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The Characteristics of the Appearance and Health Risks of Volatile Organic Compounds in Industrial (Pohang, Ulsan) and Non-Industrial (Gyeongju) Areas

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Objectives: The aim of this study was to identify the health and environmental risk factors of air contaminants that influence environmental and respiratory diseases in Gyeongju, Pohang and Ulsan in South Korea, with a focus on volatile organic compounds (VOCs).

Methods: Samples were collected by instantaneous negative pressure by opening the injection valve in the canister at a fixed height of 1 to 1.5 m. The sample that was condensed in -150℃ was heated to 180℃ in sample pre-concentration trap using a 6-port switching valve and it was injected to a gas chromatography column. The injection quantity of samples was precisely controlled using an electronic flow controller equipped in the gas chromatography-mass spectrometer.

Results: The quantity of the VOC emissions in the industrial area was 1.5 to 2 times higher than that in the non-industrial area. With regards to the aromatic hydrocarbons, toluene was detected at the highest level of 22.01 ppb in Ulsan, and chloroform was the halogenated hydrocarbons with the highest level of 10.19 ppb in Pohang. The emission of toluene was shown to be very important, as it accounted for more than 30% of the total aromatic hydrocarbon concentration.

Conclusions: It was considered that benzene in terms of the cancer-causing grade standard, toluene in terms of the emission quantity, and chloroform and styrene in terms of their grades and emission quantities should be selected for priority measurement substances.

Key words: Benzene, Carcinogenic substances, Chloroform , Toluene, Volatile organic compounds

INTRODUCTION

The emission of hazardous chemical substances, such as hazardous air pollutants and polycyclic aromatic hydrocarbons (PAHs) have increased globally due to excessive energy consumption, industrialization and urbanization. However, the emission quantity has been decreasing from 2005 through the efforts on the reduction such as leak detection and repair, regenerative thermal oxidizer system, vapor recovery unit, process improvement, quality control, and material improvement in Korea [1,2]. These contaminants have resulted in reduced biodiversity and the destruction of ecosystems, and are emerging as environmental problems, regardless of the nation and area investigated. It has been revealed that hazardous chemicals and environmental contaminants are the main causes of asthma, atopy, dermatitis and allergies. With the ever-increasing number of environmental diseases, human interest in this area has been increasing [3-8]. The numbers of asthma and atopy patients have been increasing steadily over the last 30 years in advanced countries, such as the USA and Europe, with comparative prevalence rates as follows: UK (over 15%), New Zealand (15.1%), Australia (14.7%) and USA (10.9%). Also, more than 100 asthmatic patients per day for every 100,000 of the population in Japan are treated in hospital. The prevalence rates of asthma and atopy in Korea have been increasing, and the prevalence rate of asthma in primary and middle school student has increased more than 30% between 2002 and 2008 according to a report from the Korean Academy of Pediatric Allergy

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and Respiratory Disease [4,8,9]. The result analyzed from health insurance payment data from 2002 to 2008 for patients with environmental diseases, such as atopy, asthma, allergic rhinitis and chronic bronchitis, showed that the prevalence rates in 2008 had increased by 8.7% compared to those in 2007, with a 6.4% increase in the yearly average from 631 in 2002 to 1,034 in 2008 per 10,000 of the population. The main reason for this is air pollution, which can be categorized into two groups. Firstly, indoor air pollution that causes fatigue, headaches, dizziness, and reduced concentration in indoor residents due to sick house syndrome, as well as multi-chemical sensitivity. Secondly, outdoor air pollution due to the increased emissions of VOCs, particulate matters and liquid state contaminants from the increased use of oil and organic solvents, increased landfill use and the increased incineration of waste.

Investigating the emerging features of VOCs as contaminants that are influential on national health is considered to be important [4-6]. Therefore, to identify hazardous factors, including the types and concentration of pollutants, found in air contaminants, which are influential to national health, is essential for the healthcare of the residents in that area. Accordingly, this study aimed to identify the health and environmental risk factors of air contaminants that influence environmental and respiratory diseases in Gyeongju, Pohang and Ulsan in South Korea, with a particular focus on VOCs. The characteristics of the emergence of VOCs in industrial and non-industrial areas were compared.

