ sites} \times 247 \frac{\text{days}}{\text{yr}}$

 $Q_{chem_yr} = 7,000 \frac{kg \ chemical}{yr}$

Occupational Exposure Assessments

Total Number of Workers (Equation 5-1)

$$N_{\text{workers}} = N_{\text{machinist}} + (N_{\text{worker_shift}} \times N_{\text{shift}})$$

$$N_{workers} = 46 \frac{workers}{site} + \left[1 \frac{worker}{shift - site} \times 2 \text{ shifts}\right]$$

 $N_{workers} = 48 \frac{workers}{site}$

Transfer of Neat Metalworking Fluid (Exposure A)

The default number of workers for this activity ranges from 2 (typical) to 46 (high-end) workers per site. The default days of exposure for this activity are up to 247 days per year.

Inhalation (Equation 5-2):

EXP_{inhalation} = Negligible

Dermal (Equation 5-3):

 $EXP_{dermal} = Q_{liquid_skin} \times AREA_{surface} \times N_{exp_incident} \times F_{chem_neat}$

$$EXP_{dermal} = 0.7 \text{ to } 2.1 \frac{\text{mg neat MWF}}{\text{cm}^2 \text{ - incident}} \times 840 \text{ cm}^2 \times 1 \frac{\text{incident}}{\text{day}} \times 0.3 \frac{\text{kg chemical}}{\text{kg neat MWF}}$$

 $EXP_{dermal} = 176 \text{ to } 529 \frac{\text{mg chemical}}{\text{day}} \text{ over } 247 \frac{\text{days}}{\text{yr}}$

Cleaning of Transport Containers (Exposure B)

The default number of workers for this activity from 2 workers per site. The default days of exposure for this activity are 11 days per year ($N_{cont site yr}$).

Inhalation (Equation 5-4):

EXP_{inhalation} = Negligible

Dermal (Equation 5-5):

 $EXP_{dermal} = Q_{liquid_skin} \times AREA_{surface} \times N_{exp_incident} \times F_{chem_neat}$

 $EXP_{dermal} = 0.7 \text{ to } 2.1 \frac{\text{mg neat MWF}}{\text{cm}^2 - \text{incident}} \times 840 \text{ cm}^2 \times 1 \frac{\text{incident}}{\text{day}} \times 0.3 \frac{\text{kg chemical}}{\text{kg neat MWF}}$

 $EXP_{dermal} = 176 \text{ to } 529 \frac{\text{mg chemical}}{\text{day}} \text{ over } 11 \frac{\text{days}}{\text{yr}}$

Mixing and Transfer of Diluted Metalworking Fluid (Exposure C)

The chemical of interest is used in water-based metalworking fluids; therefore, Exposure C is applicable. The default number of workers for this activity ranges from 2 (typical) to 46 (high-end) workers per site. The default days of exposure for this activity are up to 247 days per year.

Inhalation (Equation 5-2):

EXP_{inhalation} = Negligible

Dermal (Equation 5-3):

$$EXP_{dermal} = Q_{liquid_skin} \times AREA_{surface} \times N_{exp_incident} \times F_{chem_trough}$$

 $EXP_{dermal} = 0.7 \text{ to } 2.1 \frac{\text{mg trough MWF}}{\text{cm}^2 - \text{incident}} \times 840 \text{ cm}^2 \times 1 \frac{\text{incident}}{\text{day}} \times 0.03 \frac{\text{kg chemical}}{\text{kg trough MWF}}$

 $EXP_{dermal} = 18 \text{ to } 53 \frac{\text{mg chemical}}{\text{day}} \text{ over } 247 \frac{\text{days}}{\text{yr}}$

Metal Shaping Operations (Exposure D)

The default number of workers for this activity is 46 workers per site. The default days of exposure for this activity are 247 days per year.

Inhalation (Equation 5-8, 5-10):

The type of metalworking fluid is unknown; therefore, assume the neat metalworking fluid is 60 percent water (See Table 0-3) and that the mist concentration is 0.24 (typical) to 1.10 (high-end) milligrams of mist per cubic meter.

$$F_{\text{chem_mist}} = \frac{F_{\text{chem_neat}}}{(1 - F_{\text{water neat}})} = \frac{0.3}{1 - 0.6} = 0.75 \frac{\text{mg chemical}}{\text{mg mist}}$$

$$\text{EXP}_{\text{inhalation}} = \text{C}_{\text{shape}_{\text{mist}}} \times \text{RATE}_{\text{breathing}} \times \text{TIME}_{\text{exposure}} \times \text{F}_{\text{chem}_{\text{mist}}}$$

$$\text{EXP}_{\text{inhalation}} = 0.24 \text{ to } 1.10 \frac{\text{mg mist}}{\text{m}^3} \times 1.25 \frac{\text{m}^3}{\text{hr}} \times 8 \frac{\text{hr}}{\text{day}} \times 0.75 \frac{\text{mg chemical}}{\text{mg mist}}$$

$$EXP_{inhalation} = 1.8 \text{ to } 8.3 \frac{\text{mg chemical}}{\text{day}} \text{ over } 247 \frac{\text{days}}{\text{yr}}$$

Dermal (Equation 5-11):

$$EXP_{dermal} = Q_{liquid_skin} \times AREA_{surface} \times TIME_{exposure} \times F_{chem_trough}$$

$$EXP_{dermal} = 2.9 \frac{\text{mg trough MWF}}{\text{cm}^2 - \text{hr}} \times 840 \text{ cm}^2 \times 8 \frac{\text{hr}}{\text{day}} \times 0.03 \frac{\text{kg chemical}}{\text{kg trough MWF}}$$

$$EXP_{dermal} = 585 \frac{mg \ chemical}{day} over 247 \frac{days}{yr}$$

Filtering and Other Recycling Operations (Exposure E)

The default number of workers for this activity is 46 workers per site. The default days of exposure for this activity are 247 days per year.

Inhalation (Equation 5-12):

EXP_{inhalation} = Negligible

Dermal (Equation 5-13):

 $EXP_{dermal} = Q_{liquid_skin} \times AREA_{surface} \times N_{exp_incident} \times F_{chem_neat}$

$$EXP_{dermal} = 0.7 \text{ to } 2.1 \frac{\text{mg neat MWF}}{\text{cm}^2 \text{ - incident}} \times 840 \text{ cm}^2 \times 1 \frac{\text{incident}}{\text{day}} \times 0.3 \frac{\text{kg chemical}}{\text{kg neat MWF}}$$

 $EXP_{dermal} = 176 \text{ to } 529 \frac{\text{mg chemical}}{\text{day}} \text{ over } 247 \frac{\text{days}}{\text{yr}}$

Transferring Spent Metalworking Fluid and Cleaning of Shaping Machine and Trough (Exposure F)

The default number of workers for this activity ranges from 2 (typical) to 46 (high-end) workers per site. The default days of exposure for this activity are 247 days per year.

Inhalation (Equation 5-14):

EXP_{inhalation} = Negligible

Dermal (Equation 5-15):

$$EXP_{dermal} = Q_{liquid_skin} \times AREA_{surface} \times N_{exp_incident} \times F_{chem_trough}$$

 $EXP_{dermal} = 0.7 \text{ to } 2.1 \frac{\text{mg trough MWF}}{\text{cm}^2 - \text{incident}} \times 840 \text{ cm}^2 \times 1 \frac{\text{incident}}{\text{day}} \times 0.03 \frac{\text{kg chemical}}{\text{kg trough MWF}}$

 $EXP_{dermal} = 18 \text{ to } 53 \frac{\text{mg chemical}}{\text{day}} \text{ over } 247 \frac{\text{days}}{\text{yr}}$

On-Site Waste Treatment Operations (Exposure G)

Exposures during on-site waste treatment operations are expected to be negligible compared to other activities.

DATA GAPS/UNCERTAINTIES AND FUTURE WORK

This ESD is primarily based on extensive information collected by EPA during the proposal development phase of the Metal Products and Machinery (MP&M) industry effluent limitation guidelines, occupational exposure data collected by NIOSH, and information provided by ILMA in response to requests for technical input. The effluent guidelines data were collected from actual field surveys and are specific to the use of metalworking fluids. The occupational exposure data were obtained through personal monitoring studies at 79 metalworking shops in the U.S. These sources allow this document to provide a thorough overview of the industry and the chemicals used in metalworking fluids, industry-specific environmental release estimates based on a detailed survey of the industry and occupational exposure estimates based on actual inhalation and dermal monitoring data, and extensive information on onsite wastewater treatment technologies, engineering controls, and personal protective equipment (PPE).

However, EPA wishes to make this ESD as detailed and up-to-date as possible, such that the risk-screening assessments reflect current industrial practices. Reviewers should feel free to provide additional information and data that could further enhance and improve the methods described in this ESD, as well as to recommend additional resources that may be useful to the development of this ESD.

The key data gaps are summarized below. Note that the data gaps are listed in order of importance (the first being most important):

- Data on the current, relative prevalence of ultrafiltration, oil/water separation, and contract hauling were not found.
- Use rate estimates are currently based on smaller "job shops" (see Section 3.3). Data were not found for larger part manufacturers.
- Data on dermal exposures during metal shaping operations are limited to seven samples collected for one machinist.
- Data on dermal exposures to the transfer of metalworking fluids and to the transfer of shaped parts were not found.
- The media of release for container residue is uncertain. No information on the prevalence of any media was found.

REFERENCES

The specific information researched in the development of this document include process description, operating information, chemicals used, wastes generated, worker activities, and exposure information. Specific sources investigated in the development of this document include documents and data from the following sources:

- U.S. Environmental Protection Agency (EPA);
- U.S. Occupational Safety and Health Administration (OSHA); •
 - U.S. National Institute for Occupational Safety and Health (NIOSH);
- U.S. Census Bureau;
- Organisation for Economic Co-operation and Development (OECD);
- Environment Canada:
- North Carolina Division of Pollution Prevention and Environmental Assistance;
- Kirk-Othmer Encyclopedia of Technology;
- Various trade association websites (e.g., Independent Lubricant Manufacturers Association - www.ilma.org); and
- Industrial hygiene journals (e.g., AIHA Journal, Journal of Occupational and Environmental Hygiene, and Annals of Occupational Hygiene)

While each of these sources was reviewed for information, not all provided information specific to the laundering process. The references specifically cited in this ESD are provided below.

(Abrams, 2000) Abrams, L., N. Seixas, T. Robins, H. Burge, M. Muilenberg, A. Franzblau, 2000. "Characterization of Metalworking Fluid Exposure Indices for a Study of Acute Respiratory Effects", Applied Occupational and Environmental Hygiene, 15:6, 492-502.

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- (CEB, 2000) Memorandum: Revision to CEB's Method for Screening Level Assessments for Dermal Exposure from Greg Macek of CEB to CEB staff and contractors; June 1, 2000.
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Appendix A

ESTIMATION EQUATION SUMMARY AND DEFAULT PARAMETER VALUES

Summary of Release and Exposure Estimation Equations

Table A-1 summarizes the equations introduced in Section 0, which are used to calculate the general facility parameters. Tables A-2 and A-3 summarize the equations used in evaluating releases of and exposures to components of metalworking fluids used in metal shaping operations. Table A-4 summarizes the parameters for each equation, the default value if applicable and the source. The default values for the ChemSTEER models are presented in Appendix B.

