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Analysis of risk trade-off relationships between organic solvents and aqueous agents: case study of metal cleaning processes

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ABSTRACT

When substance substitution is implemented to reduce the target risk of production processes, countervailing risks may occur. The goal of this study is to analyze the risk trade-off relationships between organic solvents and aqueous agents in the case study of metal cleaning processes. Global environmental impacts and local risks were evaluated for the eight scenarios by life cycle and risk assessments, respectively. The results show that the contribution of the processes using chlorinated solvents to photochemical ozone creation, human toxicity, ozone depletion, and ecotoxicity was larger than processes using aqueous detergents, while the contribution of aqueous processes to eutrophication was larger than chlorinated processes. Neighbors' health risk around a cleaning site using chlorinated solvents was sufficiently small in all scenarios, whereas ecological risk due to surfactants which are contained in aqueous detergents and emitted to the local aquatic environment should be reduced. Cleansing agents and process facilities should be selected on the basis of the comprehensive analysis of risk trade-off relationships for feasible and cleaner production.

1. Introduction

Various chemical substances are used in industry as product materials and process chemicals. As issues related to the environment and human health are considered important, possible risks of production processes need to be identified and reduced at the process design stage (Cano-Ruiz and McRae, 1998; Chen and Shonnard, 2004). Organic solvents are used for many purposes, e.g., as cleansing agents in metal cleaning processes and as components of inks and paints in printing and painting processes. Some organic solvents have been an issue of public concern in Japan owing to their human toxicity and contribution to air pollution (METI-Kanto, 2009). The replacement of volatile organic compounds (VOC) with a chemical substance that is less toxic or less volatile has been recommended, and aqueous agents have been suggested as alternatives (Verschoor and Reijnders, 2001). For example, aqueous detergents have been substituted for chlorinated organic solvents, such as dichloromethane, trichloroethylene, and perchloroethylene in the cleaning industry (Rydberg, 1994). As a result, the sales volume of aqueous detergents in Japan increased from 22,978 ton in 1999 to 37,247 ton in 2007 (JICC, 2001; METI, 2009b). Water-based inks and paints have been developed as alternatives to conventional solvent-based inks and paints in the printing and painting industries (Geldermann and Rentz, 2004; Vachon and Klassen, 2006).

Although VOC emission can be reduced by substance substitution, the adverse effects of alternative aqueous agents originating from their hazards have not been taken into account. Processes using aqueous agents generally emit a large amount of wastewater, and thus adverse effects of contaminants in wastewater may occur as a result of the substitution (Lavoué et al., 2003). Such a phenomenon in which the countervailing risk is generated by an intervention to reduce the target risk is referred to as a risk trade-off relationship (Graham and Wiener, 1997). The countervailing risk may offset reductions in the target risk (Gray and Hammitt, 2000), or the type and affected population of the countervailing risk are different from those of the target risk (Hofstetter et al., 2002). Thus, it is necessary to evaluate various risks originating from chemical substances and identify risk trade-off relationships among them in order to design an appropriate cleaner process.

Life cycle assessment (LCA) is a tool for quantifying potential impacts on the environment by analyzing emissions of chemical substances from processes throughout the whole life cycle of a product. It enables the evaluation and comparison of design options for process modifications with regard to various impacts on the global environment, e.g., global warming, acidification, ozone depletion, and eutrophication (Azapagic, 1999). In general, the absolute magnitude of such impacts is not important in LCA,

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because evaluation results are presented with marginal values that indicate changes in environmental impacts due to process modifications. In contrast, risk assessment (RA) (Kolluru et al., 1996), which has been used as an assessment tool in process design, is aimed at evaluating the absolute magnitude of risks by comparing evaluation results with absolute standards (Cowell et al., 2002). The acceptability of risks should be the major concern of a process plant, particularly for the health risk of workers and neighbors around the plant, and the ecological risk in the local environment. RA can be applied to the evaluation of such local risks. The integration of LCA and RA has been discussed in several studies. Similarities and differences between LCA and RA are examined (Cowell et al., 2002; Tukker, 2002), and procedures and required information for the integration are clarified (Kikuchi and Hirao, 2009). The application of the integrated LCA and RA to process evaluation has been studied (Kikuchi and Hirao, 2008a, 2010; Sonnemann et al., 2000), and the framework to evaluate both of the environmental performance and local health and safety issues related to solvents has been proposed (Capello et al., 2007) by implementing case studies.

The utilization of organic solvents in industry has been the subject of many studies. Technologies for treating VOC in exhausted gas have been developed (Peishi et al., 2004; Stehlik et al., 2004), and their engineering and economic performance have been evaluated (Mulholland and Dyer, 1999). Technological tests on alternative solvents and their hazard assessment have been implemented (Sikdar and El-Halwagi, 2000; Trivedi et al., 2004). The impacts of chlorinated organic solvents in metal cleaning processes have also been analyzed by LCA (Hellweg et al., 2005; Kikuchi and Hirao, 2008b) and by integrated LCA and RA (Kikuchi and Hirao, 2008a, 2010). As to the comparison between organic solvents and alternative aqueous agents, an LCA study was performed for metal parts degreasing processes (ECSA, 1996). It is necessary to evaluate and compare organic solvents and aqueous agents in terms of both global impacts and local risks. Risk reduction measures including substance substitution should be selected on the basis of a comprehensive interpretation of such evaluation results.

In this study, the risk trade-off relationships between organic solvents and aqueous agents are analyzed in a case study of metal cleaning processes. Impacts on the global environment and risks in the local environment are evaluated by LCA and RA, respectively, for cleaning processes using chlorinated solvents and aqueous detergents. The cleaning processes evaluated in the case study are those using washing machines and other process facilities that are conventionally used in Japan. Risk trade-off relationships are illustrated by clarifying the differences in the major risks between organic solvents and aqueous agents on the basis of comprehensive interpretation of LCA and RA results.

2. Materials and methods

2.1. Introduction to metal cleaning

Metal cleaning is an essential process in metal processing, e.g., metal finishing, fabrication, and assembly. Metal parts are greased before cutting or pressing in order to reduce friction. As process oils on the surface of metal parts can be impurities in the following process, cleaning processes are needed to remove them with cleansing agents. A variety of chemical substances are used as cleansing agents. They can be categorized into three groups: solvents, aqueous detergents, and semiaqueous detergents. Although various solvents, such as chlorinated organic solvents, brominated organic solvents, hydrocarbons, fluorocarbons, and alcohols, are used according to cleaning requirements, chlorinated solvents are most widely used in Japan, accounting for 31% of the total shipment of cleansing agents in 2007. This is followed by aqueous detergents (27%), hydrocarbons (19%), and alcohols (16%) (METI, 2009b).