MATERIALS AND METHODS

I. Survey Area

The locations of the sampling sites are shown in Figure 1. The Pohang Steel Management Industry Complex (A point, industrial area, TM 35.9782, 129.37942, 627 Ho-dong, Nam-gu, Pohang, South Korea) and the Yeocheon industry complex (B point, industrial area, TM 35.51932, 129.34462 896-1, Yeocheon-dong, Nam-gu, Ulsan, South Korea) were selected to represent the characteristics of Pohang and Ulsan. As reference areas, Sungdong-dong in Gyeongju (C point, commercial area, TM 35.84442, 129.21772 40, Sungdong-dong, Gyeongju, South Korea) and Yonggang-dong (D point, residential area, TM 35.86762, 129.2236 956-3, Yonggang-dong, Gyeongju, South Korea) where were selected as the residential sampling sites. The industrial area, commercial area, and residential area were set according to the land use plan of the Ministry of Land and Maritime Affairs and the standard for installation of the air quality monitoring stations for hazardous air contaminants, such as VOCs and PAHs, were obtained from the Ministry of the Environment [1,10].

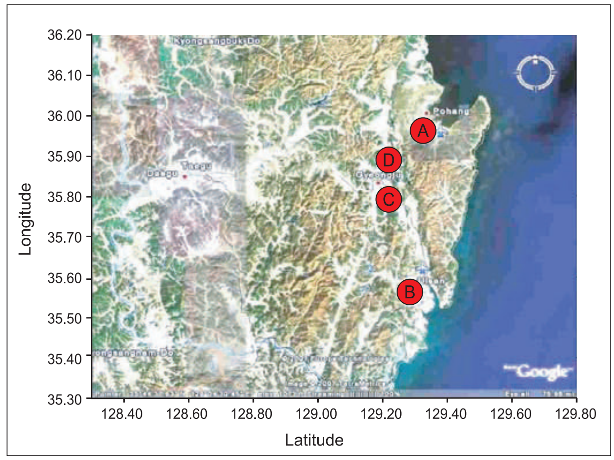

Figure 1. Locations of sampling sites at Pohang (A), Ulsan (B), and Gyeongju (C, D).

II. Period and Method of Specimen Sampling

The specimen samples for the collection of VOC concentration data were taken on January 22,2007, May 21,2007 and September 17,2007. The specimens were sampled for 1 hour from 09:00 AM to 10:00 AM. The specimens were collected twice from 4 spots in January, March, and May. A 6 L canister made of stainless steel, purchased from the Restek Company, was used for collecting the samples. The impurities in the canister were removed by cleaning it more than 6 times with high purity nitrogen gas, using a canister cleaner (ENTECH, Model 3100, CA, USA). Once the canisters were cleaned, they were connected to the analysis system. Samples were collected by instantaneous negative pressure by opening the injection valve in the canister at a fixed height of 1 to 1.5 m.

III. Analysis

In this study, due to the very low VOC concentrations in the air, the enrichment and desorption of VOCs were conducted automatically via the assembly of a sample pre-concentration trap (SPT) to a gas chromatography-mass spectrometer (GC-MS). The quantity of the sample used for the concentration step was precisely controlled using a mass flow controller (MFC), and the sample was analyzed for 5 minutes with a flow rate of 80 mL/min. The sample that was condensed at -150℃ was heated to 180℃ in a SPT using a 6 port switching valve, following which it was injected to GC column. The injection quantity of the sample was precisely controlled with an electronic flow controller equipped in the GC-MS. The operation conditions for VOC analysis by the Saturn 2000 GC-MS (Varian, Oshawa, Canada) of the Varian Company are shown in Table 1.

Table 2 shows the items analyzed in this study, as well as their specific characteristics and classifications. The VOCs frequently detected in the air, which draw attention in terms

Table 1. Experimental conditions of GC-MS

Model	GC-MS (Varian, Saturn 2000)
Condensation method	Low temperature condensation by SPT
Condensation conditions	-150℃ (5 min) condensation → 200℃ desorption
Sample amount	50 mL/min× 5 min → 250 mL (split ratio 100:1)
Column	CP-Sil 5CB (60 m× 0.32 mm× 1 um)
Column flow	2.7 mL/min He
Oven condition	-30℃ (5 min) → 10℃/min → 150℃ (5 min)
MS condition	Ion trap: 140℃, manifold : 50℃, transfer line 180℃

GC-MS, gas chromatography-mass spectrometer; SPT, sample preconcentration trap.

