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EMISSION SCENARIO DOCUMENT (ESD) ON INDUSTRIAL USE OF INDUSTRIAL CLEANERS

Series on Emission Documents
No. 33

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Series on Emission Scenario Documents
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IOMC
INTER-ORGANIZATION PROGRAMME FOR THE SOUND MANAGEMENT OF CHEMICALS
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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 release pathways of chemicals used in industrial cleaning, so as to help estimate the amounts of chemicals released into the environment.

This ESD should be seen as a living document that provides the most updated information available. As such, the ESD can be updated to take account of changes and new information. It can also be extended to cover industries in countries other than the lead country, Japan. Users of the document are encouraged to submit comments, corrections, updates, and new information to the OECD's Environment, Health and Safety Division (env.riskassessment@oecd.org). The comments received will be forwarded to the lead country so that the lead country can update the document. The comments will also be made available to users within the OECD web site (http://www.oecd.org/env/riskassessment).

How to use this document

The user of this ESD needs to consider how the information in the ESD covers the situation for which they wish to estimate releases of chemicals. The document can be used as a framework to identify the information needed, or alternatively the approaches in the document can be used together with the suggested default values to provide estimates. Where specific information is available, it should be used in preference to the defaults. At all times, the values inputted and the results should be critically reviewed to assure their validity and appropriateness.

How this document was developed

This ESD was produced mainly on the basis of Japanese data. The proposal to develop this ESD was approved by the OECD Task Force on Exposure Assessment (TFEA) in March 2011. The original document (with identical technical content) was created and published by the National Institute of Advanced Industrial Science and Technology, Japan, in December 2010.

In Japan, this ESD was created as a part of a NEDO (New Energy and Industrial Technology Development Organization) project entitled "*Development of Methodologies for Risk Trade-off Analysis towards Optimum Chemical Substance Management*" (2007–2011) (hereinafter referred to as "the RTA project"). The RTA project focuses on the trade-off of risks faced when one chemical is substituted for another for various reasons. Material substitution can be effective in reducing the risks inherent in the material to be replaced. However, selecting and substituting one material for another, if not done carefully, can introduce new risks. In some cases, the risk reduction afforded by the substitution is negated by new risks introduced by the new material. In other cases, the risk may in fact increase because of the substitution.

This ESD provides a method of estimating emission quantity in the absence of sufficient empirical data to support an analysis of the substitution of one industrial cleaner for another. It also aims to provide data on each parameter. Among scenarios that are highly likely to occur (as determined by analysing trends in the substitution of cleaning chemicals), possible combinations of currently used substances and their substitutes are focused. Changes in operating conditions and cleaning equipment due to the use of substitute materials are also examined.

Coverage

The cleaners targeted in this ESD are for use on metallic parts used in machinery and in various metal industries. The OECD has not published any ESDs that refer specifically to industrial cleaners. The OECD's Series No. 12 *Metal Finishing* is an ESD that corresponds to ours, but its primary focus is on surface-treatment processes such as plating, not on cleaning processes.

This ESD covers the use of chemicals in the industrial cleaning process. The industry categories relevant to this ESD are industrial category (IC) 4 (electrical/electronic industry) and IC 8 (Metal extraction, refining and processing). The seven industries targeted by this ESD are manufacture of iron and steel; manufacture of non-ferrous metals and products; manufacture of fabricated metal products; manufacture of general machinery; manufacture of electrical machinery, equipment, and supplies; manufacture of transportation equipment; and manufacture of precision instruments and machinery. Hereinafter these are referred to as "the seven industries."

The focal application is the cleaning of metallic parts (electrical and electronics parts, printed circuit boards, surface-mounted components, precise machining parts, automotive parts, and metal parts). In all seven industries, oil-based contaminants become attached to metallic parts and products during cutting, pressing and processing. The common feature of these processes is that these oil-based contaminants need to be removed (e.g. the parts need to be degreased) in the washing process. Also, chlorinated-type cleaners are being replaced by alternatives (e.g. aqueous or hydrocarbon types) within the abovementioned industries. For these reasons it was decided to categorize these seven industries as one group.

This ESD excludes the textile industry, the rubber and plastics industry, and the cleaning industry, even though these industries use industrial cleaners extensively, because the objects to be cleaned (shape, material quality and size), the components of the contaminants, and the cleaning equipment required differ markedly between these groups of industries and our seven-industry group. Also excluded from this ESD are households, even though they use large quantities of cleaners, because once again the objects to be cleaned, the types of contaminants, and the cleaning equipment differ from those used in our seven-industry group.

Also, in 2002, development of a British-focused ESD on Industrial Surfactants began, but it is currently focusing on the use of cleaners in industrial and mass cleaning (e.g. textile-processing, laundering, and dishwashing), construction, and emulsion polymerization. All three applications differ from the focus of this ESD; not only are the industries and application classifications considered in this ESD different, but also, unlike the British-focused ESD, this one considers cleaners substitution.

This document is published under 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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1 INTRODUCTION

1.1 Background

1. This Emission Scenario Document (ESD) was created as a part of a New Energy and Industrial Technology Development Organization (NEDO) project entitled "*Development of Methodologies for Risk Trade-off Analysis towards Optimum Chemical Substance Management*"(2007–2011) (hereinafter referred to as the RTA project). The term "risk trade-off" refers to a situation in which one chemical substance is substituted for another for reasons such as toxicity, but the initial risk is simply replaced by a new risk, resulting in zero net risk reduction.

2. The main goals of the RTA project are to analyse the nature of risk trade-off when one material is substituted for another, and to develop a systematic method that makes risk trade-off analysis possible. In order to analyse risk trade-off when a substance is being substituted for another, a method of estimating information such as emission quantity, amount of exposure, and toxicity without necessarily having enough data is necessary.

3. This ESD aims to provide a method of estimating emission quantity in the absence of sufficient empirical data to support an analysis of the substitution of one industrial cleaner for another, and to provide data on each parameter. Among scenarios that are highly likely to occur (as determined by analysing trends in cleaner substitutions), possible combinations of currently used substances and their substitutes, and changes in operating conditions and cleaning equipment due to the use of substitute materials are focused.[1]

1.2 Scope of the ESD and reasons for choosing this scope

4. This ESD can be an asset in risk trade-off evaluation in the substitution of industrial cleaners. The seven industries targeted for this ESD are manufacture of iron and steel; manufacture of non-ferrous metals and products; manufacture of fabricated metal products; manufacture of general machinery; manufacture of electrical machinery, equipment and supplies; manufacture of transportation equipment; and manufacture of precision instruments and machinery (hereinafter referred to as "the seven industries"). The focal application is the cleaning of metallic parts (electrical and electronics parts, printed circuit boards, surface-mounted components, precise machining parts, automotive parts, and metal parts). In all seven industries, oil-based contaminants become attached to metallic parts and products during cutting, pressing, and processing.

5. The common feature of these processes is that these oil-based contaminants need to be removed (e.g. the parts need to be degreased) in the washing process. Also, chlorinated-type cleaners are being replaced by alternatives (e.g. aqueous or hydrocarbon types) within the abovementioned industries. For these reasons it was decided to categorize these seven industries as one group. This ESD excludes the textile industry, the rubber and plastics industry, and the cleaning industry, even though these industries use industrial cleaners extensively, because the objects to be cleaned (shape, material quality, and size), the components of the contaminants, and the cleaning equipment required differ markedly between these

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[1] Refer to Appendix C for trends in the substitution of chlorinated-type cleaners in Japan.

groups of industries and our seven-industry group. Also excluded from this ESD are households, even though the quantities of cleaners used are high, because once again the objects to be cleaned, the types of contaminants, and the cleaning equipment differ from those used in our seven-industry group.

6. It is common practice to categorize cleaners into 5 separate categories: chlorinated hydrocarbon type (hereafter referred to as “chlorinated type”), halogenated hydrocarbon type (hereafter referred to as “halogenated type”, which includes brominated type and fluorinated type), hydrocarbon type, aqueous type, and semi-aqueous type. Study of these five types of cleaners provides a good understanding of the industries and applications discussed in this ESD.

7. Details of each cleaner are given in Chapter 2.

2 TYPES OF CLEANERS AND CLEANING EQUIPMENT AND THEIR CHARACTERISTICS

2.1 Use of Industrial Cleaners

8. Industrial cleaners are classified as shown in Table 2.1. Aqueous type, semi-aqueous type, and non-aqueous type are the basic classifications. Classifying non-aqueous-type cleaners is difficult, particularly when considering applications and emissions, because of the wide variety of these cleaners available. Therefore, non-aqueous-type cleaners have subdivided into smaller groups and only the major characteristics and components of each group were considered.

Table 2.1 Cleaner classifications

Classification (type)			Property or component		Group classification
Non-aqueous	Non-flammable	Chlorinated hydrocarbon	Methylene chloride (dichloromethane) Trichloroethylene Tetrachloroethylene		Chlorinated type
		Fluorinated hydrocarbon	Hydrofluoroethers Hydrofluorocarbons Hydrochlorofluorocarbons Perfluorocarbons		Halogenated type
		Brominated hydrocarbon	n-propyl bromide (1-bromopropane)		
	Flammable	Hydrocarbon	n-paraffin Isoparaffin Naphthene Aromatic		Hydrocarbon type
		Alcohol	Isopropyl alcohol (IPA) Methanol, ethanol, others		
		Other	Silicon Terpene		
Aqueous	Alkaline		Inorganic alkaline Organic alkaline		Aqueous- type
	Neutral				
	Acidic		Inorganic acid Organic acid		
Semi-aqueous			Nonflammable	Glycol ether n-methylpyrrolidone (NMP)	Semi-aqueous type
			Flammable	Terpene Hydrocarbon type Silicone	

Note: Japan Industrial Conference on Cleaning (JICC) (1999a, 2001a, 2009), Mizuho Information & Research Institute (MIRI) (2009)

9. The total usage of industrial cleaners in Japan is about 100 000 tonne/year (Table 2.2). Chlorinated cleaners account for 36% of the total, aqueous cleaners for 32% and hydrocarbons for 23%.

Table 2.2 Industrial cleaner usage by manufacture in Japan (tonne/year) (2007)

Substance name	Iron & steel	Non-ferrous metals & products	Fabricated metal products	General machinery	Elec. mach., equipment & supplies	Transportation equipment	Precision instruments & mach.	Total
Chlorinated								
Dichloromethane	9	1 835	10 041	1 893	3 187	56	1 835	18 856
Trichloroethylene	1 334	958	3 183	1 996	3 183	2 373	2 145	15 172
Tetrachloroethylene	505	194	557	287	379	285	194	2 401
Subtotal	1 848	2 987	13 781	4 176	6 749	2 714	4 174	36 429
Hydrocarbon								
n-Paraffin type	216	1 326	1 402	950	1 378	1 313	1 417	8 002
Isoparaffin type	7	3	1 668	433	822	1 468	832	5 233
Naphthene type	509	691	2 705	1 541	771	3 768	8	9 993
Other hydrocarbon	0	0	57	78	96	74	129	434
Subtotal	732	2 020	5 832	3 002	3 067	6 623	2 386	23 662
Semi-aqueous								
Glycol ether admix.	0	0	71	1	2 414	82	651	3 219
n-Methylpyrrolidone admixture	0	0	0	0	7	0	3	10
Terpene admixture	0	0	0	0	0	1	0	1
Hydrocarbon admix.	9	9	19	0	19	0	0	56
Other semi-aqueous	0	0	0	0	0	0	0	0
Subtotal	9	9	90	1	2 440	83	654	3 286
Aqueous								
Alkaline	12 961	278	1 379	1 723	2 606	4 752	1 264	24 963
Neutral	22	144	1 059	1 124	2 273	1 636	915	7 173
Acidic	62	127	76	12	21	30	44	372
Other aqueous	0	0	1	0	12	0	0	13
Subtotal	13 045	549	2 515	2 859	4 912	6 418	2 223	32 521
Halogenated								
HFC (fluorinated)	8	8	0	8	153	37	332	546
HFE (fluorinated)	8	8	0	8	164	83	160	431
HCFC-225 (fluo.)	30	12	118	59	177	59	236	691

HCFC-141b (fluo.)	52	0	603	323	343	0	343	1 664
n-Propylbromide (brominated)	0	0	67	0	534	332	862	1 795
Other halogenated	0	0	0	0	0	0	0	0
Subtotal	98	28	788	398	1 371	511	1 933	5 127
Total	15 732	5 593	23 006	10 436	18 539	16 349	11 370	101 025

Sources: Ministry of Economy, Trade and Industry, Japan and Ministry of the Environment, Japan (METI and MoE) (2009) for chlorinated types; MIRI (2009) for other types.

2.2 Composition and characteristics of cleaners

10. After being allocated to groups, industrial cleaners were organized by composition and characteristics for each detailed category.

11. The characteristics considered included general properties, cleaning performance (e.g. drying characteristics and penetrability), environmental performance (effect on environment and recyclability), legislation, solvent attack of objects to be cleaned, cost, contaminants to be removed, and cleaning processes and objects.

12. Some aqueous, semi-aqueous, and hydrocarbon-type cleaners are composed of mixtures of unknown substances. In order to determine the physical properties of these cleaners, an industrial cleaner list (Japan Industrial Conference on Cleaning (JICC), 1999a) that lists the characteristics of each product was analysed for substance behaviour and conditions of use.

2.2.1 Chlorinated-type cleaners

13. Table 2.3 gives the sub-categories and characteristics of chlorinated-type cleaners. Methylene chloride (dichloromethane), trichloroethylene and tetrachloroethylene are the three types of chlorinated-type cleaners currently in use. They have characteristics such as non-combustibility, high Kauri-butanol ((Kb) value[2], strong solvent power, low viscosity, low surface tension, high osmotic strength, potential for use in vapour washing because of their high vapour density, and potential for reuse of their waste solutions through distillation. They are conventionally used for degreasing.

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[2] An index used to indicate the performance of organic solvents

Table 2.3 Sub-categories and characteristics of chlorinated-type cleaners

Cleaner	Characteristics	Targeted contaminants	Objects to be cleaned	Field of use
Methylene chloride (dichloromethane)	・Have been used as cleaners for a long time ・Low cost ・Non-combustible ・Good cleaning performance at low temperature ・Vapour washing possible ・Dissolves organic substances well ・Good penetrability ・Good drying characteristics ・Waste liquid can be recovered through distillation and reused ・Toxicity is well known. Designated as PRTR (Pollutant Release and Transfer Register) Class I Designated Chemical Substances and regulated by various regulations	・Machine contaminants, machining oils, etc.	・Machines, electrical and electronic parts	・Degreasing before and after processing
Trichloroethylene				
Tetrachloroethylene				

Sources: JICC (1999a, 2001a, 2009) and MIRI (2009)

2.2.2 Halogenated-type cleaners

14. This document groups fluorinated and brominated types cleaners together as “halogenated-type cleaners”; chlorinated-type cleaners are used so commonly that they are categorised of their own. Table 2.4 shows the characteristics of halogenated-type cleaners. Halogenated-type cleaners can be largely divided into brominated- and fluorinated-type cleaners.

15. Fluorinated-type cleaners can be further subdivided on the basis of the materials used. They have non-combustibility and good drying characteristics. Fluorinated-type cleaners have ozone-depletion potential and/or global warming potential (table2.4).

16. Brominated-type substances may use n-propylbromide (1-bromopropane). This substance has a high Kb value, much like those of chlorinated-type substances, and has high solvent power, low viscosity, low surface tension, and high osmotic strength. Many brominated-type cleaners are recycled, or their waste solutions are recovered by the manufacturers of these cleaners. More toxicity data-gathering and evaluation are required, because little is known about the toxicity of these substances.

Table 2.4 Sub-categories and characteristics of halogenated cleaners

Cleaner		Characteristics		Targeted contaminants	Objects to be cleaned	Field of use, etc
Fluorinated	HFEs	・Expensive ・Waste liquid can be recovered through distillation and reused ・ Noncombustible ・Good drying characteristics ・Toxicity of some components not known (testing incomplete) ・Vapor washing possible	・Comparatively low degreasing power ・Often used for rinse or precision washing ・Sometimes used as co-solvent after washing with other cleaners, in addition to use by itself ・Zero ozone-depletion potential ・Comparatively low global warming potential	Machining oil, dust, etc.	Machines, metallic parts, etc.	Degreasing, finishing
	HFCs					
	HCFCs		・High degreasing power ・Low boiling point, and volatile (tends to have large losses) ・Comparatively high ozone-depletion potential and global warming potential			
	PFCs		・Low degreasing power ・Used as rinse and drying agent ・Zero ozone-depletion potential ・High global warming potential			
Brominated	n-propyl bromide (1-bromopropane)		・Similar usage as DCM, TCE, PCE			

TCE, trichloroethylene; DCM, dichloromethane: PCE, tetrachloroethylene.

Sources: JICC (1999a, 2001a, 2009) and MIRI (2009)

2.2.3 Hydrocarbon-type cleaners

17. Hydrocarbon-type cleaners can be largely divided into paraffin (normal-, iso-), naphthene, and aromatic. They are flammable and are thus governed by Fire Service Act regulations on their storage and use. Cleaning equipment used with these substances must be designed to be explosion proof. The solubility parameters of hydrocarbon-type cleaners are similar to those of mineral-type machine oils. The cleaners are close to being chemically neutral and have little interaction with most metals. Hence, they are often used for degreasing of metallic products, including non-ferrous metals. Also, the large difference in boiling point between the cleaners and the contaminants they are used to treat allows recycling of the cleaners through distillation. Generally, additives are not used, but surfactants etc. may be added, depending on the contaminant to be removed. Table 2.5 shows the types of hydrocarbon-type cleaners and their major characteristics.

Table 2.5 Sub-categories and characteristics of hydrocarbon-type cleaners

Cleaner	Main component (example)	Characteristics	Solubility[1]	Targeted contaminants	Objects to be cleaned	Field of use, etc.
n-paraffin	(n-decane)	・Generally used without additives, but sometimes used with surfactants and additives. ・Solubility close to those of mineral-based machining oils. Good solubility and permeability performance ・Distillation recycling possible ・Little interaction with metals ・Flammable, regulated by Fire Service Act	Low	・Oils for machining (press oils, cutting oils, anti-corrosion oils, etc.)	・ Sheet steel, automotive and machine parts, electrical and electronics parts	・Degreasing in metallic processing
Isoparaffin	(isohexane, isooctane, isododecane)					
Naphthene	(cycloparaffin)		↕	・Oils for machining (press oils, cutting oils, anti-corrosion oils, etc.)	・ Automotive and precision machines, general machines, metal and plastic parts of electrical and electronics equipment (printed substrates, car bumpers)	・Degreasing before and after processing
Aromatic	(1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene)		High	・Various machine oils, waxes, fluxes, etc.	・ Metallic parts (needs erosion testing for plastic parts)	・Degreasing after processing ・Wax, and flux removal

1 Cleaners are listed in ascending order of solubility.

Sources: JICC (1999a, 2001a, 2009), Mizuho Information & Research Institute (2009)

18. To determine the properties of hydrocarbon-type cleaners, 51 products were reviewed out of 135 non-aqueous-type cleaners listed as industrial cleaners (JICC (1999a)) of the hydrocarbon type and used only with hydrocarbon-type organic solvents (e.g. without mixing). Analysis categories were their (1) properties (specific gravity, ignition point, surfactant), and (2) use conditions (cleaning temperature).

2.2.3.1 Behaviour of hydrocarbon-type cleaners

2.2.3.1.1 Specific gravity

19. Table 2.6 shows the specific gravities of 52 hydrocarbon-type cleaners, as well as the numbers of cleaners in each range of specific gravities and ignition points. Note that approximately 95% of the cleaners had specific gravities of 0.7 or higher and under 0.9. This point supports the result of interviews stating that it is difficult to determine limits of use from changes in specific gravity, because hydrocarbon-type cleaners and their target contaminants (e.g. machining oils) have similar specific gravities.

Table 2.6 Specific gravities of hydrocarbon-type products

Specific gravity	<0.7	0.7–<0.8	0.8–<0.9	0.9–<1.0	1.0–<1.1	≥1.1	Not listed	Total
Number of products	1	34	15	1	0	0	1	52
Ratio	1.9%	65.4%	28.8%	1.9%	0.0%	0.0%	1.9%	100.0%

2.2.3.1.2 Ignition point

20. Table 2.7 shows the ignition points of the 52 hydrocarbon-type cleaners. Less than 20% of the products had ignition points of 85 ºC or above. This supports the general requirement that equipment used with hydrocarbon-type cleaners needs to be explosion proof.

Table 2.7 Ignition points of hydrocarbon-type products

Ignition point °C	<21	21–<40	40–<55	55–<70	70–<85	≥85	Not listed	Total
Number of products	2	4	20	5	11	9	1	52
Ratio	3.8%	7.7%	38.5%	9.6%	21.2%	17.3%	1.9%	100.0%

2.2.3.1.3 Use of surfactants

21. Only one product out of 52 hydrocarbon-type cleaners had surfactant added. This indicates that hydrocarbon-type cleaners are generally used without additives.

2.2.3.2 Use temperature

22. Table 2.8 shows the use temperatures of hydrocarbon-type cleaners. Multiple use temperatures are listed for 26 products. Therefore, the total number of products listed in Table 2.8 includes some

products with multiple operating temperatures. Over 90% of products had use temperatures of ≤60 ºC to prevent explosion. Of the 52 products, three had no listed operating temperature and 26 had two or more listed temperature ranges.

Table 2.8 Use temperatures of hydrocarbon type products

Temperature °C	<25	25–<40	40–<60	60–<80	≥80	Total
Number of products	24	31	20	5	1	81
Ratio	29.6%	38.3%	24.7%	6.2%	1.2%	100.0%

2.2.4 Aqueous-type cleaners

23. Aqueous-type cleaners use water as a solvent. Their action against contaminants is as follows:

i) Surface-activation effects as a result of the contaminants being scattered, emulsified, and solubilized into the water because of permeation between the contaminant and the object to be cleaned, along with a reduction in the surface tension of the water and the oil-based contaminants;

ii) Prevention of scattering of contaminants into water owing to the generation of electrostatic repulsion on the contaminants by negative charging of the particle surfaces, and prevention of the particles from re-attaching to the objects to be cleaned.

24. Table 2.9 gives the details and characteristics of aqueous-type cleaners. The cleaners can be largely divided into alkaline, neutral and acidic in terms of the properties of their main components. Alkaline cleaners may use a building effect (e.g. enhancement of the effectiveness of surfactants) to clean or to degrade contaminants that require removal.

25. The main components of neutral cleaners are surfactants. They exhibit good cleaning performance against oil-based contaminants because the composition of the surfactants can be controlled relatively freely to remove various contaminants. They also show little corrosion of various metals.

26. Acidic cleaners are often used to remove scale formed from calcium ions or rust in pipes by chemical reactions (e.g. degradation and dissolution). Sometimes they are used to form a protective coating on metal surfaces in processes involving phosphate.

27. Other components of aqueous-type cleaners include anti-corrosion agents, anti-foaming agents and chelating agents for capturing and removing metal ions.

28. The ratio of these components to water varies depending on the product. The liquid concentrates that are supplied to customers are often diluted before use.

29. To determine the characteristics of commercially available aqueous-type cleaners, a total of 172 products from 32 companies (1 to 14 products per company) as listed by JICC (1999a) were analysed. Note that the listed numbers do not reflect sales or manufacturing volumes. Instead, the parameters are the numbers of different brands of the products that are commercially available. Hence, these values should help in understanding trends in the uses and characteristics of the cleaners.

30. Analysis categories were (1) product family, (2) trends in components (surfactants, organic solvents, builders, water content), and (3) concentration and recommended temperature for use.