Fig. 1(a) shows a typical metal cleaning process using chlorinated solvents with an open-top washing machine. The process entails washing, rinsing, vapor washing, and drying. An open-top washing machine has three tanks equipped with heaters at the bottom for heating solvents and coolers for recovering vaporized solvents. A significant amount of solvents, which are not condensed and recovered by coolers, is emitted from the top of the machine. To reduce solvent emission from cleaning machines, semiclosed washing machines equipped with a shutter are installed in some cleaning sites. Solvent emission can be reduced by 75–90% compared with that of an open-top machine if the shutter is closed while input metal parts are automatically conveyed inside a machine (T.C.C., 2006).

Using an alternative cleansing agent is another possible measure of eliminating the adverse effects of chlorinated solvents from the perspective of hazard management. Some Japanese cleaning sites have substituted aqueous detergents for chlorinated solvents (MOE, 2007). Alkaline detergents, which are the most used aqueous detergents in Japan, are composed of inorganic alkali compounds, surfactants, and other additives. A typical cleaning process using aqueous detergents is shown in Fig. 1(b). This process entails washing, rinsing, and drying. Washing tanks are filled with a water solution of aqueous detergents, and rinsing tanks are filled with water. The number of tanks and the purity of water for washing and rinsing may vary according to required cleanliness. Rinsed metal parts are dried using drying machines such as a hot-air-blowing dryer and a spin dryer.

There are similarities and differences between chlorinated solvents and aqueous detergents used in metal cleaning processes. They both play a role as process chemicals rather than as product materials. Chlorinated solvents dissolve and detach oils from the surface of metal parts, whereas aqueous detergents saponify or emulsify them (JICC, 2004). They are removed after playing their role: Chlorinated solvents are vaporized, and aqueous detergents are rinsed. Regarding their differences, chlorinated solvents are emitted mainly to the atmosphere during and after utilization, because they can be easily vaporized and released from a process. On the other hand, aqueous detergents are released as part of wastewater and released into public water bodies or sewers.

2.2. Analysis of risk trade-off relationships

When aqueous detergents are used as an alternative to chlorinated solvents, risk trade-off relationships result. First, the trade-off relationships of global impacts may appear between processes using chlorinated solvents and aqueous detergents. VOC emitted from processes using chlorinated solvents to the atmosphere can create photochemical ozone and cause air pollution, while wastewater emitted from processes using aqueous detergents can contribute to eutrophication.

Second, local risks that appear in a cleaning site and its surrounding environment differ between processes using chlorinated solvents and aqueous detergents. If a large amount of chlorinated solvents is emitted from a washing machine, human health risks in the neighborhood are a serious concern. Meanwhile, if components of aqueous detergents contained in wastewater are emitted to the local aquatic environment, they may pose risks to aquatic lives. As locations where those risks may be posed and populations bearing the risks are clearer than potential impacts on the global environment, the acceptability of each local risk should be carefully considered.

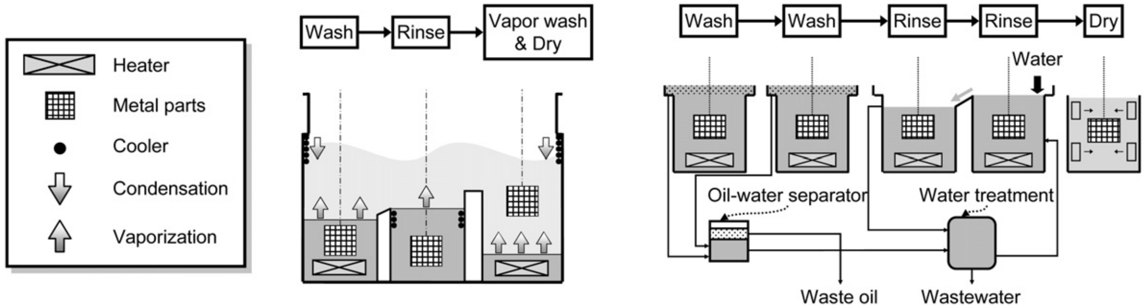

Fig. 1. Typical metal cleaning processes in Japan: (a) process using an open-top washing machine and a chlorinated organic solvent (Kikuchi and Hirao, 2008a) and (b) process using an aqueous detergent.

2.3. LCA and RA

Although LCA and RA are both evaluation tools for products and processes by quantifying the impacts of the emission of chemical substances on the environment and humans, they differ in data used for evaluation and in information obtained from evaluation results. Environmental impacts evaluated in LCA are related to a functional unit that is a measure of the service delivered during the life cycle of a product under study. The amount of all chemical substances emitted from the life cycle is calculated in life cycle inventory analysis (LCI). Although those chemical substances may be emitted on different temporal and spatial scales, they are summed up in order to evaluate their potential impacts on the global environment (Tukker, 2002). In life cycle impact assessment (LCIA), midpoint indicators of impact categories, such as global warming and ozone depletion, can be used to measure the potencies of such impacts on the global environment. Endpoint indicators are available in some LCIA methods in order to analyze damage to areas of protection (AoP) as a result of the impacts. Changes in global impacts, rather than the absolute magnitude of impacts, are quantified in LCA, because LCA results are mainly used for the purpose of environmental improvements (Sonnemann et al., 2000), i.e., LCA results show the relative magnitude of potential impacts on the global environment.

In contrast, RA is aimed at evaluating the likelihood and severity of a specific harmful effect originating from products or processes (Cowell et al., 2002). It generally focuses on toxicological risks due to emissions of individual chemical substances. As local risks that may be posed in one or a limited number of sites are a concern in RA, the location of emission sources and the temporal variation in the emission of chemical substances need to be defined during evaluation (Tukker, 2002). The significant feature of RA is that its results show the absolute magnitude of actual risks. The acceptability of risks can be judged by comparing risk indicators and absolute standards.