Table A-1. General Facility Parameter Calculation Summary

General Facility Estimates				
Days of Operation (TIME _{working_days}):				
$TIME_{working days} = 247 days/year$ (Default from Table 0-2)				
Annual Facility Metalworking Fluid Use Rate (Q _{neat_site_yr}):				
$Q_{neat_site_yr} = V_{neat_site_yr} \times RHO_{neat} \times 3.785 \frac{L}{gal}$	(Eqn. 3-1)			
Concentration of Chemical of Interest (F _{chem_neat} , F _{chem_trough}):				
$F_{chem_trough} = F_{chem_neat} \times F_{neat_trough}$	(Eqn. 3-2)			
Annual Use Rate of the Chemical of Interest (Q _{chem_site_yr}):				
$Q_{chem_site_yr} = \frac{Q_{neat_site_yr} \times F_{chem_neat} \times N_{mwf_site_chem}}{N_{mwf_site_total}}$	(Eqn. 3-3)			
Daily Use Rate of the Chemical of Interest (Qchem_site_day):				
$Q_{chem_site_day} = \frac{Q_{chem_site_yr}}{TIME_{working_days}}$	(Eqn. 3-4)			
Number of Sites (N _{sites}):				
$N_{sites} = \frac{Q_{chem_yr}}{Q_{chem_site_day} \times TIME_{working_days}}$	(Eqn. 3-5)			
Annual Number of Metalworking Fluid Containers (N _{cont_site_yr}):				
$N_{cont_site_yr} = \frac{Q_{chem_site_day} \times TIME_{working_days}}{V_{container} \times RHO_{neat} \times F_{chem_neat}}$	(Eqn. 3-6)			

Source	Possible Media	Daily Release Rates (kg/site-day), Elocal (for Given Sources)	Equation
Release 1: Container Residue	Uncertain: Water Land Incineration	Estimate if number of containers is fewer than days of operation (kg/site-day): Elocal _{container_residue_disp} = $V_{container} \times RHO_{neat} \times F_{chem_neat} \times F_{container_residue} \times 1 \frac{container}{site-day}$ This release will occur over [N _{cont_site_yr}] days/year from [N _{sites}] sites Estimate if number of containers is greater than or equal to the days of operation (kg/site-day): Elocal _{container_residue_disp} = $Q_{chem_site_day} \times F_{container_residue}$	(Eqn. 4-1) (Eqn. 4-2)
Release 2: Dragout Losses	On-site Treatment	This release will occur over [TIME _{working days}] days/year from [N _{sites}] sites $Elocal_{dragout_losses} = Q_{chem_site_day} \times (1 - F_{container_residue}) \times F_{dragout_losses}$ This release will occur over [TIME _{working_days}] days/year from [N _{sites}] sites	(Eqn. 4-3)
Release 3: Filter and Other Recycling Wastes	Uncertain: Water Land Incineration	$Elocal_{recycle_wastes} = Q_{chem_site_day} \times (1 - F_{container_residue}) \times F_{recycle_wastes}$ This release will occur over [TIME _{working_days}] days/year from [N _{sites}] sites	(Eqn. 4-4)
Release 4: Spent MWF Discharge	Water-based: On-site Treatment Straight Oil: Incineration	$Elocal_{trough_discharge} = Q_{chem_site_day} \times (1 - F_{container_residue}) \times (1 - F_{dragout_losses} - F_{recycle_wastes})$ This release will occur over [TIME _{working_days}] days/year from [N _{sites}] sites	(Eqn. 4-5)
Effect of On-Site Waste	Treated Wastewater: POTW	$Elocal_{water_WWT} = Elocal_{dragout_losses} \times (1 - F_{eff_WWT})$ This release will occur over [TIME _{working_days}] days/year from [N _{sites}] sites	(Eqn. 4-6)
Treatment	Concentrate: Incineration	$Elocal_{concentrate} = Elocal_{dragout_losses} \times F_{eff_WWT}$ This release will occur over [TIME _{working_days}] days/year from [N _{sites}] sites	(Eqn. 4-7)
		Mass Balance: $Q_{chem_yr} = (Q_{chem_site_day} \times F_{container_residue} + Elocal_{dragout_losses} + Elocal_{recycle_wastes} + Elocal_{trough_discharge})$ $\times N_{sites} \times TIME_{working_days}$	(Eqn. 4-8)

Table A-2. Environmental Release Calculation Summary

Occupational Exposure Calculations	
Number of Workers Exposed Per Site:	
$N_{workers} = N_{machinist} + (N_{worker_shift} \times N_{shift})$	(Eqn. 5-1)
Transfer of Neat Metalworking Fluid (Exposure A):	
Number of Workers: Ranges from 2 (shift workers) to 46 (machine workers) workers per site.	
Inhalation: EXP _{inhalation} = Negligible (Eqn. 5-2) Dermal:	
$EXP_{dermal} = Q_{liquid_skin} \times AREA_{surface} \times N_{exp_incident} \times F_{chem_neat}$	(Eqn. 5-3)
Cleaning of Transport Containers (Exposure B): Number of Workers: 2 shift workers per site. Inhalation: EXP _{inhalation} = Negligible (Eqn. 5-4) Dermal:	
$EXP_{dermal} = Q_{liquid_skin} \times AREA_{surface} \times N_{exp_incident} \times F_{chem_neat}$	(Eqn. 5-5)
Transfer of Diluted Metalworking Fluid (Exposure C): Number of Workers: Ranges from 2 (shift workers) to 46 (machine workers) workers per site over (usually the sam discussed in Exposure A).	ne workers as
Inhalation: EXP _{inhalation} = Negligible (Eqn. 5-6) Dermal: EXP _{dermal} = $Q_{liquid_skin} \times AREA_{surface} \times N_{exp_incident} \times F_{chem_trough}$	(Eqn. 5-7)

Table A-3. Occupational Exposure Calculation Summary

Occupational Exposure Calculations	
Metal Shaping Operation (Exposure D):	
Number of Workers: 46 machine workers per site.	
Inhalation: $F_{chem_mist} = \frac{F_{chem_concentrate}}{(1 - F_{water_concentrate})} $ (Eqn. 5-8)	
$F_{chem_{mist}}$ should never be greater than 1, but if $F_{chem_{mist}}$ is greater than 1, assume:	
$F_{\text{chem_mist}} = 1 \frac{\text{mg of chemical}}{\text{mg of mist}}$ (Eqn. 5-9)	
$EXP_{inhalation} = C_{shape_mist} \times RATE_{breathing} \times TIME_{exposure} \times F_{chem_mist}$	(Eqn. 5-10)
Dermal: $EXP_{dermal} = Q_{liquid_skin} \times AREA_{surface} \times TIME_{exposure} \times F_{chem_trough}$	(Eqn. 5-11)
Filtering and Other Recycling Operations (Exposure E):	
Number of Workers: 46 machine workers per site.	
Inhalation: EXP _{inhalation} = Negligible (Eqn. 5-12) Dermal:	
$EXP_{dermal} = Q_{liquid_skin} \times AREA_{surface} \times N_{exp_incident} \times F_{chem_neat}$	(Eqn. 5-13)
Transferring Spent Metalworking Fluid and Cleaning of Shaping Machine and Trough (Expo	osure F):
<i>Number of Workers:</i> Ranges from 2 (shift workers) to 46 (machine workers) workers per site (usually the same worker in Exposures A and C).	s as discussed
Inhalation: EXP _{inhalation} = Negligible (Eqn. 5-14) Dermal:	
$EXP_{dermal} = Q_{liquid_skin} \times AREA_{surface} \times N_{exp_incident} \times F_{chem_dilute}$	(Eqn. 5-15)

Variable	Variable Description	Default Value	Data Source
AREA _{surface}	Surface area of contact	840 cm ² , 2 hands	CEB, 2000
C _{shape_mist}	Metalworking fluid mist concentration in the air at workers' breathing zone for shaping operations	See Table 0-2; water- based fluids: 0.24 mg/m ³ (typical), 1.10 mg/m ³ (high-end); straight oils: 0.39 mg/m ³ (typical), 1.42 mg/m ³ (high-end)	Piacitelli, 2001 Piacitelli, 2006
RHO _{neat}	Density of neat metalworking fluid	1 kg/L	(CEB assumption)
F _{chem_neat}	Weight fraction of the chemical of interest in the neat metalworking fluid	See Table 0-3; water- based fluids: 0.35 kg chem./kg neat MWF, straight oils: 0.4 kg chem/kg neat MWF	ILMA, 2005a Byers, 2006 OECD, 2004
F_{neat_trough}	Weight fraction of the neat metalworking fluid in the trough	See Table 0-6; 0.1 kg neat MWF/kg dilute MWF	Whodeck, 1997
$F_{container_residue}$	Fraction of neat metalworking fluid remaining in the container as residue	0.03 for drums; 0.006 for small containers; 0.002 for bulk containers	CEB, 2002
F _{eff_WWT}	Wastewater treatment efficiency	No on-site treatment = 0, chemical precipitation = 0, oil/water separation = 0.5 (default), ultrafiltration = 0.7,	USEPA, 2000a
F _{water_neat}	Weight fraction of water in the neat metalworking fluid	See Table 0-3; 0.54 kg of water/kg neat MWF	ILMA, 2005a
N _{exp} incident	Number of exposure incidents per day	1 incident/day	(CEB assumption)
N _{machines}	Number of machines per site	See Table 0-2; 48 machines/site	USEPA, 2000a
N _{shift}	Number of shifts	See Table 0-2; 2 shifts	USEPA, 2000a
N _{worker_shift}	Number of workers supervising per shift	1 worker/shift-site	(CEB assumption)
Qliquid_skin	Quantity of liquid remaining on skin	Varies depending on activity, see Equations 5-3, 5-5, 5-7, 5-11, 5-13, and 5-15	CEB, 2000
RATE _{breathing}	Typical worker breathing rate	1.25 m³/hr	NIOSH, 1976
TIME _{exposure}	Duration of exposure	8 hour/day	ILMA, 2006a
V _{container}	Volume of container	208 L (55-gal drum)	(CEB assumption)
V _{neat_site_yr}	Annual volume of metalworking fluid used per site	4,260 gal/site-yr (typical) 12,000 gal/site-yr (high- end)	Piacitelli, 2001 Piacitelli, 2006

Table A-4. Parameter Declaration and Documentation Summary

Appendix B

BACKGROUND INFORMATION AND EQUATIONS/DEFAULTS FOR THE STANDARD CEB ENVIRONMENTAL RELEASE AND WORKER EXPOSURE MODELS

B.1. INTRODUCTION

This appendix provides background information and a discussion of the equations, variables, and default assumptions for each of the standard release and exposure models used by EPA in estimating environmental releases and worker exposures. The models described in this appendix are organized into the following five sections:

- Section B.2: Chemical Vapor Releases & Associated Inhalation Exposures;
- Section B.3: Container Residue Release Models (non-air);
- Section B.4: Process Equipment Residue Release Models (non-air);
- Section B.5: Dust Emissions from Transferring Solids Model;
- Section B.6: Chemical Particle Inhalation Exposure Models; and
- Section B.7: Dermal Exposure Models.

Please refer to the guidance provided in the ESD for estimating environmental releases and worker exposures using these standard models, as it may suggest the use of certain overriding default assumptions to be used in place of those described for each model within this appendix.