Table 2. Physical characteristics of VOCs and their carcinogenesis classification

No.	VOCs	Molecular formula	CAS No.	Molecular weight	Classification [2,11]	
					WHO (IARC)	EPA (IRIS)
1	Difluorodichloromethane (Freon-12)	CCl_2F_2	75-71-8	120.91	-	-
2	Chloromethane	CH_3Cl	74-87-3	50.49	-	-
3	1,2-dichlorotetrafluoroethane (Freon-114)	$C_2Cl_2F_4$	76-14-2	170.92	-	-
4	Vinyl chloride	$H_2C{=}CHCl$	75-01-4	62.5	1	A
5	1,3-butadiene	$H_2C{=}CHCH{=}CH_2$	106-99-0	54.09	2A	B2
6	Bromomethane	CH_3Br	74-83-9	94.94	-	-
7	Chloroethane	CH_2ClCH_3	75-00-3	64.52	-	-
8	Trichlorofluoromethane (Freon-11)	CCl_3F	75-69-4	137.37	-	-
9	Acrylonitrile	CH_2CHCN	107-13-1	53.06	-	-
10	1,1-dichloroethene	$H_2C{=}CCl_2$	75-35-4	96.94	-	-
11	Methylene chloride	CH_2Cl_2	75-09-2	84.93	2B	B2
12	1,1,2-trichlorotrifluoroethane (Freon-113)	$CF_2ClCFCl_2$	76-13-1	187.38	-	-
13	1,1-dichloroethane	$ClCH_2CH_2Cl$	75-34-3	98.96	-	-
14	cis-1,2-dichloroethylene	$ClCH{=}CHCl$	156-59-2	96.94	-	-
15	Chloroform	$CHCl_3$	67-66-3	119.38	2B	B2
16	1,2-dichloroethane	$ClCH_2CH_2Cl$	107-06-2	98.96	2B	B2
17	1,1,1-trichloroethane	CH_3CCl_3	71-55-6	133.4	D	-
18	Benzene	C_6H_6	71-43-2	78.11	1	A
19	Carbon tetrachloride	CCl_4	56-23-5	153.82	2B	B2
20	1,2-dichloropropane	$CH_3CH(Cl)CH_2Cl$	78-87-5	112.99	-	-
21	Trichloroethylene	$ClCH{=}CCl_2$	79-01-6	131.39	2A	B2
22	cis-1,3-dichloropropene	$ClCH_2CH{=}CHCl$	10061-01-5	110.97	-	-
23	trans-1,3-dichloropropene	$ClCH_2CH{=}CHCl$	10061-02-6	110.97	-	-
24	1,1,2-trichloroethane	$ClCH_2CHCl_2$	79-00-5	133.4	3	C
25	Toluene	$C_6H_5CH_3$	108-88-3	92.14	3	D
26	1,2-dibromoethane	CH_2BrCH_2Br	106-93-4	187.87	-	-
27	Tetrachloroethylene	$Cl_2C{=}CCl_2$	127-18-4	165.83	2A	-
28	Chlorobenzene	C_6H_5Cl	108-90-7	112.56	-	D
29	Ethylbenzene	$C_6H_5C_2H_5$	100-41-4	106.17	-	D
30	m-Xylene	$C_6H_4(CH_3)_2$	108-38-3	106.17	3	D
31	p-Xylene	$C_6H_4(CH_3)_2$	106-42-3	106.17	3	D
32	Styrene	$C_6H_5CH{=}CH_2$	100-42-5	104.15	2B	-
33	o-Xylene	$C_6H_4(CH_3)_2$	95-47-6	106.17	3	D
34	1,1,2,2-tetrachloroethane	$Cl_2CHCHCl_2$	79-34-5	167.85	-	-
35	1,3,5-trimethylbenzene	$C_6H_3(CH_3)_3$	108-67-8	120.19	-	-
36	1,2,4-trimethylbenzene	$C_6H_3(CH_3)_3$	95-63-6	120.19	-	-
37	1,3-dichlorobenzene	$C_6H_4Cl_2$	541-73-1	147	-	-
38	1,4-dichlorobenzene	$C_6H_4Cl_2$	106-46-7	147	2B	C
39	1,2-dichlorobenzene	$C_6H_4Cl_2$	95-50-1	147	-	-
40	1,2,4-trichlorobenzene	$C_6H_3Cl_3$	120-82-1	181.45	D	-
41	Hexachloro-1,3-butadiene	$Cl_2C{=}CClCCl{=}CCl_2$	87-68-3	260.76	C	-

WHO (IARC)	EPA (IRIS)
Group 1: the agent is carcinogenic to humans	Group A: human carcinogen
Group 2A: the agent is probably carcinogenic to humans	Group B1: probable carcinogen, limited human evidence
Group 2B: the agent is possibly carcinogenic to humans	Group B2: probable carcinogen, sufficient evidence in animals
Group 3: the agent is not classifiable with respect to its carcinogenicity to humans	Group C: possible human carcinogen
	Group D: not classifiable as to human carcinogenicity
Group 4: the agent is probably not carcinogenic to humans.	Group E: evidence of non-carcinogenicity for humans

VOCs, volatile organic compounds; IARC, International Agency for Research on Cancer; IRIS, Integrated Risk Information System.

