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Health risk assessment of exposure to selected volatile organic compounds emitted from an integrated iron and steel plant

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Abstract

Workplace air samples from sintering, cokemaking, and hot and cold forming processes in the integrated iron and steel industry were analyzed to determine their volatile organic compound (VOC) concentration. Sixteen VOC species including three paraffins (cyclohexane, n-hexane, methylcyclohexane), five chlorinated VOC species (trichloroethylene, 1,1,1-trichloroethane, tetrachloroethylene, chlorobenzene, 1,4-dichlorobenzene), and eight aromatics (benzene, ethylbenzene, styrene, toluene, m,p-xylene, o-xylene, 1,2,4-trimethylbenzene, 1,3,5 trimethylbenzene) were selected to measure their noncancer risk for workers. Concentrations of toluene, xylene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, dichlorobenzene, and trichloroethylene were high in all four processes. Carbon tetrachloride and tetrachloroethylene concentrations were high in the hot and cold forming processes. The noncancer risk followed the increasing order: cokemaking > sintering > hot forming > cold forming. 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene contributed 44% to 65% and 13% to 20% of noncancer risk, respectively, for the four processes. Benzene accounted for a high portion of the noncancer risk in cokemaking. The hazard index (HI: 17–108) of the average VOC concentrations suggests that health risks can be reduced by improving workplace air quality and protecting workers.

Keywords: *Volatile organic compound (VOC); integrated iron and steel plant; health risk*

Introduction

The coke oven, the blast furnace (BF), and sintering, basic oxygen steelmaking (BOS), casting and rolling equipment are the main facilities used to produce steel in an integrated iron and steel plant. Generally, coal is used as a raw material, and coke oven gas (COG)—which includes coal tar, CO, CO₂, particles, hydrocarbons (i.e., methane, benzene and toluene, etc.), ammonia, NOx, and SOx—was the main by-product of the cokemaking process [\(Considine et](#page-7-0) al., 2001). A basic oxygen furnace (BOF) is used to produce molten iron from the BF. 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. 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. The iron and steel industry is a high energy- and

material-consumption operation, causing serious workplace and environmental pollution, especially air pollution, which is attributed to the application of complex compositions of raw materials in various manufacturing facilities. According to a European investigation, coke ovens and metal ore roasting or sintering installations for the production of pig iron or steel are important sources of nonmethane hydrocarbons [\(Lagoudi](#page-8-0) et [al., 2001](#page-8-0)).

A number of studies have investigated the human health effects of VOCs. It has been found that trichloroethylene, toluene, and benzene emitted from a PVC film production factory can have a clastogenic effect (Kim et [al., 2003](#page-8-1)); toluene, trichloroethylene, and perchloroethylene can have an inhibitory effect on the nervous system [\(Bushnell et](#page-7-1) al., 2005); CO and benzene can cause hematological problems and cancer ([Kampa and Castanas, 2008\)](#page-7-2); and VOCs emitted from the TFT-LCD were associated with kidney dysfunction in TFT-LCD

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workers [\(Chang et](#page-7-3) al., 2010). More seriously, some VOC species (i.e., aromatics and halogenated VOCs: benzene and trichloroethylene, etc.) are carcinogenic ([IARC, 1982](#page-7-4); IARC, [1997](#page-7-5)).

In addition, aromatic and chlorinated VOC species have been found to cause a health risk in offices ([Destaillats et](#page-7-6) al., [2008](#page-7-6)) and urban environments, that is, transportation [\(Chan](#page-7-7) et [al., 2003\)](#page-7-7). The health risk of indoor air associated with benzene and chlorinated VOC species, that is, 1,1-dichloroethene, chloroform, was significant. In addition, benzene contributed over 40% of the risk for various indoor environments (Guo et [al., 2004\)](#page-7-8). Ohura et [al. \(2006\)](#page-8-2) investigated the VOC risk near an industrial harbor and found that the risk was derived mainly from benzene and carbon tetrachloride. [Lee](#page-8-3) et [al. \(2006\)](#page-8-3) investigated the health risk of BTEXS (benzene, toluene, ethylbenzene, xylenes, and styrene) in photocopy centers and found that the hazard indices ranged from 1.8 to 26. Vitali et al. analyzed organic compounds such as toluene, benzene, ethylbenzene, 1,2-dicholoropropane, and the like in car painting shops and found that benzene was associated with high exposure risk for workers (Vitali et [al., 2006](#page-8-4)). Leung et al. investigated VOC exposure in printing plants and found that ethylbenzene, methylene chloride, toluene, 1,3,5-trimethylbenzene, and xylene were the important compounds. Local exhaust ventilation is an important factor reducing the exposure level of workers ([Leung et](#page-8-5) al., 2005).