This appendix includes a list of the key reference documents that provide the background and rationale for each of the models discussed. These references may be viewed in their entirety through the ChemSTEER Help System. To download and install the latest version of the ChemSTEER software and Help System, please visit the following EPA web site:

http://www.epa.gov/oppt/exposure/pubs/chemsteer.htm

B.2. CHEMICAL VAPOR RELEASES & ASSOCIATED INHALATION EXPOSURES

This section discusses the models used by EPA to estimate chemical vapor generation rates and the resulting volatile releases to air and worker inhalation exposures to that chemical vapor. The volatile air release models (discussed in B.2.1) calculate both a vapor generation rate ($Q_{vapor_generation}$; g/sec) and the resulting daily release rate of the chemical vapors to air. The *EPA/OPPT Mass Balance Inhalation Model* (discussed in Section B.2.2) uses the value of $Q_{vapor_generation}$, calculated by the appropriate release model, to estimate the resulting inhalation exposure to that released vapor.

B.2.1 Vapor Generation Rate and Volatile Air Release Models

The following models utilize a series of equations and default values to calculate a chemical vapor generation rate ($Q_{vapor generation}$; g/sec) and the resulting daily volatile air release rate (Elocal_{air}; kg/site-day):

- *EPA/OPPT Penetration Model* evaporative releases from an exposed liquid surface located indoors;
- *EPA/OPPT Mass Transfer Coefficient Model* evaporative releases from an exposed liquid surface located outdoors; and

[**B-1**]

• *EPA/OAQPS AP-42 Loading Model* – releases of volatile chemical contained in air that is displaced from a container being filled.

Each of these models is described in greater detail in the following sections:

B.2.1.1 EPA/OPPT Penetration Model

Model Description and Rationale:

The *EPA/OPPT Penetration Model* estimates releases to air from evaporation of a chemical from an open, exposed liquid surface. This model is appropriate for determining volatile releases from activities that are performed *indoors*¹² or when air velocities are expected to be *less than or equal to 100 feet per minute*.

A draft paper (Arnold and Engel, 1999) evaluating the relative performance of this model and the *Mass Transfer Coefficient Model* against experimentally measured evaporation rates described laminar airflow conditions existing up to 100 feet per minute. The paper compared the *Penetration Model* to experimental evaporation rate data measured under laminar (less than 100 feet per minute) and turbulent (above 100 feet per minute) airflow conditions. While the *Penetration Model* did not provide accurate estimates of evaporation rates under turbulent air flow conditions (relative to the *Mass Transfer Coefficient Model*), the results modeled under laminar flow conditions were found to more closely approximate the experimental data (usually within 20 percent). It is assumed that the conditions of an indoor work area most closely approximate laminar airflow conditions.

The model was originally developed using Fick's second law of diffusion. Model results were tested against experimental results of a study on evaporation rates for 15 compounds studied at different air velocities and temperatures in a test chamber. The experimental data confirmed the utility and accuracy of the model equation. Sample activities in which the *Penetration Model* may be used to estimate volatile releases to air are sampling liquids and cleaning liquid residuals from smaller transport containers (e.g., drums, bottles, pails).

Model Equations:

The model first calculates the average vapor generation rate of the chemical from the exposed liquid surface using the following equation:

$$Q_{\text{vapor_generation}} = \frac{(8.24 \times 10^{-8}) \times MW_{\text{chem}}^{0.835} \times F_{\text{correction_factor}} \times VP_{\text{chem}} \times \left(\frac{1}{29} + \frac{1}{MW_{\text{chem}}}\right)^{0.25} \times \text{RATE}_{\text{air_speed}}^{0.5} \times \text{AREA}_{\text{opening}}}{\text{TEMP}_{\text{ambient}}^{0.05} \times D_{\text{opening}}^{0.5} \times P_{\text{ambient}}^{0.5}}$$

Where:

Qvapor_generation=Average vapor generation rate (g of chemical/sec)MWchem=Molecular weight of the chemical of interest (g/mol)

¹²Similar air releases from surfaces located at *outdoor* locations (air speeds > 100 ft/min) are calculated using the *Mass Transfer Coefficient Model* (see the description provided in this section of Appendix B).

Fcorrection_factor	=	Vapor pressure correction factor (EPA default =1) ¹³
VP _{chem}	=	Vapor pressure of the chemical of interest (torr)
RATE _{air_speed}	=	Air speed (EPA default = 100 feet/min; value must be ≤ 100
		feet/min for this model)
AREA _{opening}	=	Surface area of the static pool or opening $(cm^2; B \times D_{opening}^2)$
		4)
TEMP _{ambient}	=	Ambient temperature (EPA default = 298 K)
D _{opening}	=	Diameter of the static pool or opening (cm; See Table B-1 for
		appropriate EPA default values)
Pambient		Ambient pressure (EPA default = 1 atm)
Note: The factor 8.24	· × 1	0^{-8} in Equation B-1 accounts for various unit conversions. See
Arnold and Engel, 19	99,	for the derivation of this constant.

Using the vapor generation rate (Q_{vapor_generation}) calculated in Equation B-1, the model then estimates the daily release to air for the activity using the following equation:

Elo	$\operatorname{cal}_{\operatorname{air}} = \operatorname{Q}_{\operatorname{val}}$	$\text{appor}_{\text{generation}} \times \text{TIME}_{\text{activity}_{\text{hours}}} \times \frac{3600 \text{ sec/hour}}{1000 \text{ g/kg}} $ [B-2]	2]
Where:			
Elocal _{air}	=	Daily release of the chemical vapor to air from the activity (kg/site-day)	
$Q_{vapor_generation}$	=	Average vapor generation rate (g of chemical/sec; see Equation B-1)	m
$TIME_{activity_hours}$	=	Operating hours for the release activity per day (hours/site-day See Table B-1 for appropriate EPA default values)	y;

References:

- Arnold, F.C. and Engel, A.J. Pre-publication draft article entitled, *Evaporation of Pure Liquids from Open Surfaces*. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. October 1999.
- U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1 (Equation 4-24 and Appendix K). U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

¹³The default vapor pressure correction factor, $F_{correction_factor}$, assumes that the chemical-containing material in the evaporating pool exhibits the vapor pressure of the chemical of interest, as a worst case (i.e., effective VP of the evaporating material = $F_{correction_factor} \times VP_{chem}$). Alternatively, Raoult's Law may be assumed (i.e., effective VP = mole fraction of the chemical in the material $\times VP_{chem}$), thus the $F_{correction_factor}$ may be set equivalent to the chemical's mole fraction in the material, if known. Note: in the absence of more detailed data, the chemical's weight fraction within the material formulation may be used to approximate its mole fraction.

B.2.1.2 EPA/OPPT Mass Transfer Coefficient Model

Model Description and Rationale:

The *EPA/OPPT Mass Transfer Model* estimates releases to air from the evaporation of a chemical from an open, exposed liquid surface. This model is appropriate for determining this type of volatile release from activities that are performed *outdoors*¹⁴ or when air velocities are expected to be *greater than 100 feet per minute*. A draft paper (Arnold and Engel, 1999) evaluating the relative performance of this and the *Penetration Model* against experimentally measured evaporation rates, described laminar airflow conditions existing up to 100 feet per minute. It is assumed that the conditions of an indoor process area most closely approximate laminar air flow conditions, while outdoor conditions approximate turbulent airflow conditions above 100 feet per minute.

As discussed in the draft paper, the model is predicated on the solution of the classical mass transfer coefficient model with the gas-phase mass transfer coefficient estimated by the correlation of Mackay and Matsugu. Results were tested against experimental results on 19 compounds generated by four different experimenters over a wide range of experimental conditions. While the *Mass Transfer Coefficient Model* matched the data well (usually within 20 percent), it was found that the *Penetration Model* (see description in previous section) outperformed the *Mass Transfer Coefficient Model* under laminar flow (i.e., "indoor") conditions. Therefore, the *Penetration Model* is used as a default for estimating indoor evaporation rates, while the *Mass Transfer Coefficient Model* is used for outdoor rates. Sample activities in which the *Mass Transfer Coefficient Model* may be used to estimate volatile releases to air are cleaning liquid residuals from process equipment and bulk transport containers (e.g., tank trucks, rail cars).

Model Equations:

The model first calculates the average vapor generation rate of the chemical from the shallow pool using the following equation:

$$Q_{\text{vapor_generation}} = \frac{(1.93 \times 10^{-7}) \times \text{MW}_{\text{chem}}^{0.78} \times \text{F}_{\text{correction_factor}} \times \text{VP}_{\text{chem}} \times \left(\frac{1}{29} + \frac{1}{\text{MW}_{\text{chem}}}\right)^{0.33} \times \text{RATE}_{\text{air_speed}}^{0.78} \times \text{AREA}_{\text{opening}}}{\text{TEMP}_{\text{ambient}}^{0.4} \times \text{D}_{\text{opening}}^{0.11} \times \left(\text{TEMP}_{\text{ambient}}^{0.5} - 5.87\right)^{2/3}}$$

Where:

Q _{vapor generation} =	=	Average vapor generation rate (g of chemical of interest/sec)
	=	Molecular weight of the chemical of interest (g/mol)
F _{correction factor} =	=	Vapor pressure correction factor (EPA default =1) ¹⁵
VP _{chem} =	=	Vapor pressure of the chemical of interest (torr)

¹⁴Similar air releases from surfaces located at *indoor* locations (air speeds \leq 100 ft/min) are calculated using the *Penetration Model* (see the description provided in this section of Appendix B).

¹⁵The default vapor pressure correction factor, $F_{correction_factor}$, assumes that the chemical-containing material in the evaporating pool exhibits the vapor pressure of the chemical of interest, as a worst case (i.e., effective VP of the evaporating material = $F_{correction_factor} \times VP_{chem}$). Alternatively, Raoult's Law may be assumed (i.e., effective VP = mole fraction of the chemical in the material $\times VP_{chem}$), thus the $F_{correction_factor}$ may be set equivalent to the chemical's mole fraction in the material, if known. Note: in the absence of more detailed data, the chemical's weight fraction within the material formulation may be used to approximate its mole fraction.

RATE _{air_speed}	=	Air speed (EPA default = 440 feet/min; value must be > 100
		feet/min for this model)
AREA _{opening}	=	Surface area of the static pool or opening (cm ² ; $B \times D_{opening}^2$ /
		4)
TEMP _{ambient}	=	Ambient temperature (EPA default = 298 K)
Dopening	=	Diameter of the static pool or opening (cm; See Table B-1 for
		appropriate EPA default values)
Note: The factor 1.93	× 1	0^{-7} in Equation B-3 accounts for various unit conversions See

Note: The factor 1.93×10^{-7} in Equation B-3 accounts for various unit conversions. See Arnold and Engel, 1999, for the derivation of this constant.

Using the vapor generation rate ($Q_{vapor_generation}$) calculated in Equation B-3, the model then estimates the daily release to air for the activity using the following equation:

$$Elocal_{air} = Q_{vapor_generation} \times TIME_{activity_hours} \times \frac{3600 \text{ sec/hour}}{1000 \text{ g/kg}}$$
[B-4]

Where:

Elocal _{air}	=	Daily release of the chemical vapor to air from the activity
		(kg/site-day)
Qvapor_generation	=	Average vapor generation rate (g of chemical/sec; see Equation
		B-3)
TIME _{activity_hours}	=	Operating hours for the release activity per day (hours/site-day;
		See Table B-1 for appropriate EPA default values)

References:

- Arnold, F.C. and Engel, A.J. Pre-publication draft article entitled, *Evaporation of Pure Liquids from Open Surfaces*. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. October 1999.
- U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

B.2.1.3 EPA/OAQPS AP-42 Loading Model

Model Description and Rationale:

The EPA's Office of Air Quality Planning and Standards (OAQPS) *AP-42 Loading Model* estimates releases to air from the displacement of air containing chemical vapor as a container/vessel is filled with a liquid. This model assumes that the rate of evaporation is negligible compared to the vapor loss from the displacement.