3. Case study

3.1. Scenario settings

Fig. 2 shows the life cycles of chlorinated solvents and aqueous detergents used in metal cleaning processes. The life cycle of chlorinated solvents comprises four stages: agent production, cleaning, distillation recycle, and incineration. Waste fluid containing solvents and process oils can be recycled by distillation. A residue of the waste fluid, which is mostly composed of process oils, is incinerated. The life cycle of aqueous detergents includes wastewater treatment and sludge incineration as well as agent production and cleaning. Wastewater from the processes using aqueous detergents contains process oils and aqueous detergents. The effluent standards established by the Water Pollution Control Act (MIC, 2009) in Japan restrict the concentration of toxic substances and the values of water quality indices, such as pH, chemical oxygen demand (COD), and phosphorus content, for wastewater to be discharged into public water bodies and sewers. They are further restricted by the ordinance of some municipalities. To satisfy such restrictions, contaminants contained in wastewater from the cleaning site need to be treated before discharging. The neutralization of inorganic alkali compounds in wastewater is implemented in most cleaning sites, and additional equipment for oil–water separation and coagulation sedimentation is installed in some cleaning sites. Wastewater may be further diluted before discharging in order to lower the concentration of contaminants, although dilution is not recommended by the pollution control ordinance in some municipalities. Finally, treated wastewater is discharged into public water bodies or sewers, while sludge composed of process oils, surfactants, and phosphates is incinerated.

Eight scenarios were developed and evaluated in this case study. Metal cleaning processes using chlorinated solvents were analyzed in three scenarios (SOL1-3), and processes using aqueous detergents were analyzed in five scenarios (AQU1-5). Table 1 shows a summary of the conditions of the eight scenarios. Primitive cleaning processes that are still operated in some cleaning sites in Japan were analyzed in SOL1 and AQU1. An open-top machine is used in the process of SOL1. Processes that are modified to reduce expected risk were investigated in SOL2 and SOL3 in order to see the effectiveness of risk reduction measures implemented in Japan. An open-top washing machine in the process of SOL2 can recover more solvents than that in the process of SOL1, because its chiller is improved. The process of SOL3 uses a semiclosed washing machine that can significantly reduce solvent emission.

Aqueous processes of AQU2 and AQU3 differ from that of AQU1 in the purity of water used for cleaning and wastewater treatment. Although the purity of water affects cleanliness, and thus these three processes have different functions of metal cleaning, the processes were still evaluated to see how water selection can affect environmental impacts. Although wastewater is treated by only neutralization, and then diluted to meet the effluent standards in AQU1-3, additional equipment for removing organic contaminants and phosphates is installed in AQU4 and AQU5. An oil–water separator installed for the processes of the two scenarios can separate process oils. In the process of AQU5, coagulation sedimentation equipment, which can remove not only process oils but also surfactants and phosphates, is installed in addition to the oil–water separator. Finally, treated wastewater is discharged into public water bodies, whereas collected sludge is incinerated.

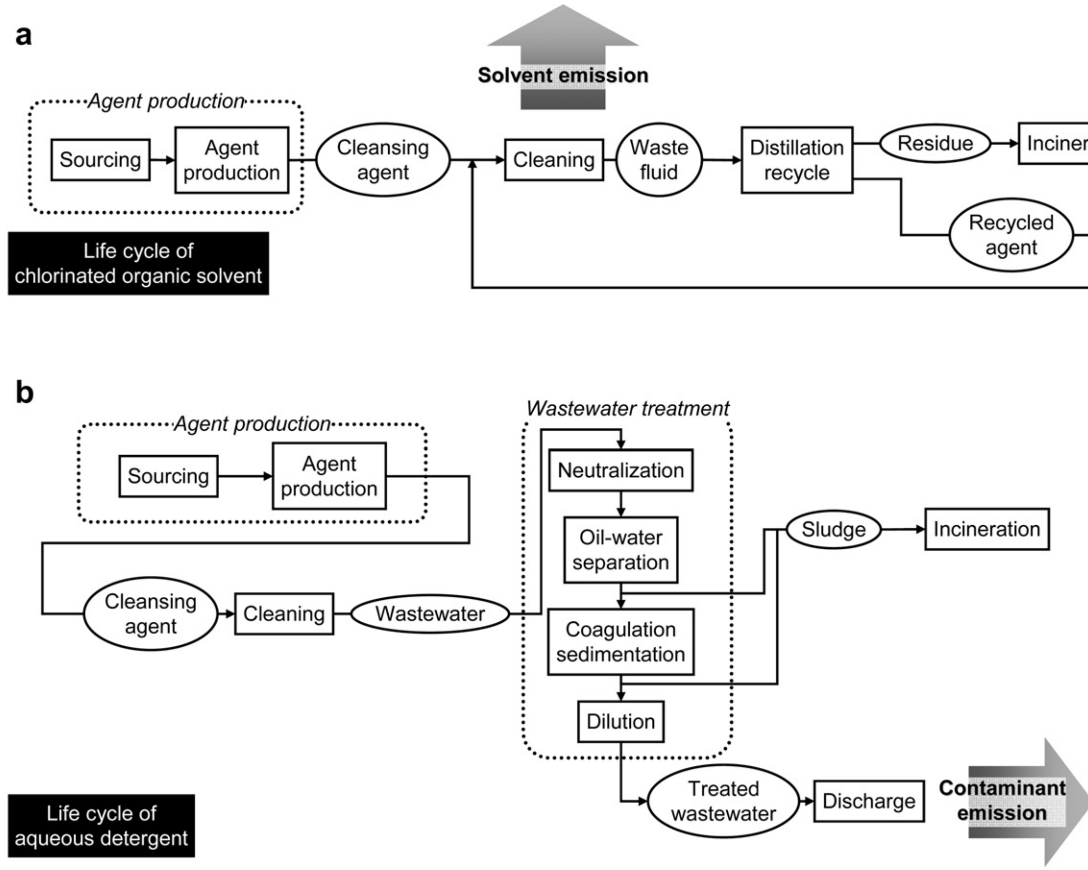

Fig. 2. Life cycle of cleansing agents: (a) chlorinated organic solvent (Kikuchi and Hirao, 2008a) and (b) aqueous detergent.

3.2. Analysis settings

Detailed data used for evaluation are summarized in Table 2. Process data of cleaning processes owned by electroplating plants were obtained from the literature (JMF, 1993) and used in evaluation, although some data were assumed on the basis of statistics from the cleaning industry. Trichloroethylene (TCE) is used in processes of SOL1-3. The amount of inputted solvents including recycled solvents is the largest in SOL1. Reductions in solvent emissions in SOL2 and SOL3 would lead to reduced solvent consumption by 47% and 90%, respectively. Aqueous detergents were assumed to be composed of sodium hydroxide, sodium silicate, sodium phosphate, sodium carbonate, and polyoxyethylene alkyl ether (POER) on the basis of the typical composition of aqueous detergents used in Japan (Mamiya, 1998). The oil–water separator installed in the processes of AQU4 and AQU5 can separate 90% of oils from wastewater as sludge, and the coagulation sedimentation equipment installed in the process of AQU5 can separate 99% of oils, 96% of surfactants, and 90% of phosphates as sludge (MITI, 1980). It was assumed that treated wastewater is discharged into the Tama River in Japan.