VOC species are important precursors of other pollutants including PAHs (polyaromatic hydrocarbons; [BjØrseth et](#page-7-9) al., [1978](#page-7-9)), dioxins and furans (Quaβ et [al., 2004\)](#page-8-6). [Al Zabadi et](#page-7-10) al. [\(2008\)](#page-7-10) investigated the carcinogenic effects of PAHs and VOC species during the occupational exposure of sewage workers and found that these pollutants can cause DNA damage. [Wilson et](#page-8-7) al. (2007) indicated that hexane, acetone, and toluene are the main VOCs of worker exposure in the vehicle repair industry. [Ryan \(2002\)](#page-8-8) investigated the VOC exposure of waste comminglers and found that methylene chloride, chloroform, toluene, m,p-xylene, benzene, ethylbenzene, and chlorobenzene were the most prevalent compounds. However, few studies have focused on VOC emissions from the production of steel.

Generally, time-activity patterns play an important role in exposure levels [\(Delgado-Saborit et](#page-7-11) al., 2009; [Edwards et](#page-7-12) al., [2006](#page-7-12); [Mielke et](#page-8-9) al., 2005;). [Tompa et](#page-8-10) al. (2005) investigated the benzene exposure of refinery workers and suggested that zero tolerance and strict health control were necessary. [Rappaport et](#page-8-11) al. (2005) explained that the variability of VOC species (i.e., benzene, perchloroethylene, and acrylonitrile) is the important factor for exposure estimation using a physiologically based toxicokinetic model. 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 factors in determining the health risk of workers.

Generally, risk analysis is best used to develop insights and not to develop numerical results, which might suggest an inappropriate degree of precision [\(North, 1995\)](#page-8-12). 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 ([Hoffman & Hammonds, 1994](#page-7-13)). Therefore, a comprehensive framework was applied to identify the sensitivity or uncertainty of parameters and developed a control approach method of workplace air.

The National Institute for Occupational Safety and Health (NIOSH) and several partners developed the National Occupational Research Agenda (NORA), which identified indoor air environment improvement as the most important issue for the health of workers [\(Mendell et](#page-8-13) al., 2002). Based on the above-cited literature, the aromatic and chlorinated VOC species are important species affecting human health in the workplace and other indoor environment. Few studies have focused on the risks of VOC species in the workplace air of iron and steel industries. Therefore, working conditions (exposure time, VOC concentration distribution, and pollution control efficiency of workplace air) were addressed in this study. In addition, the hazard index (HI) of noncancer risk and cancer risk was measured for workers of the sintering, cokemaking, hot forming, and cold forming processes in an integrated iron and steel plant.

Materials and methods

Operational conditions of four facilities

Four facilities were selected—sintering, cokemaking, hot forming, and cold forming processes—in an integrated iron and steel plant, and the workplace air VOC samples were the target airborne pollutants.

Generally, the sintering plant collects the ash from the BF and BOF, returns fines from the sintering plant (130–180 t/h), and blends these with ore (450–600 t/h), serpentine, limestone, and coke breeze (25–25 t/h) to manufacture sintering ore (400–600 t/h) at temperatures ranging from 1050°C to 1150°C. Coal (30–200 t/h) is used as the raw material, and blast furnace gas (BFG) and coke oven gas (COG) are used as fuel (19100–62000 Nm3 /h) to produce coke (20–160 t/h) at 1230°C to 1260°C 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. It takes about 140–175 t/h of cold-rolled coil and about 8000 Nm3 /h to generate the cold-rolled coil at 840°C. In addition, slab (rectangular type) steel (165–260 t/h) is rolled, milled, and heated (COG as fuel: 9270-12000 Nm³/h) to about 1200°C, then rolled, leveled, and cooled in the hot forming process. Finally, slab steel is manufactured to form hot-rolled coils (160–260 t/h).