This model is used as the default for estimating volatile air releases during both loading activities and unloading activities. This model is used for unloading activities because it is assumed while one vessel is being unloaded another is assumed to be loaded. The *EPA/OAQPS AP-42 Loading Model* is used because it provides a more conservative estimate than either the *EPA/OPPT Penetration Model* or the *Mass Transfer Coefficient Model* for unloading activities.

Model Equations:

The model first calculates the average vapor generation rate of the chemical from the displacement during loading/filling operation using the following equation:

		[B-5]
F _{saturation}	$_{\rm L_{factor}} \times \rm{MW}_{\rm chem}$	$\times \left(V_{\text{cont_empty}} \times \frac{3785.4 \text{cm}^3}{\text{gal}} \right) \times \left(\frac{\text{RATE}_{\text{fill}}}{3600 \text{sec/hour}} \right) \times F_{\text{correction_factor}} \times \left(\frac{\text{VP}_{\text{chem}}}{760 \text{torr/atm}} \right)$
$Q_{vapor_generation} =$		$R \times TEMP_{ambient}$
Where:		
Qvapor_generation	=	Average vapor generation rate (g of chemical/sec)
F _{saturation_factor}	=	Saturation factor (See Table B-1 for appropriate EPA default values)
MW _{chem}	=	Molecular weight of the chemical of interest (g/mol)
V_{cont_empty}	=	Volume of the container (gallons; see Table B-1 for appropriate EPA default values)
$RATE_{fill}$	=	Fill rate (containers/hour; see Table B-1 for appropriate EPA default values)
Fcorrection_factor	=	Vapor pressure correction factor (EPA default =1) ¹⁶
VP _{chem} [–]		Vapor pressure of the chemical of interest (torr)
R		Universal Gas Constant (82.05 atm-cm ³ /mol-K)
TEMP _{ambient}	=	Ambient temperature (EPA default = 298 K)

Using the vapor generation rate ($Q_{vapor_generation}$) calculated in Equation B-5, the model then estimates the daily release to air for the activity using the following equation:

$$Elocal_{air} = Q_{vapor_generation} \times TIME_{activity_hours} \times \frac{3600 \text{ sec/hour}}{1000 \text{ g/kg}}$$
[B-6]
Where:
Elocal_{air} = Daily release of the chemical vapor to air from the activity
(kg/site-day)
Q_{vapor_generation} = Average vapor generation rate (g of chemical/sec; see Equation
B-5)
TIME_{activity_hours} = Operating hours for the release activity per day (hours/site-day;
see Table B-1 for appropriate EPA default values)

¹⁶The default vapor pressure correction factor, $F_{correction_factor}$, assumes that the chemical-containing material in the evaporating pool exhibits the vapor resure of the chemical of interest, as a worst case (i.e., effective VP of the evaporating material = $F_{correction_factor} \times VP_{chem}$). Alternatively, Raoult's Law may be assumed (i.e., effective VP = mole fraction of the chemical in the material $\times VP_{chem}$), thus the $F_{correction_factor}$ may be set equivalent to the chemical's mole fraction in the material, if known. Note: in the absence of more detailed data, the chemical's weight fraction within the material formulation may be used to approximate its mole fraction.

Reference:

U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1 (Equation 4-21). U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

Activity Type (Location)	V _{cont empty} (gallons)	D _{opening} (cm)	RATE _{fill} (containers/hour)	F _{saturation factor}	TIME _{activity hours} (hours/site-day)
Container-Related Act	tivities (e.g., filling, unload	ing, cleaning, op	en surface/evaporativ	ve losses):	
Bottles (Indoors)	1 (Range: <5)	5.08 (<5,000 gals)	60	Typical: 0.5 Worst Case: 1	Number of containers handled per site-day_) RATE _{fill}
Small Containers (Indoors)	5 (Range: 5 to <20)				
Drums (Indoors)	55 (Range: 20 to <100)		20		
Totes (Indoors)	550 (Range: 100 to <1,000)				
Tank Trucks (Outdoors)	5,000 (Range: 1,000 to <10,000)	7.6 (≥5,000 gals)	2	1	
Rail Car (Outdoors)	20,000 (Range: 10,000 and up)		1		
Equipment Cleaning A	Activities:				
Multiple Vessels (Outdoors)	Not applicable	92	Not applicable	1	4
Single, Large Vessel (Outdoors)					1
Single, Small Vessel (Outdoors)					0.5
Sampling Activities:					
Sampling Liquids (Indoors)	Not applicable	Typical: 2.5 ^a Worst Case: 10	Not applicable	1	1

Table B-1. Standard EPA Default Values Used in Vapor Generation Rate/Volatile Air Release Models

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Activity Type (Location)	V _{cont empty} (gallons)	D _{opening} (cm)	RATE _{fill} (containers/hour)	F _{saturation factor}	TIME _{activity hours} (hours/site-day)
Other Activities:					
Continuous Operation	If other scenario-specific a			1	24
Batch Operation	the vapor generation rate/air release models described in this section, the ESD will describe the model and provide appropriate default values for the model parameters.				Lesser of: (Hours/batch × Batches/site-day) or 24

a - The "typical" diameter default value of 2.5 cm was adopted as a policy decision in 2002, which supersedes the previous default value of 7 cm shown in the 1991 U.S. EPA reference document.

B.2.2 <u>Chemical Vapor Inhalation Model</u>

The following sections describe the EPA standard model for estimating worker inhalation exposures to a chemical vapor, utilizing a vapor generation rate ($Q_{vapor generation}$).

B.2.2.1 EPA/OPPT Mass Balance Model

Model Description and Rationale:

The *EPA/OPPT Mass Balance Model* estimates a worker inhalation exposure to an estimated concentration of chemical vapors within the worker's breathing zone. The model estimates the amount of chemical inhaled by a worker during an activity in which the chemical has volatilized and the airborne concentration of the chemical vapor is estimated as a function of the source vapor generation rate $(Q_{vapor_generation})$. This generation rate may be calculated using an appropriate standard EPA vapor generation model (see Equation B-1, Equation B-3, or Equation B-5) or may be an otherwise known value.

The *EPA/OPPT Mass Balance Model* also utilizes the volumetric ventilation rate within a given space and includes simplifying assumptions of steady state (i.e., a constant vapor generation rate and a constant ventilation rate) and an assumed mixing factor for non-ideal mixing of air. The default ventilation rates and mixing factors provide a typical and worst case estimate for each exposure. The airborne concentration of the chemical cannot exceed the level of saturation for the chemical.

An evaluation of the model was performed against collected monitoring data for various activities (see the 1996 AIHA article). This evaluation confirmed that the Mass Balance Model is able to conservatively predict worker inhalation exposures within one order of magnitude of actual monitoring data and is an appropriate model for screening-level estimates.

Model Equations:

The model first calculates the volumetric concentration of the chemical vapor in air using the following equation:

$$C_{\text{chem_volumetric}} = \frac{(1.7 \times 10^{\circ}) \times \text{TEMP}_{\text{ambient}} \times Q_{\text{vapor_generation}}}{\text{MW}_{\text{chem}} \times \text{RATE}_{\text{ventilation}} \times F_{\text{mixing_factor}}}$$
[B-7]

Where:

C _{chem_volumetric}	=	Volumetric concentration of the chemical vapor in air (ppm)
Qvapor generation	=	Average vapor generation rate (g of chemical/sec; see Equation
1 _0		B-1, Equation B-3, or Equation B-5, as appropriate)
TEMP _{ambient}	=	Ambient temperature (EPA default = 298 K)
MW _{chem}	=	Molecular weight of the chemical of interest (g/mol)
RATE _{ventilation}	=	Ventilation rate (ft ³ /min; see Table B-2 for appropriate EPA
		default values)
Fmixing factor	=	Mixing factor (dimensionless; see Table B-2 for appropriate
		EPA default values)
Note: The factor 17	×	10^5 in Equation B-7 accounts for various unit conversions. See

Note: The factor $1.7 \times 10^{\circ}$ in Equation B-7 accounts for various unit conversions. See Fehrenbacher and Hummel, 1996, for the derivation of this constant.

Note that the airborne concentration of the chemical vapor cannot exceed the saturation level of the chemical in air. Equation B-8 calculates the volumetric concentration at the saturation level based on

Raoult's Law. Use the lesser value for the volumetric concentration of the chemical vapor (C_{chem volumetric}) calculated in either Equation B-7 or Equation B-8 in calculating the mass concentration of the chemical of interest in the air (see Equation B-9).

$$C_{\text{chem_volumetric}} = F_{\text{correction_factor}} \times VP_{\text{chem}} \times \frac{10^6 \text{ ppm}}{P_{\text{ambient}}}$$
[B-8]

Where:

C_{chem} volumetric

Volumetric concentration of the chemical of interest in air =(ppm) = Vapor pressure correction factor (EPA default =1)¹⁷ F_{correction factor} = Vapor pressure of the chemical of interest (torr) VP_{chem} = Ambient pressure (Default = 760 torr) Pambient Note: Raoult's law calculates the airborne concentration as a mole fraction. The factor 10^6 in

Equation B-8 accounts for the unit conversion from mole fraction to ppm.

The volumetric concentration of the chemical of interest in air (calculated in either Equation B-7 or Equation B-8) is converted to a mass concentration by the following equation:

$$C_{\text{chem}_{mass}} = \frac{C_{\text{chem}_{volumetric}} \times MW_{\text{chem}}}{V_{\text{molar}}}$$
[B-9]

Where:

C _{chem_mass}	=	Mass concentration of the chemical vapor in air (mg/m ³)
C _{chem_volumetric}	=	Volumetric concentration of the chemical vapor in air (ppm,
_		see Equation B-7 or B-8, as appropriate)
MW _{chem}	=	Molecular weight of the chemical of interest (g/mol)
V _{molar}	=	Molar volume (Default = 24.45 L/mol at 25°C and 1 atm)

Assuming a constant breathing rate for each worker and an exposure duration for the activity. the inhalation exposure to the chemical vapor during that activity can be estimated using the following equation:

$$EXP_{inhalation} = C_{chem mass} \times RATE_{breathing} \times TIME_{exposure}$$
[B-10]

Where:

EXPinhalation	=	Inhalation exposure to the chemical vapor per day (mg
		chemical/worker-day)
C _{chem_mass}	=	Mass concentration of the chemical vapor in air $(mg/m^3; see$
_		Equation B-9]
RATE _{breathing}	=	Typical worker breathing rate (EPA default = $1.25 \text{ m}^3/\text{hr}$)

 $^{^{17}}$ The default vapor pressure correction factor, $F_{correction_{factor}}$, assumes that the chemical-containing material in the evaporating pool exhibits the vapor pressure of the chemical of interest, as a worst case (i.e., effective VP of the evaporating material = $F_{correction_{factor}} \times VP_{chem}$). Alternatively, Raoult's Law may be assumed (i.e., effective VP = mole fraction of the chemical in the material × VP_{chem}), thus the $F_{correction factor}$ may be set equivalent to the chemical's mole fraction in the material, if known. Note: in the absence of more detailed data, the chemical's weight fraction within the material formulation may be used to approximate its mole fraction.