Table 2.9 Sub-categories and characteristics of aqueous-type cleaners

Cleaner		Main component (example)	Other components	General characteristics	Other characteristics	Targeted contaminants	Objects to be cleaned	Field of use, etc.
Alkaline	Inorganic alkaline	・Inorganic salt (sodium hydroxide, potassium hydroxide, silicate sodium, sodium carbonate, sodium phosphate) ・Water		・Inexpensive ・Noncombustible ・Not very toxic ・Little effect on polymers ・Requires wastewater treatment equipment ・Cannot be reused ・Does not penetrate well into small areas ・Slow to dry ・Long process required	・Utilizes scattering effect of contaminant particles by alkaline water solution ・Corrosive against metals	Cutting oil, rolling oil, machining oil, polishing powder, cutting powder	Steel sheet, wire, metallic parts, glass	・Preprocessing for plating and painting of metals ・Cleaning of metal parts
	Organic alkaline	・Organic salt (alkanolamine) ・Water	・Surfactant ・Organic chelator (polyphosphoric acid) ・Solvent ・Anti-corrosion agent		・Can gain building effect of alkaline by use with surfactant ・No residue of salt of metal ・Corrodes metals			
Neutral		・Surfactant (nonionic, anionic, amphoteric) ・Water	・Builder (sodium carbonate, silicate sodium) ・Chelating agent (polyphosphate, polycarboxylate) ・Aqueous solvents (glycol ether, alcohol) ・Anti-foaming agent (silicone oil, mineral oil) ・Anti-corrosion		・Washing by solubilization, scattering, and emulsification of surfactant ・Not very corrosive to metals	Machining oil, pitch, liquid crystal, wax	Precision parts, aluminium parts, liquid crystal panels, optical lenses	

			agent (organic acid salt, benzotriazole)					
Acidic	Inorganic acid	・Inorganic acid (sulfuric acid, hydrochloric acid, phosphoric acid, nitric acid) ・Water	・Surfactant ・Anti-corrosion agent		・Washing by degradation and dissolution of chemical reactions ・Corrodes metals	Rust, calcium ions	Steel sheet, wire, pipes, heat exchangers	・Scale removal ・Preprocessing for plating, chemical conversion treatment, and painting
	Organic acid	・Organic acid (citric acid, glycolic acid, sulfamic acid) ・Water						

Sources: JICC (1999a, 2001a, 2009) and MIRI (2009)

2.2.4.1 Families of aqueous-type cleaners

31. Figure 2.1 shows the proportions of acidic, alkaline and neutral aqueous-type cleaners sold commercially. The basis of this categorization comes from pH values listed by JICC (1999a). If a cleaner's pH was 6 or less, it was classified as acidic; if over pH 6 and under 8, it was classified as neutral; and if 8 or more it was classified as alkaline. With this categorisation, approximately 2/3 of 172 products were alkaline. Only about 1% of the products were classified as acidic.

Figure 1.

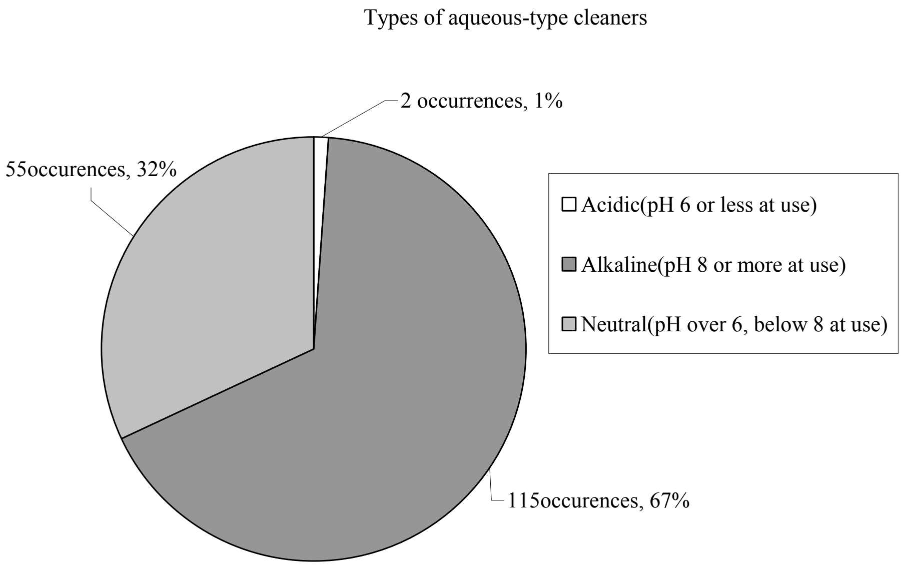

Figure 2.1 Types of aqueous-type cleaners

2.2.4.2 Components of aqueous-type cleaners

2.2.4.2.1 Surfactants

32. Table 2.10 shows the numbers of products that contain surfactants (per type). Less than 5% of the products did not contain surfactants. Of the 172 products, 89% contained nonionic-type surfactants.

Table 2.10 Numbers of products that contain surfactants (per type)

Surfactant	Number of occurrences	Occurrence as a percentage of the number of products
Includes anionic type	64	37.2%
Includes nonionic type	153	89.0%
Includes cationic type	3	1.7%
Includes zwitterionic type	6	3.5%
Not included	8	4.7%
No answer	4	2.3%
Total occurrences	238	138.4%

2.2.4.2.2 Organic solvents

33. Table 2.11 shows the numbers of aqueous-type cleaners that contain organic solvents (per type). Approximately 60% of all products did not contain organic solvents. If organic solvents were present, they tended to be glycol or glycol ether series; about 30% of the 172 products contained these.

Table 2.11 Numbers of products containing organic solvents (per type)

Organic solvent component	Number of occurrences	Occurrence as a percentage of the number of products
Includes hydrocarbon type	1	0.6%
Includes alcohol type	9	5.2%
Includes glycol/glycol ether type	48	27.9%
Includes terpene type	0	0.0%
Others	4	2.3%
Does not include organic solvent	106	61.6%
No answer	6	3.5%
Total occurrences	174	101.2%

2.2.4.2.3 Builders

34. Components that enhance the effectiveness of surfactants are called builders. Table 2.12 shows the numbers of aqueous-type cleaners that contained builders (per type). Approximately 30% of the cleaners (this figure includes those cleaners for which there was no builder-related information) did not contain builders. The rest (70%) of the products contained some sort of builder.

Table 2.12 Numbers of products containing builders (per type)

Component	Number of occurrences	Occurrence as a percentage of the number of products
Includes organic builder	68	39.5%
Includes inorganic builder	84	48.8%
Does not include builder	42	24.4%
No answer	6	3.5%
Total occurrences	200	116.3%

2.2.4.2.4 Water content

35. Figure 2.2 shows the percentage water contents of products. Products that contained 50% to 90% water were most common; 60% of products had water contents in this range.

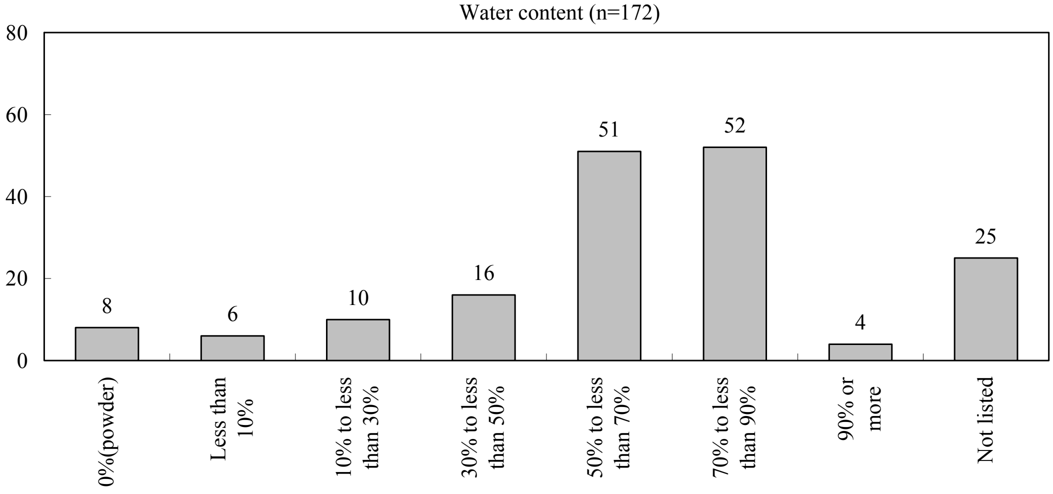

Figure 2.2 Percentage water contents of aqueous-type cleaners

2.2.4.3 Use conditions of aqueous-type cleaners

2.2.4.3.1 Concentration of cleaners within cleaning solutions

36. Cleaners are often diluted before use. Figure 2.3 shows the percentage concentrations of aqueous-type cleaners within cleaning solutions at the time of use. The arithmetic mean was 14.2% and the geometric mean was 6.7%.

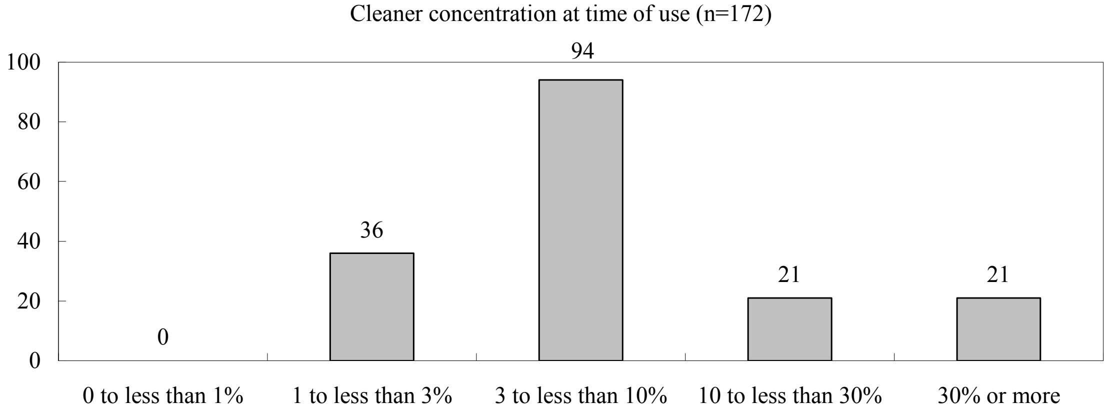

Figure 2.3 Percentage concentrations of aqueous-type cleaners within cleaning solutions at the time of use

2.2.4.3.2 Cleaning solution temperature

37. One hundred and sixty-six products were left by excluding products for which there was no temperature information and products for which there were no limitations on the use temperatures. The use temperature arithmetic mean was 53.5 ºC; the geometric mean was 51.9 ºC; the maximum temperature was 80 ºC; and the minimum temperature was 25 ºC.

2.2.5 Semi-aqueous-type cleaners

38. Table 2.13 shows types of semi-aqueous-type cleaners and their characteristics. Compositions of semi-aqueous-type cleaners vary depending on the product, but they can be largely divided into flammable and non-flammable cleaners. Flammable-type cleaners are solvent-based and contain water-soluble solvents and surfactants so that they can be washed off with water; the cleaning process may therefore include washing with a cleaner (non-aqueous type) and then rinsing with water. Non-flammable cleaners contain water-compatible solvent mixed with a small amount of water to make them non-flammable. If surfactants are not present, the cleaning process may not require rinsing with water.

39. According to the literature (JICC 1999a, 2004) and interviews conducted with cleaner manufacturers, glycol ether solution seemed to be the solution most commonly used for semi-aqueous-type cleaners.

40. The list (JICC 1999a) of 80 industrial cleaners was analysed for (1) trends in components (surfactants, organic solvents, builders and water content ratio) and (2) use conditions (cleaner concentration at use and temperature) in order to estimate the representative properties of semi-aqueous-type cleaners.

Table 2.13 Sub-categories and characteristics of semi-aqueous-type cleaners

Cleaner		Main component (example)	Other components	Characteristics	Targeted contaminants	Objects to be cleaned	Fields of use, etc.
Nonflammable (small amount of water present in cleaner)	Glycol ether	Diethylene glycol ether, propylene glycol ether.	Surfactant, water	・Good solubility for polar contaminants	Flux, wax, solder masks, marking ink, conductive derivatives, resistive paste, general oils, heavy oils	Electrical and electronics parts, metal parts	Degreasing
	n-methylpyrrolidone (NMP)	n-methylpyrrolidone	Water, builder	・No ignition point ・Organic solvent compatible with water	Cutting oil, machining oil, fingerprints, resin	Metal parts	Degreasing
Flammable (washing with non-aqueous type, rinsing with water)	Terpene	Terpene (d-limonene)	Surfactant	・Good cleaning performance at room temperature ・Biodegradable	Rosin flux	Electrical and electronics parts	Removal of contaminants
	Hydrocarbon	Paraffin-type solvent Isoparaffin-type solvent Naphthene-type solvent Aromatic-type solvent	Surfactant, water	・Good solubility, good penetrability ・Flammable ・Washes by the solubility of the organic solvent ・ Select materials with solubility for targeted contaminants	Mineral oil, grease, wax, mold lubricant	Metal parts	Degreasing, removal of contaminants
	Silicone	Low-molecular-weight silicone (volatile siloxane)	Water	・Good drying characteristics		Optical parts such as lenses, metals, ceramics, plastics	Cleaning, drying

Sources: JICC (1999a, 2001a, 2009) and MIRI (2009)

2.2.5.1 Components of semi-aqueous-type cleaners

2.2.5.1.1 Solvents

41. Figure 2.4 shows the solvents used in semi-aqueous-type cleaners. Five products from a total of 80 products did not contain solvents. The remaining cleaners contained some kind of solvent (12 products contained two types of solvents). The most common solvents used were glycol and glycol ether types; 70% of the products that contained solvents used them. Glycol-ether-type solvents were the most common. These results were consistent with the results of interviews conducted with the cleaner manufacturers.

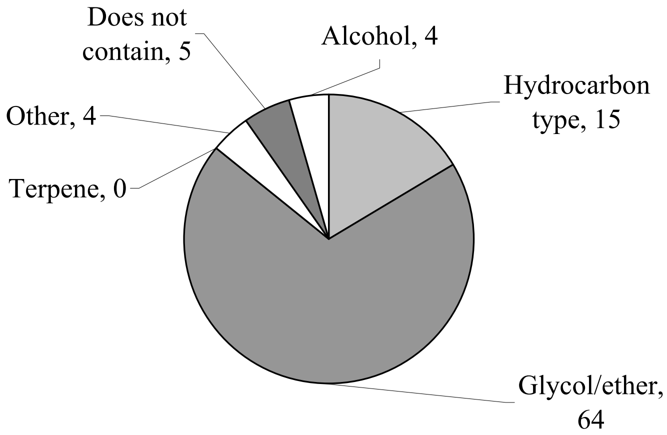

Figure 2.4 Types of solvents used in semi-aqueous-type cleaners

Ehftqd rgnvr sgd mtladq ne oqnctbsr hm sgd bnqqdronmchmf sxod-

2.2.5.1.2 Surfactants

42. Table 2.14 shows the numbers of each type of surfactant used in semi-aqueous-type cleaners. Approximately 50% of products did not include surfactants. Unlike the case with aqueous-type cleaners, 95% of which contained surfactants, it can be supposed that semi-aqueous-type cleaners contain surfactants not as the main component, but only as secondary components added to target specific contaminants.

Table 1. Table 2.14 Use of surfactants in 80 semi-aqueous-type cleaners

Type of surfactant	Number of products in which used
Anionic type	3
Nonionic type	30
Not included	43
No answer	6
Total	82

Note: Two products used two types of surfactant.

2.2.5.1.3 Builders

43. Figure 2.5 shows the numbers of cases in which builders were used in semi-aqueous-type cleaners. Of the 80 products, 69 (86%) did not contain builders. Products that contained surfactants rarely contained builders as well.

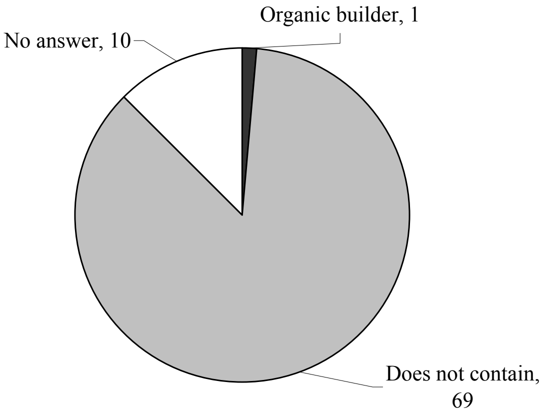

Figure 2.5 Numbers of semi-aqueous-type cleaners containing builders

2.2.5.1.4 Percentage water contents

44. Figure 2.6 shows the percentage water contents of semi-aqueous-type cleaners. About 80% of the 80 products had water contents above 1% but below 30%.

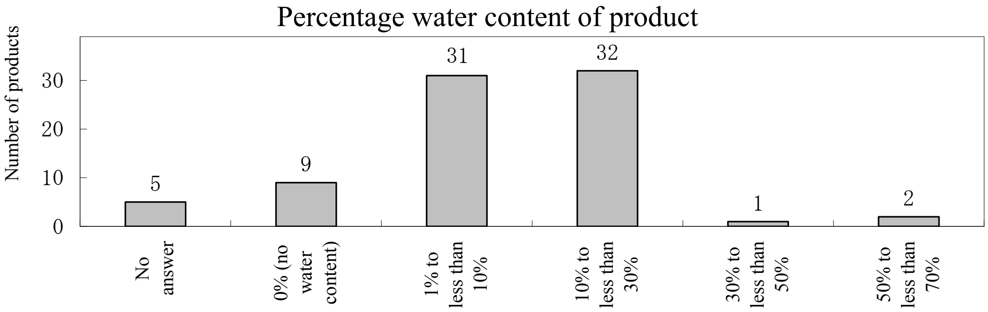

Figure 2.6 Percentage water contents of semi-aqueous-type cleaners

2.2.5.2 Use conditions

2.2.5.2.1 Concentration of cleaners within cleaning solutions

45. Figure 2.7 shows the concentrations of semi-aqueous-type cleaners in cleaning solutions at the time of use. Seventy-one products (89%) were used without dilution.

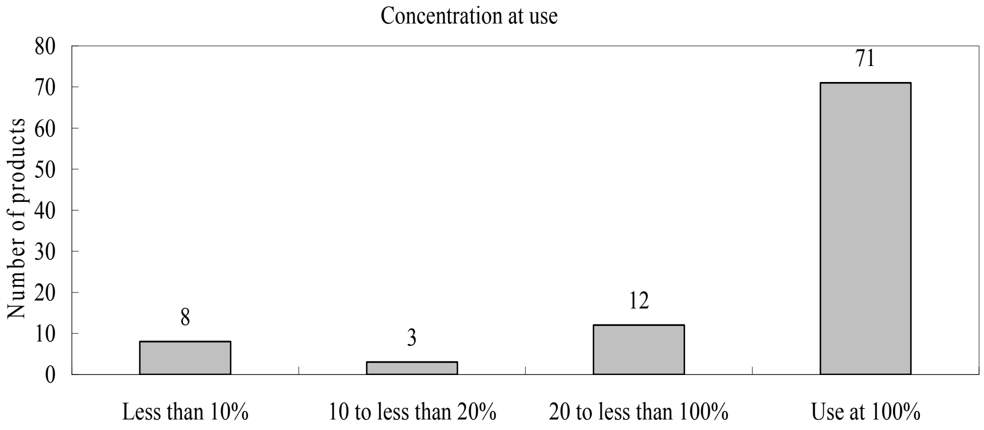

Figure 2.7 Concentrations of semi-aqueous-type cleaners in cleaning solutions at time of use

"Concentration at use" means the unit amount of the stock concentrate as a percentage of that of the cleaning solution. Whether this is by weight or by volume is unknown.

2.2.5.2.2 Cleaning solution temperature

46. The product reference materials listed use temperatures. Figure 2.8 shows the numbers of products in each temperature class. Operating temperatures were listed for all 80 products. Because two or more temperature classes were listed for 27 products, the grand total came to 118. Fifty-two products (44%) fell in the temperature class range of 40 to 60 ºC.

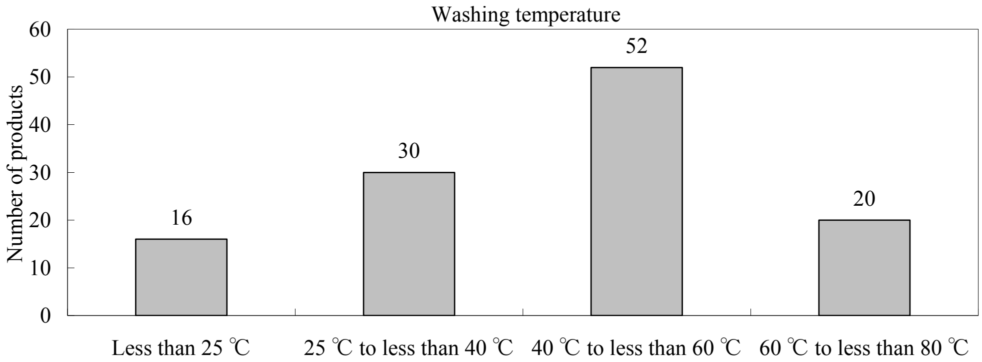

Figure 2.8 Recommended temperatures for use of semi-aqueous-type cleaners

2.3 Substances used in cleaners, and their properties

47. The characteristics of cleaners are determined by the characteristics of the substances used in them. Properties like saturated vapour pressure are important factors in estimating emissions. If the name of the main component in each product is not listed in any of the available reference materials, in order to obtain suitable parameters similar to those of the actual main components of a cleaner, this ESD refers to data (e.g. on boiling points) that are available as part of the product information accompanying commercially available products.

48. Table 2.15 shows boiling point, density and saturated vapour pressure at near room temperature (25 ºC) for the substances presumed to be in each industrial cleaner group. For hydrocarbon-type products, it was assumed that there was one material for each carbon (C) contained in the structural formula if the substance names were not known. On the basis of interviews conducted with the manufacturers, for aqueous-type products, among the surfactants presumed to be the main components (section 2.2.4). Poly (oxyethylene) = alkyl ether (C = 12 to 15) (AE) was assumed the mainstream surfactant contained in industrial cleaners. For semi-aqueous type substances, glycol-ether-based solvents can be presumed to be the main components (section 2.2.5). Also, from interviews with cleaner manufacturers, the diethylene glycol type are considered to be mainstreamed. Fluorinated (halogenated) substances were assumed to be used in large quantities, as mentioned in Appendix A1 of this ESD.