The functional unit in LCA was defined as "daily cleaning of 300 kg metal parts."' The second version of the Life cycle Impact assessment Method based on Endpoint modeling (LIME2) (Itsubo and Inaba, 2003, 2005) was used as an LCIA method. The environmental impacts of nine categories were evaluated: global warming, ozone depletion, acidification, urban air pollution, eutrophication, photochemical ozone creation, human toxicity, ecotoxicity, and waste. Background inventory data, such as utilities required for the production of cleansing agents and associated

Table 1
Conditions of the eight scenarios analyzed in this case study.

Scenario	Cleansing agent	Washing machine		Wastewater treatment	Water for cleaning and dilution	Fuels for distillation and recycle
		Type	Utility			
SOL1	Trichloroethylene	3 tanks, open-top	Electricity	–	–	Kerosene, electricity
SOL2		3 tanks, open-top, chiller is improved	Electricity	–	–	Kerosene, electricity
SOL3		Semiclosed	Electricity	–	–	Kerosene, electricity
AQU1	Aqueous detergent	4 tanks (washing	Electricity	Neutralization, dilution	City water	–
AQU2		(2 tanks), rinsing,	Electricity	Neutralization, dilution	Industrial water	–
AQU3		drying)	Electricity	Neutralization, dilution	Deionized water	–
AQU4			Electricity	Neutralization, oil–water separation, dilution	City water	–
AQU5			Electricity	Neutralization, oil–water separation, coagulation sedimentation, dilution	City water	–

Table 2
Data used for evaluation in this case study.

		SOL1	SOL2	SOL3	AQU1	AQU2	AQU3	AQU4	AQU5
Throughput of metal parts [kg day^{-1}]		300	300	300	300	300	300	300	300
Cleansing agent	Composition	Trichloroethylene			Aqueous detergent (sodium hydroxide (15%), sodium silicate (10%), sodium phosphate (25%), sodium carbonate (40%) and POER (10%))				
	Input [kg day^{-1}]	47	25	4.7	5.9	5.9	5.9	5.9	5.9
Washing machine	Electricity use [kWh day^{-1}]	18	18	24	16	16	16	16	16
Wastewater	Removal rate from wastewater	–	–	–	–	–	–	Oil: 90%	Oil: 99%, surfactants: 96%, phosphates: 90%
	Process oil content [kg day^{-1}]	–	–	–	0.12	0.12	0.12	0.012	0.000059
	Phosphate content [kg day^{-1}]				1.5	1.5	1.5	1.5	0.15
	Discharged into	–	–	–	The Tama River				
	Effluent standard	–	–	–	COD: 20 mg L^{-1}				
Data for risk assessment	Emission of cleansing agent [kg day^{-1}]	Trichloroethylene emission to the neighborhood (from cleaning sites)			POER emission to the river				
		44	22	1.7	0.59	0.59	0.59	0.59	0.022
	Threshold	NOAEL of trichloroethylene: 22 mg kg^{-1} day^{-1}			NOEC of POER: 0.15 mg L^{-1}				
	Background concentration	2.5 μg m^{-3}			48 μg L^{-1}				
	UFs	100			10				

emissions, which are necessary for calculating these impacts, were obtained from several databases (JEMAI, 2007; JLCA, 2009).

With regard to RA, the health risk to neighbors around a cleaning site due to TCE emission was evaluated for processes using chlorinated solvents, while the ecological risk in the Tama River due to the emission of POER contained in aqueous detergents as a surfactant was evaluated for processes using aqueous detergents. Margin of exposure (MOE) (US-EPA, 2009), which is given by Eq. (1), was used as the indicator.

$$\mathrm{MOE} = (\text{no observed adverse effect level})/(\text{actual exposure level}) \tag{1}$$

No observed adverse effect level (NOAEL) can be derived from animal experiments and epidemiological studies. The amount of intake of a chemical substance by humans can be used as the actual exposure level for humans. In the case of the human health risk due to inhalational exposure to a chemical substance, it is given by.

$$\mathrm{PDI_{inh}} = \left(V_{\mathrm{inh}}/\mathrm{h_{day}}\right)\cdot\sum_i \left(C_i\cdot\Delta t_{\mathrm{exposure},\ i}\right) \tag{2}$$

where $\mathrm{PDI_{inh}}$ [mg of intake person^{-1} day^{-1}] is the predicted daily intake per person, C_i [mg m^{-3}] is the concentration of the chemical substance in the air to which the person is exposed, V_{inh} [m^3 person^{-1}] is the daily inhalation volume per person (20 m^3 person^{-1}), $\Delta t_{\mathrm{exposure,\ i}}$ [h] is the exposure time at C_i, and $\mathrm{h_{day}}$ [h day^{-1}] is hours per day (24 h day^{-1}).

Meanwhile, the concentration of a chemical substance in an aquatic environment is often adopted as the actual exposure level to evaluate ecological risk. It is common to compare MOE with uncertainty factors (UFs), which explain interspecific, interindividual, and other variabilities of the adopted NOAEL, in order to judge whether risks are negligible or not. If MOE is larger than UFs, the risk can be considered sufficiently small.

The NOAEL of TCE, which was 22 mg kg^{-1} day^{-1}, was adopted. This was derived from epidemiological studies of people exposed to TCE (Nakanishi et al., 2008). The total uncertainty of the NOAEL was 100, which was derived from the interindividual variability (10) and the use of data of short-term exposure to evaluate risks of chronic exposure (10). The TCE concentration in the selected neighborhood was estimated using METI-LIS, (Ministry of Economy, Trade and Industry – Low rise Industrial Source dispersion Model) (METI, 2009a), a type of software for simulating the behavior of pollutants emitted from industrial plants into the atmosphere. The monthly averaged concentration of 0.075 km^2 around a cleaning site was simulated using METI-LIS, assuming that TCE is emitted during working hours from AM 9:00 to PM 5:00. The MOE of neighbors' health risk was then estimated.