TIME _{exposure}	=	Duration of exposure for the activity (hours/worker-day; see
		Table B-2 for appropriate EPA default values (≤ 8
		hours/worker-day))

References:

- Fehrenbacher, M.C. and Hummel, A.A¹⁸. "Evaluation of the Mass Balance Model Used by the EPA for Estimating Inhalation Exposure to New Chemical Substances". *American Industrial Hygiene Association Journal*. June 1996. 57: 526-536.
- U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1 (Equation 4-21). U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

¹⁸Note: This reference is currently <u>not available</u> for viewing in the ChemSTEER Help System.

Activity Type (Location)	V _{cont empty} (gallons)	RATE _{fill} (containers/hour)	RATE _{air speed} (feet/min)	RATE _{ventilation} ^a	F _{mixing factor}	TIME _{exposure} (hours/day)
Container-Related Act	tivities (e.g., filling, ur	loading, cleaning, o	pen surface/evap	orative losses):		
Bottles (Indoors)	1 Range: <5	60	100 (Indoors)	Typical: 3,000 Worst Case: 500	Typical: 0.5 Worst Case: 0.1	Lesser of:
Small Containers (Indoors)	5 Range: 5 to <20			(Indoors)		(Number of containers handled per site-day)) RATE _{fill}
Drums (Indoors)	55 Range: 20 to <100	20				or 8
Totes (Indoors)	550 Range: 100 to <1,000					
Tank Trucks (Outdoors)	5,000 Range: 1,000 to <10,000	2	440 (Outdoors)	Average: 237,600 Worst Case:		
Rail Car (Outdoors)	20,000 Range: 10,000 and up	1		$\begin{array}{c} 26,400 \times \\ (60 \times \text{RATE}_{\text{air_speed}}) 5,280)^3 \\ (\text{Outdoors}) \end{array}$		
Equipment Cleaning A	Activities:		I	I		L
Multiple Vessels (Outdoors)	Not app	plicable	440 (Outdoors)	Average: 237,600	Typical: 0.5 Worst Case: 0.1	4
Single, Large Vessel (Outdoors)	essel			Worst Case: 26,400 × $(60 \times RATE_{air speed}) 5,280)^3$		1
Single, Small Vessel (Outdoors)				$(00 \wedge \text{KATE}_{air_speed})$ 5,280) (Outdoors)		0.5
Sampling Activities:			1	1	1	1
Sampling Liquids (Indoors)	Not applicable		100 (Indoors)	Typical: 3,000 Worst Case: 500 (Indoors)	Typical: 0.5 Worst Case: 0.1	1

Table B-2. Standard EPA Default Values Used in the EPA/OPPT Mass Balance Inhalation Model

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Activity Type (Location)	V _{cont empty} (gallons)	RATE _{fill} (containers/hour)	RATE _{air speed} (feet/min)	RATE _{ventilation} ^a	F _{mixing} factor	TIME _{exposure} (hours/day)
Other Activities:						
-	-			ne of the vapor generation rate		
		anodels with the <i>Mass Balance Inhalation Model</i> described in this section, the ESD will Worst Case: 0.1 ≤ 8				<u><</u> 8

a - If the appropriate vapor generation rate model is the *EPA/OAQPS AP-42 Loading Model* (see Equation B-5) for an <u>outdoor</u> activity, the RATE_{air_speed} should be set to 440 feet/min, as a default in determining the worst case RATE_{ventilation}.

B.3. CONTAINER RESIDUE RELEASE MODELS (NON-AIR)

Model Description and Rationale:

EPA has developed a series of standard models for estimating the quantity of residual chemical remaining in emptied shipping containers that is released to non-air media (e.g., water, incineration, or landfill) when the container is either rinsed or disposed. All of the residue models assume a certain portion or fraction of the chemical remains in the emptied container to be later rinsed or discarded with the empty container.

The default parameters of model are defined based upon the particular size/type of container (e.g., small containers, drums, or large bulk), as well as the physical form of the chemical residue (e.g., liquid or solid). These defaults are based upon data collected during a 1988 EPA-sponsored study of residuals in containers from which materials have been poured or pumped.

Model Equation:

All of the models discussed in this section utilize the following common equation for calculating the amount of chemical residue:

$$Elocal_{container_residue_disp} = F_{container_residue} \times Q_{total_daily_container}$$
[B-11]

Where:

$Elocal_{container_residue_disp}$		Daily release of the chemical residue to water, incineration, or landfill from the cleaning or disposal of empty shipping containers (kg/site-day)
$F_{container_residue}$	=	Fraction of the amount of the total chemical in the shipping container remaining in the emptied container (dimensionless; see Table B-3 for appropriate EPA default values)
$Q_{total_daily_container}$	=	Total (daily) quantity of the chemical contained in the shipping containers prior to emptying (kg of chemical/site-day; see Table B-4 for appropriate EPA default values)

Each model, however, utilizes unique default values within that equation based upon the relative size of the container and the physical form of the chemical residue. These default values are summarized in Table B-3 and Table B-4. The following models are the standard EPA models for estimating container residues:

- EPA/OPPT Small Container Residual Model;
- EPA/OPPT Drum Residual Model;
- EPA/OPPT Bulk Transport Residual Model; and
- EPA/OPPT Solid Residuals in Transport Containers Model.

The default frequency with which the container residues are released (TIME_{days_container_residue}, days/site-year) must be appropriately "paired" with the total daily quantity of chemical contained in the containers ($Q_{total_daily_container}$) used in calculating the daily release. Thus, Table B-4 also contains the appropriate EPA default values for TIME_{days container} residue.

References:

- U.S. EPA. Chemical Engineering Branch. Memorandum: *Standard Assumptions for PMN Assessments*. From the CEB Quality Panel to CEB Staff and Management. October 1992.
- U.S. EPA. Office of Pesticides and Toxic Substances. *Releases During Cleaning of Equipment*. July 1988.

Chemical Form	Container Type	V _{cont empty} (gallons)	Model Title	F _{container} residue
Liquid	Liquid Bottle	1 Range: <5	EPA/OPPT Small Container Residual Model	Central Tendency: 0.003 High End: 0.006
	Small Container	5 Range: 5 to <20		
	Drum	55 Range: 20 to <100	EPA/OPPT Drum Residual Model	Central Tendency: 0.025 High End ^b : 0.03 (for <u>pumping</u> liquid out of the drum)
				Alternative defaults: Central Tendency: 0.003 High End: 0.006 (for <u>pouring</u> liquid out o the drum)
	Tote	550 Range: 100 to <1,000	EPA/OPPT Bulk Transport Residual Model	Central Tendency: 0.000 High End: 0.002
	Tank Truck	5,000 Range: 1,000 to <10,000		
	Rail Car	20,000 Range: 10,000 and up		
Solid	Any	Any	EPA/OPPT Solid Residuals in Transport Containers Model	0.01

a - These defaults are based on the 1988 EPA study investigating container residue and summarized in the 1992 internal EPA memorandum (see *References* in this section for the citations of these sources).

b - The 1992 EPA memorandum reference document contains the previous default of 0.04 for the high-end loss fraction ($F_{container_residue}$) for the *Drum Residual Model*; however, this value was superseded by an internal policy decision in 2002. Per 40 CFR 261.7(b)(1) of the Resource Conservation and Recovery Act (RCRA), "a container or an inner liner removed from a container that has held any hazardous wastes, except waste that is a compressed gas or that is identified as an acute hazardous waste...is empty if...(ii) no more than 2.5 centimeters (1 inch) remain on the bottom of the container or liner or (iii)(A) no more than 3 percent by weight of the total capacity of the container remains in the container or inner liner if the container is equal to or less than 110 gallons in size...". The 3 percent high-end default is consistent with the range of experimental results documented in the 1988 EPA study (see *References* in this section for a citation of this study).

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Table B-4. Standard EPA Methodology for Calculating Default Q_{total_daily_container} and TIME_{days_container_residue} Values for Use in the Container Residual Models

Number of Containers Emptied per Day	Q _{total daily container} (kg/site-day)	TIME _{days} container residue (days/year)
1 or more	(Mass quantity of chemical in each container (kg/container)) × (Number of containers emptied per day)	Total number of operating days for the facility/operation
Less than 1	Mass quantity of chemical in each container (kg/container)	Total number of containers emptied per site-year

B.4. PROCESS EQUIPMENT RESIDUE RELEASE MODELS (NON-AIR)

Model Description and Rationale:

EPA has developed two standard models for estimating the quantity of residual chemical remaining in emptied process equipment that is released to non-air media (e.g., water, incineration, or landfill) when the equipment is periodically cleaned and rinsed. The residue models assume a certain portion or fraction of the chemical remains in the emptied vessels, transfer lines, and/or other equipment and is later rinsed from the equipment during cleaning operations and discharged with the waste cleaning materials to an environmental medium.

The default parameters of the model are defined based upon whether the residues are being cleaned from a *single* vessel or from *multiple* pieces of equipment. These defaults are based upon data collected during an EPA-sponsored study of residuals in process equipment from which materials have pumped or gravity-drained.

Model Equation:

The models discussed in this section utilize the following common equation for calculating the amount of chemical residue:

$$Elocal_{equip_cleaning} = F_{equip_residue} \times Q_{total_chem_capacity}$$
[B-12]

Where:

$Elocal_{equip_cleaning}$	=	Daily release of the chemical residue to water, incineration, or landfill from cleaning of empty process equipment (kg/site- day)
$F_{equip_residue}$		Fraction of the amount of the total chemical in the process equipment remaining in the emptied vessels, transfer lines, and/or other pieces (dimensionless; see Table B-5 for appropriate EPA default values)
$Q_{equip_chem_capacity}$	=	Total capacity of the process equipment to contain the chemical in question, prior to emptying (kg of chemical/site- day; see Table B-6 for appropriate EPA default values)

Each model, however, utilizes unique default values within that equation based upon whether the residues are cleaned from a single vessel or from multiple equipment pieces. These default values are summarized in Table B-5 and Table B-6. The following models are the standard EPA models for estimating process equipment residues:

- EPA/OPPT Single Process Vessel Residual Model; and
- EPA/OPPT Multiple Process Vessel Residual Model.

The default frequency with which the equipment residues are released (TIME_{days_equip_residue}, days/site-year) must be appropriately "paired" with the total capacity of the equipment to contain the chemical of interest ($Q_{equip_chem_capacity}$) used in calculating the daily release. Thus, Table B-6 also contains the appropriate EPA default values for TIME_{days_equip_residue}.

References:

- U.S. EPA. Chemical Engineering Branch. Memorandum: *Standard Assumptions for PMN Assessments*. From the CEB Quality Panel to CEB Staff and Management. October 1992.
- U.S. EPA. Office of Pesticides and Toxic Substances. *Releases During Cleaning of Equipment*. July 1988.

Table B-5. Standard EPA Default Values for Use in the Process Equipment Residual Release Models

Model Title	F _{equip} residue
EPA/OPPT Single Process Vessel Residual Model	Conservative: 0.01 (for <u>pumping</u> process materials from the vessel)
	*Alternative defaults: Central Tendency: 0.0007 High End to Bounding: 0.002 (alternative defaults for <u>gravity-draining</u> materials from the vessel)
EPA/OPPT Multiple Process Vessel Residual Model	Conservative: 0.02

a - These defaults are based on the 1988 EPA study investigating container residue and summarized in the 1992 internal EPA memorandum (see *References* in this section for the citations of these sources).