Table 2.15 Examples of substances potentially used in each cleaner, and their properties

Cleaner		Example of material	Molecular formula	Molecular mass	Boiling point	Density (g/cm^3) at 25 °C	Saturated vapor pressure (Pa) at 25 °C	Key [7]
Hydrocarbon	Naphthene	cyclooctane	C_8H_{16}	112.2	151	0.83	721.1 [5]	HC-N-1
		n-propylcyclohexane	C_9H_{18}	126.2	157	0.79	558.6	HC-N-2
		n-butylcyclohexane	$C_{10}H_{20}$	140.3	181	0.80	175.2	HC-N-3
		1-cyclopentylhexane	$C_{11}H_{22}$	154.3	203	0.79	48.1 [5]	HC-N-4
		1-cyclopentylheptane	$C_{12}H_{24}$	168.3	224	0.81	14.6 [5]	HC-N-5
	Paraffin	n-nonane	C_9H_{20}	128.3	151	0.72	593.3 [5]	HC-P-1
		n-decane	$C_{10}H_{22}$	142.3	174	0.73	190.1	HC-P-2
		n-undecane	$C_{11}H_{24}$	156.3	196	0.74	54.9	HC-P-3
		n-dodecane	$C_{12}H_{26}$	170.3	216	0.75	18.1	HC-P-4
		n-tridecane	$C_{13}H_{28}$	184.4	235	0.75	7.4	HC-P-5
	Isoparaffin	isooctane (2,2,4-trimethylpentane)	C_8H_{18}	114.2	99	0.69	6576.8	HC-I-1
		isononane (2-methyloctane)	C_9H_{20}	128.3	143	0.71	830.1	HC-I-2
		isodecane (2-methylnonane)	$C_{10}H_{22}$	142.3	167	0.72	251.3	HC-I-3
	Aromatic	1,3,5-trimethylbenzene	C_9H_{12}	120.2	165	0.86	330.4	HC-A-1
Chlorinated		dichloromethane	CH_2Cl_2	84.9	40	1.32	57728.4	CL-1
		trichloroethylene	C_2HCl_3	131.4	87	1.46	9828.5	CL-2
		tetrachloroethylene	C_2Cl_4	165.8	121	1.61	2471.8	CL-3
Semi-aqueous		diethylene glycol monomethyl ether	$C_5H_{12}O_3$	120.1	194	1.02	24.0	SA-1
		diethylene glycol monobutyl ether	$C_8H_{18}O_3$	162.2	231	0.95	2.9	SA-2
Halogenated	Brominated	1-bromopropane	C_3H_7Br	123.0	71	1.35	18505.1	H-1
	Halogenated	HCFC-141b (1,1-dichloro-1-fluoroethane) [1]	$C_2H_3Cl_2F$	116.9	32	1.25 [3]	79993.2	H-2
Aqueous	Surfactant	poly (oxyethylene) = alkyl ether (C=12 to 15) [2]	Cm+2nH$_2$+2m+4nO$_1$+n	626.9		1.02 [4]	– [6]	-

Source: Yaws (1997), excluding [1] and [2]

[1] Hazardous Substances Data Bank (HSDB) (National Library of Medicine) database, http://toxnet.nlm.nih.gov/cgi-bin/sis/ htmlgen?HSDB

[2] National Institute of Technology and Evaluation (NITE) website, www.safe.nite.go.jp/risk/files/pdf_hyoukasyo/307riskdoc.pdf

[3] Density at 10 °C

[4] Specific gravity of C12(AE) at 20 °C

[5] Value calculated using the Antoine coefficient with Yaws (1997), even though the temperature is out of range

[6] Presumably liquid or solid at room temperature

[7] Key to Figure 2.9

49. Figure 2.9 shows the saturated vapour pressures (Pa) of each substance at 25 ºC. The figure does not include surfactants (aqueous type) that do not vaporize at room temperature. The figure indicates a tendency for chlorinated- and halogenated-type cleaners to vaporize more easily, and for semi-aqueous-type cleaners to vaporize less easily. Table 2.15 gives a key to identifying the chemical substances present in each cleaner.

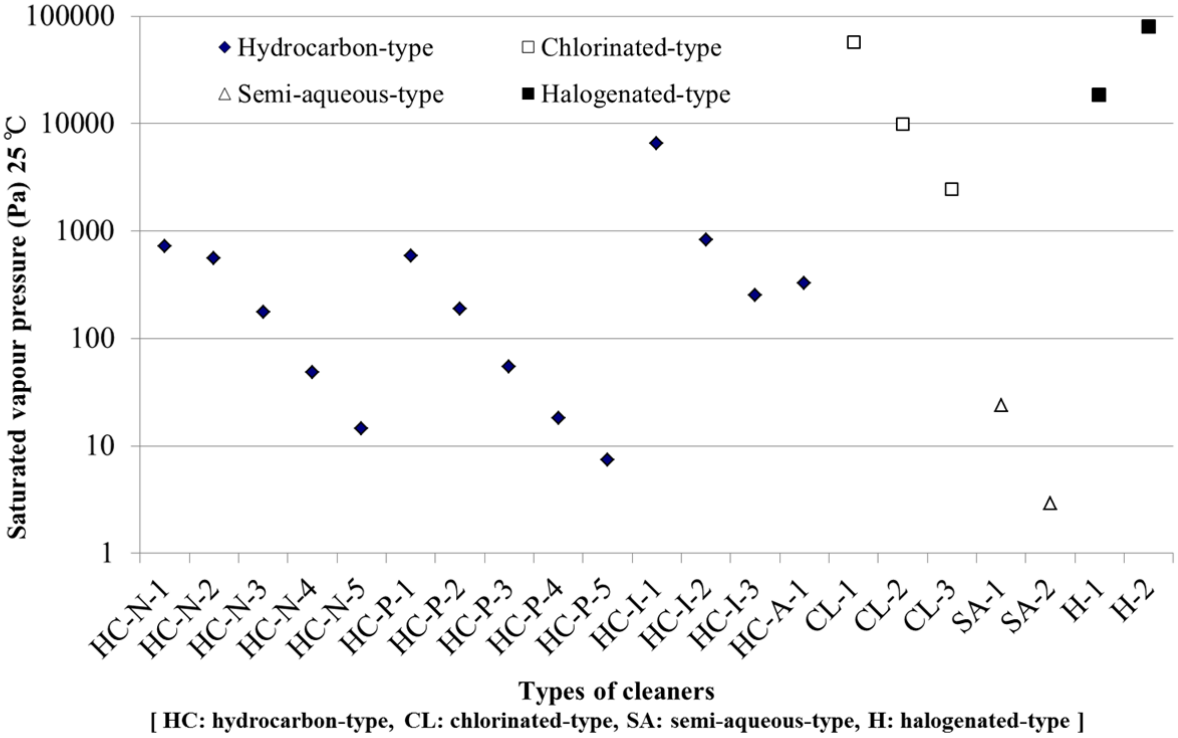

Figure 2.9 Examples of saturated vapour pressures (at 25 °C) of substances used in cleaners

50. Figure 2.10 shows saturated vapour pressure curves obtained for some of the substances listed in Table 2.15 by using Antoine coefficients A through E, shown in the work of Yaws (1997), with the Antoine equation;

$\log_{10} P = A + B / T + C \log_{10} T + D T + E T^2$

A, B, C, D, E: Antoine coefficients
P: atmospheric pressure (mm Hg)
T: temperature (K).

51. The figure shows that saturated vapour pressure curves can be used to calculate emissions from vaporizing cleaners at a given temperature.

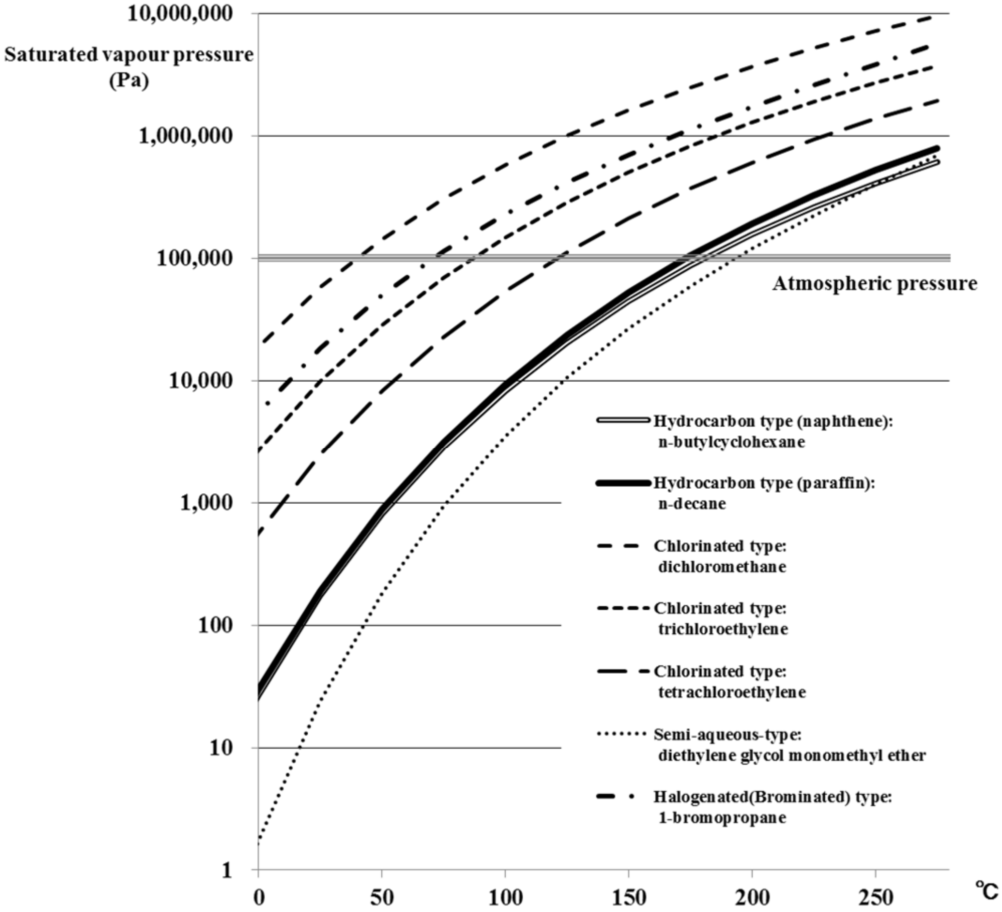

Figure 2.10 Vapour pressure curves of some of the substances used in each type of cleaner

2.4 Types of cleaning equipment and their characteristics

52. Cleaning methods can largely be divided into wet cleaning which uses cleaning solution, and dry cleaning which uses particles, vapour and light. This ESD focuses on wet cleaning methods.

53. There are various ways to differentiate cleaning equipment, and it may therefore be difficult to systematically categorize all of them. In this section, the characteristics of each category of cleaning equipment are discussed. Names of cleaning equipment are given for each category. The categorization method was based on (1) the three basic types of cleaning process, namely washing, rinsing and drying with wet-type cleaning equipment; and (2) the overall cleaning system used; and (3) the cleaners used.

2.4.1 Categorization by cleaning method

54. The data listed in Table 2.16 were obtained from JICC (1999a); these are the factors fundamental to the cleaning methods used with wet-type cleaning equipment.

Table 2.16 Factors that contribute to cleaning

Factor		Action
Chemical	Solubility	Water, solvent
	Surface action	Surfactant
	Chemical reactivity	Acid, alkaline
Physical	Heat	Acceleration of reactions of cleaning factors, physical change in properties of contaminants, physical change in properties of objects to be cleaned
	Ultrasonication	Ultrasonic energy (shockwaves of several thousand MPa), cavitation, acceleration, separation of contaminants using rectilinear flow, scattering
	Pressurization	Acceleration of contaminant removal by spray energy (shower spray jet)
	Agitation (oscillation, rotation)	Agitation to accelerate contact between fresh cleaning solutions and the surface of the objects to be cleaned; enhanced efficiency of washing by uniformalisation; mechanical acceleration of separation of contaminants from the surfaces of objects to be cleaned Prevention of re-attachment of contaminants to the already cleaned surface by scattering and retaining contaminant into the cleaning solution
	Depressurization	Removal of contaminants by expanding them by allowing reduced-pressure solution to penetrate into hard-to-reach areas
	Polishing	Hand and machine polishing, or blasting to remove contaminants
	Frictional force	Acceleration of contaminant removal through scrubbing with brushes, etc.

Source: JICC (1999a) (partly altered)

55. Table 2.17 lists the characteristics of cleaning methods after their classification according to the physical properties given in Table 2.16. Cleaning methods can be classified into immersion type, by which the objects to be cleaned are immersed in a washing tank containing cleaning solution and non-immersion type, in which the objects to be cleaned are not immersed but spray-cleaned with the solution.

Table 2.17 Classification of cleaning methods

Cleaning method (equipment)			Overview	Cleaners primarily used	Characteristics
Immersion cleaning	Objects to be cleaned are put into washing tank with cleaners	Ultrasonic cleaning	Ultrasound generated in the washing tank.	Virtually all cleaners	Handles relatively small objects to be cleaned. Possible to wash complex shapes, narrow gaps, and grooves.
		Jet washing	Cleaning liquid made into a jet in the washing tank by a pump.	Aqueous type, semi-aqueous type, hydrocarbon type	Difficulty handling concave depressions in complex shapes.
		Oscillate (rotate) washing	The objects to be cleaned moved up and down or side to side, or spun around in a basket to give vigorous contact with the washing liquid.	Virtually all cleaners	Requires mechanisms for oscillation.
		Mechanical vibration stirring	A vibrating plate hung inside the washing tank is oscillated up and down.	Virtually all cleaners	Stable emulsion tends to form from the removed oily substance, making it difficult to separate oil and water.
		Bubble washing	Washing liquid is stirred by the ascending bubbles, which are formed by scattered jet.	Semi-aqueous type, some aqueous types	The simplest agitation mechanism, but the agitation effect is not very significant.
		Reduced-pressure (vacuum) washing	A washing technique that maintains a vacuum by pressure reduction inside the sealed washing tank.	Hydrocarbon type, semi-aqueous type, some aqueous types	Precision wash is possible because the cleaning liquid permeates well. Vacuum drying can be performed with this equipment.
Non-immersion cleaning	Washing liquid is applied to the objects to be cleaned	Jet (spray, shower) washing	Contaminants removed through the shock of liquid colliding with the objects to be cleaned as a jet.	Aqueous type, some semi-aqueous types (some fluorinated and chlorinated types with the shower method)	Possible to accommodate large objects but maintain a relatively simple structure.
		Steam washing (Vapour degreasing)	A washing technique that places the objects to be cleaned within air filled with solvent (cleaner) vapour.	Cleaners other than aqueous type and semi-aqueous type	Need explosion-proof provisions for flammable solvents.

Sources: JICC (1999b, 2004)

56. Table 2.17 assumes that each type of cleaning equipment uses one method of cleaning. In reality, many types of cleaning equipment use a combination of cleaning methods to suit the characteristics of the cleaning solution, the required cleanliness, the shapes and materials of the objects to be cleaned, and the characteristics of the targeted contaminants.

2.4.2 Examples of classification by system mechanism

57. Many names are used for referring to cleaning equipment, because such equipment is sometimes given names related to the shape of the cleaning tanks, the method of transportation of the objects to be cleaned, or other characteristics. Major system mechanism of equipment is explained below.

2.4.2.1 Closed-type cleaning equipment

58. This name is given to wet-type cleaning systems in which it is ensured that vaporized cleaning solutions do not leak to the outside of the cleaning equipment, particularly when cleaners with low boiling points are used. The term "closed-type cleaning equipment" refers to equipment that has mechanisms to prevent this leakage. These mechanisms may include the use of cooling coils, a lid for the top of the cleaning tank, a buffer zone to prevent contact between the cleaning solution and the outside of the equipment, and mechanisms to recover vaporized cleaners. This type of system is the opposite of the open-type cleaning system.

2.4.2.2 Co-solvent cleaning equipment

59. This cleaning system uses two types of cleaner, namely one with a good contaminant removal performance as a cleaner, and another with good drying characteristics as a rinsing agent.

2.4.2.3 Batch cleaning system

60. In this system, washing, rinsing and drying are all conducted in the one tank. Washing is done by supplying pre-cleaning solution, finishing solution, etc., to the washing tank. This system is used in places where available space may be limited.

2.4.2.4 Other systems

61. Other systems include de-aerating cleaning, direct path cleaning, steam cleaning, supercritical cleaning, electrolytic cleaning and non-rinsing cleaning.

2.4.3 Example of classification based on cleaners used

62. Mentioned below are types of cleaning equipment named according to the cleaners used. Some of these types of cleaners have already been mentioned in this ESD. Note that these classifications are for the purpose of introducing and organizing the commonly used classifications of cleaning equipment.

2.4.3.1 Solvent-based cleaning equipment

63. This is a generic name for all cleaning equipment that removes contaminants by using a dissolving mechanism. They use cleaners other than aqueous type, semi-aqueous type, or non-aqueous type, excluding alcohol-type cleaners. The cleaners can be largely divided into two categories. One category of equipment uses flammable solvents (e.g. hydrocarbon type, silicone type, terpene type), and the other uses non-flammable solvents (e.g. chlorinated type, fluorinated type, brominated type). The design of the cleaning mechanisms and explosion-proof mechanisms differ depending on the type of cleaner used; this results in a diverse range of equipment.

2.4.3.2 Alcohol-based cleaning equipment

64. This is a generic name for cleaning equipment that uses various alcohols, including ethanol, methanol and Isopropyl alcohol (IPA) for cleaning. Ketones and esters have the same uses. A mainstream process would consist of wash (immersion, ultrasonic wash), rinse, finishing rinse and then dry. Sometimes the risk of flashing is lowered by using these substances as combined solvents with water (but only in the case of those that have low flash points and can therefore be mixed with water).

2.4.3.3 Aqueous-type cleaning equipment

65. In these cleaning systems, cleaners (alkaline, neutral and acidic) are diluted with water. These systems include processes that use moistening osmotic effects, emulsifying scattering, solubilisation and saponification to remove contaminants. The process finishes with rinsing with water. The components include washing, rinsing, drying and other auxiliary mechanisms. The system may be equipped with wastewater treatment and a purified water recycling system. For the washing mechanism itself, a spray wash (classified according to the method of transfer of the objects to be cleaned), ultrasonic wash and reduced-pressure ultrasonic wash may be used.

2.4.3.4 Semi-aqueous-type cleaning equipment

66. These cleaning systems use cleaners without diluting them and remove contaminants by dissolving them. This is generally followed with rinsing with water. The system varies depending on the cleaning solution’s main component and concentration. The system is equipped with a moisture meter for managing the concentration of the cleaning solution inside the washing tank, a concentration meter for measuring the concentration of the cleaner and the contaminants, and a conductance meter. Waste solution from rinsing passes through a distillation regeneration device, a pure water regeneration device, or a rinse water cleaning device and is not disposed of.

2.5 Types of auxiliary devices and their characteristics

67. In this section, parts of the cleaning systems are discussed. They do not directly clean but that may have significant impacts on cleaner use and on system emissions.

2.5.1 Dryers

2.5.1.1 Hot-air drying

68. This is a widely used process in which an air blower blows heated air onto the objects to be cleaned and elevates the temperature of the cleaning solution to dry the objects by evaporating the liquid. The temperature and the drying speed are approximately proportional to each other.

2.5.1.2 Reduced-pressure (vacuum) dryer

69. The cleaning solutions adhering to the objects to be cleaned are vaporized by creating a vacuum (reduced pressure) inside the drying chamber. The solutions are then sucked into the pump that is generating the vacuum. In this way, the cleaning solution continues to be vaporized to dry the objects to be cleaned. This method is suitable for cleaning blind holes and complex shapes because the objects to be cleaned are entirely under a reduced-pressure (vacuum) environment.

2.5.1.3 Vapour drying

70. The objects being cleaned are placed within the cleaner's vapour atmosphere. The cleaner is liquefied because the temperature of the surface of the objects to be cleaned is lower than that of the vapour. The liquefied cleaner then runs down the surface of the objects to be cleaned to give a finishing touch to the wash. The objects to be cleaned remain in the cleaner's vapour, and eventually the surfaces of the objects reach the same temperature as the vapour. At this point, the vaporized cleaner no longer liquefies on the surface of the objects, allowing the objects to be taken out "dry" from the system.

71. Other drying methods include indirect-heat drying, air blow-drying, spin drying, water displacement drying and radiant heat drying. Details of these drying methods are not given here. A particular drying method is selected on the basis of such considerations as the objects to be cleaned and the cleaners being used. In some cases, a dryer is used as a single unit, but in many cases multiple methods may be combined or dryers may be integrated as a part of a cleaning system.

2.5.2 Exhaust gas treatment devices

72. This device removes dust from the air, dirt components from the objects to be cleaned, water, and cleaner contained in the exhaust before exhausting to the outside of the establishment to protect the environment and ensure fire safety. Major exhaust gas treatment devices are briefly described below.

2.5.2.1 Burner device

73. If the concentration of flammable organic substances contained in the exhaust gas is high enough for combustion, the exhaust gas is led into a burner mechanism (e.g. a boiler) and then burned. Supplementary fuel (e.g. LPG) is often added to support burning.

2.5.2.2 Absorption device

74. A liquid that has the ability to absorb a targeted component contained within the cleaning equipment exhaust gas is used as a collection medium. The exhaust gas is allowed to come into contact with the absorption solution and becomes dissolved in the solution. The device then exhausts the gas, from which targeted substances have been removed by mist separation.

2.5.2.3 Activated carbon adsorption device

75. This device adsorbs emitted gases that contain a targeted substance with a packed bed that uses activated carbon as its adsorption material. Activated carbon has weaker polarity than many other adsorption materials. The system exhibits good adsorption performance to nonpolar materials (e.g. saturated hydrocarbon) compared with polar materials (e.g. water and alcohol). Performance is especially good for hydrocarbons with large carbon numbers.

2.5.3 Wastewater treatment devices

76. The term "wastewater treatment device" refers to a device or a facility that removes contaminated materials (e.g. cleaner components, dirt removed from the objects to be cleaned) from wastewater discharged from cleaning equipment that uses a water-soluble cleaner. This removal is done before the wastewater reaches sewage or other public waters. Table 2.18 lists major wastewater treatment devices and their classifications, along with their removal rates and degradation rates for each targeted component.

77. Natural sedimentation, coagulating sedimentation, microbiological degradation, membrane filtration, and activated carbon adsorption are some of the classifications for wastewater treatment devices.

Natural sedimentation method is excluded from this discussion, because it has removal and degradation rates of zero for dissolved organic and inorganic compounds. Refer to European Union (2003) for the efficiencies of removal of individual substances.

Table 2.18 Removal and degradation ratios (%) of wastewater treatment devices

Treatment device classification		Chemical compound classification							
		Suspended inorganic compound [2]		Suspended organic compound [2]		Dissolved organic compound [3]		Dissolved organic compound [3]	
		Removal ratio	Degradation ratio	Removal ratio	Degradation ratio	Removal ratio	Degradation ratio	Removal ratio	Degradation ratio
Natural sedimentation device	Representative value	40	0	20	0	0	0	0	0
	Min. to max.	40–50	–	20–50	–	–	–	–	–
	Factors determining min. or max.	Particle size of suspended matter				–	–	–	–
Coagulation - sedimentation equipment	Representative value	80	0	70	0	0	0	0	40
	Min. to max.	66–95	–	90–95	–	0–10	–	0–10	–
	Factors determining min. or max.	Particle size of suspended matter				Type of flocculating agent			
Microorganism decomposition device (aerobic) [1]	Representative value	70	0	70	30	0	0	60	40
	Min. to max.	70–80	0	70–80	30	–	–	60–95	40–70
	Factors determining min. or max.	Sludge adsorption characteristic				–	–	Degradability of material	
Membrane filtration device	Representative value	100	0	100	0	0	0	0	0
	Min. to Max.	–	–	–	–	70–98*	0	90–95	0
	Factors determining min. or max.	–	–	–	–	* if reverse osmosis (RO) membrane used			
Activated carbon adsorption device	Representative value	10	0	10	0	20	0	80	0
	Min. to Max.	0–10	0	0–10	0	0–20	0	80–90	0
	Factors determining min. or max.	Material adsorption characteristic							

[1] Values are for materials that persist in treatment devices that use aerobic microorganisms (e.g. activated sludge treatment, immersed filtration method, contact oxidation method, rotating disk method).

[2] The term "suspended" (inorganic compound, organic compound) refers to targeted objects that are in particle form in wastewater.

[3] The term "solvent" (inorganic and organic compounds) refers to wastewater in which the targeted objects are already dissolved.

Source: METI and MoE (2004)

2.5.3.1 Coagulation - sedimentation equipment

78. Coagulating sedimentation is the most widely used water treatment method. It is a separation method that conducts coagulation and sedimentation operations in a single device. The targeted suspended objects are colloidally dispersed particles 0.001 to 1 µm in diameter that cannot be separated by sedimentation in a given time.

2.5.3.2 Microbiological degradation devices (aerobic)

79. Sometimes referred to as biotreatment, this method uses aerobic microorganisms to degrade and remove organic substances within wastewater. Active sludge treatment is believed to be the most widely used organic industrial wastewater treatment. It allows microorganisms to come into contact with organic substances that are floating evenly.

2.5.3.3 Membrane filtration devices

80. The reverse osmosis membrane (listed in Table 2.18) is a membrane that allows water to pass through but does not allow solute to permeate. A membrane filtration device uses this characteristic to remove only water from a solution in which the targeted object is dissolved. Membrane filtration relies on pressure difference as its power source.

2.5.3.4 Activated carbon adsorption

81. Activated carbon adsorption is normally used to remove minute amounts of organic matter that cannot be removed by other means (e.g. coagulating sedimentation, filtration, biotreatment). It is generally believed that larger objects with high hydrophobicity are more easily adsorbed, as opposed to objects with low molecular mass and high hydrophilicity, because the surface of activated carbon is highly hydrophobic.

