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Inhalation risk assessment of exposure to the selected volatile organic compounds (VOCs) emitted from the facilities of a steel plant

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Concentrations of volatile organic compounds (VOCs) were investigated in the workplace air of four processes: sintering, cokemaking, hot forming, and cold forming in an integrated iron and steel plant. In addition, the cancer risk was measured for workers in these 4 processes. Seven VOCs (chloroform, carbon tetrachloride, 1,1,2-trichloroethane, trichloroethylene, tetrachloroethylene, benzene, and ethylbenzene) were selected for cancer risk measurement. Trichloroethylene concentrations are high in the 4 processes, and carbon tetrachloride and tetrachloroethylene concentrations are high in both the cold and hot forming processes. The sequence of the total cancer risk of the 7 species was as follows: cokemaking > sintering > cold forming ≅ hot forming. About 66–93% of the cancer risk of the four processes was caused by trichloroethylene. The cancer risks (3.7×10^{-3}–30×10^{-3}) of the average VOC concentrations suggest that improvement of workplace air quality and protection of workers are necessary to reduce cancer risks.

Keywords: Volatile organic compounds (VOCs), integrated steel plant, cancer risk.

Introduction

In an integrated iron and steel plant, the main facilities used to produce steel include the coke oven, the blast furnace (BF), and sintering, basic oxygen steelmaking (BOS), casting and rolling equipment. Most of the pollutants are emitted from the sintering process, cokemaking, the heating furnace and the BF.

During the cokemaking process, coal is used as a raw material, and coke oven gas (COG) is a product that includes coal tar, CO, CO_2, particles, hydrocarbons (i.e., methane, benzene and toluene etc.), ammonia, NOx, and SOx as the main by-products of this process.[1] Iron ore fines, pollution-controlled dusts, coke breeze, sludge, recycled iron-rich materials (i.e., mill scale and processed slag) and flux were fed into the sintering furnace to form a porous mass for charging a BF. A basic oxygen furnace (BOF) is used to produce molten iron from the BF. Flux, alloy materials and scrap are added to the molten iron and refined by injecting high-purity oxygen to produce the molten steel, which is then cast into slabs, beams or billets. Therefore, the iron and steel industry is associated with high energy and material consumption with the potential to cause serious workplace and environmental pollution, especially air pollution.

Based on a European investigation, coke ovens and metal ore roasting or sintering installations for the production of pig iron or steel are important sources of non-methane VOCs.[2] Polyaromatic hydrocarbons, [3,4] dioxins and furans [5,6] and metal constituents[7] in the particulate matter, as well as criteria gas pollutants (i.e., CO, NOx and SOx) and VOCs in the exhaust during the iron and steel production processes, were mentioned in most of the literature.

Quaβ et al.[5] measured the sinter plants and reported that they may represent the highest industrial source of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) in Europe.[7] Chlorinated VOCs in the exhaust could be the precursors of dioxins in iron and steel processes, especially in a sintering plant. Some studies noted that the cokemaking process was an important source of PAHs (polyaromatic hydrocarbons),[8] and VOCs could be their precursors.

Human health effects and VOC risks have been investigated by some researchers. For example, it has been shown that VOCs (i.e., trichloroethylene, toluene, benzene, etc.) emitted from a Polyvinylchloride (PVC) film

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Table 1. Operating conditions and baseline information of four processes in the integrated iron and steel plant.

Processes	*Raw materials* (*t/h*)[a]	*Fuel* (*gas*:$Nm^{3(b)}$/*h*)	(*Temperature* °*C*)	*Flue gas flow rate* (Nm^3/*min*)	*Products* (*t/h*)
Sintering	Flux: 20–40 Return fine: 130–180 Blended ore: 450–600	COG: 1200–1320 Coke: 25–35 t/h	1050–1150	9000–17000	Sintering ore: 400–600
Cokemaking	Coal: 30–200	BFG[c]/COG[d]: 19100–62000	1230–1260	2100–3500	Coke: 20–160
Cold forming	Cold-rolled coil: 140–175	COG: 7000–8500	830–850	1100–1500	Cold-rolled coil: 140–175
Hot forming	Plate and billet: 165–260	COG: 9270–12000	1150–1270	1300–1800	160–260

[a]t/h: ton/hr.
[b]Gas condition at 1 atm and 0°C.
[c]Blast furnace gas.
[d]Coke oven gas.

production factory can cause a clastogenic effect[9]; toluene, trichloroethylene and perchloroethylene can have an inhibitory effect on the nervous system[10]; and CO and benzene can cause haematological problems and cancer,[11] respectively, at sufficient dosage.