Process Type	Number of Batches per Day	Q _{equip} chem. capacity (kg/site-day)	TIME _{days equip} residue (days/year)
Batch	1 or more	(Mass quantity of chemical in each batch (kg/batch)) × (Number of batches run per day)	Total number of operating days for the facility/operation
	Less than 1	Mass quantity of chemical in each batch (kg/batch)	Total number of batches run per site- year
Continuous	Not applicable	Daily quantity of the chemical processed in the equipment (kg/site-day)	Total number of operating days for the facility/operation

Table B-6. Standard EPA Methodology for Calculating Default Q_{equip_chem_capacity} and TIME_{days_equip_residue} Values for Use in the Process Equipment Residual Models

Note: Please refer to the ESD for any overriding default assumptions to those summarized above. Equipment cleaning may be performed periodically throughout the year, as opposed to the default daily or batch-wise cleaning frequencies shown above. For example, facilities may run dedicated equipment for several weeks, months, etc within a single campaign before performing equipment-cleaning activities, such that residuals remaining in the emptied are released less frequently than the standard default $TIME_{days_equip_residue}$ summarized above in Table B-6. Care should be given in defining the appropriate $Q_{total_daily_container}$ and $TIME_{days_container_residue}$ to be used in either of the standard EPA process equipment residue models.

B.5. DUST EMISSIONS FROM TRANSFERRING SOLIDS MODEL

EPA has developed the *EPA/OPPT Dust Emissions from Transferring Solids Model* to estimate the releases from dust generation during the unloading/transferring of solid powders. While there are multiple potential industrial sources of dust (e.g., grinding, crushing), the scope of this model is limited to transferring/unloading of solids. Specifically, this can be defined as activities where packaging/transport materials are opened and contents are emptied either into a feed system and conveyed or directly added into a process tank (e.g., reactor, mixing tank).

Model Description and Rationale:

The EPA/OPPT Dust Emissions from Transferring Solids Model estimates that 0.5% of the solid powder transferred may be released from dust generation. This model is based on 13 sources, including site visit reports, Oganisation for Economic Co-operation and Development (OECD) Emission Scenario Documents (ESD), EPA's AP-42 Emission Factors, and Premanufacture Notice submissions (EPA's new chemicals review program). Each source contained estimates of the quantity of solid powder that may be lost during transfers for a specific industry. The different sources contained dust loss data or loss fraction estimates from a variety of industries including paint and varnish formulation, plastic manufacturing, printing ink formulation, rubber manufacturing, and chemical manufacturing. These estimates ranged from negligible to 3% of the transferred volume. The mean of the upper bound from each data set was 0.5%.

Additionally, dust generation test data were reviewed. A study by Plinke, et al. investigated key parameters for developing a theoretical approach for estimating dust losses based on moisture content, particle size, drop height, and material flow (Plinke, 1995). Dust generation rates during unloading and transfers were measured for four materials. The highest measured dust generation rate was 0.5%. These data further justified the adoption of a 0.5% loss fraction as a conservative estimate.

For the media of release of the dust generated, most facilities utilize some type of control device(s) to collect fugitive emissions. Many facilities collect fugitive dust emissions from these operations in filters and dispose of the filters in landfills or by incineration. Wet scrubbers may also be utilized by industry. However, in some cases, uncontrolled/uncollected particulates may be small enough to travel several miles from the facility, resulting in environmental and human exposures to the chemical of interest beyond the boundaries of the site. Fugitive dust emissions may also settle to facility floors and are disposed of when floors are cleaned (water if the floors are rinsed or land or incineration if the floors are swept). Therefore, as a conservative assumption the model assumes an uncontrolled release to air, water, incineration, or landfill.

If facility-specific information states a control technology is employed, the release may be partitioned to the appropriate media. If the control technology efficiency information is not available, the *CEB Engineering Manual* may be utilized for control technology efficiencies. Table B-7 provides estimated efficiencies for common control technologies.

			Default Media of
	Default Control		Release for
	Technology Capture		Controlled
Control Technology	Efficiency (%)	Notes/Source	Release
None (default)	0	No control technology	N/A
		should be assumed as	
		conservative.	

Table B-7. Default Control Technology Efficiencies

Filter (such as a	99	For particles > 1 um.	Incineration or Land
baghouse)		CEB Engineering Manual.	
Cyclone/Mechanical	80	For particles > 15 um	Incineration or Land
Collectors		CEB Engineering Manual.	
Scrubber	Varies	Consult Table 7-1 of the	Water
	95 may be assumed	CEB Engineering Manual.	

Model Equation:

Based on these data, the model estimates the portion of the release that is not captured or the uncontrolled release using the following equation. As a default this material is assumed released to air, water, incineration, or land.

$$Elocal_{dust_fugitive} = Q_{transferred} \times F_{dust_generation} \times (1 - F_{dust_control})$$
[B-13]

Where:

$Elocal_{dust_fugitive}$	=	Daily amount not captured by control technology from transfers or unloading (kg/site-day)
Qtransferred	=	Quantity of chemical transferred per day (kg chemical/site-day)
$F_{dust_generation}$	=	Loss fraction of chemical during transfer/unloading of solid
		powders (Default: 0.005 kg released/kg handled)
F _{dust_control}	=	Control technology capture efficiency (kg captured/kg processed)
		(Default: If the control technology is unknown, assume capture efficiency = 0 kg captured/kg processed, see Table B-7).

The following equation estimates the portion of dust release captured by the control technology. The default media of release for this material should be selected based on the information presented in Table B-7.

$$Elocal_{dust_captured} = Q_{transferred} \times F_{dust_generation} \times F_{dust_control}$$
[B-14]

Where:

Elocal _{dust captured}	=	Daily amount captured by control technology from transfers or
		unloading (kg/site-day)
Qtransferred	=	Quantity of chemical transferred per day (kg chemical/site-day)
F _{dust_generation}	=	Loss fraction of chemical during transfer/unloading of solid
		powders (Default: 0.005 kg released/kg handled)
$F_{dust_control}$	=	Control technology capture efficiency (kg captured/kg processed)
		(Default: If the control technology is unknown, assume capture
		efficiency = $0 \text{ kg captured/kg processed}$, see Table B-7).

References:

- U.S. EPA. Chemical Engineering Branch. "Generic Model to Estimate Dust Releases from Transfer/Unloading Operations of Solid Powders". November 2006.
- U.S. EPA. Chemical Engineering Branch. CEB Manual for the Preparation of Engineering Assessment, Volume 1 (page 4-11). U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

Plinke, Marc A.E., et al. "Dust Generation from Handling Powders in Industry." *American Industrial Hygiene Association Journal*. Vol. 56: 251-257, March 1995.

B.6. CHEMICAL PARTICLE INHALATION EXPOSURE MODELS

The following EPA standard models may be used to estimate worker inhalation exposures to particles containing the chemical of interest:

- EPA/OPPT Small Volume Solids Handling Inhalation Model; and
- OSHA Total Particulates Not Otherwise Regulated (PNOR) Permissible Exposure Limit (PEL)-Limiting Model.

Each of these models is an alternative default for calculating worker inhalation exposures during the following particulate-handling activities, based upon the relative daily amount of particulate material being handled:

- Unloading and cleaning solid residuals from transport containers/vessels;
- Loading solids into transport containers/vessels; and
- Cleaning solid residuals from process equipment.

For amounts up to (and including) 54 kg/worker-shift, the *EPA/OPPT Small Volume Solids Handling Inhalation Model* is used, as it more accurately predicts worker exposures to particulates within this range than the *OSHA Total PNOR PEL-Limiting Model*. The *Small Volume Solids Handing Inhalation Model* is based on exposure monitoring data obtained for workers handling up to 54 kg of powdered material. Beyond this data-supported limit, EPA assumes that exposures within occupational work areas are maintained below the regulation-based exposure limit for "particulates, not otherwise regulated".

The *EPA/OPPT Small Volume Solids Handling Model* is also the exclusive model used for any solids sampling activity. Each of these models is described in detail in the following sections.

B.6.1 EPA/OPPT Small Volume Solids Handling Inhalation Model

Model Description and Rationale:

The *EPA/OPPT Small Volume Solids Handling Inhalation Model* utilizes worst case and typical exposure factors to estimate the amount of chemical inhaled by a worker during handling of *small volumes*¹⁹ (i.e., \leq 54 kg/worker-shift) of solid/powdered materials containing the chemical of interest. The handling of these small volumes is presumed to include scooping, weighing, and pouring of the solid materials.

The worst case and typical exposure factor data were derived from a study of dye weighing and adapted for use in situations where workers are presumed to handle small volumes of solids in a manner similar to the handling in the study. The maximum amount of dye handled in the study was 54 kg/worker-shift, so the *Small Volume Solids Handling Inhalation Model* is presumed to be valid for

¹⁹Worker inhalation exposures to particulates handled in amounts greater than 54 kg/worker-shift are calculated using the OSHA Total PNOR PEL-Limiting Model (see the description provided in this section of Appendix B).

quantities up to and including this amount. In the absence of more specific exposure data for the particular activity, EPA uses these data to estimate inhalation exposures to solids transferred at a rate up to and including 54 kg/worker-shift. This model assumes that the exposure concentration is the same as the concentration of the chemical of interest in the airborne particulate mixture.

Note that the amount handled per worker per shift is typically unknown, because while the throughput may be known, the number of workers and the breakdown of their activities are typically unknown. For example, while two workers may together handle 100 kg of material/day, one worker may handle 90 kg of material/day and the other may only handle 10 kg of material/day. Therefore, as a conservative estimate EPA assumes that the total throughput ($Q_{facility_day}$; kg/site-day) is equal to the amount handled per worker ($Q_{shift handled}$; kg/worker-shift), if site-specific information is not available.

Model Equation:

The model calculates the inhalation exposure to the airborne particulate chemical using the following equation:

$$EXP_{inhalation} = (Q_{shift handled} \times N_{shifts}) \times F_{chem} \times F_{exposure}$$
[B-15]

Where:		
EXPinhalation	=	Inhalation exposure to the particulate chemical per day (mg chemical/worker-day)
$Q_{shift_handled}$	=	Quantity of the solid/particulate material containing the chemical of interest that is handled by workers each shift (kg/worker-shift; see Table B-8 for appropriate EPA default values; must be \leq 54 kg/worker-shift for this model to be valid)
${{N_{shifts}}^{20}}$	=	Number of shifts worked by each worker per day (EPA default = 1 shift/day)
F _{chem}	=	Weight fraction of the chemical of interest in the particulate material being handled in the activity (dimensionless; refer to the ESD discussion for guidance on appropriate default value)
F _{exposure}	=	Exposure factor; amount of total particulate handled that is expected to be inhaled (EPA defaults: 0.0477 mg/kg (typical) and 0.161 mg/kg (worst case))

²⁰Note that this value is the number of shifts worked by *each worker* per day. This value would only be greater than one if a worker worked for over eight hours in a given day.