Workplace VOCs

Workplace air samples were taken using the stainless steel canister sampling method for $C_3 - C_{11}$ hydrocarbon analysis. The canister sampler was placed on the platform, and the height of the sampling probe was about 1.5 m from the ground to simulate the human breathing area. 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 [\(EPA, 1988\)](#page-8-14).

Based on the questionnaires and investigations, the hot and cold forming processes were operated from 0600 to 2300 each day, and the cokemaking and sintering processes were operated for 24h a day. Three sampling periods per day (0700–1100, 1300–1700, and 1900–2300) were taken for the hot and cold forming processes, and four sampling periods per day (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-day sampling schedules were followed to enable representative samples to be collected for each process. In total, 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 preconcentrated in a purge-andtrap 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 (nonpolar 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.

Duplicated analyses were done for every five 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 95±8% (propene) to 106±5% (p-ethyltoluene), and the method detection limit varied from 0.02 (n-decane) to 0.15 (propene) ppb.

Health risk measurement

Based on the VOC data in this study, an exposure assessment was conducted to evaluate the potential VOC uptake by inhalation. According to the questionnaire survey, the exposure time per day of workers for the four processes is 5h for the sintering process, 7h for cokemaking, and 1h for both hot forming and cold forming.

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.

Noncarcinogenic hazards from chronic exposure were evaluated for workers. The noncancer risk of *i*th VOC species

is expressed in terms of the hazard quotient (HQ_i) , which is defined as follows:

$$
HQ_i = \frac{(C_i \times IR \times ET \times EF \times ED \times f)}{(AT \times BW) \times RfD_i}
$$
\n(1)

where C_i is the concentration of *i* species VOC in workplace air (mg/m³), IR is the inhalation rate (m³/h), ET is the exposure time (h/day), EF is the exposure frequency (day/year), ED is the exposure duration (year), f is the conversion factor, AT is the average time (ED years×EF days/year), BW is the body weight (70kg was assumed in this study), and R*f*D is a numerical estimate of the daily exposure of the human population. The average lifetime of 70 years was used for the VOC carcinogenic assessment, and the total exposure time was 30 years. In addition, the parameters applied to the health risk assessment are as shown in [Table 1](#page-3-0).

The noncancer risk is expressed in terms of the HI, which is defined as follows:

$$
HI = \sum_{i=1}^{i=n} HQ_i
$$
 (2)

where HI is expressed as the hazard index, which is measured by the calculation of HQ_i for a VOC species and summing of all HQ_i (*i* is a VOC species) to be the HI value.

VOC exposure below the reference level, HI < 1, is unlikely to be associated with adverse health effects. The potential for adverse effects increases as exposures exceed the reference dose obtained from the Integrated Risk Information System ([IRIS, 2010](#page-7-14)) and Risk Assessment Information System [\(RAIS,](#page-8-15) [2010](#page-8-15)).

The inhalation reference dose $(RfD_i$ _{*n*} mg/kg-day, shown as [Table 1](#page-3-0)) of 16 components including trichloroethylene (1.14×10−2), 1,1,1-trichloroethane (1.43), tetrachloroethylene (1.71×10−1), benzene (8.57×10−3), cyclohexane (1.71), n-hexane (2.00×10−1), chlorobenzene (1.42×10−2), 1,4-dichlorobenzene (2.29×10^{-1}) , methylcyclohexane (8.60×10^{-1}) , ethylbenzene (2.86×10−1), styrene (2.86×10−1), toluene (1.43), m-m,p-xylene, o-xylene (2.80×10−2), 1,2,4-trimethylbenzene (2.00×10^{-3}) , and 1,3,5-trimethylbenzene (1.71×10^{-3}) were measured to determine the HI for the four processes examined in this study.