Table 3. Summary of the VOC concentrations at Pohang, Ulsan, and Gyeongju (unit: ppb)

No.	VOCs	Pohang A	Ulsan B	Gyeongju C	Gyeongju D
1	Difluorodichloromethane (Freon-12)	0.92 ± 0.44	1.59 ± 2.18	0.65 ± 0.43	1.04 ± 0.69
2	1,2-dichlorotetrafluoroethane (Freon-114)	N.D	N.D	N.D	N.D
3	Bromomethane	N.D	N.D	N.D	N.D
4	Trichlorofluoromethane (Freon-11)	0.52 ± 0.54	3.21 ± 5.56	0.32 ± 0.29	0.52 ± 0.52
5	1,1-dchloroethene	N.D	N.D	N.D	N.D
6	Methylene chloride[1]	0.15 ± 0.26	N.D	0.19 ± 0.33	N.D
7	1,1,2-trichlorotrifluoroethane (Freon-113)	N.D	N.D	N.D	N.D
8	1,1-dichloroethane	N.D	N.D	N.D	N.D
9	cis-1,2-dichloroethylene	N.D	N.D	N.D	N.D
10	Chloroform[1]	10.19 ± 16.54	8.00 ± 12.81	5.39 ± 4.83	3.00 ± 4.38
11	1,2-dichloroethane[1]	0.16 ± 0.12	0.20 ± 0.19	0.14 ± 0.04	0.17 ± 0.07
12	1,1,1-trichloroethane[1]	N.D	N.D	N.D	N.D
13	Benzene[1]	0.64 ± 0.57	0.53 ± 0.36	0.37 ± 0.32	0.75 ± 0.76
14	Carbon tetrachloride[1]	0.29 ± 0.49	N.D	0.27 ± 0.47	N.D
15	1,2-dchloroporpane	7.29 ± 9.19	5.39 ± 4.67	4.31 ± 3.76	9.76 ± 9.01
16	Trichloroethylene[1]	0.33 ± 0.50	0.13 ± 0.22	0.26 ± 0.45	0.20 ± 0.35
17	cis-1,3-dichloropropene	N.D	N.D	N.D	0.10 ± 0.09
18	trans-1,3-dichloropropene	N.D	N.D	N.D	N.D
19	1,1,2-tichloroethane[1]	N.D	N.D	N.D	N.D
20	Toluene[1]	19.74 ± 16.65	22.01 ± 24.13	8.77 ± 4.01	11.927 ± 5.65
21	1,2-dibromoethane	N.D	N.D	N.D	N.D
22	Tetrachloroethylene[1]	N.D	N.D	N.D	N.D
23	Chlorobenzene[1]	N.D	N.D	N.D	N.D
24	Ethylbenzene[1]	4.46 ± 1.26	1.72 ± 0.27	2.39 ± 0.36	1.96 ± 1.09
25	m,p-Xylene[1]	5.04 ± 2.87	2.55 ± 0.69	2.92 ± 0.56	2.96 ± 1.38
26	Styrene[1]	2.54 ± 1.71	1.69 ± 2.20	0.82 ± 0.23	0.82 ± 0.75
27	o-Xylene[1]	2.37 ± 0.21	1.40 ± 0.40	1.56 ± 0.34	1.86 ± 1.17
28	1,3,5-trimethylbenzene	0.51 ± 0.14	0.34 ± 0.20	0.33 ± 0.04	0.51 ± 0.34
29	1,2,4-trimethylbenzene	1.05 ± 0.26	0.78 ± 0.20	0.80 ± 0.20	0.89 ± 0.43
30	1,3-dichlorobenzene	0.13 ± 0.22	0.17 ± 0.16	0.15 ± 0.13	0.16 ± 0.14
31	1,4-dichlorobenzene[1]	0.15 ± 0.26	0.20 ± 0.18	0.17 ± 0.16	0.18 ± 0.17
32	1,2-dichlorobenzene	N.D	N.D	N.D	N.D
33	1,2,4-trichlorobenzene[1]	N.D	N.D	N.D	N.D
34	Hexachloro-1,3-butadiene[1]	N.D	N.D	N.D	N.D