Activity Type	Default Q _{shift handled} ²¹ (kg/worker-day)
Loading and Unloading Containers	Quantity of material in each container (kg/container) × Number of containers/worker-shift
Container Cleaning	Quantity of residue in each container (kg/container) × Number of container/worker-shift
Process-Related Activity (equipment cleaning, sampling):	
Continuous process: Batch process (<1 batch per day): Batch process (>1 batch per day):	Daily throughput of material / Number of shifts per day Quantity of material per batch Quantity of material per batch × Number of batches per shift

Table B-8. Standard EPA Default Values for Q_{daily_handled} in the EPA/OPPT Small Volume Solids Handling Inhalation Model

References:

U.S. EPA. Chemical Engineering Branch. Generic Scenario: Textile Dyeing. October 15, 1992.

- U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1 (page 4-11). U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.
- U.S. EPA Economics, Exposure and Technology Division²². *Textile Dye Weighing Monitoring Study*. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington D.C., EPA 560/5-90-009. April 1990.

B.6.2 OSHA Total PNOR PEL-Limiting Model

Model Description and Rationale:

The OSHA Total Particulates Not Otherwise Regulated (PNOR) Permissible Exposure Limit (PEL)-Limiting Model estimates the amount of chemical inhaled by a worker during handling of solid/powdered materials containing the chemical of interest. The estimate assumes that the worker is exposed at a level no greater than the OSHA PEL for Particulate, Not Otherwise Regulated, total particulate. Operations are generally expected to comply with OSHA's federal regulation regarding total particulate exposures. This model assumes that the exposure concentration is the same as the concentration of the chemical of interest in the airborne particulate mixture.

²¹The appropriate quantity of material handled by each worker on each day may vary from these standard CEB defaults, per the particular scenario. Be sure to consult the discussion presented in the ESD activity description in determining the most appropriate default value for Q_{daily handled}.

²²Note: This reference is currently available for viewing in the ChemSTEER Help System.

The OSHA Total PNOR PEL-Limiting Model is used in cases where workers are handling quantities of solid/powdered materials in excess of 54 kg/worker-shift²³. As stated in Section B.6.1, the Small Volume Solids Handling Model, based on monitoring data, provides a more realistic estimate of worker inhalation exposures to smaller quantities particulate material. The data used by the Small Volume Solids Handling Model are supported up to and including 54 kg solid material handled per worker-shift. Beyond this amount, EPA assumes the occupational exposures are maintained below the regulatory exposure limit contained in the OSHA Total PNOR PEL-Limiting Model, although the exposures provided by this model are considered to be worst-case, upper-bounding estimates.

Refer to Table B-8 for the standard EPA assumptions used in determining the appropriate quantity of particulate material handled to determine the applicability of this model to a given activity.

NOTE: The OSHA Total PNOR PEL (used as the basis for the model calculations) is an 8-hour time-weighted average (TWA); therefore, *worker exposures must be assumed to occur over an 8-hour period* for the OSHA Total PNOR PEL-Limiting Model estimate to be valid basis for the calculated inhalation exposure estimate.

Model Equations:

The model first calculates the mass concentration of the airborne particulate chemical using the following equation:

$$C_{\text{chem}_{mass}} = C_{\text{total}_{mass}} \times F_{\text{chem}}$$
[B-16]

Where:

C _{chem_mass}	=	Mass concentration of the chemical in air (mg/m^3)
C _{total_mass}	=	Mass concentration of total particulate (containing the
_		chemical) in air (EPA default = 15 mg/m^3 , based on the OSHA
		Total PNOR PEL, 8-hr TWA)
F _{chem}	=	Weight fraction of the chemical of interest in the particulate
		material being handled in the activity (dimensionless; refer to
		the ESD discussion for guidance on appropriate default value)

Similar to Equation B-10 in the *EPA/OPPT Mass Balance Inhalation Model*, the *OSHA Total PNOR PEL-Limiting Model* then uses the mass airborne concentration of the chemical (C_{mass_chem}) in Equation B-16, to calculate the inhalation exposure to the particulate chemical using the following equation:

$$EXP_{inhalation} = C_{chem_mass} \times RATE_{breathing} \times TIME_{exposure}$$
[B-17]

Where:

WINCIC.		
EXPinhalation	= Inhalation exposure to the airborne particulate chemica	l per
	day (mg chemical/worker-day)	
C _{chem_mass}	= Mass concentration of the particulate chemical in air (r	ng/m ³ ;
	see Equation B-17)	
RATE _{breathing}	= Typical worker breathing rate (EPA default = $1.25 \text{ m}^3/2$	hr)

²³Worker inhalation exposures to particulates handled in amounts up to and including 54 kg/worker-shift are calculated using the EPA/OPPT Small Volume Handling Inhalation Model (see the description provided in this section of Appendix B).

TIME _{exposure}	=	Duration of exposure for the activity (EPA default = 8
		hours/worker-day ²⁴)

References:

U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1 (Equations 4-1 and 4-11). U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

B.7. DERMAL EXPOSURE MODELS

Model Description and Rationale:

EPA has developed a series of standard models for estimating worker dermal exposures to liquid and solid chemicals during various types of activities. All of these dermal exposure models assume a specific surface area of the skin that is contacted by a material containing the chemical of interest, as well as a specific surface density of that material in estimating the dermal exposure. The models also assume *no use of controls or gloves* to reduce the exposure. These assumptions and default parameters are defined based on the nature of the exposure (e.g., one hand or two hand, immersion in material, contact with surfaces) and are documented in the references listed in this section.

In the absence of data, the EPA/OPPT standard models for estimating dermal exposures from industrial activities described in this section can be used. The models for exposures to liquid materials are based on experimental data with liquids of varying viscosity and the amount of exposure to hands was measured for various types of contact. Similar assessments were made based on experimental data from exposure to solids.

Model Equation:

All of the standard EPA models utilize the following common equation for calculating worker dermal exposures:

$$EXP_{dermal} = AREA_{surface} \times Q_{remain \ skin} \times F_{chem} \times N_{event}$$
[B-18]

Where:

EXP _{dermal}	=	Dermal exposure to the liquid or solid chemical per day (mg
		chemical/worker-day)
AREA _{surface}	=	Surface area of the skin that is in contact with liquid or solid
		material containing the chemical (cm ² ; see Table B-9 for
		appropriate EPA default values)
Qremain skin	=	Quantity of the liquid or solid material containing the chemical
_		that remains on the skin after contact (mg/cm ² -event; see Table
		B-9 for appropriate EPA default values)

²⁴Since the OSHA Total PNOR PEL is an 8-hr TWA, the exposure duration must be assumed as 8 hours/worker-day for the model defaults to apply.

F _{chem}	=	Weight fraction of the chemical of interest in the material being
		handled in the activity (dimensionless; refer to the ESD
		discussion for guidance on appropriate default value)
N _{event} ²⁵	=	Frequency of events for the activity (EPA default = 1
		event/worker-day)

Each model, however, utilizes unique default values within that equation based upon the nature of the contact and the physical form of the chemical material. These default values are summarized in Table B-9. The following models are the standard EPA models for estimating worker dermal exposures:

- EPA/OPPT 1-Hand Dermal Contact with Liquid Model;
- EPA/OPPT 2-Hand Dermal Contact with Liquid Model;
- EPA/OPPT 2-Hand Dermal Immersion in Liquid Model;
- EPA/OPPT 2-Hand Dermal Contact with Container Surfaces Model; and
- EPA/OPPT 2-Hand Dermal Contact with Solids Model.

For several categories of exposure, EPA uses qualitative assessments to estimate dermal exposure. Table B-10 summarizes these categories and the resulting qualitative dermal exposure assessments.

References:

U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

U.S. EPA. Chemical Engineering Branch. *Options for Revising CEB's Method for Screening-Level Estimates of Dermal Exposure – Final Report.* U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. June 2000.

²⁵Only one contact per day (N_{event} = 1 event/worker-day) is assumed because Q_{remain_skin}, with few exceptions, is not expected to be significantly affected either by wiping excess chemical material from skin or by repeated contacts with additional chemical material (i.e., wiping excess from the skin does not remove a significant fraction of the small layer of chemical material adhering to the skin and additional contacts with the chemical material do not add a significant fraction to the layer). Exceptions to this assumption may be considered for chemicals with high volatility and/or with very high rates of absorption into the skin.

Default Model	Example Activities	AREA _{surface} ^a (cm ²)	Q _{remain} skin (mg/cm ² - event)	Resulting Contact AREA _{surface} × Q _{remain skin} (mg/event)
Physical Form: Liquids				
EPA/OPPT 1-Hand Dermal Contact with Liquid Model	Liquid sampling activitiesLadling liquid/bench-scale liquid transfer	420 (1 hand mean)	Low: 0.7 High: 2.1	Low: 290 High: 880
EPA/OPPT 2-Hand Dermal Contact with Liquid Model	 Maintenance Manual cleaning of equipment and containers Filling drum with liquid Connecting transfer line 	840 (2 hand mean)	Low: 0.7 High: 2.1	Low: 590 High: 1,800
EPA/OPPT 2-Hand Dermal Immersion in Liquid Model	Handling wet surfacesSpray painting	840 (2 hand mean)	Low: 1.3 High: 10.3	Low: 1,100 High: 8,650
Physical Form: Solids				
EPA/OPPT 2-Hand Dermal Contact with Container Surfaces Model	 Handling bags of solid materials (closed or empty) 	No defaults	No defaults	< 1,100 ^c
EPA/OPPT 2-Hand Dermal Contact with Solids Model	 Solid sampling activities Filling/dumping containers of powders, flakes, granules Weighing powder/scooping/mixing (i.e., dye weighing) Cleaning solid residues from process equipment Handling wet or dried material in a filtration and drying process 	No defaults	No defaults	< 3,100 ²³

Table B-9. Standard EPA Default Values for Use in the Worker Dermal Exposure Models

a - These default values were adopted in the 2000 EPA report on screening-level dermal exposure estimates (see *References* in this section for the citations of this sources) and are the mean values for men taken from the EPA Exposure Factors Handbook, 1997.

b - These default values were adopted in the 2000 EPA report on screening-level dermal exposure estimates (see *References* in this section for the citation of this source). The report derived the selected ranges of values for liquid handling activities from: U.S. EPA. A Laboratory Method to Determine the Retention of Liquids on the Surface of Hands. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Exposure Evaluation Division. EPA 747-R-92-003. September 1992.

c - These default values were adopted in the 2000 EPA report on screening-level dermal exposure estimates (see *References* in this section for the citation of this source). The report derived values for dermal contact for solids handling activities from: Lansink, C.J.M., M.S.C. Breelen, J. Marquart, and J.J. van Hemmen: Skin Exposure to Calcium Carbonate in the Paint Industry. Preliminary Modeling of Skin Exposure Levels to Powders Based on Field Data (TNO Report V 96.064). Rijswijk, The Netherlands: TNO Nutrition and Food Research Institute, 1996.

Table B-10. EPA Default Qualitative Assessments for Screening-Level Estimates of Dermal
Exposure

Category	Dermal Assessment
Corrosive substances (pH>12, pH<2)	Negligible
Materials at temperatures >140°F (60°C)	Negligible
Cast Solids (e.g., molded plastic parts, extruded pellets	Non-Quantifiable (Some surface contact may occur if manually transferred)
"Dry" surface coatings (e.g., fiber spin finishes, dried paint)	Non-Quantifiable (If manual handling is necessary and there is an indication that the material may abrade from the surface, quantify contact with fingers/palms as appropriate)
Gases/Vapors	Non-Quantifiable (Some contact may occur in the absence of protective clothing)

Source: U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

Appendix C

SUMMARY OF RELEASE DATA FROM MP&M EFFLUENT GUIDELINES DATABASE

During the development of the MP&M effluent guidelines, EPA collected discharge data for metal shaping operations, including machining and grinding. This appendix presents the data from the MP&M Database (USEPA, 2000a) used to generate Table 0-2 and Table 0-2. Data handling for the development of these tables is consistent with the data handling during the development of the effluent guidelines, such as the removal of data from several facilities due to incomplete surveys and/or data irregularities. Each facility was statistically weighted to better characterize the industry; the averages presented below are weighted averages. Tables C-1 through C-3 summarize the data from the MP&M Database presented in Table 0-2.