2.5.4 Recovery and recycling systems

82. In this section, the configuration and types of recovery and recycling systems that are integrated into cleaning processes are discussed.

2.5.4.1 Rinsing water (including cleaner) recycling systems

83. These cleaning systems may use aqueous-type cleaners and rinse with water. The system is made up of (1) an oil–water separation system used to reduce the frequency of exchange of solution by removing dirt (oil) from the cleaner, thereby extending the life of the cleaning solution; and (2) a system that filters the used rinse water to remove contaminants (oil) and cleaner so the rinse water and cleaner can be reused.

2.5.4.2 Solvent gas treatment and recovery devices

84. This device uses a gaseous form of cleaner and works to prevent the targeted components generated by local ventilation near the cleaning tank and drying process from escaping into the environment. Activated carbon adsorption and cryogenic distillation methods are two of the major methods used.

2.5.4.3 Distillation recycling devices

85. Distillation recycling devices for cleaners may be attached to some cleaning and rinsing systems that use hydrocarbon-type cleaners. Reduced-pressure distillation devices are among the most common types. These devices distil cleaner that already contains contaminants by utilizing differences in boiling point between the contaminants and the cleaners.

2.5.5 Other peripheral devices

86. Here, the following devices are listed, which relates to emission, treatment and recovery of components targeted by cleaners.

2.5.5.1 Local ventilation devices

87. These devices are used in processes that involve volatile cleaners. To improve the working environment, the device is installed near the source of the volatile substance to provide local ventilation. Suction is provided by an air blower through a hood. Hood types include surrounding type, booth type, receiver type and external type.

2.5.5.2 Oil – separator

88. These extend the service life of cleaning and rinsing solutions. They stabilize the cleaning quality by reducing the oil concentration within the washing and rinsing water to below a certain value by removing oily substances using flotation separation, filtration or other means. They are used with aqueous- and semi-aqueous-type cleaners.

2.6 Relationship between cleaners and targeted contaminants

89. Here the term "contaminants" refers to the materials that are attached to the objects to be cleaned, and that need to be removed. The type of contaminant is an important determinant of the choice of cleaning process. There are many different kinds of contaminants. Table 2.19 divides them into organic and inorganic types.

90. By further subdivision, greasy contaminants, for example, can be classified into aqueous type and mineral oil type. In some cases, contaminants attached to the objects to be cleaned may be of multiple types and will require a comprehensive cleaning method.

91. A quantitative measure of contaminants may be the amount of contaminant (volume or mass) per unit targeted object (weight and surface area).

Table 2.19 Examples of targeted contaminants

Organic contaminants (organic compounds)	Greasy type (mineral oil type and water soluble): cutting oil, machining oil, rolling oil, pressing oil, anti-corrosion oil, heat-treatment oil, greases, lubricants. Other (solid organics, etc.): flux (rosin type, amines), waxes, adhesives, liquid crystal, resin, mould lubricant, fibre waste, ion-based contaminants.
Inorganic contaminants (metals, inorganic compounds)	Inorganic solids: processing waste, abrasive powder, cutting powder, abrading agents, dusts. Oxidized films, surface layer films.

Sources: JICC (1999a, 1999b, 2004, 2006)

92. To determine the types of cleaners used against different types of contaminants, existing research data was referred to reveal the quantities of industrial cleaners shipped (or the volumes sold, or purchased) for various types of contaminants. The source data are shown in Table 2.20. There were 11 classifications of contaminant type: mineral-based machining oil; water-soluble machining oil; flux; abrading agent; grease and lubricant; mould lubricant; anti-corrosion oil and agent; oily contaminants and stains; dusts and impurities; pitch and wax; and other.

Table 2.20 Comparison of classifications related to use of cleaners for particular contaminants in three separate questionnaires

Reference	Year	Respondents	Number of responses	Items	Total quantity of cleaner reported	Legend name shown in Fig 2.11-Fig 2.15
Japan Industrial Conference on Cleaning (JICC, 2001a)	1999	Cleaners and cleaning equipment manufacturers	79 companies	Sales volume	140 072 t	1999
Japan Industrial Conference for Ozone Layer and	2003	Industrial cleaning equipment and cleaner manufacturers	20 companies	Sales volume	29 369 t	2003 Manufacturers

Climate Protection (JICOP, 2005)		Industrial cleaning equipment and cleaner users	150 establishments	Quantity purchased	2 867 t	2003 Users
Mizuho Information & Research Institute (MIRI, 2009)	2007	Cleaner manufacturers and distributors	78 cases	Quantity shipped	135 608 t	2007

93. Figures 2.11 through 2.15 are graphs for each cleaner classification based on the questionnaires in the referenced materials (Table 2.20). The quantity of cleaner shipped (or sold or purchased) for each particular contaminant in a particular year was determined as a percentage of the overall volume shipped (or sold or purchased). The meanings of legends such as "1999" or "2003 Manufactures" are explained in Table2.20.

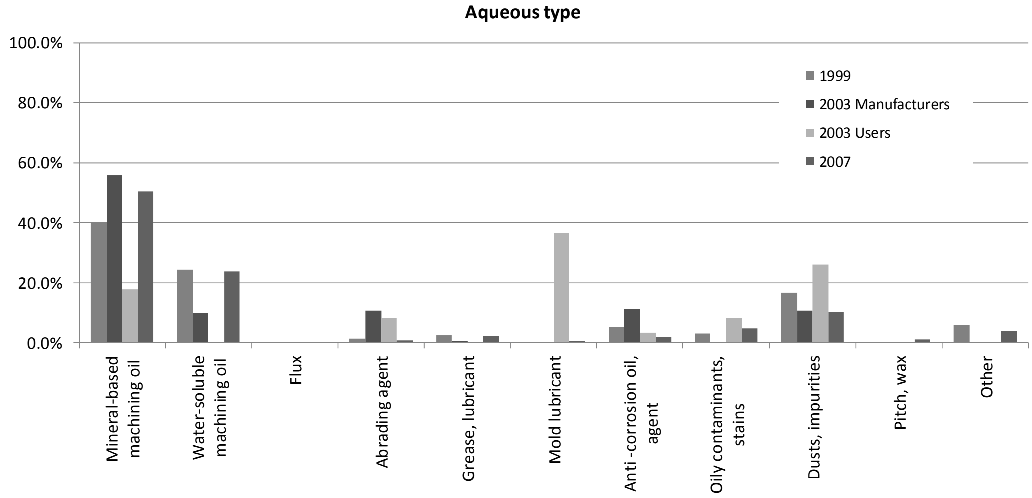

Figure 2.11 Percentages of aqueous-type cleaners sold (or shipped or purchased) for each targeted contaminant

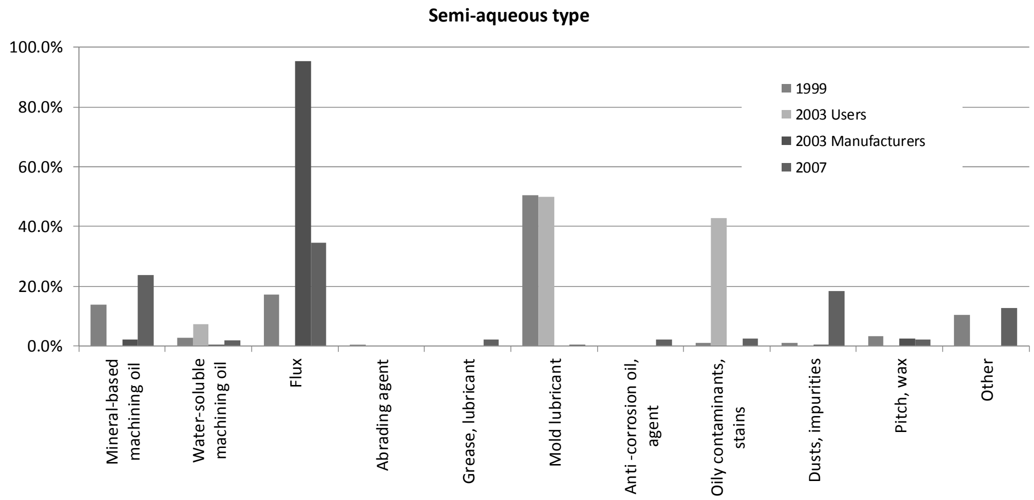

Figure 2.12 Percentages of semi-aqueous type cleaners sold (or shipped or purchased) for each targeted contaminant

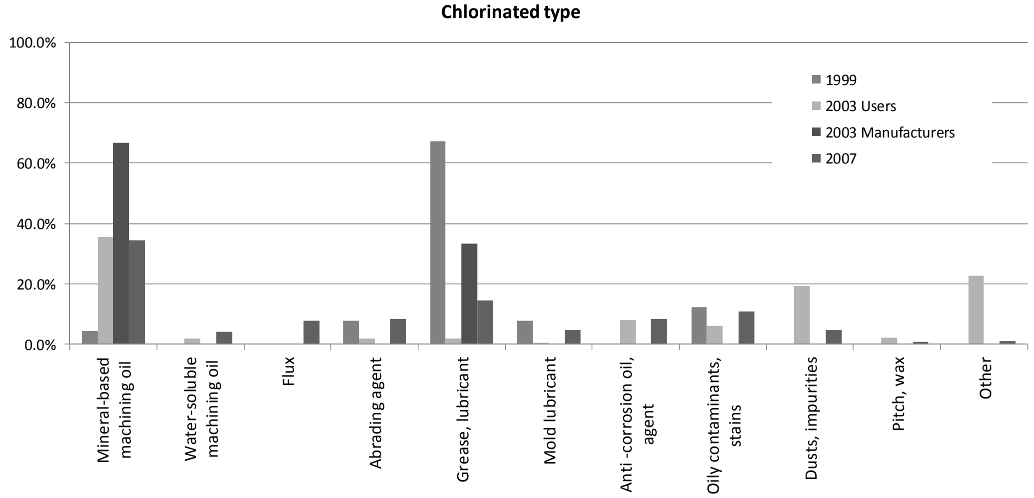

Figure 2.13 Percentages of hydrocarbon-type cleaners sold (or shipped or purchased) for each targeted contaminant

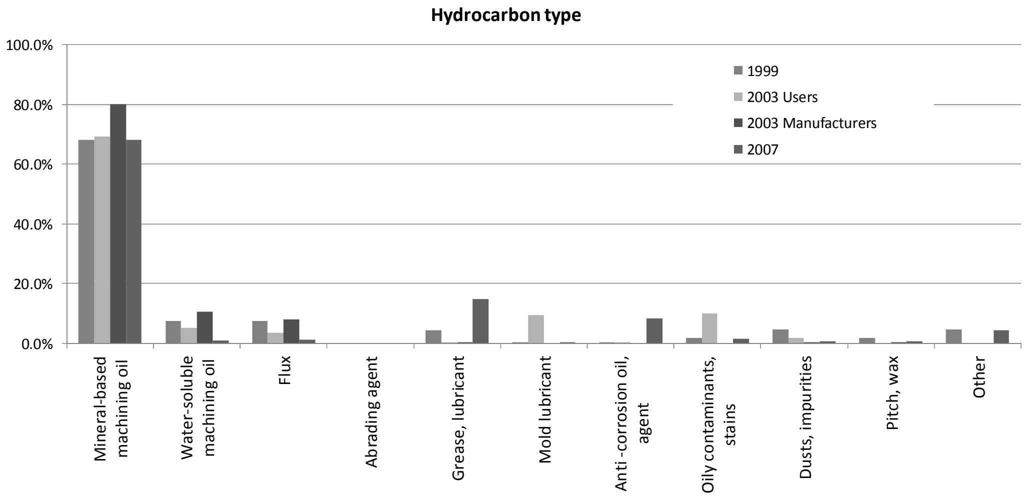

Figure 2.14 Percentages of chlorinated-type cleaners sold (or shipped or purchased) for each targeted contaminant

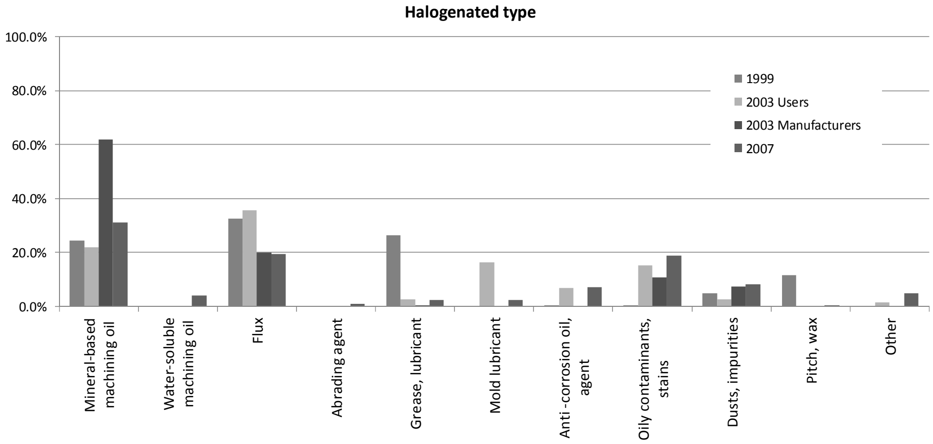

Figure 2.15 Percentages of halogenated cleaners sold (or shipped or purchased) for each targeted contaminant

94. Observation of Figures. 2.11 through 2.15 reveals that aqueous-type cleaners tend to be used for mineral-based machining oils and water-soluble machining oils. Semi-aqueous-type cleaners are used for fluxes and mould lubricants. Hydrocarbon-type cleaners are used often on mineral-based oils. Chlorinated-type cleaners are used for mineral-based machining oils, as well as for greases and lubricants that may be extremely dirty. Halogenated cleaners are used often for mineral-based machining oils, but they are also often used for fluxes and greases.

95. It is evident that, overall, the quantities of cleaners used for mineral-based machining oils is high. Particular cleaners tend to be used for what may be considered organic types of contaminants, such as fluxes, greases, lubricants, and mould lubricants. For what may be considered inorganic types of contaminants, such as abrading agents, dusts, and impurities, there are no specific trends in the use of particular cleaners, with the exception of the application of aqueous-type cleaners to dusts and impurities. These trends are summarized in Table 2.21. The symbols ***, **, and * (refer to the descriptions at the bottom of the table) are used to indicate the amounts of specific types of cleaners used as percentages of overall use for the year.

Table 2.21 Types of cleaners used for each type of contaminant

	Aqueous type	Semi-aqueous type	Hydrocarbon type	Chlorinated type	Halogenated type
Mineral-based machining oil	***	**	***	***	***
Water-soluble machining oil	**	*	*	*	*
Flux	—	***	*	*	**
Abrading agent	*	—	—	*	*
Grease, lubricant	*	*	*	***	**
Mold lubricant	**	***	*	*	*
Anti-rust oil and agents	*	*	*	*	*
Oily contaminants, stains	*	**	*	*	*
Dusts, impurities	**	*	*	*	*
Pitch, wax	*	*	*	*	*

*** At least 50% of the total quantity was used for this type of contaminant for the year.

** At least 20% but less than 50% of the total quantity was used for this type of contaminant for the year.

* Less than 20% of the total quantity was used for this type of contaminant for the year.

3 ESTIMATION AND EMISSION QUANTITIES

3.1 Estimation of emission quantities for cleaner substitution

96. By simplifying the cleaning process to the disposal of used cleaners as waste solution or release into the environment (Figure. 3.1), Eq. 3.1 can be used to calculate the environmental emissions after substituting cleaners. To simplify the calculation, the cleaners are assumed to be composed of a single substance. The input variables used and the calculated emission are shown in Table 3.1.

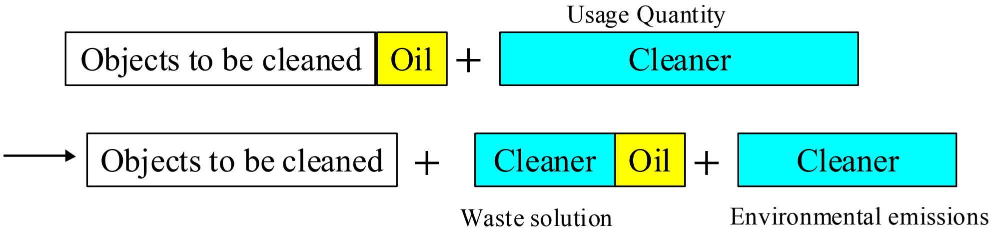

Figure 3.1 Conceptualized simplified cleaning process

$$ELEM_{emission\_2} = \frac{EF_{\_2}}{1-EF_{\_2}} \cdot \frac{1-R_{oil\_2}}{R_{oil\_2}} \cdot \frac{R_{oil\_1}}{1-R_{oil\_1}} \cdot \frac{1-EF_{\_1}}{EF_{\_1}} \cdot ELEM_{emission\_1} \quad \ldots\ 3.1$$

Table 3.1 Input variables used for calculating environmental emissions after substituting cleaners, and output variable

Term	Definition	Unit
Input variables		
EF_{1}	Emission coefficients of cleaners before substitution	–
EF_{2}	Emission coefficients of cleaners after substitution	–
$R_{oil\ 1}$	Ratio of oil content within waste cleaning solution before substitution	–
$R_{oil\ 2}$	Ratio of oil content within waste cleaning solution after substitution	–
$ELEM_{emission\ 1}$	Environmental emission of cleaners before substitution	kg/h
Output variable		
$ELEM_{emission\ 2}$	Environmental emission of cleaners after substitution	kg/h

97. Eq. 3.1 is derived from Eq. 3.2, and Eq.3.2 shows that the amount of oil removed by washing is the same before and after cleaners are substituted:

$$ELEM_{emission\_1} \cdot \frac{1-EF_{\_1}}{EF_{\_1}} \cdot \frac{1-R_{oil\_1}}{R_{oil\_1}} = ELEM_{emission\_2} \cdot \frac{1-EF_{\_2}}{EF_{\_2}} \cdot \frac{1-R_{oil\_2}}{R_{oil\_2}} \quad \ldots\ 3.2$$

98. To calculate the quantity of environmental emissions requires the parameters shown in Table 3.1. The emission coefficient and oil content in the waste solution are not independent of each other, and the emission coefficient also varies with other cleaning characteristics. Published emission coefficients and oil contents apply to individual cases, and thus are not suitable for estimating emissions after substitution, because the objects to be cleaned must be constant.

99. Parameters related to cleaning requirements—that is, the kinds of objects (e.g. material, size, mass and contaminants) to be cleaned—should not be varied depending on emission control measures such as cleaner substitution (Table 3.2). On the other hand, parameters related to the cleaning process—that is, the methods (e.g. cleaners, equipment and operation)—can be varied.

100. In this ESD, an estimation equation suitable for use in cleaner substitution cases is presented. The equation is derived from the relationships among the cleaning process parameters when the cleaning requirement parameters, which are for example shown in the boxes surrounded by a dashed line in Figure 3.3, are fixed.

Table 3.2 Cleaning requirement parameters and cleaning process parameters

Use	Parameter	Content
Cleaning requirement	Timing of cleaning	Pre-treatment, post-treatment
	Cleaning precision	Precise, general, rough
	Cleaning quantity	Mass, volume
	Objects to be cleaned	Materials, shapes, stability, contaminant
Cleaning process	Cleaner	Cleaner type
	Cleaning equipment	Transportation type, system, heating method, recovery device, etc.
	Cleaning operation	Operating time, operation ratio, treatment rate, operators, etc.

Source: Kikuchi and Hirao (2008a).

101. The rest of this chapter shows typical flows for cleaning processes that use certain types of cleaners. Equations that represent the quantity of cleaner to be used, emission quantity and emission coefficient are derived.

3.2 Cleaning with chlorinated or halogenated cleaners

102. Figure 3.2 shows a conceptualized process flow for a chlorinated or halogenated cleaner. The objects to be cleaned are first submerged in the immersion-washing tank to remove oils, and then transferred to the rinsing tank, where the cleaning solution is cleaner than that in the washing tank. Finally, the vapour of the cleaning solution contacts the objects in the upper part of the heated vapour-washing tank and condenses on the surface of the objects, washing them (vapour washing). At the same time, new (or recovered) cleaning solution is supplied to the rinsing tank. Excess solution overflows into the washing tank, displacing solution into the vapour-washing tank. Therefore, the cleaning solution is cleanest in the rinsing tank, then the immersion-washing tank and then the vapour-washing tank. A cooling coil with cooling water is wrapped around the upper part of the cleaning equipment to condense the vapour back to liquid. Vapour that escapes from the openings of the cleaning tank is recovered by the emission gas treatment and recovery device for reuse. When the oil content of the cleaning solution in the vapour-washing tank exceeds a given amount, the cleaning solution is drawn off for industrial waste treatment.

103. The conceptualized flow relies on five assumptions:

1. All solution is either emitted to the atmosphere or treated as waste;
2. All recovered solution is reused;
3. Emission into public waters is negligible;
4. An oily substance separator is not used;
5. The cleaner is removed continuously (in reality, the cleaning solution in the washing tank is exchanged with new solution when the oil content exceeds a given value).

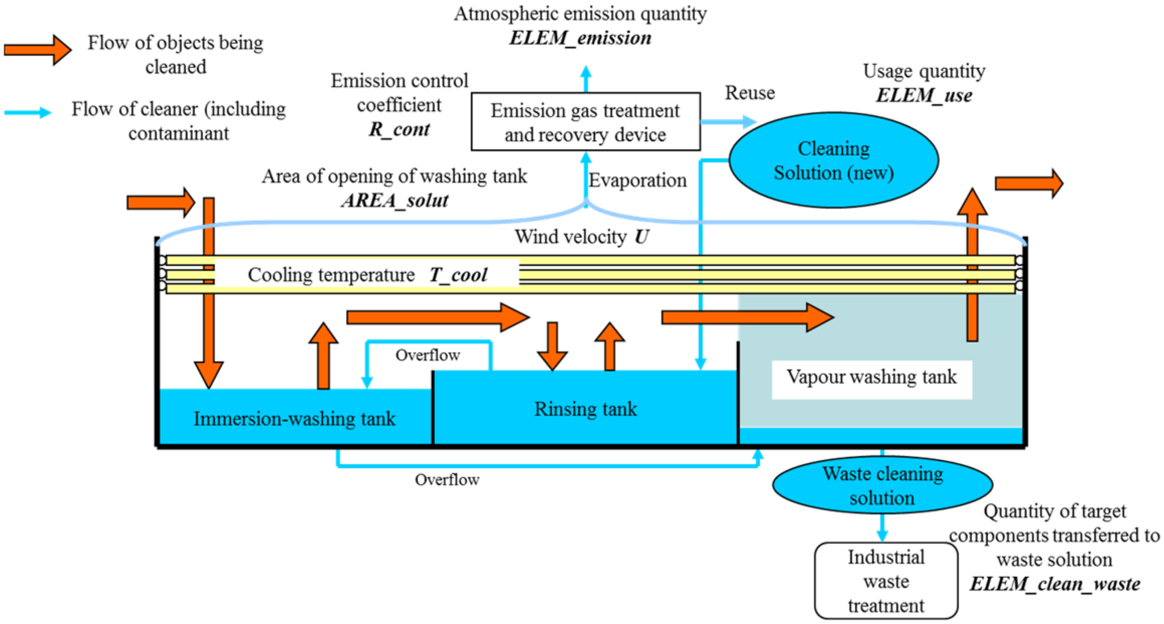

Figure 3.2 A conceptualized process using chlorinated or halogenated cleaners

Sources:JRCC (2001a, 2002) and MoE (2007a).