Generally, the health risk of indoor air associated with benzene and chlorinated VOCs (i.e., 1,1-dichloroethene, chloroform) was significant. The total lifetime risk ranged from 9.2×10^{-6} (classroom) to 1.5×10^{-4} (smoker's home) fordifferent indoor environments, and benzene contributed over 40% of the risk.[12] Ohura et al.[13] investigated the VOC risk near an industrial harbor and found that it was derived mainly from benzene and carbon tetrachloride. Lee et al.[14] investigated the health risk of BTEXS (benzene, toluene, ethylbenzene, xylenes, and styrene) in photocopy centers and found that the lifetime cancer risk ranged from 8.5×10^{-5} to 2.5×10^{-3}. Furthermore, aromatic VOCs caused the health risk in offices[15] and urban environments.[16] Therefore, exposure to VOCs could be an important source of human health risk via air pathways.

Most of the studies were focused on dioxins, furans, and PAHs. Few studies have focused on the risks of VOCs in the workplace air of iron and steel industries. At sufficient concentration, VOCs can be harmful to humans, causing eye and skin irritation, as well as damage to the bronchus. More seriously, some VOCs (i.e., aromatics and halogenated VOCs: benzene and trichloroethylene etc.) are carcinogenic.[17,18]

Edwards et al.[19] investigated the use of health-based standards to protect the exposed fraction of the population. Generally, time-activity patterns play an important role in exposure levels.[20,21] Tompa et al.[22] investigated the benzene exposure of refinery workers and suggested that zero tolerance and strict health control were necessary. Many studies have focused on the airborne pollution risk of workers, but few have investigated the health risk of workers in the integrated iron and steel industry. In addition, working conditions (i.e., working hours, workplace ventilation, and the use of personal protective equipment or workplace air control systems) are important issues in determining the health risk of workers.

Therefore, working conditions (exposure time, VOC concentration distribution, and pollution control efficiency of workplace air) were addressed in this study. In addition, the cancer risks were measured for workers of the sintering, cokemaking, hot forming and cold forming processes in an integrated iron and steel plant.

Methods

Operating conditions of facilities

Workplace air samples were taken from an integrated iron and steel plant located in southern Taiwan. The operating conditions of four processes (sintering, cokemaking, hot forming, and cold forming) are shown in Table 1.

In this study, the sintering plant collects the ash from the BF and BOF, returns fines from the sintering plant, and blends these with ore, serpentine, limestone and coke breeze to manufacture sinter. Coal is used as the raw material in the cokemaking process. In the cold forming process, the hot-rolled bands are pickled by hydrochloric acid and then cold-rolled at room temperature to form thinner coils. Slab (rectangular type) steel is rolled, milled and heated to 1200°C, then rolled, leveled, and cooled in the hot forming process. Finally, slab steel is manufactured to form hot-rolled coils.

Workplace VOCs sampling and analysis

Workplace air samples were collected for C_3-C_{11} hydrocarbon analysis using the stainless steel canister sampling method. Six-liter stainless steel-polished canisters were cleaned in the laboratory, pressurized with humidified zero air at ~100°C prior to sampling, and certified as described by U.S. EPA Method TO-14.[23] The canister sampler was placed on the platform, with the sampling probe about 1.5 m from the ground to simulate the human breathing area.

Based on the questionnaires and investigations, the hot and cold forming processes were operated from 0600–2300 per day, and the cokemaking and sintering processes were operated for 24 hrs per day. Therefore, 3 sampling periods (0700–1100, 1300–1700, and 1900–2300) were taken for the hot and cold forming processes, and 4 sampling periods (0100–0500, 0700–1100, 1300–1700, and 1900–2300) were taken for the sintering and cokemaking processes. Four sampling sites were selected in the vicinity (a distance of less than 1 m) of the manufacturing facilities. Three-run (1 day per run) sampling schedules were investigated to obtain representative samples for each process. A total of 36 VOC samples was taken for the hot and cold forming processes, and 48 samples were taken for the cokemaking and sintering processes. These samples were sufficient to represent the concentration of VOCs emitted from the various types of facilities.