The chronic toxicity of POER to aquatic lives has been indicated by a number of ecological toxicity tests. The no observed effect concentration (NOEC) of POER, which was 0.15 mg L^{-1} (Nakanishi and Rin, 2007), was adopted for calculating MOE. POER is contained not only in aqueous detergents for metal cleaning processes but also in detergents for household and other purposes. As POER can be removed by a sewage treatment system, the background POER concentration originating from other emission sources would be high in densely populated areas with an insufficient-sewage treatment system. It is reported that the POER concentrations of the Tama River basin under such conditions ranged from 5.9 to 48 μg L^{-1} (Nakanishi and Rin, 2007). A background POER concentration of 48.1 μg L^{-1} was adopted in this study, and it is assumed that wastewater from the metal cleaning site using aqueous detergents is discharged to this basin. An increase in POER concentration due to the emission of wastewater from the cleaning site was estimated using AIST-SHANEL (National Institute of Advanced Industrial Science and Technology - Standardized Hydrology-based AssessmeNt tool for chemical Exposure Load) (AIST, 2005), a type of software for the exposure assessment of chemical substances in Japanese rivers. MOE was then calculated and compared with the uncertainty factors of the NOEC (10), which are derived from the uncertainty due to the use of results of experimental toxicity tests.

3.3. Results

3.3.1. LCA results

Among the environmental impacts of the nine impact categories evaluated by LCA, the five in which the contribution of metal cleaning processes is expected to be relatively large are presented in Fig. 3: global warming, urban air pollution, eutrophication, photochemical ozone creation, and human toxicity. The LCA results at the midpoint level are shown herein except for the impact of urban air pollution, whose characterization factors for the midpoint assessment are not developed in LIME2. As to urban air pollution,

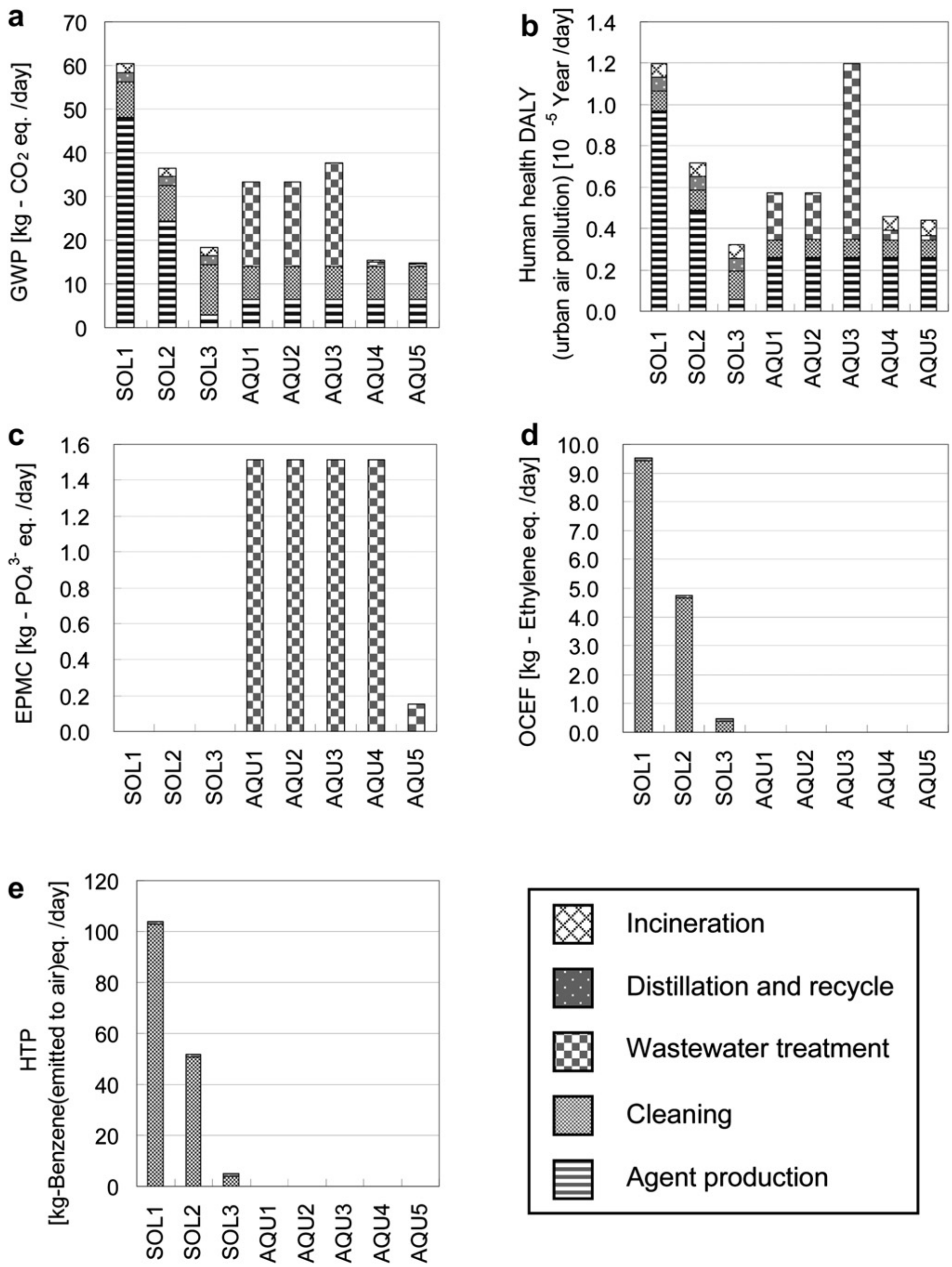

Fig. 3. Life cycle environmental impacts by impact categories of LIME2: (a) global warming presented by Global Warming Potential (GWP), (b) urban air pollution presented by Disability Adjusted Life Years (DALY), (c) eutrophication presented by Eutrophication Potential considered marine Material Circulation (EPMC), (d) photochemical ozone creation presented by Ozone Conversion Equivalency Factor (OCEF), (e) human toxicity presented by Human Toxicity Potential (HTP).

the results at the endpoint level are presented, using disability adjusted life years (DALY) to quantify its impacts on human health.

In the evaluation results of global warming shown in Fig. 3(a), the impact of solvent production accounts for 80% of the total global warming impact in SOL1. Reductions in solvent consumption in SOL2 and SOL3 would lead to a marked decrease in the impact of solvent production. The results also show that the total global warming impact of the process using chlorinated solvents and a semiclosed washing machine in SOL3 is less than or comparable to that of the processes using aqueous detergents. As to the processes using aqueous detergents, the results of AQU1 show that the impact of wastewater treatment accounts for approximately 60% of the total. This is mainly due to the consumption of a large amount of water for diluting wastewater to meet the effluent standards. Installing additional equipment for wastewater treatment can reduce water consumption, leading to a reduction in the total impact by approximately 55%, as can be seen from the results of AQU4 and AQU5. The use of deionized water in the process of AQU3 resulted in a 13% increase in the total impact from that of AQU1.