104. Figure 3.3 shows the mathematical relationships of the parameters shown in Figure 3.2.

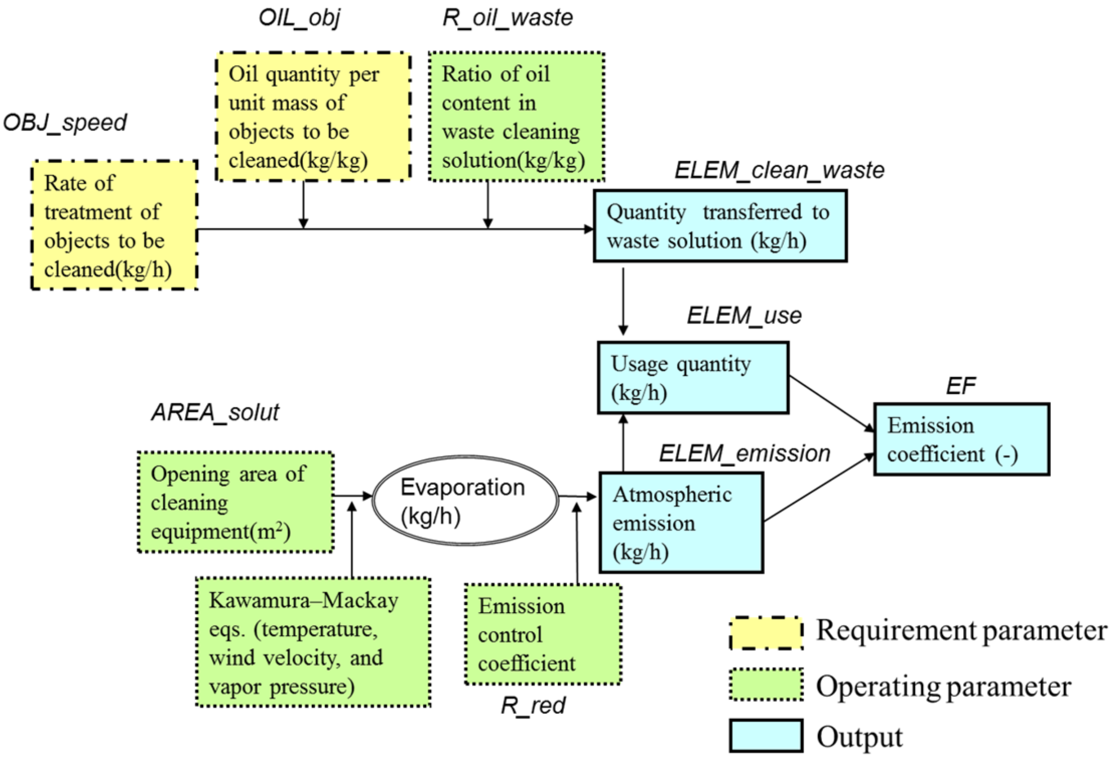

Figure 3.3 Relationships of parameters

105. Under the five assumptions, the quantity used is the sum of atmospheric emission and waste solution. The emission coefficient is the ratio of atmospheric emission to quantity used:

$$ELEM\_use = ELEM\_emission + ELEM\_clean\_waste \qquad \ldots 3.3$$

$$EF = ELEM\_emission \,/\, ELEM\_use$$
$$= ELEM\_emission \,/\, (ELEM\_emission + ELEM\_clean\_waste) \qquad \ldots 3.4$$

where “ELEM” refers to the target components. The terms are described in Table 3.3.

Table 3.3 Variables used in estimating emissions of chlorinated cleaners

Term	Definition	Unit
ELEM_use	Quantity of target components used per hour	kg/h
ELEM_emission	Atmospheric emission of target components per hour	kg/h
ELEM_clean_waste	Quantity of target components transferred to waste solution per hour	kg/h
EF	Emission coefficient (emission quantity / usage quantity)	–
AREA_solut	Opening area of cleaning equipment (area of cleaning solution that contacts air)	m^2
Mw	Molecular weight	kg/kmol
P_v	Saturated vapour pressure of target components at temperature *T*	Pa
T_cool	Cooling temperature	K
R_gas	Gas constant	J/K/kmol

Term	Definition	Unit
R_cont	Emission control coefficient (based on recovery device or equipment shape)	–
Km	Material transfer coefficient	m/s
U	Control wind velocity around upper part of washing tank	m/s
Z	Length of cleaning solution surface along wind direction	M
Sc	Schmidt number	–
OBJ_speed	Rate of treatment of objects to be cleaned	kg/h
OIL_obj	Oil quantity per unit mass of objects to be cleaned	kg/kg
R_oil_waste	Ratio of oil content in waste cleaning solution	kg/kg
R_elem_solut	Ratio of target components within cleaning solution	kg/kg

3.2.1 Estimation of atmospheric emissions

106. The quantity of cleaners dragged out from the equipment by clinging to the objects is assumed to be zero, because in a chlorinated type cleaning system as shown in Fig. 3.2, the cleaning solution that clings to the objects evaporates off in the vapour washing area (stippled area in Fig. 3.2). Hence, the atmospheric emission can be accounted for by the evaporation of the cleaning solution from the openings of the washing tank. The rate of evaporation of the cleaning solution can be calculated by Kawamura–Mackay Eqs. 3.5 and 3.6 (Kawamura et al., 1987):

$$ELEM\_emission = AREA\_solut \times Km \times 3600 \times \{(\mathrm{Mw} \times P\_v) / (\mathrm{R\_gas} \times T\_cool)\} \times (1 - R\_cont) \quad \ldots\ 3.5$$

$$Km = 0.0048 \times U \times Z^{-1/9} \times \mathrm{Sc}^{-2/3} \quad \ldots\ 3.6$$

107. The emission quantity is assumed to be proportional to the area of the openings of the washing tank (*AREA_solut*) and to the material transfer coefficient (*Km*), and the emission quantity is assumed to be controlled by the emission gas treatment and recovery device and the shape of the cleaning equipment.

108. The Kawamura–Mackay equations were originally formulated to estimate the rate of evaporation of solvent components from solvent pools located outside. In this ESD, a solution surface of temperature *T_cool* in the washing tank opening is assumed, because the vapour is condensed in the upper part of the washing tank (Fig. 3.2). Further, the evaporation is assumed to arise from that solution surface, making possible the use of the Kawamura–Mackay equations for estimating the rate of evaporation from the washing tank. The emission control wind velocity of the cleaning equipment is used as the wind velocity.

109. A report by the Cleaning Subcommittee of the Commission for Investigating Measures for Emission Control of Volatile Organic Compounds (Ministry of the Environment, 2005a), which is part of the Central Environment Council, also uses the Kawamura-Mackay equation to estimate the amount of emission from cleaning equipment.

110. Note that Kawamura et al. (1987) adjust the wind velocity at 10 m above the ground to the ground-level wind velocity by using $U^{7/9}$ in equation 3.6, but the wind velocity is not adjusted in this ESD because the controlled wind velocity within devices is substituted into the equation.

3.2.2 Estimation of target components in waste cleaning solution

111. The quantity of the target components (*ELEM_clean_waste*) that would be disposed of as waste cleaning solution (for industrial waste treatment) is estimated as:

$$ELEM\_clean\_waste = OBJ\_speed \times OIL\_obj \times \\ ((1 - R\_oil\_waste) / R\_oil\_waste) \times R\_elem\_solut \qquad \ldots 3.7$$

112. When the quantity of oil (or contaminant) in the cleaning solution reaches a certain ratio (*R_oil_waste*), the solution is disposed of as waste. Recycling ratios can be taken into consideration by adjusting "*R_oil_waste.*"

3.3 Cleaning with hydrocarbon cleaners

113. The emission of hydrocarbons was estimated from open and closed cleaning equipment.

3.3.1 Open equipment

114. Figure 3.4 shows a conceptualized process flow for open equipment. The objects are moved from the immersion-washing tank into the rinsing tank, as in the process using chlorinated cleaners. Because hydrocarbon cleaners do not evaporate quickly, the cleaning solution clinging to the objects is forcefully dried within the dryer. Therefore, unlike the cleaning process that uses chlorinated cleaners, there is no vapour-washing step, and cooling coils are not required. New (or recovered) cleaning solution is supplied to the rinsing tank, and the overflow from there enters the immersion-washing tank. The overflow is distilled and returned to the rinsing tank. When the oil content of the cleaning solution in the distillation-recycling device reaches a certain amount, the cleaning solution is drawn off for industrial waste treatment. Although some equipment is fitted with multiple rinsing tanks, a single tank is assumed. The number of tanks does not affect the equations.

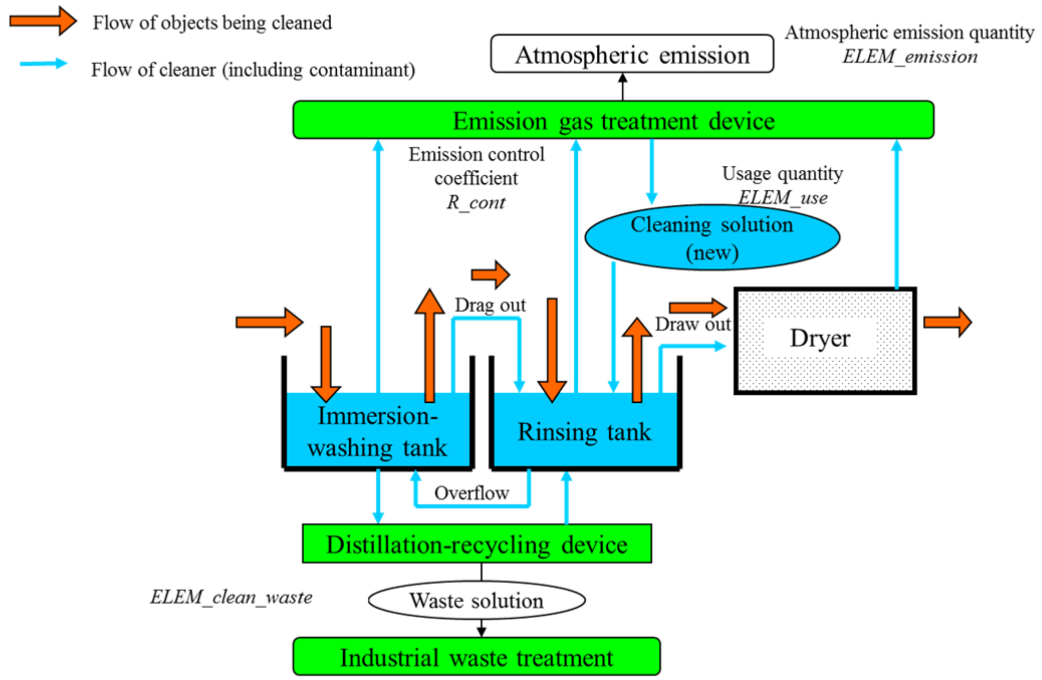

Figure 3.4 Conceptualized open process using hydrocarbon cleaners

3.3.1.1 Estimation of atmospheric emissions

115. As in the chlorinated process, cleaning solution evaporates from the surface. However, because there is no vapour washing step, all of the cleaning solution removed on the objects is assumed to evaporate in the drying process. The atmospheric emission is expressed as:

$$\mathit{ELEM\_emission} = [\underline{\mathit{AREA\_solut} \times \mathit{Km} \times 3600 \times \{(\mathrm{Mw} \times \mathit{P\_v}) / (\mathrm{R\_gas} \times \mathit{T\_solut})\}} + \mathit{DRAG\_unitweight} \times \mathit{OBJ\_speed} \times \rho\mathit{\_solut} \times \mathit{R\_elem\_solut}] \times (1 - \mathit{R\_cont}) \qquad \dots 3.8$$

116. The underlined part of the equation represents the evaporation of cleaning solution from the washing tank and is equivalent to Eq. 3.5[3]. The area of the openings of the cleaning equipment (*AREA_solut*) is the sum of all openings of the immersion-washing tank and the rinsing tank. The temperature is that of the cleaning solution (*T_solut*), not that of the cooling water (*T_cool*), because the installation of cooling tubes is not assumed in this ESD. The remainder of Eq. 3.8 represents the quantity of cleaner removed. Eq. 3.6 is used to calculate the material transfer coefficient (*Km*), as for the chlorinated type. The terms are defined in Table 3.4.

Table 3.4 Variables used in estimating emissions of hydrocarbon cleaners (see also Table 3.3)

Term	Definition	Unit
T_solut	Cleaning solution temperature	K
DRAG_unitweight	Quantity of cleaning solution taken out by objects to be cleaned	L/kg
ρ_solut	Specific gravity of cleaning solution	kg/L
SOLUT_generate	Quantity of cleaning solution vapour generated per unit time in the depressurizing vapour generation mechanism	kg/h
P_v	Cleaning solution saturated vapour pressure inside condenser at cooling temperature	Pa
P_atm	Atmospheric pressure	Pa
T_cool	Cooling temperature inside condenser	K

3.3.2 Closed equipment

117. Figure 3.5 shows a conceptualized process flow for closed equipment. The objects are cleaned and dried in the single washing and drying tank. First, the lid of the tank is opened and the objects are inserted. Next, the tank is depressurized by a vacuum pump, and cleaning solution is fed in as vapour from the depressurizing vapour generator to clean the objects. The tank is again depressurized by the vacuum pump, which evaporates the cleaning solution from the objects. The vapour from the tank is cooled and condensed and then returned to the vapour generator. When the oil content of the cleaning solution in the vapour generator reaches a certain amount, the solution is drawn off for industrial waste treatment.

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[3] It is possible that the Kawamura–Mackay equations are not suitable for use in open hydrocarbon systems, because the process does not use vapor washing within the vapor zone, as in the chlorinated process. However, we used it because the quantity of vapor that escapes from the openings is very small compared with the quantity evaporated after the objects are taken out.

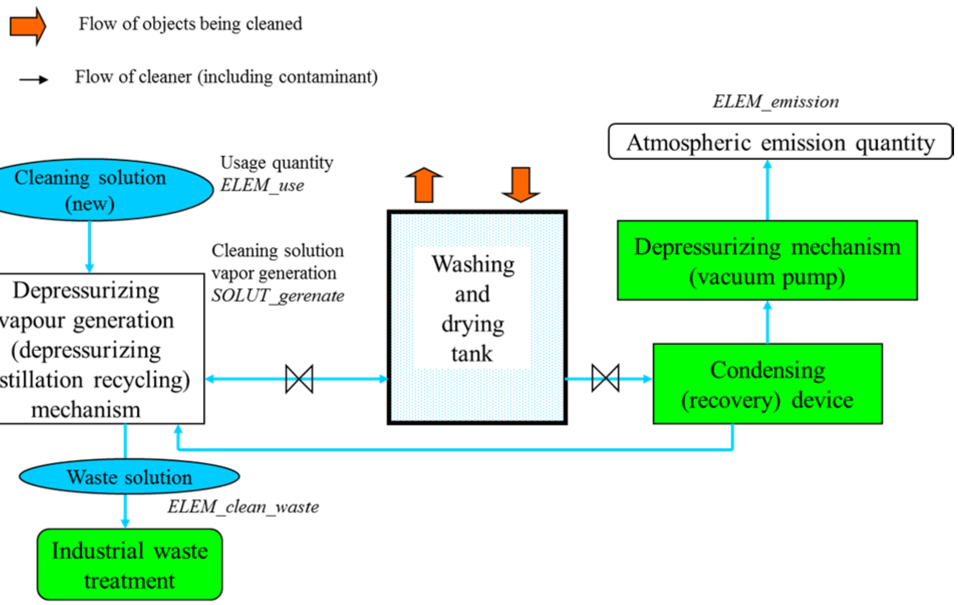

Figure 3.5 Conceptualized closed process using hydrocarbon cleaners

118. Atmospheric emission from closed equipment (JICOP, 2005) is written as:

$$ELEM\_emission = SOLUT\_generate \times R\_elem\_solut \times (P\_v / P\_atm) \qquad \ldots 3.9$$

119. (P_v / P_atm) indicates that from the amount generated as vapour in the condenser, only the proportion at atmospheric pressure is exhausted[4].

120. In processes using hydrocarbon cleaners, Eqs. 3.3, 3.4, and 3.7 give the quantity of cleaner used, the emission coefficient, and the quantity of waste cleaning solution.

3.4 Cleaning with aqueous cleaners

121. Figure 3.6 shows a conceptualized process flow for aqueous cleaners. The process flow is the same as for the open hydrocarbon equipment. Multiple rinsing tanks are often installed; two tanks were assumed, but the number does not affect the equations. Pure water is supplied to the secondary rinsing tank (or to the final rinsing tank if there are three or more), and the overflow is supplied to the primary rinsing tank (or into the tank just prior). Therefore, the final rinsing tank is the cleanest, and the primary rinsing tank has the highest concentration of cleaning solution[5] and oil. The overflow from the primary tank is treated as rinsing wastewater. The dashed lines in Fig. 3.6 show the case where rinsing wastewater is transferred directly to industrial waste treatment or into public waters (or the sewer) without being treated as wastewater. The cleaning solution in the washing tank is replaced with new solution when the contaminant content reaches a certain level.

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[4] During drying, the pressure is reduced (to about 100 to 10 mm Hg according to interviews). Therefore, it has been suggested that the ratio of the pressure within the equipment to the saturated vapour pressure should be considered, instead of the ratio of the atmospheric pressure to the saturated vapour pressure (P_v / P_atom). If the former is used in Eq. 3.9, the atmospheric emission (*ELEM_emission*) will be larger.

[5] In this ESD, a cleaning solution is defined as a liquid-type aqueous cleaner diluted with water at the time of use.

122. Figure 3.6 shows the main components of the equipment used at the site where aqueous cleaner is used, as determined by interviews. It includes the following assumptions:

1. The solution volume and the concentration of the cleaner in the washing tank change with evaporation and removal of cleaning solution on the cleaned objects, but cleaner and water are added to maintain a steady state;

2. All oil is removed from the objects within the washing tank and accumulates there (e.g. oil is not transferred to the rinsing tank). The emissions of cleaner components from oil separators are negligible in volume.

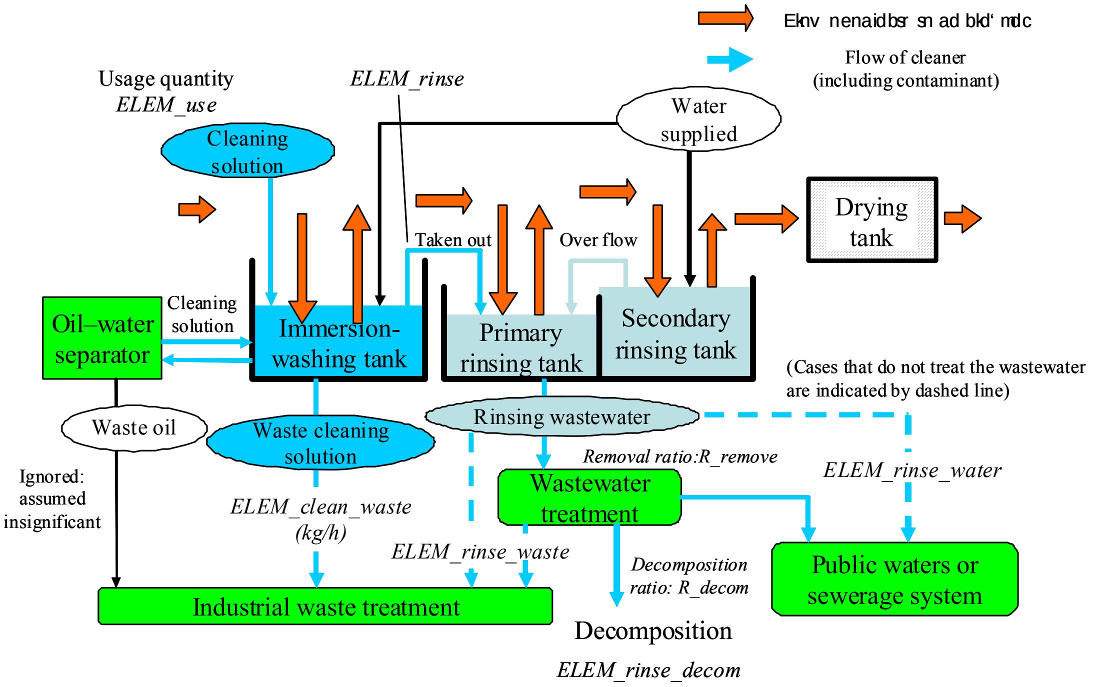

Figure 3.6 Conceptualized process using aqueous cleaners

123. The relationship between the usage quantity, emission quantity and disposal quantity of cleaner components is defined as follows:

$$ELEM\_use = ELEM\_clean\_waste + ELEM\_rinse \quad \ldots 3.10$$

124. The terms are described in Table 3.5. The used cleaner components are disposed of with the waste cleaning solution or are treated with the rinsing wastewater.

Table 3.5 Variables used in estimating emissions of aqueous cleaners (see also Tables 3.3 and 3.4)

Term	Definition	Unit
ELEM_rinse	Quantity of target components that goes through wastewater treatment as rinsing wastewater	kg/h
R_remove	Ratio of removal by wastewater treatment	–
R_decom	Ratio of decomposition by wastewater treatment	–
ELEM_rinse_waste	Quantity of target components transferred to waste material	kg/h
ELEM_rinse_water	Quantity of emission released into public waters or sewer	kg/h
ELEM_rinse_decom	Quantity of decomposition by wastewater treatment	kg/h

3.4.1.1 Estimation of rinse wastewater

125. Because the quantity of target components (*ELEM_rinse*) treated as rinsing wastewater is equal to the quantity of target components transferred from the washing tank into the rinsing tank, the following equation can be used to calculate the quantity:

$$ELEM\_rinse = DRAG\_unitweight \times OBJ\_speed \times \rho\_solut \times R\_elem\_solut \quad \ldots\ 3.11$$

3.4.1.2 Ratio of decomposition and removal by wastewater treatment

126. The target components within the rinsing wastewater are assumed to be treated on-site and either removed or decomposed. The target components that are not removed are released into public waters or into the sewer. It is also assumed that the quantity removed minus the decomposed quantity ends up as industrial waste (sludge etc.), and the decomposed portion transforms into other substances. In other words, after being treated as wastewater, the target components are (1) transferred as waste material (primarily as active sludge), (2) released into public waters or the sewer, or (3) decomposed into other substances, as follows:

$$ELEM\_rinse\_waste = ELEM\_rinse \times (R\_remove - R\_decom) \qquad \ldots\ 3.12$$

$$ELEM\_rinse\_water = ELEM\_rinse \times (1 - R\_remove) \qquad \ldots\ 3.13$$

$$ELEM\_rinse\_decom = ELEM\_rinse \times R\_decom \qquad \ldots\ 3.14$$

127. These scenarios are based on the *PRTR Emissions Calculation Manual* (Ministry of Economy, Trade and Industry, Japan, and Ministry of the Environment, Japan (METI and MoE) 2004).

128. The emission into public waters and the sewer was calculated by substituting Eq. 3.13 into Eq. 3.11. Public water and sewerage were not distinguished, as this would be based on the locations of the treatment plants.

$$\begin{aligned} ELEM\_rinse\_water = {} & DRAG\_unitweight \times \\ & OBJ\_speed \times \rho\_solut \times R\_elem\_solut \times (1 - R\_remove) \qquad \ldots\ 3.15 \end{aligned}$$

129. Eq. 3.7 is used to calculate the content in the waste cleaning solution. The emission coefficient is obtained as the emission (Eq. 3.15) divided by the quantity used (Eq. 3.10).

3.5 Cleaning with semi-aqueous cleaners

130. Figure 3.7 shows a conceptualized process flow for semi-aqueous cleaners. The process flow, the supply of pure water and overflows are the same as for aqueous cleaners. In contrast, the solvent components in the cleaner are evaporated from the immersion-washing tank, and all rinsing wastewater is disposed of as waste. This section shows how to calculate the emissions of the solvent component within semi-aqueous cleaners[6].