	Оро			
Operation	Average	Low	High	Number of Data Points
Grinding	12.7	1	24	124
Machining	13.3	1	24	122
Overall	13.0	1	24	246

Table C-1.	Summary	of Data fron	ı the MP&M	Database fo	r Operating Hours

Table C-2. Summary of Data from the MP&M Database for Operating Da	Table C-2.	. Summary of I	ata from the	e MP&M Database	for Operating Days
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	Оро			
Operation	Average	Low	High	Number of Data Points
Grinding	249	1	365	124
Machining	246	1	365	122
Overall	247	1	365	246

Table C-3.	Summary of Data	from the	MP&M Database	for Number	of Machines per Site
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	Number			
Operation	Average	Low	High	Number of Data Points
Grinding	17	1	298	36
Machining	93	1	976	25
Overall	48	1	976	61

Tables C-4 and C-5 summarize the data collected on the quantity of dilute metalworking fluid from trough discharge and cleanout, and the quantity lost to dragout (fluid remaining on the parts as they are removed from the shaping machine). Facilities reported these releases either by weight or by volume. If volume was reported, a density of 1 kg/L (similar to water) was assumed.

	Trough Dischar F			
Operation	Average	Low	High	Number of Data Points
Grinding	2021.5	15.8	134,000	84
Machining	1268.9	0	75,700	148
Overall	1535.0	0	134,000	232

Table C-4. Summary of Data from the MP&M Database for Trough Discharge Releases

Table C-5. Summary of Data from the MP&M Database for Dragout Releases

	Dragout Relea	Number of Data		
Operation	Average	Low	High	Points
Grinding	1374.9	0	5,450	76
Machining	230.3	0	11,400	228
Overall	314.5	0	11,400	304

Tables C-6 and C-7 summarize the collected data on the quantity of process sludge generated and the quantity of filter residue or wet sludge removed from the recycle loop. Since facilities reported the percent solids of the sludge waste streams, the solids fraction has been removed from the data presented below. Most facilities reported these releases by weight; however a few facilities reported by volume. If volume was reported, a density of 1 kg/L (similar to water) was assumed. These two releases were summed to present the value for sludge and filtration releases in Table 0-2.

Table C-6. Summary of Data from the MP&M Database for Process Sludge

	Liquid Fraction			
Operation	Average	Low	High	Number of Data Points
Grinding	1160.4	0	79,600	568
Machining	210.6	0	33,100	368
Overall	534.1	0	79,600	954

	Recycle L			
Operation	Average	Low	High	Number of Data Points
Grinding	793.6	0	20,300	48
Machining	210.8	0	1,930	50
Overall	514.0	0	11,400	98

Appendix D

TOC REMOVAL EFFICIENCY DATA

The following TOC removals information is based on data in the long-term average database for the MP&M Phase II proposed effluent guidelines (USEPA, 2000a). These data were gathered during sampling episodes to a variety of MP&M facilities. Only data points with no quality control concerns have been included. The data are presented separately for each type of treatment system. Average influent and effluent TOC concentrations were calculated for each sampled site. The percent TOC removals for each site were calculated from the corresponding average influent and effluent concentrations. The final average removals of TOC for each treatment system were calculated as the average of the percent TOC removals for each site, which is the same procedure used for the MP&M proposed effluent guidelines with TOC being the indicator parameter (USEPA, 2000a).

The following tables provide the raw data used to determine the average percent removal of TOC, which is used as the default for treatment in this ESD. Table D-1 presents the average percent removal and range of removal percentages for each form of treatment.

Table D-1.	Summar	of TOC Percent	Removals by Treatment
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Treatment	Average Percent Removal	Range of Percent Removal
Precipitation	8.35	-44 to 56
Chemical Emulsion Breaking with Oil Water Separation	50.4	32 to 82
Ultrafiltration	70.3	11 to 97

Table D-2 presents the data used to determine the percent TOC removal for chemical precipitation. Metal shaping unit operations are in bold.

Table D-2. Chemical Precipitation

Episode	Unit Operations	%TOC Removal (Average)
CP1	Grinding	47.6
	Impact Deformation	
	Machining	
	Acid Treatment	
	Alkaline Cleaning	
	Chemical Conversion Coating	
	Electroplating	
CP2	Acid Treatment	-16.1
	Alkaline Treatment	
	Anodizing	
	Chemical Conversion Coating	
	Electroplating	
CP3	Impact Deformation	17.9
	Machining	
	Pressure Deformation	
	Acid Treatment	
	Alkaline Cleaning	
	Chromate Conversion Coating	
	Electroplating	
CP4	Machining	26.9
	Acid Treatment	
	Alkaline Treatment	
	Electroplating	
CP5	Conversion Coating	30.4
	Electrocoating	
	Painting	
CP6	Etcher Rinsewater	30.6
CP7	Acid Treatment	55.8
	Alkaline Treatment	
	Electroplating	
CP8	Alkaline Cleaning	-7.3
	Acid Cleaning	
	Conversion Coating	
	Electroplating	
CP9	Acid Treatment	-26
	Alkaline Treatment	
	Conversion Coating	
CP10	Impact Deformation	0
	Acid Treatment	
	Alkaline Treatment	
	Electroplating	

Episode	Unit Operations	%TOC Removal (Average)
CP11	Impact Deformation	-15.4
	Aqueous degreasing	
	Conversion Coating	
	Acid Treatment	
	Electroplating	
CP12	Aqueous Degreasing	-4.9
	Conversion Coating	
	Acid Treatment	
CP13	Alkaline Cleaning	-44.5
	Acid Treatment	
	Electroplating	
CP14		21.9
	AVG % Removal =	8.35
	Median % Removal =	8.95

Table D-3 presents the data used to determine the percent TOC removal for chemical emulsion breaking with oil/water separation. Metal shaping unit operations are in bold.

Episode	Unit Operations	%TOC Removal (Average)
OW1	Grinding	41.5
	Machining	
	Alkaline Cleaning	
OW2	Grinding	31.65
	Impact Deformation	
	Machining	
	Aqueous Degreasing	
OW3	Machining	81.8
	Impact Deformation	
	Chemical Conversion Coating	
OW4	Grinding	46.6
	Impact Deformation	
	Machining	
	Alkaline Cleaning	
	Aqueous Degreasing	
	Solvent Degreasing	
	AVG % Removal =	50.4
	Median % Removal =	44.0

Table D-3. Chemical Emulsion Breaking with Oil/Water Separation

Table D-4 presents the data used to determine the percent TOC removal for ultrafiltration. Metal shaping unit operations are in **bold**.

Table D-4. Ultrafiltration

Episode	Unit Operations	%TOC Removal (Average)
UF1	Grinding	65
	Machining	
	Solvent Degreasing	
	Acid Treatment	
	Alkaline Cleaning	
UF2A	Impact Deformation	89.8
UF2B	Alkaline Cleaning	91.1
UF3	Grinding	94.9
	Machining	
	Acid Treatment	
	Alkaline Cleaning	
UF4	Machining	93.9
	Grinding	
UF5	Grinding	97.4
	Impact Deformation	
	Machining	
	Pressure Deformation	
	Acid Treatment	
	Alkaline Treatment	
	Solvent Degreasing	
UF6	Machining	59.3
	Grinding	
UF7	Machining	92.2
	Grinding	
	Impact Deformation	
UF8	Machining	11.2
	Acid Treatment	
	Alkaline Cleaning	
UF9	Machining	64.8
UF10A	Machining	36.2
UF10B	Machining	48.2
	AVG % Removal =	70.3
	Median % Removal =	77.4

Appendix E

EU RELEASE ESTIMATES FROM WASTEWATER TREATMENT

The EU Harmonisation of Environmental Emission Scenarios for Biocides used as Metalworking Fluid Preservatives (Product Type 13) estimates that the majority of releases from the use of metalworking fluids occurs from releases from wastewater treatment from dragout losses and spent metalworking fluids.

The EU provides two methods of estimating water releases, for emulsifiable metalworking fluids and water soluble metalworking fluids. These equations include terms to account for the degradation of biocides during the use phase. The user of the scenario may include the fraction when necessary. Equations E-1 and E-2 describe water releases for emulsifiable metalworking fluids:

$$Elocal_{water} = C_{proc,emul} * V_{proc,emul} * F_{form} / (F_{conc/water} * K_{OW}+1) * (1-F_{elim}) * (1-F_{degr})$$
[E-1]

$$C_{\text{proc,emul}} = (F_{\text{conc}} * \text{RHO}_{\text{MWF}}) / (1-F_{\text{conc}})$$

[E-2]

Where:

Elocal _{water}	=	Emission to wastewater (kg/day)
C _{proc} ,emul	=	Concentration of the chemical in the concentrated emulsifiable MW fluid (kg/m^3)
V _{proc,emul}	=	Treated volume of MW fluid (EU default = $200 \text{ m}^3/\text{day}$)
F _{form}	=	Fraction of MW fluid with chemical in treated volume (EU
		default = 1)
F _{conc/water}	=	Volume ratio of concentrate/water phase (dimensionless)
K _{OW}	=	Octanol/Water partition coefficient (dimensionless)
F _{elim}	=	Fraction of elimination of chemical during physical or chemical treatment (EU default = 0)
F_{degr}	=	Fraction of chemical degraded during industrial use (EU default $= 0$)
RHO _{MWF}	=	Density of MW fluid (EU default = $1,000 \text{ kg/m}^3$)
F _{conc}	=	Weight fraction of the chemical of interest in concentrate (dimensionless)

Equations E-1 and E-2 describe water releases for emulsifiable metalworking fluids:

$$Elocal_{water} = C_{proc,sol} * V_{proc,w.s} * F_{conc/water} * (1-F_{elim}) * (1-F_{degr}) * F_{form}$$
[E-3]

$$C_{\text{proc,sol}} = (F_{\text{conc}} * \text{RHO}_{\text{MWF}}) / (1 - F_{\text{conc}})$$
[E-4]

Where:

Elocal _{water}	=	Emission to wastewater (kg/day)
C _{proc,sol}	=	Concentration of the chemical in the concentrated emulsifiable
		MW fluid (kg/m ³)
V _{proc,w.s.}	=	Treated volume of MW fluid (EU default = $40 \text{ m}^3/\text{day}$)
F _{form}	=	Fraction of MW fluid with chemical in treated volume (EU
		default = 1)

F _{conc/water}		Volume ratio of concentrate/water phase (dimensionless)
K _{OW}	=	Octanol/Water partition coefficient (dimensionless)
F _{elim}	=	Fraction of elimination of chemical during physical or chemical treatment (EU default = 0.8)
F _{degr}	=	Fraction of chemical degraded during industrial use (EU default $= 0$)
RHO _{MWF}	=	Density of MW fluid (EU default = $1,000 \text{ kg/m}^3$)
F _{conc}	=	Weight fraction of the chemical of interest in concentrate (dimensionless)