Fig. 3(b) shows the impact of urban air pollution due to emissions of NO_x, SO_2, and particulate matter. As to the processes using chlorinated solvents, trends similar to that of global warming can be observed. The impact of the process using a semiclosed machine in SOL3 is the least among the impacts of all the scenarios. The impact of wastewater treatment for the processes of AQU1-3 account for 40%, 40%, and 71%, respectively. They are due to water production for diluting wastewater. The impact of the process using deionized water in AQU3 is twice as much as that of the process using city water in AQU1 or industrial water in AQU2. Water consumption for dilution can be decreased by installing additional equipment for wastewater treatment although the impact of the incineration of residual sludge may be increased.

In the evaluation results of eutrophication shown in Fig. 3(c), the impact of the processes using chlorinated solvents are negligible compared with that of the processes using aqueous detergents. Process oils, surfactants, and phosphates contained in wastewater from the processes using aqueous detergents can cause eutrophication when they are released to the aquatic environment. Although the oil–water separator installed in the aqueous process of AQU4 can remove process oils from wastewater, it cannot separate phosphates whose impact factor is much larger than organic contaminants. As a result, installing an oil–water separator contributed to only a small reduction in the impact, while installing coagulation sedimentation equipment that can remove phosphates in AQU5 led to a reduction of 90% from AQU1.

Fig. 3(d) and (e) shows the impacts of photochemical ozone creation and human toxicity. TCE released from cleaning processes and during its distillation for recycling is the main causative agent of these impacts, and thus similar trends can be recognized in their results. Improving a chiller in SOL2 and installing a semiclosed washing machine in SOL3 would lead to reduction in the impacts by 50% and 95%, respectively, relative to that of SOL1. The impact of the processes using aqueous detergents would be negligible compared with that of the processes using chlorinated solvents.

3.3.2. RA results

Fig. 4 shows RA results. Neighbors' health risks of the processes using chlorinated solvents and the ecological risks of the processes using aqueous detergents are presented with MOE. The MOE of neighbors' health risks due to TCE emissions is much larger than the uncertainty factors of 100 in all the scenarios of the processes using chlorinated solvents. This means that neighbors' health risks are sufficiently small even in the primitive process of SOL1. Process modifications may not be necessary for the purpose of reducing neighbors' health risks.

Meanwhile, the MOE of the ecological risks due to POER emissions is less than the uncertainty factors of 10 in all the

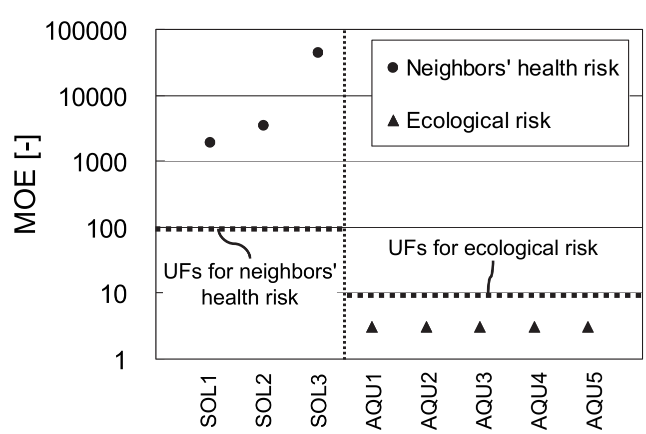

Fig. 4. Results of risk assessment presented with MOE. Neighbors' health risk around a cleaning site using trichloroethylene (TCE) and the ecological risk due to polyoxyethylene alkyl ether (POER) emission from a cleaning site using aqueous detergents were evaluated. [–] after MOE means that MOE is a non-dimensional index. The uncertainty factors (UFs) of the NOAEL for TCE were 100 (interindividual variability of 10 and the use of data of short-term exposure to evaluate risks of chronic exposure of 10), while those of the NOEC for POER was 10 (the use of results of experimental toxicity tests).

scenarios of the processes using aqueous detergents. The results indicate that the ecological risks are not negligible in the analyzed area of the Tama River. The contribution of wastewater from the metal cleaning site was further analyzed as follows. First, MOE was calculated from the POER concentration derived from household, agricultural, and industrial emission sources other than the cleaning site. The MOE calculated in this way was 3.1, which is less then the uncertainty factor. Second, MOE was calculated from the POER concentration derived from all the emission sources including the cleaning site. The difference between the two values of MOE (ΔMOE) was then calculated and regarded as a change in the ecological risk due to emissions of wastewater from the cleaning site. Negative values of ΔMOE mean an increase in the ecological risk due to wastewater from the cleaning site. The ΔMOE values were -5.0×10^{-7} in AQU1-3, -5.0×10^{-7} in AQU4, and -1.8×10^{-8} in AQU5. The ΔMOE values of AQU2 and AQU3 were the same as that of AQU1, because the amount of POER emissions and the wastewater treatment equipment used were the same in these scenarios. As the additional oil–water separator installed in the process of AQU3 cannot remove POER, there was no difference in ΔMOE between AQU1 and AQU4. Installing coagulation sedimentation equipment that can remove surfactants in AQU5 would lead to a 96% reduction in ΔMOE compared with that of AQU1.

4. Risk trade-offs between organic solvents and aqueous detergents

Table 3 shows a summary of the evaluation results of this case study. As to the global impacts evaluated by LCA, the results of each impact category were compared among the scenarios and rated in three levels: large, comparative, and small. If the results of all the solvent scenarios are larger than those of any of the aqueous detergent scenarios, the impacts of the processes using chlorinated solvents and aqueous detergents are rated as large and small, respectively, and vice versa. If their relations of magnitude vary among the scenarios, the impacts are rated as comparative. The contribution of the processes using chlorinated solvents is larger in terms of the impact of ozone depletion, photochemical ozone creation, human toxicity, and ecotoxicity. TCE emitted to the atmosphere is the main causative substance of photochemical ozone creation, human toxicity, and ecotoxicity in these scenarios. Solvent emissions from the processes using chlorinated solvents with an open-top washing machine can be markedly reduced by improving the chiller of such a machine or by substituting a semiclosed machine. Such process modifications can be also effective to reduce the impact of global warming, acidification, urban air pollution, and waste, which are rated as comparative. As the contribution of solvent production is large in these impact categories, solvent emission reductions and associated solvent consumption reductions would also reduce the impacts. Meanwhile, the contribution of the processes using aqueous detergents is larger in terms of the impact of eutrophication. Equipment for wastewater treatment that can remove not only organic contaminants but also phosphates is needed to reduce this impact. Installing additional equipment for wastewater treatment can also reduce water consumption, leading to a reduction in the other impacts rated as comparative.