VOC species were pre-concentrated in a purge-and-trap system (Entech 7100 instrument) and subsequently analyzed in a GC/MS (Gas Chromatograph (HP-6890) and Mass Spectrometer (HP 5973N)). The GC was equipped with a fused silica capillary column (non-polar RTx-1, 105 m × 0.25 mm ID × 1.0 μm film thickness). Calibration standards were prepared by diluting a certified standard gas (56 Enviro-Mat Ozone Precursor, Matheson, USA) with ultra-high-purity nitrogen (99.995%) in dilution bottles. VOC analysis included the analysis of halogenated VOCs and standard gases prepared by Matheson Gas Products, Georgia, USA.

Two duplicated analyses were done for every 10 samples to obtain representative samples. The performance of the GC/MS was evaluated with perfluorotributylamine for quality control. The relative standard deviation for all VOCs was <15%, the accuracy ranged from 91 ± 6% (propane) to 103 ± 9% (p-ethyltoluene), and the method detection limit varied from 0.03 (n-decane) to 0.20 (propane) ppb.

Health risk estimation

Based on the VOC data in this study, an exposure assessment was conducted to evaluate the potential VOC uptake by inhalation. In this study, inhalation was assumed as the main route of VOC uptake by workers in the integrated iron and steel facilities. Risk assessment focused on the chronic exposure to VOCs that may cause cancer or other toxic effects, rather than on acute toxicity from exposure to VOCs. The receptors were full-time workers of the four processes in the integrated iron and steel plant. Inhalation was the investigated exposure pathway in this study.

Carcinogenic risks from chronic exposure were evaluated for workers. The inhalation intake "I" was measured by the average daily intake over the exposure periods. Carcinogenic intake of VOCs for workers was calculated as follows:

$$I = \frac{(C_{ia} \times I_h \times E_t \times E_f \times E_d)}{(A_t \times B_w)} \quad (1)$$

where I is the inhalation intake (mg/kg-day), C_{ia} is the VOC i species concentration in workplace air (mg/m^3), I_h is the inhalation rate (m^3/h), E_t is the exposure time (h/day), E_f is the exposure frequency (day/year), E_d is the exposure duration (year), A_t is the average time (70 years × 365 days/year), and Bw is the body weight (70 kg was assumed in this study). An average lifetime of 70 years was used for the VOC carcinogenic assessment (although the average lifetime for the Taiwanese is about 78 years, which could cause about a 10% difference in the measurement of cancer risk),[26] and the total exposure time was 30 years. In addition, the parameters applied to the health risk assessment are as shown in Table 2.

The lifetime cancer risks of various VOC species were calculated by incorporating exposure assessment and toxicity values (slope factors). Generally, the lifetime cancer risk was calculated as follows:

$$C_r = I \times S_f \quad (2)$$

where C_r is the cancer risk and S_f is the cancer slope factor (kg-day/mg).

The potential for adverse effects increases as exposures exceed the reference dose. The sources of slope factor (S_f) were obtained from the Integrated Risk Information System[27] and Risk Assessment Information System.[28,29] Only seven VOCs were classified as having the potential for cancer risk and used in determining the slope factor (S_f), which could be a limitation of this study. The S_f of seven components including benzene, chloroform, ethylbenzene,

Table 2. Parameters of health risk estimation.

Parameters	*Unit*	*Values*	*Reference*
VOCs in workplace	mg/m^3	see Table 3	This study
Inhalation rate (IR)	m^3/hr	1.68[1]	USEPA[24]
Exposure time (ET)	hr/day	0.17, 0.5, 1, 2, 4, 6, 8	This study
Exposure duration (ED)	year	30	USEPA[24]
Exposure frequency (EF)	day/year	250	USEPA[25]
Body weight (BW)	kg	70[2]	DOH[26]
Average time (AT)	day	Cancer risk: 70×365	USEPA[24]

[1]The value of inhalation rate was based on the average of construction workers, carpenters and iron workers (1.44–1.86 m^3/hr)
[2]Based on the investigation of Taiwan's department of health (DOH), the average weight of adult (age: 24–64) was 70.67 kg. Therefore, 70 kg of body weight was selected, and this value is commonly used as the body weight of an adult in Taiwan.

tetrachloroethylene, 1,1,2-trichloroethane, trichloroethylene, and carbon tetrachloride was 2.73×10^{-2}, 8.05×10^{-2}, 3.85×10^{-3}, 2.07×10^{-2}, 5.60×10^{-2}, 4.00×10^{-1} and 5.25×10^{-2} kg-day/mg, respectively, were measured as the drivers of cancer risk.

Based on the questionnaire survey that collected data about the activity patterns of workers in the plant, the exposure time of workers for the four processes is 5 hrs for the sintering process, 7 hrs for cokemaking, and 1 hr for both the hot and cold forming processes.