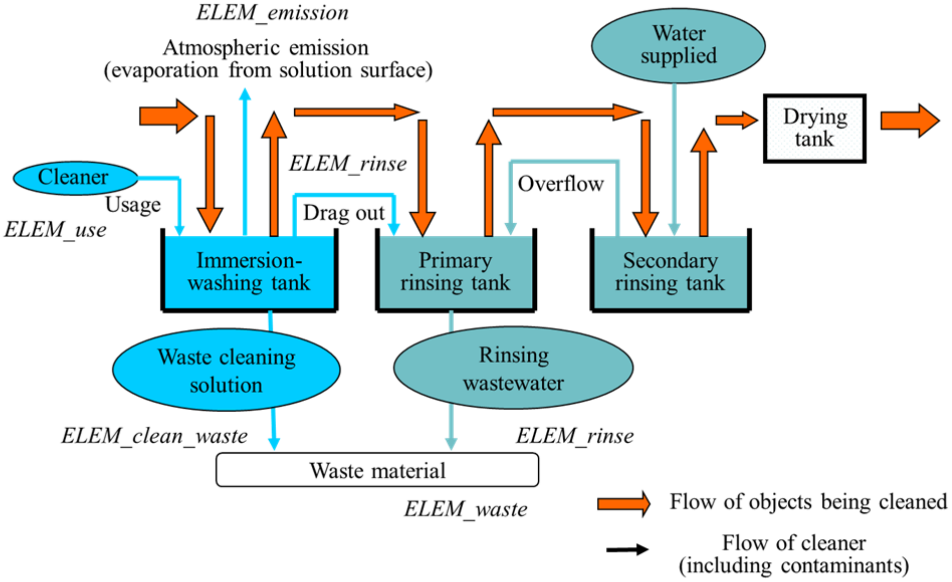

Figure 3.7 Conceptualized process using semi-aqueous cleaners

131. The relationship between the usage, emission and disposal of cleaner components is defined as follows:

$$ELEM\_use = ELEM\_emission + ELEM\_clean\_waste + ELEM\_rinse \qquad \ldots 3.16$$

3.5.1 Estimation of atmospheric emission

132. Atmospheric emission is calculated as:

$$ELEM\_emission = AREA\_clean \times Km \times 3\,600 \times \{(\mathrm{Mw} \times P\_v) / (\mathrm{R\_gas} \times T\_solut)\} \qquad \ldots 3.17$$

where *Km* is calculated by Eq. 3.6.

133. In this process, because the cleaning solution in the rinsing tank is largely water, the area of the immersion-washing tank (*AREA_clean*) is used as the area of the opening. The terms are described in Table 3.6.

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[6] Nonvolatile components, like surfactants, were not considered, because they are sent to industrial waste treatment as wastewater.

Table 3.6 Variables used in estimating emissions of semi-aqueous cleaners (see also previous tables)

Term	Definition	Unit
$AREA\_clean$	Area of the opening of immersion-washing tank	m^2
$ELEM\_waste$	Quantity of target components transferred to waste material	kg/h

134. The quantity of the target components transferred to waste material is expressed as:

$$ELEM\_waste = ELEM\_clean\_waste + ELEM\_rinse \qquad \ldots 3.18$$

135. The target components in the waste cleaning solution ($ELEM\_clean\_waste$) and in rinsing wastewater ($ELEM\_rinse$) are obtained by Eqs. 3.7 and 3.11. The emission coefficient is obtained as the emission quantity (Eq. 3.17) divided by the usage quantity (Eq. 3.16).

4 REPRESENTATIVE VALUES AND VALIDATION OF PARAMETERS USED IN ESTIMATING EMISSIONS

136. The suitability of emission quantity estimation equations is verified by using characteristic parameters for each cleaner. The characteristic parameters were extracted from existing cleaning case studies. Representative values, along with distributions in some cases, were given to the parameters. This is because it is difficult to represent a characteristic parameter by a single value owing to the variation among objects to be cleaned, the variety of cleaning equipment involved, and the range of operations used. Also note that, in this ESD, the relationships between various cleaner characteristic parameters were not considered (even though the relationships are important) because there were insufficient data.

4.1 Validation of equations for estimating emissions of chlorinated cleaners

4.1.1 Evaporation quantity

137. In this section, the suitability of Kawamura–Mackay equations is validated (Chapter 3, Eqs. 3.5 and 3.6) for calculating the evaporation quantity of cleaners from cleaning equipment. Table 4.1 shows the parameter values used in Eqs. 3.5 and 3.6. Cooling water temperature (*T_cool*) and wind velocity (*U*) were given ranges in addition to representative values. Table 4.2 shows the calculated evaporation quantity.

Table 4.1 Parameter values substituted into emission rate equations

Symbol	Definition	Target component		Reasoning
		TCE [1]	DCM [1]	
AREA_solut	Washing tank opening area [m^2]	1		Assumed washing tank of 1m × 1m
Mw	Mol. weight of target components [g/mol]	131.39	84.93	Material property
T_cool	Cooling water temperature [K]	298.15 (293.15–303.15)	283.15 (278.15–288.15)	Ministry of the Environment (2007a) Representative values are taken as max.-likelihood values. Triangular distribution is assumed (min.–max. in parentheses)
P_v	Saturated vapour pressure of target components at temp. *T_cool* (Pa)	9901.9 (7808.6–12442.2)	30775.9 (24460.5–58091.2)	Material property [2]
R_cont	Emission control coefficient [–]	1		Assumed no emission control devices or measures
Z	Length of pool in wind direction [m]	1	1	Assumed washing tank of 1 m × 1 m
U	Wind velocity [m/s]	0.4 (0.1–1)	0.4 (0.1–1)	Representative value is control wind velocity for surrounding-type exhaust hood. Uniform distribution is assumed (min.–max. in parentheses)
Sc	Schmidt number[-]	1.69	1.36	National Ocean Service (2003)

[1] TCE, trichloroethylene; DCM, dichloromethane.

[2] Saturated vapor pressure (*P_v*) was calculated with the Antoine equation as a function of cooling water temperature (*T_cool*).

Table 4.2 Emissions calculated with emission rate equations

Symbol	Definition	Target component	
		TCE [1]	DCM [1]
ELEM_emission	Atmospheric emission of target components [kg/h/m^2] (2.5th–97.5th percentile)	2.56 (1.1 - 5.9)	6.26 (2.8 - 14.2)

[1] TCE, trichloroethylene; DCM, dichloromethane

138. Figure 4.1 compares the estimated and actual rates of emission (kg/h/m^2) derived from a previous cleaning case study (Table 4.3). The emission quantity in Table 4.3 was determined by multiplying the use quantity per unit time by 0.8, which is the average emission coefficient from a previous cleaning case study (Refer to Table A.1 in Appendix). Both the arithmetic mean and the geometric mean of the rate of cleaner usage fall within the estimated range (2.5th–97.5th percentile). The variability of individual emission quantities, which could not have been recreated by using an equation to estimate emission rates, was likely due to differences in the operational details of the cleaning equipment and in the objects to be cleaned, which differ in each cleaning operation. Note that the goal of this ESD is not to estimate detailed values, which will vary from operation to operation, but instead to estimate average emission quantities. Therefore, it was concluded that the equations for estimating the rate of emission are valid for average values.

139. Therefore, the approximation used in Chapter 3 with the assumption of a liquid surface cooled to *T_cool* near the washing tank opening may not be able to reproduce the variability in emissions, owing to the variety of objects to be cleaned and cleaning operations, but it is valid for calculating average values.

140. Of the 16 cases studied, 8 are within the 95% estimated range, 6 fell below it, and 2 were above it. Six out of the latter 8 cases used either *surrounding-type* or *closed-type* equipment. The emissions in many of the surrounding-type cases were well below the estimate. Therefore, the equations are effective for estimating emissions from open equipment, but require an emission control coefficient for surrounding-type equipment.

4.1.2 Emission coefficients

141. The emission estimation equations were validated by comparing emission coefficients in the literature with coefficients derived from the equations.

142. After setting the representative values for cleaning characteristic parameters shown in Tables 4.3 and 4.4, the following parameters were calculated: usage, emissions, waste solution content, and emission coefficients of trichloroethylene and dichloromethane. The value of *AREA_solut* (area of openings of washing tank) came from Table 4.4. Table 4.5 shows the calculation results.

143. Emission quantity per hour varies significantly among different cases (Fig. 4.1). This may be partly because the same number of hours of operation was assumed for those cases in Table 4.3 for which the durations of operation were unknown.

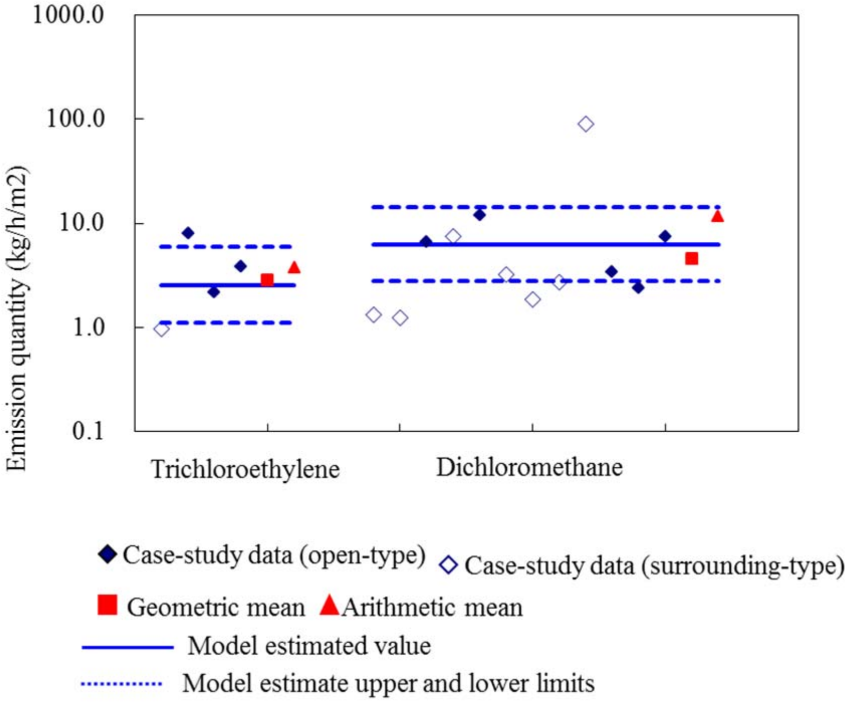

Figure 4.1 Comparison of emission rate estimation (range) with cleaning case-study data

Table 4.3 Cleaning case-study data used for validating emission estimation equations for chlorinated cleaners

No.	Cleaner used[1]	Washing tank opening			Device operating duration		Cleaner usage			Usage and emission quantity per unit area of opening		Device type	Source
		W (m)	L (m)	Area (m^2)	h/day	day/month	Value	Unit	/h of operat-ion[2] (kg/h)	Usage (kg/h/m^2)	Emission[3] (kg/h/m^2)		
1	TCE	4.5	1	4.5	8	20	875	kg/month	5.5	1.2	1.0	Surrounding-type, 2 tanks, automated	[1]
2	TCE	Unknown	Unknown	0.96	Unknown	Unknown	19 000	kg/year	9.5	9.9	7.9	Open-type	[2]
3	TCE	Unknown	Unknown	1.5	Unknown	Unknown	8 120	kg/year	4.1	2.7	2.2	Open-type	[2]
4	TCE	Unknown	Unknown	2.7	Unknown	Unknown	26 100	kg/year	13.1	4.8	3.9	Open-type	[2]
5	DCM	1.9	1.5	2.85	24	22	25,000	kg/month	4.7	1.7	1.3	Surrounding-type, single tank, automated	[1]
6	DCM	2.6	0.9	2.34	12	22	960	kg/month	3.6	1.6	1.2	Surrounding-type, 3 tanks, automated	[3]
7	DCM	0.8	1.2	0.96	10	25	2 000	kg/month	8.0	8.3	6.7	Hoop-type	[1]
8	DCM	1	1	1	8	20	1 500	kg/month	9.4	9.4	7.5	Surrounding-type, 2 pseudo-tanks	[3]
9	DCM	1.15	0.5	0.575	8	22	1 500	kg/month	8.5	14.8	11.9	Open-type, manual, 2 tanks	[3]
10	DCM	0.95	2	1.9	15	20	2 300	kg/month	7.7	4.0	3.2	Surrounding-type, manual, 3 tanks	[3]
11	DCM	0.9	0.65	0.585	10	22	300	kg/month	1.4	2.3	1.9	Surrounded-type, manual, single tank	[3]
12	DCM	Unknown	Unknown	9.1	Unknown	Unknown	62 000	kg/year	31.0	3.4	2.7	Closed-type	[2]
13	DCM	Unknown	Unknown	0.69	Unknown	Unknown	155 250	kg/year	77.6	112.5	90.0	Closed-type	[2]
14	DCM	Unknown	Unknown	1.6	Unknown	Unknown	13 675	kg/year	6.8	4.3	3.4	Open-type	[2]
15	DCM	Unknown	Unknown	3	Unknown	Unknown	17 850	kg/year	8.9	3.0	2.4	Open-type	[2]
16	DCM	Unknown	Unknown	0.8	Unknown	Unknown	14 750	kg/year	7.4	9.2	7.4	Open-type	[2]

[1] TCE, trichloroethylene; DCM, dichloromethane.

[2] In calculating usage quantity per hour of operation, we assumed 2000 hour of operation per year for the data missing the particular information (equivalent to 8 hours per day, 25 days per month).

[3] The emission quantity was assumed to be multiplied by 0.8 that of the usage quantity for all (emission coefficient: 0.8).

Sources: [1] MoE (2007a). [2] MIRI (2005). [3] Asahi Research Center (2006).

Table 4.4 Cleaning characteristic parameter values used in validation

Term	Definition	Unit	Representative value (min.–max.)	Sources & notes
OBJ_speed	Rate of treatment of objects to be cleaned	kg/h	1500 (3.1–20333)	[1–3], *n* = 24, representative value is geometric mean
OIL_obj	Oil quantity per unit mass of objects to be cleaned	kg/kg	1.6×10^{-4} (1×10^{-5}–0.087)	[1–4], *n* = 23, representative value is geometric mean
R_oil_waste	Ratio of oil content in waste solution	–	0.17 (0.07–0.5)	[2–4], *n* = 20, representative value is geometric mean
AREA_solut	Area of openings of washing tanks (chlorinated-type)	m^2	1.59 (0.575–9.1)	[1, 5–7] *n* = 16, representative value is geometric mean

Sources: [1] Asahi Research Center (2006), [2] Kikuchi & Hirao (2008a), [3] Cleaner user interviews, [4] Kikuchi & Hirao (2008b), [5] MoE (2007a), [6] Morikawa (2008), [7] MIRI (2005)

Table 4.5 Emission coefficients estimated when representative values are used for cleaning characteristic parameters

	Trichloroethylene	Dichloromethane
Atmospheric emission quantity [kg/h]	4.07	9.95
Quantity included in waste solution [kg/h]	1.17	1.17
Usage quantity [kg/h]	5.24	11.1
Emission coefficient [–]	0.78	0.89

144. The calculated emission coefficients were reasonably close to the industry's weighted coefficients (trichloroethylene, 0.80; dichloromethane, 0.77) of chlorinated cleaners (TableA.1, Appendix). Therefore, the methods for estimating emissions in this ESD reflect industrial experience relatively realistically.

145. Next, the effects of changes in the following parameters were verified: emissions, usage and emission coefficients. For untargeted parameters, the values listed in Tables 4.3 and 4.4 were used (the values in Table 4.4 were used for *AREA_solut*). For this exercise, trichloroethylene was picked up.

146. Figure 4.2 shows the changes in quantity of emission, usage quantity, and emission coefficients when the oil quantity per unit mass of objects to be cleaned (*OIL_obj*) and the ratio of oil content in waste solution (*R_oil_waste*) were varied. In the graph on the left, it is evident that when *OIL_obj* is varied from 1.0×10^{-6} to 0.1 kg/kg, atmospheric emission (*ELEM_emission*) remains constant. However, as the quantity of cleaner changes, the emission coefficient varies greatly from 1 to almost 0;[7] it is 0.81 when *OIL_obj* is 1.6×10^{-4} kg/kg, the value used in validation (Table 4.4).

147. The graph on the right of Figure 4.2 shows that when *R_oil_waste* varies from 0.05 to 0.95, the usage of cleaner gradually decreases to converge on the value of the atmospheric emission. In the range of emission coefficients at which *R_oil_waste* is in the normal range (0.07–0.5; Table 4.4), the emission coefficients generally fall between 0.5 and 0.9, within the range of case study data (Table A.1, Appendix).

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[7] Data suggest that the oil quantity per unit mass of objects to be cleaned shows inverse relationship to the rate of cleaning. This is not comprehended in this paper.

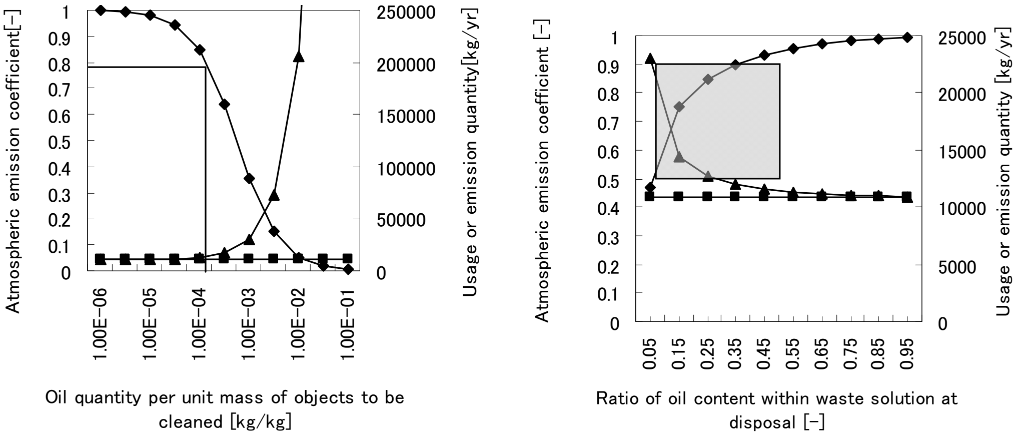

Figure 4.2 Relationship of emission coefficient to oil quantity per unit mass of objects to be cleaned and ratio of oil content contained within waste solution

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148. Figure 4.3 shows the changes in emission, usage, and emission coefficient as the cooling temperature (*T_cool*) and the control wind velocity (*U*) are varied. In the graph on the left, when *T_cool* is in the normal range (293.15–303.15 K = 20–30 °C), the emission coefficient remains within the range of the case study data (0.5–0.9). In the graph on the right, when *U* is in the normal range (0.1–1.0 m/s), the emission coefficient also remains within the range of the case study data. Therefore, the emission estimation equations are valid.

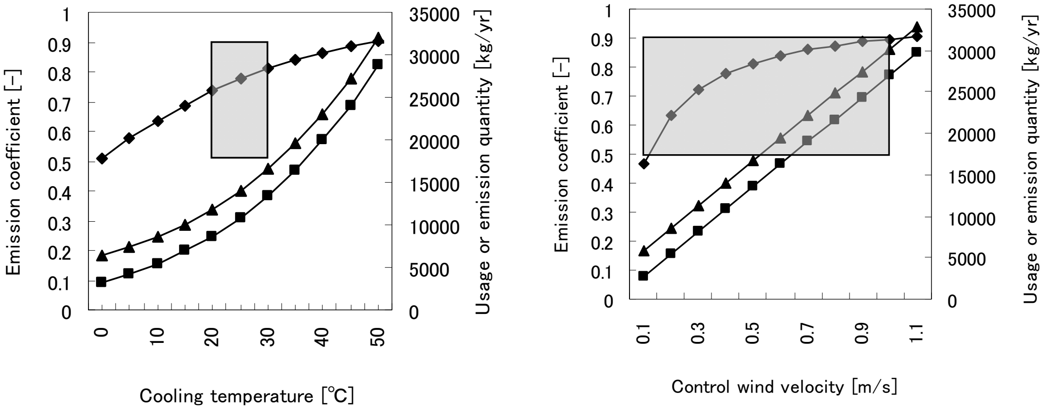

Figure 4.3 Relationships of emission coefficient to cooling temperature and wind velocity

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4.1.3 Effect of emission control measures (emission control coefficient)

149. Table 4.6 shows estimated emission control coefficients for each emission control measure. The values were derived from cleaner usage and emissions in the case studies. The coefficients for equipment with surrounding-type exhaust hoods or recovery devices are high, but those for equipment with a lid are low. However, the sample size is small, so the quantitative reliability of the data is low.

Table 4.6 Emission control coefficients derived from cleaning case-study data

Types of emission control measures	No. cases	Emission control coefficients [1]	
		Average	SD
Installation of cryogenic condensation recovery device	11	0.76	0.14
Installation of activated charcoal recovery device	4	0.49	0.31
Installation of other recovery devices	4	0.72	0.14
Enhancements to local exhaust ducts	1	0.10	–
Installation of surrounding-type exhaust hoods	1	0.80	–
Installation of automatic lid (automated open/close)	1	0.11	–
Thorough draining of solution	1	0.10	–
Enforcing lid use	2	0.23	–

[1] When only the usage data before and after the measures were available (i.e. emission data not available), a value of 0.9 was used as the emission coefficient before implementation of the emission control measure.

Sources: New Energy and Industrial Technology Development Organization (NEDO) (2003), MIRI (2005), MoE (2005b, 2007a), Asahi Research Center (2006), Morikawa (2008), Kikuchi & Hirao (2008a, b), cleaner user interviews.

4.2 Validation of equations for estimating emissions of hydrocarbon cleaners

150. The equations for estimating emissions from processes were validated. The processes use hydrocarbon cleaners against references that specifically discuss case-study data for hydrocarbon cleaners (JICOP, 2005; Tables A.5, A.6) or for chlorinated cleaners to fill in missing data.

151. Table 4.7 shows the values of the parameters used for open- and closed-type equipment. We assumed *n*-decane to be the most representative substance for hydrocarbon cleaners, on the basis of interviews conducted with users and manufacturers. Table 4.8 (open-type) and Table 4.9 (closed-type) show estimates.

Table 4.7 Cleaning characteristic parameters used in emission estimation equations for hydrocarbon cleaners, and the reasons for the chosen values

Equipment (open/closed)	Term	Contents	Condition 1	Condition 2	Reasons
Common	*OBJ_speed*	Rate of treatment of objects [kg/h]	120	100	JICOP (2005)
Common	*OIL_obj*	Oil quantity per unit mass of objects [kg/kg]	0.0034	0.0028	Ditto
Common	*DRAG_unitweight*	Quantity drag out per unit mass of objects [L/kg]	0.0068	0.0159	Ditto
Common	*Mw(chem)*	Molecular weight of target substance [g/mol]	142.3	142.3	Material property
Common	*ρ_solut*	Specific gravity of cleaning solution [kg/L]	0.7	0.7	Material property
Common	*R_oil_waste*	Ratio of oil content in waste cleaning solution [kg/kg]	0.4356	0.4356	JICOP (2005)
Common	*R_elem_solut*	Ratio of target components within cleaner [kg/kg]	1	1	Assumed single component
Common	*R_cont*	Emission control coefficient for exhaust gas treatment etc. [–]	0	0	No emission control device installed
Open-type	*Area_solut*	Opening area of cleaning equipment [m^2]	1.59	1.59	Table 4.4
Open-type	*Z*	Length of cleaning solution surface along wind direction [m]	1	1	Assumed opening of 1 m × 1.59 m
Open-type	*U*	Wind velocity [m/s]	0.4	0.4	Table 4.1
Open-type	*T_solut*	Cleaning solution temperature [K]	313.15	313.15	Assumed 40 °C, based on usage temp. (Table 2.8)
Open-type	*P_v*	Saturated vapour pressure at cleaning solution temperature [Pa]	493	493	Material property [1]
Closed-type	*SOLUT_generate*	Cleaning solution vapour generation [kg/h]	27.4	27.4	JICOP (2005)
Closed-type	*T_cool*	Cooling temperature in condenser (recovery device) [K]	293.15	293.15	JICOP (2005)
Closed-type	*P_v*	Saturated vapour pressure in condenser [Pa]	135	135	Material property [1]

[1] Calculated with the Antoine equation as a function of temperature (*T_solut* or *T_cool*)

Table 4.8 Estimated values (open equipment)

Symbol	Definition	Condition 1	Condition 2
ELEM_emission	Atmospheric emission of target components [kg/h]	0.78	1.3
ELEM_waste	Quantity of target components in waste solution [kg/h]	0.53	0.36
ELEM_use	Usage of target components [kg/h]	1.3	1.7
EF	Emission coefficients	0.59	0.78

Table 4.9 Estimated values (closed equipment)

Symbol	Definition	Condition 1	Condition 2
ELEM_emission	Atmospheric emission of target components [kg/h]	0.037	0.037
ELEM_waste	Quantity of target components in waste solution [kg/h]	0.53	0.36
ELEM_use	Usage of target components [kg/h]	0.57	0.40
EF	Emission coefficients	0.064	0.091

152. The emission coefficients of open equipment, calculated by using the estimating equations, are 0.59 under condition 1 and 0.78 under condition 2 (Table 4.8). These are close to the emission coefficients of 0.53 and 0.76 (Table A.4), as noted in the existing literature (JICOP, 2005) described in this ESD's Appendix. The emission coefficients calculated in this ESD are larger, because it considers the quantity drawn out along with evaporation from the cleaning tank.