Trade-off relationships are also identified in local risks: human health risks are an issue of concerns for the processes using chlorinated solvents, whereas the aquatic ecological risks are expected for processes using aqueous detergents. The evaluation results of neighbors' health risks show that the risks of all the scenarios were negligible. On the other hand, the ecological risks of POER exceed the negligible level in the analyzed area along the Tama River. ΔMOE, which was regarded as the contribution of wastewater from the cleaning site to the risk increase, indicates

Table 3
Comparison of the global impacts and local risks between chlorinated organic solvents and aqueous detergents used in metal cleaning processes.

		Chlorinated organic solvent	Aqueous detergent
Global impact	Global warming	Comparative: solvent consumption needs to be reduced.	Comparative: wastewater treatment to remove organic contaminants is needed.
	Ozone depletion	Large: solvent consumption needs to be reduced.	Small
	Acidification	Comparative: solvent consumption needs to be reduced.	Comparative: wastewater treatment to remove organic contaminants is needed.
	Urban air pollution	Comparative: solvent consumption needs to be reduced.	Comparative: Wastewater treatment to remove organic contaminants is needed.
	Eutrophication	Small	Large: wastewater treatment to remove phosphates as well as organic contaminants is needed.
	Photochemical ozone creation	Large: solvent emission needs to be reduced.	Small
	Human toxicity	Large: solvent emission needs to be reduced.	Small
	Ecotoxicity	Large: solvent consumption needs to be reduced.	Small
	Waste	Comparative: solvent consumption needs to be reduced.	Comparative: the purity of water may have an effect.
Local risk	Human health	Neighbors' health risk due to solvent emission is negligible. Measures to reduce workers' health risk are needed.	–
	Environment	–	Ecological risk in the river where cleaning wastewater is released is not negligible. Surfactants in wastewater need to be removed before discharging to public water bodies.

that installing coagulation sedimentation equipment would be effective in reducing the contribution.

Trade-off relationships may also occur between the global impacts evaluated by LCA and the local risks evaluated by RA. In the case study, cleansing agents emitted to the outside of cleaning sites are the causative agents of both global impacts and local risks. Chlorinated solvents pose neighbors' health risk and have impacts on photochemical ozone creation and human toxicity. Surfactants contained in aqueous detergents pose aquatic ecological risk. Phosphates, also one of the components of aqueous detergents, contribute to eutrophication. Therefore, reduced emissions of cleansing agents would lead to reductions in both the global impacts and the local risks and would result in no trade-off relationships between them. If the risks that can be posed inside a cleaning site are further taken into account, such trade-offs may result, as has been demonstrated in a study entailing the assessment of metal degreasing processes using chlorinated solvents (Kikuchi and Hirao, 2008a). Occupational health risks due to the inhalation of chlorinated solvents are often a serious concern, and ventilation systems are equipped in cleaning sites to avoid solvent emission to the workplace. Although solvent emission to the workplace can be decreased by increasing ventilation rate, more solvents would be lost from a washing machine and emitted to the environment outside cleaning sites through a ventilation system. In other words, the measure of reducing occupational health risk may lead to an increase in global impact.

5. Discussion

The LCA results of this case study show the trade-off relationships of the global impacts between the cleaning processes using chlorinated solvents and aqueous detergents. These impacts can be aggregated into a single index in order to avoid such trade-off relationships. Fig. 5 shows the environmental impacts of the nine categories aggregated by a single index of LIME2. The results show that photochemical ozone creation accounts for a large fraction of the total impact in SOL1, whereas eutrophication is a significant impact of AQU1. When they are compared, the impact of photochemical ozone creation in SOL1 is larger than that of eutrophication in AQU1. The partial improvement of a washing machine in SOL2 and the substitution of a semiclosed machine in SOL3 would reduce the total impact by 49% and 93%, respectively, compared with that in the case of SOL1. The total impact of SOL3 is comparable to that of AQU5, which is the smallest of all.

Fig. 6 shows the evaluation results of the eight scenarios in this case study. The horizontal axis means total global impact in Fig. 5, and the vertical axis shows MOE of neighbors' health risk and the ecological risk presented in Fig. 4. Pareto-optimal scenarios in terms of global impacts and local risks would appear on the lower left side. The evaluation results of the three scenarios using chlorinated solvents can be recognized on the lower side. Although the local risks of these processes are low, global impact can vary according to the washing machines used in the processes. Meanwhile, the evaluation results of the five scenarios using aqueous detergents can be found on the upper left side, and the differences among the scenarios are small. Although the global impacts of the processes using aqueous detergents are relatively small, their local risks are high and non-negligible.

The results of the analysis of risk trade-off relationships can be used to support decision making for cleaner process design. The results indicate that the substitution of aqueous detergents for chlorinated solvents would lead to a marked reduction in total global impact. Local health risks originating from the toxicity of chlorinated solvents can also be eliminated. However, instead of their reduction, the countervailing risks might be posed as a result of the substitution. The local ecological risk in the river where

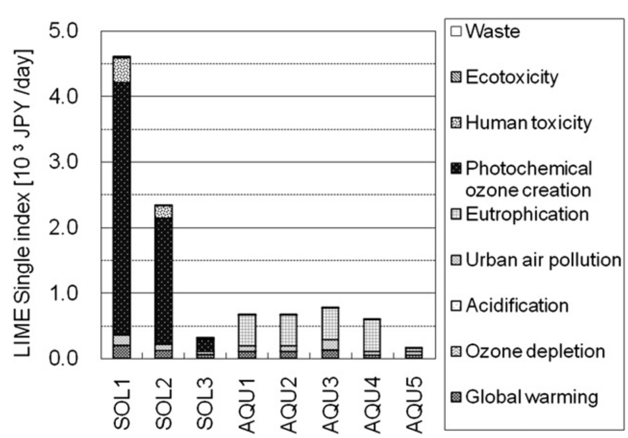

Fig. 5. Results of the aggregation of the life cycle environmental impacts of the nine impact categories by LIME2. JPY means Japanese Yen.