According to the working conditions and VOC concentration, the health risk from inhalation was about 4×10^2 to 3×10^3 times that from the derma. Therefore, inhalation was regarded as the dominant exposure pathway for workers in the iron and steel industry.

Although a 10^{-6} cancer risk is typically used as the level in risk management of environmental contamination, many agencies, including the U.S. EPA, have indentified a range of increased cancer incidence risks. Generally, 10^{-4} to 10^{-6} is considered an acceptable risk range depending on the situation and conditions of exposure.[30–32] In addition, a health risk of 10^{-3} is suggested by OSHA (Occupational Safety and Health Administration).[33] Therefore, cancer risk levels of 10^{-6}–10^{-3} are discussed in this study.

Exposure reduction scenarios

Based on the VOC concentrations in the workplace, the concentration distribution was measured to evaluate the cancer risk associated with VOCs in the workplace. The percentile of various VOC concentration distributions in the workplace air was present as C_{i0} (where i was the percentage of VOC concentration distribution under no workplace air control strategy). In this study, VOC concentration distribution was simulated by Crystal Ball 2000.2.[34] Based on the software analysis, the VOC concentrations of the 4 processes could be fit to the gamma (γ) distribution better than to others (i.e., normal or log normal distributions). Therefore, the γ distribution was used to recalculate the percentage of VOC concentrations from low (5%) to high (99.97%). In addition, for the workplace air control efficiency ($\eta = (C_{ib}/C_{i0}) \times 100\%$, η is the workplace air control efficiency (%), C_{ib} is the VOC concentration (mg/m^3) of worker breathing after the control methods, and C_{i0} is the VOC concentration (mg/m^3) of workplace air) in current conditions.

Working hours in the vicinity of manufacturing equipment (exposure time) and VOC concentration were the factors selected to determine effective exposure dosage. The workplace air control methods included ventilation-based approaches such as dilution ventilation for the entire plant and local ventilation in the vicinity of manufacturing equipment, personal protective equipment (i.e., masks), and reduction of fugitive emissions from manufacturing equipment in the workplace. The working hours in the vicinity of manufacturing equipment were regarded as the exposure time (t_e), which was lengthened or shortened based on the conditions of the plant. In this study, the VOC control efficiency of workplace air (0, 10, 30, 50, 75, 80, 95, 99 and 99.97%), exposure time (10 min, 0.5, 1, 2, 4, 6 and 8hrs), and range of concentration (5, 10, 50, 90 and 95%) were the parameters selected to assess the cancer risk.

Results and discussion

VOC concentration distribution

Table 3 shows the workplace VOC concentrations in the vicinity of the manufacturing equipment. In the sintering process, ethylbenzene was the predominant VOC, and its concentration was over 100 ppb. Trichloroethylene, chloroform, and 1,1,2-trichloroethane were detectable in the sintering process at concentrations ranging from 5.6 to 47 ppb.

Benzene and ethylbenzene were the main species in the cokemaking process. The concentration of the halogenated

Table 3. Concentration probability of VOCs (ppb) in four steel manufacturing processes.

	Sintering (n = 48)				*Cokemaking (n = 48)*				*Hot forming (n = 36)*				*Cold forming (n = 36)*			
Compounds	*10*	*50*	*90*	*Mean*	*10*	*50*	*90*	*Mean*	*10*	*50*	*90*	*Mean*	*10*	*50*	*90*	*Mean*
Benzene	1.5	12	96	34	1.4	101	1620	542	0.6	15	396	67	0.6	9. 7	130	44
Chloroform	ND	1.3	22	7.3	ND	2.6	37	12	0.5	2.4	77	9.1	ND	0.8	13	4
Ethylbenzene	2.0	23	334	113	2.3	29	307	106	2.9	66	1857	194	1.65	32	410	139
Tetrachloroethylene	ND	ND	ND	ND	ND	ND	ND	ND	0.04	21	246	84	0	1.6	111	37
1,1,2-Trichloroethane	ND	ND	0.1	—	ND	ND	0.1	—	ND	ND	ND	ND	ND	ND	ND	ND
Trichloroethylene	0.2	7.7	140	47	0.1	8.2	175	58	0	2.0	50	91	0.11	7.0	169	56
Carbon Tetrachloride	ND	ND	ND	ND	ND	ND	ND	ND	0.1	43	516	175	ND	5.4	370	124

The percentile concentration (10, 50 and 90%) is based on the gamma distribution.
n: sample number.
ND: not detectable.