Results and discussion

VOC concentration distribution

Based on this study, 67 VOC species including 26 paraffins, 9 olefins, 16 aromatics, and 16 halogenated species were analyzed. Total concentration for the 67 VOCs was 2.0ppm for the sintering process, 9.0ppm for the cokemaking process, 4.5ppm for the hot forming process, and 3.0ppm for the cold forming process. In addition, the health risk VOCs (16 selected species) contribution for the total VOCs (67 species) was 60% for sintering, 40% for cokemaking, 70% for hot forming process, and 60% for cold forming process. The halogenated VOC fractions of the 67 VOCs were 4%, 1%, 13%, and 11% for the sintering, cokemaking, hot forming, and cold forming processes,

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Table 1. Parameters of health risk measurement.

Parameters	Values	Reference
C _i (VOCs in workplace, mg/m ³)	Workplace air concentration (i.e. Figure 1)	This study
IR (Inhalation rate, m^3/h)	1.68^1	USEPA (1997)
ET (Exposure time, h/day)	$0.17 - 8$	This study
EF (Exposure frequency, day/year)	250	USEPA (1991)
ED (Exposure duration, year)	30	USEPA (1997)
AT (average time, day)	$ED \times EF$	USEPA (1997)
BW (body weight, kg)	70^{2}	DOH (2008)
RfD. (inhalation reference dose, mg/kg·day)	Benzene: 8.57×10^{-3} Chlorobenzene: 1.42×10^{-2} Ethylbenzene: 2.86×10^{-1} n-Hexane: 2.00×10^{-1} Styrene: 2.86×10^{-1} Toluene: 1.431,1,1-Trichloroethane: 1.43Xylene: 2.80×10^{-2}	IRIS $(http://www.epa.gov/iris/)$
	Cyclohexane: 1.711,4-Dichlorobenzene: 2.29×10^{-1} Tetrachloroethylene: 1.71×10^{-1} Trichloroethylene: 1.14×10^{-2} 1,2,4-Trimethylbenzene: 2.00×10^{-3} 1,3,5- Trimethylbenzene: 1.71×10^{-3} Methylcyclohexane: 8.60×10^{-1}	RAIS (http://rais.ornl.gov/)

 $\rm ^1$ The value of inhalation rate was based on the average of construction workers, carpenters and iron workers (1.44-1.86 m $\rm ^3/h$).

2 Based on the investigation of Taiwan's department of health (DOH), the average weight of adult (age: 24–64) was 70.67kg. Therefore, 70kg of body weight was selected, and this value is commonly used as the body weight of an adult in Taiwan.

respectively. The workplace air VOC profiles indicate that the aromatics ranged from 30% (cokemaking) to 70% (cold and hot forming), paraffins ranged from 10% (hot forming) to 55% (cokemaking), olefins ranged from 2% (hot forming) to 10% (cokemaking), and the halogenated group ranged from 2% (cokemaking) to 15% (hot forming).

The dominant workplace VOC concentrations in the vicinity of the manufacturing equipment are shown [Figure 1](#page-4-0). In the sintering process, toluene, m,p-xylene, 1,2,4-trimethylbenzene, and ethylbenzene were the predominant VOCs, with concentrations from 110 to 310 ppb. Trichloroethylene, dichlorobenzene chloroform, and 1,1,1-trichloroethane were detectable in the sintering process at concentrations ranging from 5.6 to 50 ppb.

Box plots depict range of concentrations, with top whisker equal to 90th percentile of concentrations, bar at the top of box equal to the 75th percentile, bar at the middle of the box equal to the 50th percentile, bar at the bottom of the box equal to the 25th percentile, and bottom whisker equal to the 10th percentile.

Toluene, benzene, m,p-xylene, 1,2,4-trimethylbenzene, n-hexane, and ethylbenzene were the main species in the cokemaking process. Most of the species were aromatics, at concentrations ranging from 110 to 1650 ppb. The concentration of the halogenated VOC species was less than 60 ppb, and trichloroethylene, dichlorobenzene, chloroform, chlorobenzene, and trichloroethane were the major species. Generally, cokemaking is a reduction condition, and the coke is an aromatic structure that can cause a high portion of aromatic compounds in the workplace air of cokemaking process.