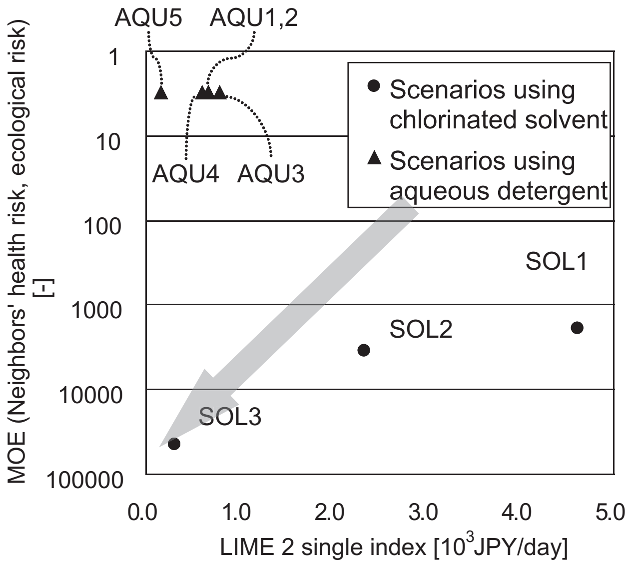

Fig. 6. Results of LCA and risk assessment. The horizontal axis means total global impact in Fig. 5, and the vertical axis shows MOE of neighbors' health risk and the ecological risk presented in Fig. 4. Pareto-optimal scenarios are shown on the lower left side.

wastewater from the cleaning site containing surfactants was discharged was high. Although the contribution of the cleaning site is smaller than that of other emission sources, this situation would be problematic in terms of social responsibility of enterprises owning metal cleaning processes.

Meanwhile, factors other than impacts on the environment and humans should also be considered in process design. The compatibility with metal parts to be cleaned is important in selecting cleansing agents. Alkali compounds contained in aqueous detergents can corrode metal parts made of aluminum. Water has a higher surface tension than solvents, and thus can less effectively penetrate a hole. Consequently, chlorinated solvents are often selected for cleaning metal parts made of aluminum or with a small hole. There are also other differences in functions as cleansing agents between chlorinated solvents and aqueous detergents. Furthermore, the choice of cleansing agents will often depend on required expense and space, because most cleaning sites in Japan are small and medium-sized enterprises (SMEs) that have severe restrictions on investible funds and available space (Kikuchi and Hirao, 2008a). The feasibility of process modifications under such restrictions should be examined in decision making for process design (Suh et al., 2005). In general, washing machines for aqueous cleaning processes are larger, and their initial cost is higher than those for solvent processes. The installation of an aqueous washing machine and equipment for wastewater treatment would require considerable space and expense. The large-scale modifications of a cleaning process would not be easily implemented under restrictions on funds and space. If chlorinated solvents are continued to be used for such reasons, design options without changing cleansing agents should be proposed for risk reduction. The results of this case study show that neighbors' health risks were sufficiently small in all the scenarios of the processes using chlorinated solvents. Installing a semiclosed washing machine instead of a primitive open-top machine led to a reduction in total global impact to a level less than or comparable to that of the processes using aqueous detergents. This would be a more feasible means of process improvement for cleaning sites where the substitution of aqueous detergents is difficult due to restrictions related to cleansing agent functions, funds and space.

LCA results presented in a single index can be applied to process design in another way. LIME2 adopts a monetary value as a single index. Integration factors were derived by conjoint analysis, which is aimed at determining the subjective values of four AoPs: human health, social welfare, biodiversity, and plant production. The value is intended to represent the amount of an environmental tax that Japanese people are willing to pay. From that viewpoint, the results presented in a single index can be regarded as the investible amount of money required to reduce the global impact due to the processes. The cost-effectiveness of process modifications aimed at the reductions in global impact can be evaluated on the basis of LCA results. For example, the difference in the results of scenarios SOL1 and SOL3 is 4300 JPY (Japanese Yen) whose functional unit is daily metal cleaning. The cost-effectiveness of installing a semiclosed washing machine in place of a primitive open-top machine can be evaluated by comparing this value with the incremental cost per day.

It must be noted, however, that there are other process modifications that may reduce the risk of cleaning processes. For instance, improving the operational conditions for the processes can be effective in reducing solvent emission. It is reported that the amount of solvent taken out by the metal parts to be cleaned can be reduced by 80% if the time for drying metal parts after washing is prolonged by 30 s (MOE, 2007). As to aqueous processes, discharging wastewater to sewers may be effective, because some surfactants can be treated before reaching public water bodies.

6. Conclusion

The global impacts and local risks due to the use of organic solvents and aqueous agents were respectively evaluated by LCA and RA in a case study of metal cleaning processes. Three scenarios using chlorinated solvents and five scenarios using aqueous detergents were developed and evaluated. Evaluation results were comprehensively analyzed to investigate the risk trade-off relationships between chlorinated solvents and aqueous detergents.

The trade-off relationships of the global impacts evaluated by LCA were identified in several impact categories. For example, the contribution of the processes using chlorinated solvents to photochemical ozone creation was much larger than that of the processes using aqueous detergents. In contrast, the contribution of aqueous processes to eutrophication was significant, whereas that of the solvent processes was negligible.

Trade-off relationships were also recognized in the local risks. Neighbors' health risks due to solvent emissions and the aquatic ecological risks due to surfactant emissions were evaluated by RA. The results show that neighbors' health risks were sufficiently small in all the scenarios developed in this case study. Meanwhile, the ecological risks in the river where wastewater from the cleaning site was discharged were not negligible. Wastewater treatment for removing surfactants is necessary for processes using aqueous detergents to reduce the contribution to the risk increase.

Substance substitution has been implemented in the industry to reduce the target risk. Decision makers who select an alternative substance should recognize the countervailing risk that may be posed as a result of the substitution. In this study, we demonstrated the trade-off relationships between chemical substances by evaluating the global impacts and local risks by LCA and RA, respectively. A comprehensive analysis of the evaluation results enables feasible and cleaner process design in which constraints beyond impacts on the environment and humans are taken into account. In this case study, the results indicate that a measure of reducing aquatic ecological risk should be implemented, when aqueous detergents are substituted for chlorinated solvents. If the use of aqueous detergents is difficult owing to constraints related to cleansing agent functions, space, and investible funds, installing a semiclosed washing machine without changing cleansing agents would be a feasible solution.

The analysis implemented in this study by LCA and RA can be applied to chemical substances used in other industrial processes. For example, in printing and painting processes where solvent-based and water-based inks and paints are used, the impacts of these substances on the environment and humans can be evaluated in a similar way.

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