Values are presented as mean ± SD.
N.D, not detected, VOCs, volatile organic compounds.
[1] Carcinogenic classification compounds.

of their risks to health and the environment, due to the cancer creating risk in the human body, were targeted for analyses [11-13]. For a quantitative or qualitative analysis, mixed standards at concentration of 1 ppm, containing 41 kinds of VOCs, were purchased from the Restek Company and were prepared using a dilution device (ENTECH, Diluter Model 4600, CA, USA).

RESULTS

1. Appearance Aspect of VOCs

Four sampling points were selected in the industrial (Pohang, Ulsan) and non-industrial (Geyongju) areas, where the attributes associated with the appearance of VOCs were expected to be different. Table 3 shows the VOCs concentrations (mean ± standard deviation) for 34 compounds available for measuring and analyzing out of a possible 41 compounds. When the data from air quality monitoring stations from the Ministry of the Environment were compared to data obtained in this study, the data from Pohang and Ulsan showed higher concentrations than the data from the measurements of air quality monitoring stations [1]. This can be ascribed to the fact that measurements from air quality monitoring stations are annual average data figures. Figure 2 shows that 16 out of 34 VOC compounds analyzed, all of which result in a cancer risk in the human body, were detected at high concentrations.

The standard deviations of the VOC concentrations in the industrial area were also high; with more severe variations in the quantities of VOC emissions than in the non-industrial area. Such results were almost the same for total hazardous chemical material emissions which were published by the National Institute of Environmental Research on Pohang, Ulsan, and Gyeongju districts in 2009 (Table 4). The total hazardous chemical emissions appeared in the following order: Pohang>Ulsan>Gyeongju [1].

Of all of the items measured, the emissions of toluene

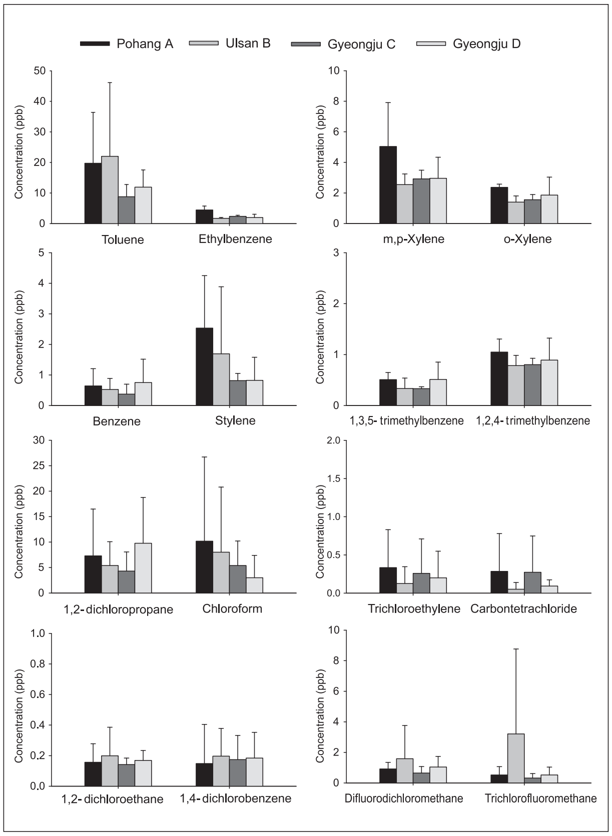

Figure 2. Comparison of the VOCs at each sampling site.

VOCs, volatile organic compounds.

were the highest regardless of the region when the sum of the concentrations of the 34 compounds were compared, with 35%, 44%, 29% and 32% in Pohang, Ulsan, the commercial area in Gyeongju and the residential area in Gyeongju, respectively. Halogenated hydrocarbons, comprising 28 out of the 34 compounds, were not detected at most of the measuring sites or were only detected at concentrations below 1 ppb, with the exception of chloroform, 1-2-dichloropropane and Freon. The Freon gases (Freon-12 and Freon-11), which are precursors of the destruction of the ozone layer, were detected at the highest levels in Ulsan, and 2 ppb of styrene, which is a second grade substance cancer-causing agent, was detected in the industrial area. This value for styrene was 2-3 times higher than in the non-industrial area. The benzene, a first grade cancer-causing substance, was detected at less than 1 ppb for all 4 points, which would satisfy the 1 ppb annual average atmospheric environmental standard in the U.K.