In the hot forming process workplace, toluene, o-xylene, m,p-xylene, 1,2,4-trimethylbenzene, styrene, ethylbenzene, and chlorobenzene were the principal species with concentrations from 170 to 860 ppb. Carbon tetrachloride, chlorobenzene, trichloroethylene, and tetrachloroethylene contributed a large fraction of chlorinated VOCs, and their concentrations were higher than 80 ppb.

In the cold forming process workplace, toluene, o-xylene, m,p-xylene, 1,2,4-trimethylbenzene, carbon tetrachloride, styrene, and ethylbenzene were the dominant VOC species with concentrations over 100 ppb. The detectable halogenated VOC species, including carbon tetrachloride, chlorobenzene, trichloroethylene, tetrachloroethylene, and dichlorobenzene, in the cold forming process work place were measured at concentrations higher than 25 ppb.

The high halogenated VOCs associated with the hot forming and cold forming process workplaces may be affected by the HCl that was used to remove steel rust. Therefore, the high chlorinated species were measured in both steel forming workplaces. To reduce the chlorinated VOCs, the use of alternative reagents could be considered.

Health risk

Sixteen species were selected to measure the noncancer risk (HI). The results indicate that the total HI of the four processes ranged from 17 to 108 (as [Table 2](#page-5-0) shown). The HI followed the increasing order: cokemaking > sintering > hot forming > cold forming. For the sintering process, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, m,p-xylene, and trichloroethylene were the dominant species causing the noncancer risk. In addition, 1,2,4-trimethylbenzene, benzene, 1,3,5-trimethylbenzene, m,p-xylene, and trichloroethylene accounted for a high portion of the noncancer risk in the cokemaking process. For the steel rolling process, 1,2,4-trimethylbenzene, 1,3,5 trimethylbenzene, m,p-xylene, o-xylene, and chlorobenzene posed the noncancer risk in hot and cold forming.

In this study, 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene contributed 44% to 65% and 13% to 20% [\(Figure](#page-5-1) 2), respectively, of the noncancer risk for the four processes. The two trimethylbenzene species contributed 78% to 85% of the risk in the sintering, hot forming, and cold forming processes. Benzene accounted for a high portion of the noncancer risk in the cokemaking process (31% for cokemaking process vs. 1% to 2% for the other processes). The contribution to the noncancer risk of other individual VOC species was less

Figure 1. Characteristics of VOC concentrations in four facilities.

than 5%, for example, trichloroethylene (about 4%) and chlorobenzene (0%–5%).

Health risk reduction scenario

Risk analysis is best used to develop insights and not to focus numerical results, which might lead an inappropriate degree of precision. Generally, some assumptions are applied in

scenarios that are commonly used in evaluating sensitivity and uncertainty associated with variable parameters for health risk analysis ([Brouwer & De Blois, 2008\)](#page-7-16).

Health risk assessment processes reveal a high degree of uncertainty via the use of the inhalation reference dose (RfD_i) of a single agent from high-dose animal studies to much lowdose human exposure. However, the procedures used could

Table 2. Hazard quotient (HQi) of VOC species at the average concentration of workplace air.

Compounds				Sintering Cokemaking Hot forming Cold forming
Benzene	1.50	33.39	0.59	0.39
Chlorobenzene	0.00	0.59	1.30	0.62
Cyclohexane	0.00	0.01	0.00	0.00
$1,4-$	0.05	0.04	0.02	0.02
Dichlorobenzene				
Ethylbenzene	0.20	0.27	0.07	0.05
n-Hexane	0.09	0.45	0.02	0.01
Styrene	0.12	0.14	0.08	0.05
Tetrachloro	0.00	0.00	0.08	0.03
ethylene				
Toluene	0.10	0.72	0.05	0.04
1, 1, 1	0.00	0.00	0.00	0.00
Trichloroethane				
Trichloroethylene	2.59	4.53	1.01	0.62
$1,2,4-$	40.58	47.78	15.36	10.38
Trimethylbenzene				
$1,3,5-$	12.43	14.49	4.59	3.28
Trimethylbenzene				
m-Xylene	2.86	3.89	1.14	0.80
o-Xylene	1.43	1.63	1.45	0.82
Methylcyclohexane	0.01	0.03	0.00	0.00
HI (Sum of HQi)	62	108	26	17