VOC species was less than 60 ppb, and trichloroethylene, chloroform, and trichloroethane were the major species.

In the hot forming process workplace, ethylbenzene was the principal species, and its concentration was 194 ppb. Carbon tetrachloride, trichloroethylene and tetrachloroethylene contributed a large fraction of chlorinated VOCs, and their concentrations were higher than 80 ppb.

In the cold forming process workplace, carbon tetrachloride and ethylbenzene were the dominant VOC species, with concentrations over 100 ppb. The detectable halogenated VOC species, including carbon tetrachloride, trichloroethylene and tetrachloroethylene in the cold forming process workplace, were measured at concentrations higher than 25 ppb.

Based on this study, 67 VOCs including 26 paraffins, 9 olefins, 16 aromatics, and 16 halogenated species were analyzed. Total concentration for the 67 VOCs was from 1,955 ppb (the sintering process) to 8,551 ppb (the cokemaking process). The halogenated VOC fractions of the 67 VOCs were 3.8, 1.4, 13 and 11% for the sintering, cokemaking, hot forming and cold forming processes, respectively. The high level of halogenated VOCs associated with the hot forming and cold forming processes workplaces may be affected by the HCl that was used for the removal of steel rust. To reduce the chlorinated VOCs, the use of alternative reagents could be considered.

Cancer risk

Seven VOC species (benzene, chloroform, ethylbenzene, tetrachloroethylene, 1,1,2-trichloroethane, trichloroethylene and carbon tetrachloride) were considered cancer risks. Benzene was classified as a human carcinogen[35] based on lowered blood cell counts in workers exposed at low levels (<1 ppm),[36] and benzene has been shown to cause leukemia at high levels of occupational exposure.[37] Trichloroethylene, chloroform, and carbon tetrachloride were classified as probable human carcinogens[38,39] on the basis of inadequate evidence in humans but sufficient evidence for carcinogenicity in animals. 1,1,2-trichloroethane has been classified as a possible human carcinogen by the U.S. EPA. Ethylbenzene has been determined to be not classifiable for human carcinogenicity due to lack of animal bioassays and human studies by the U.S. EPA,[40] but it was classified as a probable human carcinogen by the International Agency for Research on Cancer (IARC). There are some differences between IARC and the Integrated Risk Information System (IRIS) in terms of identification criteria (e.g., ethylbenzene at different levels, tetrachloroethylene and trichloroethylene classified as group 2A by IARC but not identified by IRIS). In addition, evidence of some VOCs causing cancer by inhalation exposure is lacking, as most studies have addressed exposure by the oral, subcutaneous and rectal routes (i.e., 1,1,2-trichloroethane, chloroform). Despite the lack of agreement and the dearth of data, assessment of the cancer risk to humans from exposure to VOCs by the inhalation pathway is necessary to protect the health of workers in the integrated iron and steel plant.

Table 4. Cancer risk ($\times 10^{-4}$) of VOCs at the average concentration of workplace air.

Compounds	*Sintering*	*Cokemaking*	*Hot forming*	*Cold forming*
Benzene	2.40	85.5	0.86	0.76
Chloroform	2.29	5.79	0.46	0.46
Ethylbenzene	1.53	2.73	0.50	0.48
Tetrachloroethylene	0.00	0.00	1.48	1.48
1,1,2-Trichloroethane	0.01	0.00	0.00	0.00
Trichloroethylene	81.7	207	28.2	28.5
Carbon Tetrachloride	0.00	0.00	5.82	11.6
Sum of cancer risk	87.9	301	37.3	43.3

Table 4 shows the cancer risk of these seven species for the four processes with the measured average VOC concentrations. Results indicated that the sequence of the total cancer risk of the seven species was as follows: cokemaking (3.0×10^{-2}) > sintering (8.8×10^{-3}) > cold forming (4.3×10^{-3}) ≅ hot forming (3.7×10^{-3}).

In the sintering process, 93% of the cancer risk comes from trichloroethylene; the other species, i.e., benzene, chloroform and ethylbenzene, each accounted for less than 3% of the cancer risk. In addition, trichloroethylene (69% cancer risk) and benzene (28% cancer risk) accounted for 97% of the cancer risk for the cokemaking process. For the hot forming process, the cancer risk was mainly attributed to trichloroethylene (76%) and carbon tetrachloride (16%). Trichloroethylene and carbon tetrachloride were also the main VOC species to cause cancer risk in the cold forming process. The cancer risk from the other species was less than 4%.