Table 5 shows the concentration ratios of 16 VOCs detected at high concentrations or possessing a cancer risk via their classification in the industrial area compared to the non-industrial area. The concentration ratio was high in the industrial area and non-industrial area for 16 substances which had high concentrations or were graded as carcinogens. In this study, the concentration ratio is the value obtained from the concentration of the industrial area divided by that of non-industrial area. It is recognized that a substance which has a ratio of greater than 1 is a material frequently emitted from the industrial area. The Freon-11 showed the highest concentration ratio of 4.4 in this study, and the next highest ratios were found for styrene (2.6), chloroform (2.2), toluene (2.0) and Freon-12 (1.5).

The measured substances were described by their classification as aromatic or halogenated hydrocarbons, depending on the chemical characteristics, with the sum of their average concentrations shown as a percentage for each sampling site in Table 6. The quantities emitted were in the following order: Pohang (32.6%), Ulsan (28.8%), the residential area in Gyoengju (21.4%) and the commercial area in Gyoengju (17.2%), with values for the industrial area being between 1.5 and 2 times higher than those in the non-industrial area. In addition, it was confirmed that the aromatic hydrocarbon based organic solvents toluene and xylene were used more frequently at every site, as their emissions (8 compounds out of 34 substances) were 1.5 times higher than those of the halogenated hydrocarbons (26 compounds out of 34 substances). The halogenated hydrocarbons, which are highly toxic materials, showed similar percentages regardless of the characteristics of the industrial complexes in Pohang and Ulsan. The VOC concentrations analyzed in this study are regarded as insufficient to explain the characteristics of the appearance of VOCs at each measurement site, because they are not continuously measured. However, it is meaningful as a relative comparison rather than an absolute value for the VOC concentrations, in order to obtain basic data for the VOC concentration for all of the air contaminants that can influence environmental and respiratory diseases for each district.

II. Individual VOC Risk Depending on the Detection Concentration Level

The purpose of this study was to check the degree of risk to the human body, focusing on the carcinogenic VOC

Table 4. Total emissions of hazardous chemical materials in Pohang, Ulsan, and Gyeongju (unit: ton/yr)

Sites \ Emission	Environmental			On-site landfills	Transfer			Total
	Air	Water	Total		Waste	Waste water	Total	
Ulsan	7,967.2	37.4	8,004.6	2,137.9	28,324.0	590.9	28,914.9	39,057.4
Pohang	441.1	9.9	451.0	772.6	210,948.4	39.8	210,988.2	212,211.8
Gyeongju	27.8	-	27.8	-	1,857.4	0.7	1,858.1	1,885.9

Table 5. Concentration ratios of VOCs in the industrial (IA) and non-industrial area (Non-IA) (unit: ppb)

VOCs	IA	Non-IA	Ratio
Dichlorodifluoromethane (Freon-12)	1.25	0.85	1.47
Trichlorofluoromethane (Freon-11)	1.86	0.42	4.43
Choroform	9.09	4.19	2.17
1,2-dichloroethane	0.18	0.16	1.13
Benzene	0.58	0.56	1.04
Carbontetrachloride	0.17	0.18	0.94
1,2-dichloroporpane	6.34	7.03	0.90
Trichloroethylenee	0.23	0.23	1.00
Toluene	20.87	10.34	2.02
Ethylbenzene	3.09	2.17	1.42
m,p-Xylene	3.79	2.94	1.29
Styrene	2.11	0.82	2.57
o-Xylene	1.88	1.71	1.10
1,3,5-trimethylbenzene	0.42	0.42	1.00
1,2,4-trimethylbenzene	0.92	0.85	1.08
1,4-dichlorobenzene	0.17	0.18	0.94

VOCs, volatile organic compounds.

substances that influence environmental and respiratory diseases as reported by the Environmental Protection Agency - Integrated Risk Information System (EPA - IRIS) and World Health Organization - International Agency for Research on Cancer (WHO - IARC), which are summarized in Table 3. It is well known that laborers who are occasionally exposed chloroform for 4 hours over a period of 10-24 months showed symptoms of fatigue, thirst and stimulus sensitivity at 23-35 ppm, and flatulence, fatigue, loss of appetite and disgust at 57-71 ppm [1,2,11-13]. There are thought to be no respiratory diseases caused due to exposure to high concentrations, and the average concentration of chloroform that causes malignant liver tumors was found in this study to be 3-11 ppb. However, aggressive control is considered necessary because chloroform is a B2 grade cancer-causing agent according to the EPA.