153. For closed equipment, the estimates of emission coefficients (Table 4.9) are very similar to the JICOP (2005) data. The slight differences can be accounted for by the different specific gravities used.

154. As mentioned above, the emission coefficients calculated by using the estimation equations in this ESD were close to those in the existing literature. However, note that the estimation equations in this document still bear uncertainties, because only two cases were used.

4.3 Validation of equations for estimating emissions of aqueous cleaners

155. The equations were validated for estimating emissions from processes that use aqueous cleaners by comparing emission coefficients calculated by substituting the representative values of the characteristic parameters (Table 4.10) with the emission coefficients of alcohol ethoxylate (AE), derived from Corporate Social Responsibility (CSR) data of the 23 establishments surveyed (Table A.8, Appendix). For the parameters related to wastewater treatment, we assumed that activated carbon adsorption and microorganism treatment are done in series, on the basis of on-site interviews.

156. Table 4.11 shows estimates, including emissions. The emission coefficient, 0.027, is close to that of AE calculated from the CSR data of the 23 establishments (0.03, Table A.8). Therefore, the equations used in this ESD reflect reality.

Table 4.10 Cleaning characteristic parameters used in emission estimation equations for aqueous cleaners, and the reasons for the chosen values

Term	Definition	Representative value	Reasons
OBJ_speed	Rate of treatment of objects [kg/h]	1 500	Table 4.4
OIL_obj	Oil quantity per unit mass of objects [kg/kg]	1.60E-04	Table 4.4
R_oil_waste	Ratio of oil content within waste cleaning solution [kg/kg]	0.007	JICC (2002)[1]
ρ_solut	Specific gravity of cleaning solution [kg/L]	1	Figure 2.2 [2]
DRAG_unitweight	Quantity drawn out per unit mass of objects [L/kg]	0.0114	JICOP (2005)[3]
R_elem_solut	Ratio of target components within waste solution [kg/kg]	0.005	Chapter 2 [4]
R_remove	Removal ratio [–]	0.92	METI and MoE (2004)[5]
R_decom	Rate of decomposition [–]	0.4	METI and MoE (2004)[6]

[1] Value relative to oily contaminants. [2] Assumed to be the same as the specific gravity of water, because of the large water content. [3] Average of case study (Table 4.7) for hydrocarbon cleaners. [4] We assumed the ratio of target component within cleaner to be 0.1 (Figure 2.2) and the cleaner concentration in use to be 10% (Figure 2.3). [5] Assumed to have used activated charcoal treatment (removal rate of 0.8) and microorganism treatment (removal rate of 0.6) in series. [6] Assumed to have used activated charcoal treatment (rate of detoxification of 0) and microorganism treatment (rate of detoxification of 0.4) in series.

Table 4.11 Estimated values (aqueous cleaners)

Term	Definition	Value
ELEM_rinse_water	Quantity of target components released into public waters and sewer [kg/h]	0.0068
ELEM_use	Usage of target components [kg/h]	0.26
ELEM_rinse_waste	Quantity of target components transferred to waste [kg/h]	0.21
ELEM_rinse_decom	Quantity of target component decomposed [kg/h]	0.034
EF	Emission coefficient for emission into public waters and sewer[–]	0.027

4.4 Validation of equations for estimating emissions of semi-aqueous cleaners

157. The equations were validated for estimating emissions from processes that use semi-aqueous cleaners by comparing emission coefficients calculated by substituting the representative values of the characteristic parameters (Table 4.12) with values in the literature (Appendix). We considered diethylene glycol monomethyl ether ($C_5H_{12}O_3$) and diethylene glycol monobutyl ether ($C_8H_{18}O_3$), which have different alkyl groups, as representatives of diethylene glycol monoalkyl ether, which is often used as the main component of semi-aqueous cleaners. We used case-study data on semi-aqueous cleaners for the methods of use of the cleaners, data on chlorinated cleaners for objects to be cleaned and equipment (Table 4.4) on account of the unavailability of specific data, and data on hydrocarbon cleaners for the amount drawn out (Table 4.7).

158. Table 4.13 shows estimates. The calculated emission coefficients for the two target components were 0.64% and 0.15%, agreeing well with the value of 0.4% in the literature (Appendix A.2.5). Considering that the literature does not mention any specific targets and that accurate estimation is difficult because the emission coefficients are very small (≤1%), the emission estimation equations used in this ESD are suitable, and can possibly be applied on site.

Table 4.12 Cleaner characteristic parameters used in emission estimation equations for semi-aqueous cleaners, and the reasons for the chosen values

Symbol	Contents	Target components		Reasons
		Diethylene glycol monomethyl ether	Diethylene glycol monobutyl ether	
OBJ_speed	Rate of treatment of objects [kg/h]	1 500	1 500	Table 4.4
OIL_obj	Oil quantity per unit mass of objects [kg/kg]	1.6×10^{-4}	1.6×10^{-4}	Table 4.4
AREA_solut	Solution surface area [m^2]	1.59	1.59	Table 4.4
Z	Solution surface area in wind direction [m]	1	1	Assumed opening of 1 m × 1.59 m
Mw	Molecular weight of target components [kg/kmol]	120.1	162.2	Material property
R_oil_waste	Ratio of oil content within waste cleaning solution [kg/kg]	0.05	0.05	JICC (2002)
R_elem_solut	Ratio of target components in cleaning solution [kg/kg]	0.9	0.9	Figures 2.6, 2.7
T_solut	Cleaning solution temperature [K]	333.15	333.15	Figure 2.8
P_v	Saturated vapor pressure at cleaning solution temperature [Pa]	368.2	67.2	Material property [1]
U	Wind velocity [m/s]	0.4	0.4	Table 4.1
R_cont	Emission control coefficient [–]	0	0	No emission control device installed
ρ_solut	Specific gravity of cleaning solution [kg/L]	1.02	0.95	Material property
DRAG_ unitweight	Quantity drawn out per unit mass of objects [L/kg]	0.0114	0.0114	Table 4.7 [2]

[1] Calculated with the Antoine equation as a function of temperature (*T_solut*).

[2] Average of two case studies from JICOP (2005).

Table 4.13 Estimated values (semi-aqueous cleaners)

Term	Definition	Target components	
		Diethylene glycol monomethyl ether	Diethylene glycol monobutyl ether
ELEM_emission	Atmospheric emission of target components [kg/h]	0.13	0.028
ELEM_use	Usage of target components [kg/h]	19.8	18.7
ELEM_waste	Quantity of target components transferred to waste [kg/h]	20.0	18.8
EF	Emission coefficient to air [1][–]	0.0064	0.0015

[1] It is assumed that there is no emission into water

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APPENDIX A

UTLINE OF EMISSION COEFFICIENTS STATED IN THE EXISTING LITERATURE

Introduction

This appendix outlines the estimation methods and emission coefficients of each industrial cleaner in each industry. The calculated emission coefficients are also presented. The usage and emission coefficients were determined for 2007, except where lack information necessitated the use of data for other years.

Emission coefficients

Emission coefficients for chlorinated cleaners

Emission coefficients were estimated from the usage and emissions of three chlorinated cleaners by 18 industry groups (about 600 companies) as reported in the Hazardous Air Pollutants Self-Management Reports (METI, 2002, 2003, 2005) (Table A.1).

Table A.1 Emission coefficients of chlorinated cleaners by year, substance and industry

Manufacturing industries	1999	2001	2002	2003	Average 1999–2003	Average by industry and by year
Dichloromethane						
Iron & steel	0.88	0.83	0.86	0.83	0.85	0.77
Non-ferrous metals & products	0.89	0.83	0.85	0.90	0.86	
Fabricated metal products	0.91	0.83	0.78	0.77	0.82	
General machinery	–	0.73	0.74	0.76	0.74	
Electrical machinery, equipment & supplies	–	0.67	0.62	0.58	0.62	
Transportation equipment	0.77	0.88	0.84	0.89	0.84	
Precision instruments & machinery	–	0.90	0.92	–	0.91	
Average	0.86	0.78	0.74	0.73		
Trichloroethylene						
Iron & steel	0.75	0.72	0.80	0.78	0.76	0.80
Non-ferrous metals & products	0.50	0.51	0.55	0.70	0.56	
Fabricated metal products	0.92	0.83	0.82	0.83	0.85	
General machinery	–	0.75	0.71	0.67	0.72	
Electrical machinery, equipment & supplies	–	0.46	0.54	0.39	0.47	
Transportation equipment	0.49	0.75	0.65	0.54	0.62	
Precision instruments & machinery	–	–	–	–	–	
Average	0.87	0.78	0.78	0.78		
Tetrachloroethylene						
Iron & steel	0.92	0.96	0.95	0.95	0.94	0.70
Non-ferrous metals & products	0.84	0.63	0.82	0.88	0.79	
Fabricated metal products	0.67	0.63	0.65	0.71	0.66	
General machinery	–	0.49	0.60	0.54	0.54	
Electrical machinery, equipment & supplies	–	0.82	0.90	0.71	0.82	
Transportation equipment	0.80	0.24	0.24	0.29	0.46	
Precision instruments & machinery	–	–	–	–	–	
Average	0.80	0.62	0.72	0.69		

Averages are weighted by the number of establishments.

Emission coefficient for hydrocarbon cleaners

The atmospheric emission coefficient of hydrocarbon cleaners (0.32) was calculated as the weighted average of the domestic cleaning equipment composition ratio for each washing method in the VOC Inventory (Ministry of the Environment, 2008) (Table A.2).

Table A.2 Data used in calculating the emission coefficient for hydrocarbon cleaners

Item	Depressurized vapour washing method	Hot-air drying method
Usage of oil cleaner per cleaning machine (L/h/unit)	0.6553 (a)	1.814 (d)
Domestic installation rate	78% (b)	22% (e)
Atmospheric emission coefficient (per cleaning method)	0.074 (c)	0.65 (f)
Atmospheric emission coefficient of hydrocarbon solvents	0.32	

Atmospheric emission factor (EF) = (abc + def) / (ab + de).

Sources: VOC Inventory (Ministry of the Environment, 2008). Values of a, c, d and f come from Table A.3.

Table A.3 Calculation of data in Table A.2

	Depressurized vapour washing method	Hot-air drying method
Usage of hydrocarbon cleaners by equipment (L/h)	0.6553 (a)	1.814 (d)
Fraction as proportion of total	0.265	0.735
Estimate of domestic installation ratio of equipment [1]	0.9	0.1
Ratio of domestic use to overall use of hydrocarbons	0.76	0.24
VOC emission coefficient	0.061–0.087 (mean 0.074: c)	0.53–0.76 (mean 0.65: f)

[1] Research data taken from 2003 Usage of Industrial Cleaning Device for 31 cleaning devices that use hydrocarbon cleaners, and from interviews.

Source: Asahi Research Center (2006) and Table A.4.

Table A.4 Calculation of data in Table A.3

Washing (drying) system	Depressurized vapour washing method (vacuum drying)		Hot-air drying method	
	Condition 1	Condition 2	Condition 1	Condition 2
Atmospheric emission (L/h) and setting justification	0.0468	0.0468	0.817	1.594
	Emission quantity from vacuum pump		Assume all cleaning solution exhausted to atmosphere	
Cleaner usage quantity for each condition and average usage quantity (L/h)	0.770	0.541	1.540	2.088
	0.6553 (a)		1.814 (d)	
Atmospheric emission ratio	0.061	0.087	0.53	0.76
	0.074 (c)		0.65 (f)	

Source: JICOP (2005).

Table A.5 Experimental data used for estimating emissions given in Table A.4.

		Condition 1	Condition 2
Objects to be cleaned		Rivet (aluminum)	Pressed part (material SUS304)
Weight		12 kg/basket (120 kg/h, 10 baskets/h)	10 kg/basket (100 kg/h, 10 baskets/h)
Machining oil drag-in		41 g/ basket (410 g/h, 0.482 L/h, specific gravity 0.85)	28 g/ basket (280 g/h : 0.392 L/h, specific gravity 0.85)
Cleaning solution drag-out		60 g/ basket (600 g/h, 0.817 L/h)	117 g/ basket (170 g/h, 1.594 L/h)
Cleaning solution		Hydrocarbon cleaner A (boiling point 174 °C, specific gravity 0.734, vapour pressure @ 20 °C 0.95 mm Hg)	
Allowable concentration of machining oil at discharge from reduced-pressure distillation regenerator		40%	
Cooler temperature		20 °C	
Vapor generation rate		37.5 L/h	
Exhausted to atmosphere	Emission quantity (L/h)	0.0468	
	Calculation	37.5 L/h × 0.95 mm Hg / 760 mm Hg = 0.0468 L/h	
		Vapour generation quantity × vapour pressure @ 20 °C	
	Ratio against cleaner consumption	6.1%	8.7%
Transfer as waste solution	Emission rate (L/h)	0.723	0.494
	Ratio against cleaner consumption	93.9%	91.3%
	Calculation(L/h)	(0.482 / 40%) – 0.482 = 0.723	(0.329 / 40%) – 0.329 = 0.494
		(machining oil drag-in amount ÷ allowable concentration of machining oil at emission from reduced-pressure distillation regenerator) – machining oil drag-in amount	
Cleaning solution consumption	Consumption rate (L/h)	0.770	0.541
	Calculation	0.0468 + 0.723 = 0.770 (L/h)	0.0468 + 0.494 = 0.541 (L/h)
		Atmospheric emission quantity + quantity of emission as waste solution	

Source: JICOP (2005).

Emission coefficients for aqueous cleaners

Emission coefficients used for PRTR estimation

Table A.6 lists the emission coefficients of six surfactants emitted from industrial cleaners listed in the estimated releases outside notification of the Japanese pollutant releases and transfer registers (PRTR).

These emission coefficients consider not only the seven industries considered in this ESD, but all industries except manufacture of chemical products. Data include surfactants used as cleaners and surfactants used to treat textiles.

Table A.6 Average emission coefficients of surfactants used in cleaners

Surfactant	*n*	Average emission coefficient	Annual usage (kg/year)	Annual emission (kg/year)
LAS_*	141	0.27	78 934	21 452
AO *	32	0.58	1 567	914
DAC_*	–	–	–	–
AE_*	220	0.18	177 466	31 269
OPE_*	101	0.24	17 018	4 029
NPE_*	257	0.12	229 073	26 456

Source: METI and MoE (2008).

*) LAS: Linear alkyl benzene sulfonate, AO: N,N,-Dimethyldodecylamine=N-oxide, DAC: Bis(hydrogenated tallow)dimethylammonium chloride, AE: Polyoxyethylene alkyl ether, OPE: Polyoxyethylene octylphenyl ether, NPE: Polyoxyethylene nonylphenyl ether

Emission coefficients based on PRTR reported data

The inclusion of data from industries outside of the seven fields considered in this calculated The emission coefficients were calculated with PRTR data of alcohol ethoxylates (AE), which we consider to represent surfactants used in industrial cleaners, to understand the differences between industries. The values were calculated for all industries except for manufacture of chemical products, from the PRTR data for 2006.

The emission coefficient (0.10) for the seven industries in this ESD, based on PRTR data, is only about 37% of the emission coefficient (0.27) for all industries excluding the manufacture of chemical products. This disparity indicates that emission coefficients of surfactants vary greatly depending on industry. For this reason, the emission coefficient in Table A.6 would be too high for the seven industries.

Although same industries were considered in Tables A.6 and A.7, the emission coefficient (0.27) in Table A.7 is 1.5 times higher than that in Table A.6 (0.18). Because the estimation method used for Table A.7 does not consider degradation by wastewater treatment, the emission coefficient might be excessive. So to include the effects of other industries and the effect of degradation, emission coefficients were calculated using Corporate Social Responsibility (CSR) report data, etc., in the following section.

Table A.7 Emission coefficients based on PRTR reported data (for surfactant AE)

Industry	All industries excluding manufacture of chemical products	Industries in this ESD
Emission quantity (kg/year)	186 601	20 907
Transfer quantity (kg/year)	509 645	184 266
Emission coefficient [1]	0.27	0.10
Number of reported facilities	230	64

[1] Calculated as emission quantity / (emission quantity + transfer quantity).

Source: PRTR reported data for 2006 (disclosed 2008).

Emission coefficients based on Corporate Social Responsibility reports

As the analysis in section A.2.3.2 does not consider the degradation and removal of surfactants by wastewater treatment, we analysed AE data listed in Corporate Social Responsibility (CSR) reports, which include removal, emissions and usage.

Table A.8 shows the estimated emission coefficients based on data from 23 establishments. The emission coefficient for emission into waters (emission ÷ transaction) is 0.03. Although this is smaller than the value of 0.10 (Table A.7), 0.18 (Table A.6) and 0.139 (Table A.8: removal), the amount of surfactants degraded and removed through wastewater treatment is not negligible.

Table A.8 Emission coefficient estimates based on CSR reports (for surfactant AE)

Item	kg/year	Ratio against transaction quantity
Transaction quantity	201 340	–
Atmospheric emission	170	0.001
Emission into waters	6 041	0.03
Transfer into sewage and waste	15 1470	0.752
Removal treatment	28 023	0.139
Other	3 938	0.02

Source: Mainly 2006 data, including CSR reports of 23 establishments (19 that manufacture transportation equipment and four that manufacture electrical machinery, equipment and supplies).

To confirm the distribution of coefficients shown in Table A.8, Figure A.1 shows the distribution of emission, transfer and removal quantity for individual establishments. All items show large variances. Note the large differences between individual establishments, especially for removal treatment.

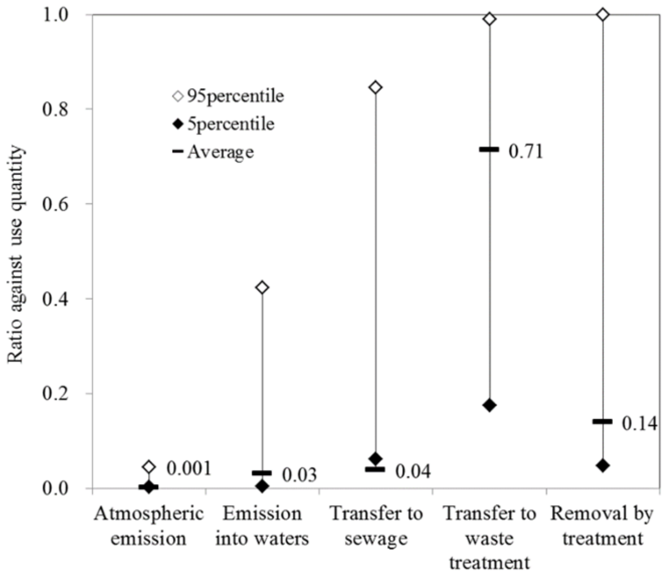

Figure A.1 Ratios of emission, transfer and removal of AE against use quantity

Source: CSR reports and websites of the 23 establishments.

The establishments' CSR reports and websites include substantial data on the manufacture of transportation equipment, but not of iron and steel, which accounts for over 30% of surfactants used. However, we have determined that the emission coefficient of 0.03 is appropriate for the surfactants, because the CSR data allowed to calculate emission coefficients from removal rates, even though some coefficients of the industries considered in this ESD could not be calculated. Although this ESD considers only AE, it is assumed that the same emission coefficients can be used for other surfactants under identical usage conditions.

As future improvement, it would be desirable to calculate the emission coefficients by gathering real case data for each industry.

Emission coefficients for other cleaners

The VOC Inventory (MoE, 2008) shows an emission coefficient for semi-aqueous cleaners of 0.004. This value is based on interviews with participants at the Japan Industrial Conference on Cleaning (MoE, 2008)[8]. Because information on emission coefficients for semi-aqueous cleaners is scarce, this value is used as representative in this ESD.

Among halogenated cleaners, the VOC Inventory shows 0.84 for fluorinated cleaners and 0.75 for others (in this case, brominated).

Summary of emission coefficients

Table A.9 summarizes the emission coefficients for 5 types of industrial cleaners considered in this ESD.

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[8] These values are said to have been obtained from interviews, but the details of the interviews (e.g. how they were conducted, and who and how many were interviewed), as well as the scope of their application, are not known.

Table A.9 Emission coefficients for each cleaner type by industry

	Iron & steel	Non-ferrous metals & products	Fabricated metal products	General machinery	Electrical machinery, equipment & supplies	Transportation equipment	Precision instruments & machinery	Average [1]
Chlorinated								
Dichloromethane	0.85	0.86	0.82	0.74	0.62	0.84	0.91	0.77
Trichloroethylene	0.76	0.56	0.85	0.72	0.47	0.62	0.80 [2]	0.80
Tetrachloroethylene	0.94	0.79	0.66	0.54	0.82	0.46	0.70 [2]	0.70
Hydrocarbon	0.32							
Semi-aqueous	0.004							
Aqueous	0.03							
Halogenated								
Fluorinated	0.84							
Brominated	0.75							

[1] Weighted average according to the number of businesses.

[2] Owing to lack of data, the emission coefficients of trichloroethylene and tetrachloroethylene used in the manufacture of precision instruments and machinery were taken as the average of the other six industries.

APPENDIX B

SAMPLE CALCULATION

Introduction

This section presents an example of how the equations introduced in Section 3 might be used to estimate usage, emission quantity, and emission factor for certain types of industrial cleaners.

The default values used in these calculations are presented in Section 4 and should be used only in the absence of site-specific information. If the equations used for estimation is unknown, the decision logic diagram presented in Figure B.1 could help identify an appropriate equation.