In this study, the cancer risk of the 4 processes was mainly attributed to trichloroethylene. Carbon tetrachloride contributed 16 and 27% cancer risk for the hot forming and cold forming process, respectively. In addition, there was a 2 to 3% cancer risk caused by benzene in the sintering, hot forming and cold forming processes. However, benzene caused a 28% cancer risk in cokemaking. Other species (chloroform, ethylbenzene and tetrachloroethylene) contributed about 1–4% cancer risk. In addition, 1,1,2-trichloroethane was detected only in the sintering process, and its concentration was low; therefore, its cancer risk was 9.9×10^{-7}. Based on the measurement of cancer risk of VOCs, most of the individual VOC species were over 10^{-5} (cancer risk of individual VOCs was 4.6×10^{-5} to 2.1×10^{-2}).

Benzene, trichloroethylene and carbon tetrachloride were the major VOCs contributing to cancer risk. Benzene is a well-known carcinogenic species. Carbon tetrachloride has been suggested to induce liver cancer in workers by inhalation exposure, although the data are inconclusive,[35] and it has been shown to produce liver tumors in animals by the oral, subcutaneous and rectal routes. Recent analysis of available epidemiological studies reports trichloroethylene exposure to be associated with several types of cancers in humans, especially cancer of the kidney, liver, cervix, and lymphatic system. Consistency across epidemiological studies is strongest for an association between trichloroethylene exposure and kidney cancer.[41] According to this study and the epidemiological and animal studies, VOCs are important factors causing cancer, therefore, it is necessary to reduce the cancer risk from the inhalation of high VOC concentrations, especially of workers.

Cancer risk reduction scenarios

The cancer risk of workers was measured under current operating conditions. The VOC-caused cancer risk of the four manufacturing process was more than 10^{-3} under the existing operating conditions; therefore control strategies for the reduction of VOC concentrations are necessary to reduce health risk. Table 5 shows the target of cancer risk conditions under current working hours at different workplace air control efficiencies and VOC concentrations.

Sintering

Figure 1a shows the cancer risk of the sintering process. In this study, even at low workplace air concentrations (5 and 10% concentration), the cancer risk is over 10^{-6}, except at low exposure time (less than 10 min). Therefore, high pollution control efficiency (> 99%) is necessary to reduce the cancer risk to less than 10^{-6}, but it is difficult to meet this target. Generally, for the 10^{-3} health risk suggested by OSHA,[33] a 50% concentration could be in the acceptable range. But at high concentration, 80% pollution control efficiency is necessary. The cancer risk could be 2.9×10^{-2} at the 95% concentration of workplace air, with no workplace air improvement and 8 hrs exposure time.

Cokemaking

Figure 1b shows the cancer risk of the cokemaking process. At 5 or 10% concentration, a pollution control efficiency greater than 80% is necessary to achieve a cancer risk in the range of 10^{-6}. Based on the 10^{-3} cancer risk, 30% pollution control efficiency is necessary to bring the risk into the acceptable range in current operating conditions. At high concentration, over 95% pollution control efficiency could control the health risk to less than 10^{-3}. If there is no workplace air control or personal protection, the cancer risk could be as high as 4.9×10^{-2} at 8 hrs exposure time. Therefore, the workplace air should be improved significantly.

Table 5. Risk reductions based on the current operating conditions of manufacturing processes.

Process	*Target of health risk*	*Workplace air control efficiency (η)*	*Percentile VOC concentrations (%)*
Sintering (5 hrs/day)	10^{-6}	95	10
	10^{-4}	10	15
		50	21
		90	51
		95	55
	10^{-3}	10	51
		50	55
		90	85
		95	95
Coke making (7 hrs/day)	10^{-6}	95	10
	10^{-4}	10	12
		50	15
		90	39
		95	51
	10^{-3}	10	42
		50	51
		90	63
		95	85
Hot forming (1 hr/day)	10^{-6}	95	14
	10^{-4}	10	42
		50	50
		90	63
		95	77
	10^{-3}	10	64
		50	77
		90	95
		95	95
Cold forming (1 hr/day)	10^{-6}	95	15
	10^{-4}	10	44
		50	50
		90	59
		95	71
	10^{-3}	10	61
		50	71
		90	95
		95	95

Hot forming

The cancer risk of the hot forming process is shown in Figure 1c. When the workplace air was low (5 or 10% concentration), the pollution control efficiency was 95%, which was still necessary to keep the cancer risk at less than 10^{-6}. If the acceptable health risk is 10^{-3}, 50% pollution control efficiency is necessary at 50% concentration. At high concentration, a health risk of 10^{-3} could be achieved with pollution control efficiency over 95%. In addition, the cancer risk could be up to 7.0×10^{-2} at 95% concentration, no pollution control improvement and 8 hrs exposure time.