1,2,4-Trimethylbenzene ⊠ 1,3,5-Trimethylbenzene Benzene 日 Xylene 日 Others

Figure 2. VOC species contributed to the hazard index of four facilities.

be a flexible method to measure the noncancer risk under the workplace contaminant air exposure and could be a method to set "safe" levels of exposure.

Based on the VOC concentrations in the workplace, the concentration distribution was measured to evaluate the noncancer risk associated with VOCs in the workplace. In this

study, the VOC control efficiency of workplace air (0%, 10%, 30%, 50%, 75%, 80%, 95%, 99%, and 99.97%), exposure time (10min, 0.5, 1, 2, 4, 6, and 8h), and range of cumulative concentration (5%, 10%, 50%, 90%, and 95%) were the selected parameters to assess the risk. VOC concentration distribution was simulated by Crystal Ball 2000.2 ([Decisionerring, 2001](#page-7-17)). Based on the software analysis, the VOC concentrations of the four 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 5%, 10%, 50%, 90%, and 95% cumulative VOC concentrations. [Figure 3](#page-6-0) shows the noncancer risk of workers under the various operating conditions.

Note: The curved surfaces from the upper to bottom layer show as first layer: 95% cumulative concentration, second layer: 90% cumulative concentration, third layer: 50% cumulative concentration, fourth layer: 10% cumulative concentration, HI=5 non- cancer risk surface, and HI=1 non-cancer risk surface.

1. Sintering process

[Figure 3A](#page-6-0) shows the noncancer risk of the sintering process. When the cumulative concentration was 50%, most of the HI values under the various conditions were less than 1. If the pollution control efficiency was increased to 80%, an HI of less than 1 could still be achieved if the exposure time was raised to 4h. When the cumulative concentration was over 90%, a high pollution control efficiency (95%) and low exposure time (2h) were necessary to reduce the noncancer risk. At 95% cumulative concentration and over 8-h exposure time, the HI value could reach 450 if no pollution control was implemented. Based on the working conditions of workers and the VOC concentration, 95% pollution control efficiency is necessary to achieve an acceptable noncancer risk level.

2. Cokemaking process

The noncancer risk of the cokemaking process is shown in [Figure 3B.](#page-6-0) The cumulative concentration was 50%, the pollution control efficiency was 80% and the exposure time was 4h; results indicated that the HI value was less than 1. When the concentration reached 90% cumulative concentration, high pollution control efficiency (95%) and low exposure time (2h) could achieve an acceptable risk condition. If the concentration reached 95% cumulative concentration, however, the HI increased to 580 if the exposure time was increased to 8h and no pollution reduction was implemented. Based on the VOC concentration of workplace air and the workplace conditions, 95% workplace air reduction or the use of personal protection should enable achievement of an acceptable noncancer risk.

3. Hot forming process

The noncancer risk of the hot forming process is shown in [Figure 3C.](#page-6-0) With the cumulative concentration at 50%, an HI of less than 1 can be achieved if the workplace air pollution is reduced by 95%. However, if the exposure time is only 30min, then an acceptable risk can be achieved at the 50% cumulative concentration with no improvement in workplace air. At 90% cumulative concentration and 30min exposure time, a

Figure 3. Non-cancer risk (Hazard index) of four processes: (a) sintering process (b) cokemaking process (c) cold forming process (d) hot forming process.

pollution control efficiency of 95% is needed to achieve an HI of less than 1. However, if the cumulative concentration is 95%, the exposure time is 8h, there is no pollution control, and the HI increases to 810. According to the VOC concentration of workplace air and the working condition of workers, 50% pollution control efficiency is necessary to keep the risk at an acceptable level for 1-h exposure.