Benzene, a first grade cancer-causing agent, which causes lymphocyte cell reduction, thrombocytopenia and leukemia, had the lowest concentration of less than 1 ppb. Bone and marrow tissue shrinkage as a result of leucopenia, which are chronic toxic symptoms in the human body, are caused by this substance. Reductions of red blood cells, white blood cells and blood platelets are also induced by benzene, with abnormalities in the nervous system, infection of the bronchus and pulmonary hemorrhage also being caused in cases of exposure to high concentrations. A hematological influence is usually caused when the human body is exposed to less than 100 ppm. Solvents, adhesives and detergents used in the home contain a small quantity of benzene, meaning that exposure to a high concentration would only result from poor handling and improper ventilation [1,2,4].

Carbon tetrachloride is used as a gasoline additive, a compound used in coolants, a solvent used for rubber bonding, a grain fumigation agent, an adjuvant and a chemical used in phosgene formation. The acute toxicity of carbon tetrachloride cause disgust, vomiting, diarrhea, headaches and paralysis, and can also be a cause of oliguria and liver damage. In extreme cases it can cause chronic toxicity damage to the liver and kidneys and can also result in visual impairment. The minimum concentration that causes abnormalities in liver function is 20 ppm [1,2,4]. Carbon tetrachloride was in the lowest concentration group of the toxic substances, as it was either not detected or was at an average concentration of less than 0.5 ppb, depending on the area being investigated.

Trichloroethylene is used for dry cleaning, printing, ink and paint production, and is also used for adhesives, as a stain remover and as a detergent for carpets in the home. Damage to the liver, kidneys and central nervous system is observed in cases of exposure to a high concentration. The impairment of psychomotor performance and object inconsistency can also be seen as a result of acute toxicity. The abnormality in the nervous system is caused following exposure to 200-500 ppm, and was observed at a similar concentration level to that of carbon tetrachloride, as previously reported [1,2,4].

Chlorobenzene is used as a paint solvent and in detergents, as well as a solvent for adhesives, waxes, polishes, medication and in the production of natural rubber. It easily evaporates into the air, and is even present in underground water sources, river water and soil due to its strong volatility [1,2,4]. However, it was suggested that there would be no risks from exposure to chlorobenzene in this study as it was not detected at any of the measurement sites.

Ethylbenzene is discharged into the air by evaporation and leakage from gas stations, automobile exhaust fumes and cigarette smoke. The target organs are the lungs and central nervous system, where it is absorbed upon exposure to high

Table 6. Mean sum and percentages of VOCs according to the chemical characteristics at each sampling site (unit: ppb)

VOCs	Aromatic hydrocarbons[1]	Halogenated hydrocarbons[2]	Total
Pohang A	36.34 (20.9)	20.38 (11.7)	56.72 (32.6)
Ulsan B	31.01 (17.8)	19.05 (11.0)	50.06 (28.8)
Gyeongju C	17.95 (10.3)	11.93 (6.9)	29.88 (17.2)
Gyeongju D	21.68 (12.5)	15.41 (8.9)	37.09 (21.4)
Σ	106.98 (61.5)	66.77 (38.5)	173.75 (100)

Values are presented as mean sum (%).
VOCs, volatile organic compounds.
[1] benzene, toluene, ethylbenzene, xylene, styrene, trimethylbenzene.
[2] all other compounds.

concentrations. This chemical can also influence the internal organs in cases of long-term exposure to low concentrations [1,2,4]. The exposure to concentrations greater than 200 ppm induces mucous membrane stimulus. However the average concentration of ethylbenzene in the areas investigated in this study was less than 5 ppb.

Xylene is emitted from coal tar, fires on mountains, evaporation from factories, as well as gasoline and diesel engines. It is also emitted when used in alkyl resins, lacquers, rubber adhesives, agrochemical sprayers and organic synthesis agents. It is generated during the transportation and storage of fuel, and in automobile exhaust fumes and from various agricultural activities. Dizziness, staggering, drowsiness and loss of sensation are caused when a high concentration of xylene is inhaled [1,2,4]. The average concentration range of xylene was about 1.4-5.0 ppb, which was in a similar concentration range to that of ethylbenzene. In this investigation, no exposure to high concentrations was found.