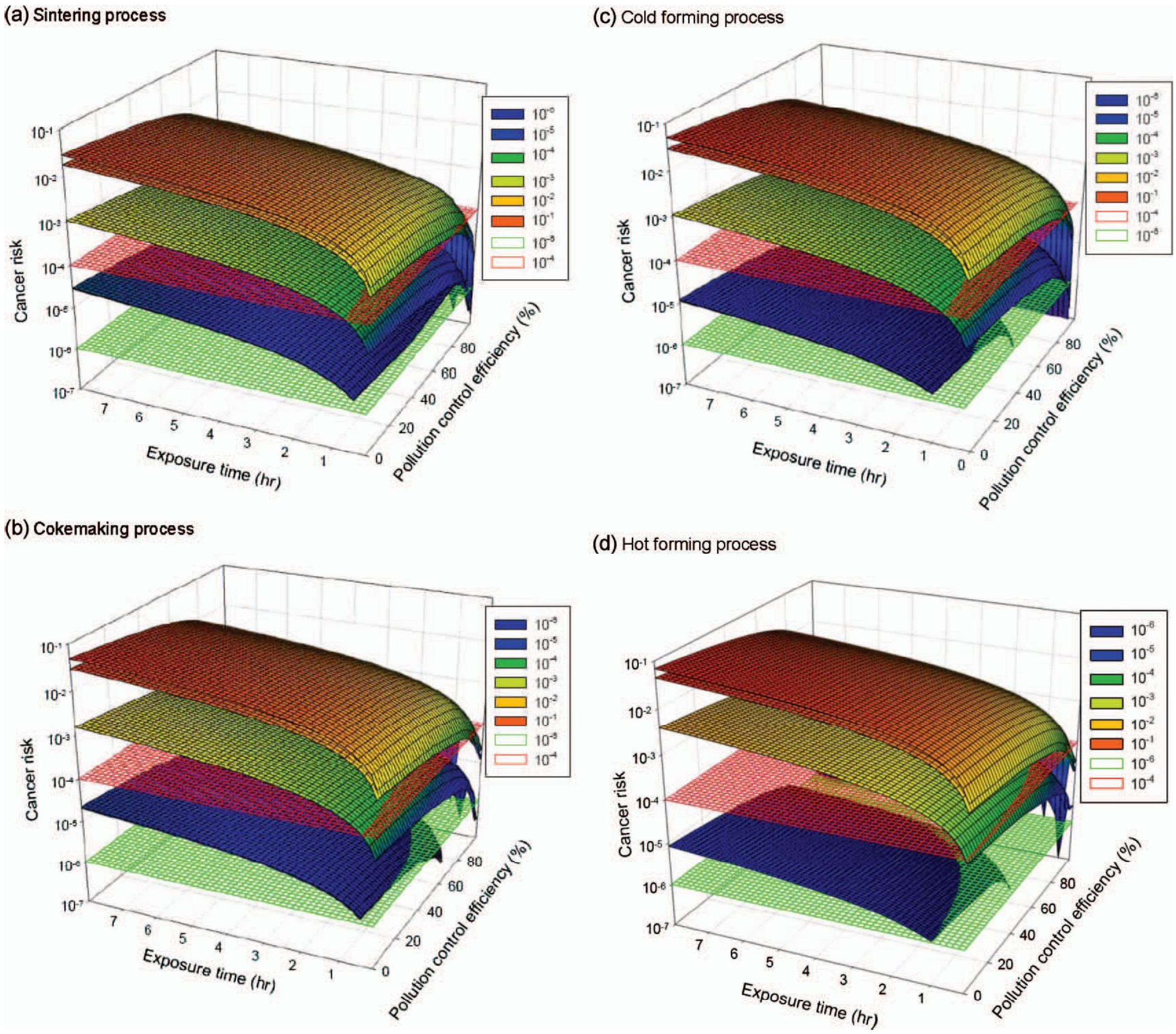

Fig. 1. Cancer risk of four processes: (a) sintering process (b) cokemaking process (c) cold forming process (d) hot forming process. Note: The curved surfaces from the upper to bottom layers show as first layer: 95% percentile concentration, second layer: 90% percentile concentration, third layer: 50% percentile concentration, fourth layer: 10% percentile concentration, 10^{-4} cancer risk surface, and 10^{-6} cancer risk surface.