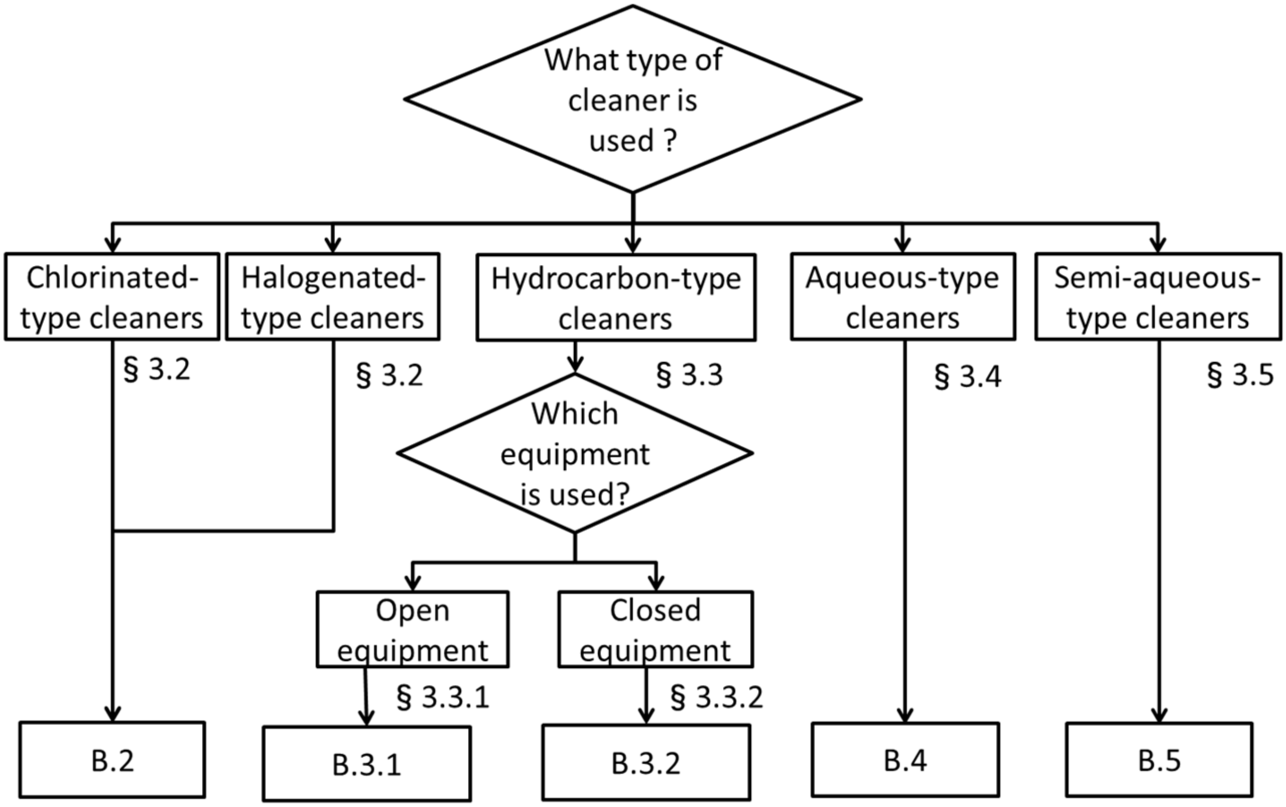

Figure B.1 Decision Logic Diagram

Chlorinated cleaners

Atmospheric emission

Parameter values

AREA_solut : Opening area of cleaning equipment: 1.59m^2 (shown in Table 4.4)

Mw : Molecular weight: 131.4 kg/kmol (shown in Table 4.1, molecular weight of TCE)

P_v : Saturated vapour pressure at T_cool: 9 901.9 Pa (shown in Table 4.1)

T_cool: Cooling temperature: 298.15 K (shown in Table 4.1)

R_gas: Gas constant: 8 314 J/K/kmol

R_cont : Emission control coefficient: 0 (no emission control device installed)

U : Wind velocity around upper part of washing tank: 0.4m/s (shown in Table 4.1)

Z : Length of cleaning solution surface along wind direction: 1.0m (shown in Table 4.1)

Sc : Schmidt number: 1.69 (TCE, shown in Table 4.1)

Km : Material transfer coefficient: 0.0135m/s ($Km = 0.0048 \times U \times Z^{-1/9} \times Sc^{-2/3}$ … 3.6)

Atmospheric emission of target components (*ELEM_emission*) is calculated by Eq. 3.5.

ELEM_emission = AREA_solut × Km ×3 600× *{(Mw × P_v) / (R_gas × T_cool)}* × *(1 – R_cont)*
= 1.59× 0.00135 × 3600 × {(131.4 × 9 901.9) / (8 314 × 298.15)} × (1 –0)
= 0.00215 ×3 600 × (1301109.7/2 478 819.1)
= 0.021465 × 3 600 × 0.524890945
= 4.1 (kg/h)

Target components in waste cleaning solution

Parameter values

OBJ_speed : Rate of treatment of objects to be cleaned: 1 500 kg/h (shown in Table 4.4)
OIL_obj : Oil quantity per unit mass of objects to be cleaned: 0.000 16kg/kg (shown in Table 4.4)
R_oil_waste : Ratio of oil content in waste solution: 0.17 (shown in Table 4.4)
R_elem_solut: Ratio of target components within cleaning solution: 1 (Assumed single component)

The quantity of the target components (*ELEM_clean_waste*) that would be disposed of as waste cleaning solution is calculated by Eq. 3.7.

ELEM_clean_waste = OBJ_speed × OIL_obj × ((1 – R_oil_waste) / R_oil_waste) × R_elem_solut
= 1 500 × 0.0016 × ((1 –0.17) /0.17) ×1
= 0.24 × (0.83/0.17) ×1
= 1.2 (kg/h)

Quantity of target components used

The quantity used is the sum of atmospheric emission and waste solution (Eq. 3.3).

ELEM_use = ELEM_emission + ELEM_clean_waste
= 4.06 + 1.17
= 5.2 (kg/h)

Emission coefficient

The emission coefficient is the ratio of atmospheric emission to quantity used (Eq. 3.4).

EF = ELEM_emission / ELEM_use
= 4.06/5.23
= 0.78

Hydrocarbon cleaners

Open equipment

Atmospheric emission

Parameter values

AREA_solut : Opening area of cleaning equipment: 1.59 m^2 (shown in Table 4.4)

OBJ_speed : Rate of treatment of objects to be cleaned: 1 500 kg/h (shown in Table 4.4)

OIL_obj : Oil quantity per unit mass of objects to be cleaned: 0.00016 kg/kg (shown in Table 4.4)

U: Control wind velocity around upper part of washing tank: 0.4m/s (shown in Table 4.1)

Z: Length of cleaning solution surface along wind direction: 1.0m (assumed washing tank of 1 m ×1.59 m)

Sc : Schmidt number: 1.75 (n-Decane, shown in Table 4.7)

Km : Material transfer coefficient: 0.0132m/s ($Km = 0.0048 \times U \times Z^{-1/9} \times Sc^{-2/3}$ ··· 3.6)

Mw : Molecular weight: 142.3 kg/kmol (n-Decane)

P_v : Saturated vapour pressure at cleaning solution temperature: 493Pa (n-Decane, shown in Table 4.7)

R_gas : Gas constant: 8 314 J/K/kmol

T_solut : Cleaning solution temperature: 313.15K (shown in Table 4.7)

DRAG_unitweight : Quantity of cleaning solution taken out by objects to be cleaned: 0.0114L/kg (average of case study shown in Table 4.7 and 4.10)

ρ_solut : Specific gravity of cleaning solution: 0.7 (n-Decane)

R_elem_solut : Ratio of target components within cleaning solution: 1 (assumed single component)

R_cont: Emission control coefficient: 0 (no emission control device installed)

Atmospheric emission of target components (*ELEM_emission*) is calculated by Eq. 3.8.

ELEM_emission = [AREA_solut × Km ×3 600× *{(Mw × Pv) / (R_gas × T_solut)} +*

DRAG_unitweight × OBJ_speed × ρ_solut × R_elem_solut] × (1 – R_cont)
= [1.59 × 0.0132 × 3 600 × {(142.3 × 493)/(8 314 × 313.15)} + 0.0114 × 1 500 × 0.7×1] × (1 – 0)
= 0.02099 × (70153.9/2603529.1) × 3 600+11.97
= 2.036 + 11.97
= 14 (kg/h)

Target components in waste cleaning solution

Parameter values

OBJ_speed : Rate of treatment of objects to be cleaned: 1 500kg/h (shown in Table 4.4)
OIL_obj : Oil quantity per unit mass of objects to be cleaned: 0.00016 kg/kg (shown in Table 4.4)
R_oil_waste : Ratio of oil content in waste cleaning solution: 0.445 (average of case study shown in Table 4.7 and 4.10)
R_elem_solut : Ratio of target components within cleaning solution: 1 (assumed single component)

The quantity of the target components (*ELEM_clean_waste*) that would be disposed of as waste cleaning solution is calculated by Eq. 3.7.

ELEM_clean_waste = OBJ_speed × OIL_obj ×
((1 – R_oil_waste) / R_oil_waste) × R_elem_solut
= 1 500 × 0.00016 × ((1-0.445)/0.445) × 1
= 0.24 × 5.05
= 1.2 (kg/h)

Quantity of target components used

The quantity used is the sum of atmospheric emission and waste solution (Eq. 3.3).

ELEM_use = ELEM_emission + ELEM_clean_waste
= 14.01 + 1.21
= 15 (kg/h)

Emission coefficient

The emission coefficient is the ratio of atmospheric emission to quantity used (Eq. 3.4).

EF = ELEM_emission / ELEM_use
= 14.01/15.22
= 0.92

Closed equipment

Atmospheric emission

Parameter values

SOLUT_generate : Quantity of cleaning solution vapour generated per unit time in the depressurizing vapour generation mechanism: 27.4kg/h (shown in Table 4.7)
R_elem_solut : Ratio of target components within cleaning solution: 1 (assumed single component)
P_v : Saturated vapour pressure in condenser: 135Pa (n-Decane, T_cool: 293.15K, shown in Table 4.7)
P_atm : Atmospheric pressure: 101 325Pa

Atmospheric emission of target components (*ELEM_emission*) is calculated by Eq. 3.9.

$$\begin{aligned}\mathit{ELEM\_emission} &= \mathit{SOLUT\_generate} \times \mathit{R\_elem\_solut} \times (\mathit{P\_v} / \mathit{P\_atm})\\ &= 27.4 \times 1 \times (135/101\,325)\\ &= 0.037\ (\mathrm{kg/h})\end{aligned}$$

Target components in waste cleaning solution

Parameter values

OBJ_speed : Rate of treatment of objects to be cleaned : 1 500kg/h (shown in Table 4.4)
OIL_obj : Oil quantity per unit mass of objects to be cleaned : 0.00016 kg/kg (shown in Table 4.4)
R_oil_waste : Ratio of oil content in waste cleaning solution: 0.445 (average of case study shown in Table 4.7)
R_elem_solut : Ratio of target components within cleaning solution: 1 (assumed single component)

The quantity of the target components (*ELEM_clean_waste*) that would be disposed of as waste cleaning solution is calculated by Eq. 3.7.

$$\begin{aligned}\mathit{ELEM\_clean\_waste} &= \mathit{OBJ\_speed} \times \mathit{OIL\_obj} \times ((1 - \mathit{R\_oil\_waste}) / \mathit{R\_oil\_waste}) \times \mathit{R\_elem\_solut}\\ &= 1\,500 \times 0.00016 \times ((1-0.445)/0.445) \times 1\\ &= 0.24 \times 5.05\\ &= 1.2\ (\mathrm{kg/h})\end{aligned}$$

Quantity of target components used

The quantity used is the sum of atmospheric emission and waste solution (Eq. 3.3).

$$\begin{aligned}\mathit{ELEM\_use} &= \mathit{ELEM\_emission} + \mathit{ELEM\_clean\_waste}\\ &= 0.0365 + 1.212\\ &= 1.2\ (\mathrm{kg/h})\end{aligned}$$

Emission coefficient

The emission coefficient is the ratio of atmospheric emission to quantity used (Eq. 3.4).

$$\begin{aligned}\mathit{EF} &= \mathit{ELEM\_emission} / \mathit{ELEM\_use}\\ &= 0.0365/1.249\\ &= 0.029\end{aligned}$$

Aqueous cleaners

Quantity of target components transferred to waste solution (Emission quantity of cleaner)

Parameter values

OBJ_speed : Rate of treatment of objects to be cleaned: 1 500 kg/h (shown in Table 4.4)
OIL_obj : Oil quantity per unit mass of objects to be cleaned: 0.00016 kg/kg (shown in Table 4.4)
R_oil_waste : Ratio of oil content within waste cleaning solution: 0.007 kg/kg (shown in Table 4.10)
R_elem_solut : Ratio of target components within waste solution: 0.005 kg/kg (shown in Table 4.10)

The quantity of the target components that would be disposed of as waste cleaning solution (ELEM_clean_waste) is calculated by Eq. 3.7.

$$ELEM\_clean\_waste = OBJ\_speed \times OIL\_obj \times ((1 - R\_oil\_waste) / R\_oil\_waste) \times R\_elem\_solut$$
$$= 1\ 500 \times 0.00016 \times (0.993/0.007) \times 0.005$$
$$= 0.17\ (\text{kg/h})$$

Quantity of target components that goes through wastewater treatment as rinsing wastewater (Disposal quantity of cleaner)

Parameter values

DRAG_unitweight : Quantity of cleaning solution taken out by objects to be cleaned: 0.0114L/kg (average of case study shown in Table 4.7 and 4.10)
OBJ_speed : Rate of treatment of objects to be cleaned: 1 500kg/h (shown in Table 4.4)
ρ_solut : Specific gravity of cleaning solution: 1 (shown in Table 4.10)
R_elem_solut : Ratio of target components within waste solution: 0.005 kg/kg (shown in Table 4.12)
R_remove : Ratio of removal by wastewater treatment: 0.92 (shown in Table 4.10)
R_decom : Ratio of decomposition by wastewater treatment: 0.4 (shown in Table 4.10)

The quantity of target components that goes through wastewater treatment as rinsing wastewater (*ELEM_rinse*) is calculated by Eq. 3.11.

$$ELEM\_rinse = DRAG\_unitweight \times OBJ\_speed \times \rho\_solut \times R\_elem\_solut$$
$$= 0.0114 \times 1\ 500 \times 1 \times 0.005$$
$$= 0.086\ (\text{kg/h})$$

Quantity of target components transferred to waste material (*ELEM_rinse_waste*) is calculated by Eq. 3.12.

$$ELEM\_rinse\_waste = ELEM\_rinse \times (R\_remove - R\_decom)$$
$$= 0.0855 \times (0.92 - 0.4)$$
$$= 0.044\ (\text{kg/h})$$

Quantity of emission released into public waters or sewer (*ELEM_rinse_water*) is calculated by Eq. 3.13.

$$ELEM\_rinse\_water = ELEM\_rinse \times (1 - R\_remove)$$
$$= 0.0855 \times (1 - 0.92)$$
$$= 0.0068 \text{ (kg/h)}$$

Quantity of decomposition by wastewater treatment (*ELEM_rinse_decom*) is calculated by Eq. 3.14.

$$ELEM\_rinse\_decom = ELEM\_rinse \times R\_decom$$
$$= 0.0855 \times 0.4$$
$$= 0.034 \text{ (kg/h)}$$

Quantity of target components used

The usage quantity of cleaner is calculated by Eq. 3.10.

$$ELEM\_use = ELEM\_clean\_waste + ELEM\_rinse$$
$$= 0.1702 + 0.0855$$
$$= 0.26 \text{ (kg/h)}$$

Quantity of emission released into public waters or sewer

The quantity of emission released into public waters or sewer (*ELEM_rinse_water*) is calculated by Eq. 3.15.

$$ELEM\_rinse\_water = DRAG\_unitweight \times OBJ\_speed \times \rho\_solut \times R\_elem\_solut \times (1 - R\_remove)$$
$$= 0.0114 \times 1\,500 \times 1 \times 0.005 \times (1 - 0.92)$$
$$= 0.0068 \text{ (kg/h)}$$

Emission coefficient

The emission coefficient (EF) is obtained as the emission (Eq. 3.15) divided by the quantity used (Eq. 3.10).

$$EF = ELEM\_rinse\_water / ELEM\_use$$
$$= 0.00684 / 0.2557$$
$$= 0.027$$

Semi-aqueous cleaners

Atmospheric emission

Parameter values

AREA_clean : Area of the opening of immersion-washing tank: 1.59m^2 (shown in Table 4.4)
U : Control wind velocity around upper part of washing tank: 0.4m/s (shown in Table 4.1)
Z : Length of cleaning solution surface along wind direction: 1.0m (shown in Table 4.12)
Sc : Schmidt number: 1.61 (National Ocean Service, 2003)
Km : Material transfer coefficient : 0.001395m/s ($Km = 0.0048 \times U \times Z^{-1/9} \times Sc^{-2/3}$ … 3.6)
Mw : Molecular weight : 120.1 kg/kmol (Diethylene glycol monomethyl ether shown in Table 4.12)
P_v : Saturated vapor pressure at cleaning solution temperature: 368.2 Pa (shown in Table 4.12)
R_gas : Gas constant: 8 314 J/K/kmol
T_solut : Cleaning solution temperature: 333.15K (shown in Table 4.12)

Atmospheric emission (*ELEM_emission*) is calculated by Eq. 3.17.

ELEM_emission = AREA_clean × Km ×3600 {(Mw × P_v) / (R_gas × T_solut)}
= 1.59 × 0.001398 × 3600 × ((120.1 × 368.2)/(8314 × 333.15))
= 0.00222282 × 3600 × (44220.82/2769809.1)
= 8.002152 × 0.015965295
= 0.13 (kg/h)

Quantity of target components transferred to waste solution

Parameter values

OBJ_speed : Rate of treatment of objects to be cleaned: 1 500kg/h (shown in Table 4.4)
OIL_obj : Oil quantity per unit mass of objects to be cleaned: 0.00016 kg/kg (shown in Table 4.4)
R_oil_waste : Ratio of oil content in waste cleaning solution: 0.05 (shown in Table 4.12)
R_elem_solut : Ratio of target components within cleaning solution: 0.9 (shown in Table 4.12, Figures 2.6 and 2.7)

The quantity of the target components that would be disposed of as waste cleaning solution (*ELEM_clean_waste*) is calculated by Eq. 3.7.

ELEM_clean_waste = OBJ_speed × OIL_obj ×((1 – R_oil_waste) / R_oil_waste) × R_elem_solut
= 1 500 × 0.00016 × (0.95/0.05) × 0.9
= 4.1 kg/h

Quantity of target components that goes through wastewater treatment as rinsing wastewater

Parameter values

DRAG_unitweight : Quantity of cleaning solution taken out by objects to be cleaned : 0.0114 L/kg (average of case study shown in Table 4.7 and Table 4.12)
OBJ_speed : Rate of treatment of objects to be cleaned: 1 500 kg/h (shown in Table 4.4)
ρ_solut : Specific gravity of cleaning solution: 1.02 (shown in Table 4.12)
R_elem_solut : Ratio of target components within waste solution: 0.9 kg/kg (shown in Table 4.12)

The quantity of target components that goes through wastewater treatment as rinsing wastewater (*ELEM_rinse*) is calculated by Eq. 3.11.

$$\begin{aligned} \mathit{ELEM\_rinse} &= \mathit{DRAG\_unitweight} \times \mathit{OBJ\_speed} \times \rho\mathit{\_solut} \times \mathit{R\_elem\_solut} \\ &= 0.0114 \times 1\,500 \times 1.02 \times 0.9 \\ &= 16 \text{ kg/h} \end{aligned}$$

Quantity of target components transferred to waste material

The quantity of target components transferred to waste material (*ELEM_waste*) is calculated by Eq. 3.18.

$$\begin{aligned} \mathit{ELEM\_waste} &= \mathit{ELEM\_clean\_waste} + \mathit{ELEM\_rinse} \\ &= 4.104 + 15.6978 \\ &= 20 \text{ kg/h} \end{aligned}$$

Quantity of target components used

The quantity of target components used (*ELEM_use*) is calculated by Eq. 3.16.

$$\begin{aligned} \mathit{ELEM\_use} &= \mathit{ELEM\_emission} + \mathit{ELEM\_clean\_waste} + \mathit{ELEM\_rinse} \\ &= 0.1278 + 4.104 + 15.6978 \\ &= 20 \text{ kg/h} \end{aligned}$$

Emission coefficient

The emission coefficient is the ratio of atmospheric emission to quantity used (Eq. 3.4).

$$\begin{aligned} \mathit{EF} &= \mathit{ELEM\_emission} / \mathit{ELEM\_use} \\ &= 0.1278/19.9296 \\ &= 0.0064 \end{aligned}$$

APPENDIX C

SUBSTITUTION TRENDS

The substitutions of chlorinated-type cleaners were reviewed; those are trichloroethylene (TCE), dichloromethane (DCM), and tetrachloroethylene (PCE) among 20 industrial groups. Table C.1 shows the numbers of substitutions of other cleaners for the three chlorinated-type cleaners by companies in each industry organization. From fiscal year 2001 to 2003 there were 166 reported substitutions of chlorinated-type substances.

The numbers of substitutions were, 79 for DCM, 64 for TCE, and 23 for PCE. The Japan Metal Heat Treatment Association (32 substitutions), the four groups including the Japan Electrical Manufacturers' Association (32), and the Federation of Electroplating Industry Associations, Japan (19) reported the greatest numbers of substitutions.

The most prominent substitute cleaners were aqueous type (60 substitutions), hydrocarbon type (51), and semi-aqueous type (22). These three accounted for 80% of all reported substitutions.

The industry group that most frequently substituted chlorinated-type cleaners with aqueous-type cleaners was the Federation of Electroplating Industry Associations, Japan (19 substitutions). The Japan Metal Heat Treatment Association had the most substitutions with hydrocarbon-type cleaners (21). The Four Groups Including the Japan Electrical Manufacturers' Association reported the greatest number of substitutions with semi-aqueous-type cleaners (14).

These findings show the industry bias in the choice of substitution. Industry-associated reasons for the bias include the following factors. In the electroplating industry, many companies already own wastewater treatment systems because they use water regularly in processing. This makes the substitution with aqueous-type cleaners easier. In contrast, in the metal treatment industry, it is more difficult for companies to substitute with aqueous and semi-aqueous-type cleaners because they deal with materials that rust. Hence they tend to use hydrocarbon-type cleaners. In the electrical industry, where companies use a wide variety of materials, semi-aqueous-type cleaners are suited to the task.

The cases used here were reported in the period between Japanese fiscal year 2001 and 2003. Therefore, note that only a very small number of cases are available for those industries that had already completed the substitution work before 2001 or that had still not yet done so.

Table C.1 Numbers of reported substitutions of other cleaners for chlorinated-type cleaners, by industry organization

Industry organizations, etc.	After substitution	Halogenated type				Hydrocarbon type				Aqueous type				Semi-aqueous type				Other/unknown				Total			
	Before substitution	TCE	DCM	PCE	Subtotal	TCE	DCM	PCE	Subtotal	TCE	DCM	PCE	Subtotal	TCE	DCM	PCE	Subtotal	TCE	DCM	PCE	Subtotal	TCE	DCM	PCE	Subtotal
Japan Automotive Manufacturers Associations, Inc.					0				0		1		1				0				0	0	1	0	1
Japan Aluminium Association					0	1	2	2	5	1	3		4		1		1		1		1	2	7	2	11
Japan Federation of Printing Industries					0				0				0				0		1		1	0	1	0	1
Society of Japanese Aerospace Companies		1			1		1		1				0		1		1		1		1	1	3	0	4
Japan Society of Industrial Machinery Manufacturers		1		1	2		1		1				0				0		3	4	7	1	4	5	10
Japan Auto Parts Industries Association			1		1	4	3		7	2	8		10				0				0	6	12	0	18
Japan Iron and Steel Federation					0				0	1			1		3	3	6				0	1	3	3	7
Japanese Electric Wire & Cable Makers' Association			2		2	1	2		3	1	1		2				0				0	2	5	0	7
Four groups including Japan Electrical Manufacturers' Association[1]		1	4		5	1	5		6	2	1		3	8	3	3	14		4		4	12	17	3	32
Glass Fiber Association					0				0				0				0		2		2	0	2	0	2
Japan Musical Instruments Association					0	1			1				0				0				0	1	0	0	1
Federation of Electroplating Industry Associations, Japan					0				0	14	5		19				0				0	14	5	0	19
Japan Wire Products Association					0				0	1	1	3	5				0		1		1	1	2	3	6
Japan Metal Heat Treatment Association					0	15	3	3	21	4	5	2	11				0				0	19	8	5	32
Japan Shoe Manufacturers Association					0				0				0				0		1		1	0	1	0	1
Japan Wool Dyers and Finishers Association, Japan Textile Dyeing and Printing Association				1	1				0				0				0				0	0	0	1	1
Japan Optical Glass Manufacturers' Association			1		1		1		1			1	1				0				0	0	2	1	3
Japan Rubber Footwear Manufacturers' Association					0				0				0				0		2		2	0	2	0	2
Japan Copper and Brass Association					0	3	2		5	1	2		3				0				0	4	4	0	8
Total		3	8	2	13	26	20	5	51	27	27	6	60	8	8	6	22	0	16	4	20	64	79	23	166

TCE, trichloroethylene; DCM, dichloromethane: PCE, tetrachloroethylene.

Source: METI (2002, 2003, 2004)

[1] The four groups including the Japan Electrical Manufacturers' Association are "Japan Electronics and Information Technology Industries Association", "Communications and Information Network Association of Japan", "Japan Business Machine and Information System Industries Association" and "Japan Electrical Manufacturers' Association.