4. Cold forming process

[Figure 3D](#page-6-0) shows the noncancer risk of the cold forming process. If the cumulative concentration is 50%, achieving a 95% reduction in workplace air pollution should result in an HI of less than 1. However, if the exposure time is only 30min, then an acceptable risk can be achieved at 50% cumulative concentration with no improvement in workplace air. With the workplace air at 90% cumulative concentration, high pollution control efficiency (95%), and low exposure time (1h), the acceptable risk condition can be achieved. With the high dose condition (95% cumulative concentration, 8-h exposure time, and non–pollution control conditions), however, the HI increases to 650.

Based on the 95% cumulative concentration and 8-h exposure time, the sequence of noncancer risk was as follows: hot forming > cold forming \cong cokemaking > sintering with no workplace pollution control improvement. At 50% cumulative VOC concentration and the predetermined exposure times for the workers (i.e., 5h for sintering, 7h for cokemaking, and 1h for hot and cold forming), the pollution control efficiency of workplace air should be up to 80% for the sintering process, 95% for the cokemaking process, 75% for the hot forming process, and 75% for the cold forming process to achieve an HI value less than 1. Measures such

as enhancing ventilation in the workplace and implementing personal protection are necessary to reduce exposure. In addition, reduction of exposure time could be another strategy to decrease the noncancer risk associated with the cokemaking and sintering processes.

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, a tight seal on the coke oven was effective in reducing the escape of VOCs. In addition, an environmentally friendly reagent could be selected for the iron rust to replace HCl in the cold and hot forming processes. This concept could reduce the formation of chlorinated VOC species during the rolling process. In addition, enhanced ventilation is necessary to improve the air exchange rate of workplace air.

In this study, 16 VOC species are regarded as health effect chemicals by IRIS and IARC; other chemicals might have a health risk effect after exposure. 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 subthreshold dose directly. Most of the dose-response data available comes from the interhuman or animal-to-human process ([Hoffman](#page-7-13) [& Hammonds, 1994](#page-7-13)). The distribution of possible risk values, that is, the uncertainty of risk, must be considered to identify the key variables (i.e., dose-response relation) and assumptions to contribute to the uncertainty of risk values ([Cooke & MacDonell, 2008;](#page-7-18) [Sassi & Ruggeri, 2008](#page-8-18)). Modeling errors could be also the source of uncertainty, deriving from parameter uncertainty, model assumptions, and oversimplification ([Van der Sluijs et](#page-8-19) al., 2005). Further research efforts are required to standardize the application of acceptable intake values of VOC species and set up a systemic methodology of health risk assessment to reduce the large variability estimation of hazard quotients.

Conclusions

VOC concentration characteristics of workplace air were investigated for the sintering, cokemaking, hot forming, and cold forming processes in the iron and steel plant. Toluene, xylene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene are the main health risk VOC species, and dichlorobenzene and trichloroethylene are the dominant halogenated VOC species of the four processes. In addition, carbon tetrachloride and tetrachloroethylene are high, up to 100 ppb, in both the cold and hot forming processes. Based on average concentration, the HI ranged from 17 to 108, and the noncancer risk followed the increasing order: cokemaking > sintering > hot forming > cold forming. 1,2,4 trimethylbenzene and 1,3,5-trimethylbenzene contributed 44% to 65% and 13% to 20%, respectively, of the noncancer risk for the four processes. According to the 50% cumulative concentration and the predetermined exposure time for the workers, the pollution control efficiency should be

over 80% for the sintering process, up to 95% for the cokemaking process, over 80% for the hot forming process, and 75% for the cold forming process to achieve a noncancer risk (HI) less than 1. These results suggest that workplace air improvement and the use of personal protective equipment for workers are necessary to reduce noncancer health risks in the current working conditions. In spite of some limitations of this study, the conclusions are informative (i.e., the reduction of VOC exposure is necessary) for both policy decision making of pollution control and new plant construction in the future.

Declaration of interest

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