Cold forming

The cancer risk of cold forming is shown as Figure 1d. When the VOC concentration of workplace air was low (5 or 10% concentration) and the pollution control efficiency was 95%, a cancer risk of less than 10^{-6} could be achieved. If the acceptable health risk is 10^{-3}, personal protective equipment (i.e., an activated carbon based mask) could control the health risk of workplace air to below 10^{-3} at 50% VOC concentration. In addition, the cancer risk could be up to 5.0×10^{-2} at 95% concentration, no pollution control improvement and 8 hrs exposure time.

Based on the 95% concentration and 8 hrs exposure time, the sequence of cancer risk was as follows: hot forming > cold forming ≅ cokemaking > sintering processes under non-workplace air improvement condition.

For the sintering and cokemaking processes, a computer auto-control system (i.e., a motor-trolley for sintering and cokemaking product) to send the sintering ore and coke to the next process could reduce the exposure of workers. Also, the seal of the coke oven could be improved to reduce the escape of VOCs. In addition, an environmentally friendly reagent could be selected to replace HCl in the cold and hot forming processes, reducing the formation of chlorinated

VOCs during the rolling process. In addition, enhanced ventilation is necessary to improve the air exchange rate.

The cancer risk was $<10^{-6}$ at high workplace air control efficiency (> 95%) and low VOC concentration (<15%) (data shown in Table 5); therefore, based on the current operating conditions of four processes, it is difficult to meet the criteria. Fugitive emission reduction, workplace ventilation improvement and personal protection improvement could reduce exposure dosage and achieve the acceptable cancer risk. Furthermore, the working-hours reduction is also an option while the workplace air control method could not completely achieve the acceptable cancer risk.

For low workplace air control efficiency (about 10%) and low VOC concentration (about 40–60%), the cancer risk could be $< 10^{-3}$. But for high concentration (i.e., 85–95%), a high level of workplace air control (>95%) was necessary to reduce the cancer risk to 10^{-3}. The workplace air of the cokemaking process should be improved ($\eta > 95\%$), as its current operating conditions pose a high cancer risk.

The risk assessment processes reveal a high degree of uncertainty via the use of the slope factor from high-dose animal studies to low-dose human exposure. But the procedures used could be a flexible method to measure cancer risk under workplace contaminant air exposure. Generally, risk analysis is best used to develop insights and not to develop numerical results, which might suggest an inappropriate degree of precision.[42] Therefore, it is necessary to discuss the uncertainty for the results of health risk assessment. However, these qualitative statements of uncertainty are difficult to assess, particularly when the assessment involves potential exposure to several contaminants transferred over a number of different pathways.[43] In this study 7 VOC species are regarded as cancer effect chemicals by IRIS and IARC; other chemicals might have a cancer effect after exposure. Only the respiration pathway was evaluated in this study. In addition, the individual exposure amount, as well as the duration and pattern of exposure to the chemical, could introduce uncertainty into exposure assessment. Few chemicals have been adequately studied in humans to accurately identify a sub-threshold dose directly. Most of dose-response data available comes from the inter-human or animal to human process.[44] Therefore, scientists typically rely on existing human epidemiologic and animal laboratory data to estimate sub-threshold doses for humans.[44] Modeling errors are also the source of uncertainty, deriving from parameter uncertainty, model assumptions, and oversimplification.[45]

Conclusions

VOC concentration characteristics of workplace air were investigated for the sintering, cokemaking, hot forming and cold forming processes. Dichlorobenzene, and trichloroethylene are the dominant halogenated VOCs of the four processes. In addition, carbon tetrachloride and tetrachloroethylene are found in high levels, up to one hundred ppb, in both the cold and hot forming processes. The total cancer risk of the seven species was in the following order: cokemaking (2.0×10^{-2}) > sintering (8.7×10^{-3}) > cold forming (2.8×10^{-3}) $\cong$ hot forming (4.5×10^{-3}). Trichloroethylene contributed 66–93% cancer risk of the four processes. In terms of control strategies for cancer risk, 10^{-6} was very difficult to achieve based on current operating conditions and manufacturing facilities. A cancer risk of 10^{-4} could be accomplished under the conditions of high workplace air control efficiency and reduction of manufacturing equipment emission. Therefore, these results suggest that workplace air improvement and the use of personal protective equipment for workers are high priority to reduce cancer health risks to less than 10^{-3}.

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