Styrene, a grade 2B cancer-causing agent according to the IARC was found at an average concentration of less than 3 ppb, but was found at levels 2-3 times higher in the industrial area compared to the non-industrial area, where petro chemical industry processing, automobiles, combustion, incinerators, plastic product manufacturing and processing were artificial contamination sources in the air. The increase in the risk of cancer has been reported for the lymph duct blood generation tissue as one impact on the human body. The styrene concentration in urine due to exposure for 8 hours with 25 ppm in the air was 150-299 mmol, with 95% reliability. It has been reported to create loss of memory, visual impairment and neuropsychological impairment [1,2,4].

1-4-dichlorobenzene is emitted from the waste of chemical compounds and manufacturing industries. About 67% is used as a space deodorant and in mothball production, with about 33% used for polyethylene sulfonate resin. The usual indoor contamination is mainly from the use of mothballs, textile products and air cleaning agents, with exposure arising for these reasons. In this study, it was observed at an average of less than 0.2 ppb, corresponding to the lowest concentration of all toxic substances.

Toluene is used for the production of other chemicals, such as in petroleum refinery processes, paints, inks, thinners, adhesives, as an element in cosmetics, and styrene. The toxicity of toluene to humans and animals results in abnormalities of the central nervous system. The eyes and neck are stimulated in cases of exposure to 400 ppm, and a medium level stimulus can be felt in the eyes and neck at levels of 200 ppm. Even though toluene is classified as a third grade cancer-causing agent, it is known to have a large contribution in terms of the quantity emitted, as more than 30% of the total chemical concentration was attributed to toluene as an individual substance. The concentration of toluene observed was 25 ppb, which is between 2 and 125 times greater than the other substances mentioned. On the other hand, 1-1-1-trichloroethane, 1-1-2-trichloroethane, tetrachloroethylene, 1-2-4-trichlorobenzene and hexachloro-1, 3-butadiene, which are also cancer-causing agents, were not detected at any of the measurement sites. Methylene chloride and 1-2-dichloroethane were detected at average concentrations of less than 0.2 ppb.

DISCUSSION

The quantity of VOCs emitted was in the order: Pohang, Ulsan, the residential area in Gyeongju and the commercial area in Gyeongju. The VOC concentrations found in the industrial area (Pohang, Ulsan) were usually higher than that of non-industrial area (Gyeongju), and the highest concentrations for most of the VOCs were observed in the industrial area. Most of the 34 VOCs shown maximum values in the industrial area, with the exceptions of benzene, 1-3-5-trimethylbenzene and 1-2-4-trimethylbenzene, which are from automobile exhaust fumes. It was also confirmed that there was a random possibility of exposure to high concentrations.

The quantity of aromatic hydrocarbon emissions, which accounted for 8 out of the 34 VOCs, appeared as high as 1.5 times the values for halogenated hydrocarbons. It was shown that aromatic organic solvents were frequently used, generally because halogenated hydrocarbons were detected at levels less than 1 ppb or were not detected at all. In addition, their use is considered to be relatively safe, because halogenated hydrocarbons containing many toxic substances were only detected at low concentrations, but the risks have to be contemplated when the potential for cancer is considered.

The study on the concentration ratios comparing industrial to non-industrial areas revealed that Freon-11, styrene, chloroform, toluene and Freon-12 had ratios exceeding 1.5, which confirmed the regional characteristics. The highest levels of Freon-12, Freon-11, and toluene were detected in Ulsan, in the Yeocheon industrial complex. The highest levels of chloroform and styrene were detected at the Pohang Steel Management Industry Complex. Other substances showed similar concentration ratios of approximately 1, regardless of the district. Therefore, it is difficult to say whether the toxic substances from the non-industrial area are safer in terms of the level of unit hazard.

The substances detected with average concentrations of more than 10 ppb from the 19 cancer-causing substances were chloroform of the halogenated hydrocarbons and toluene of the aromatic hydrocarbons. The active survey on the emission of toluene was considered meaningful, because toluene accounted for more than 30% of the total concentration of aromatic hydrocarbons. Ethylbenzene was detected at less than 5 ppb, styrene at less than 3 ppb, and all other substances were detected at either less than 1 ppb or were not detected at all. Consequently, there is a necessity to select substances for preferential control based on their cancer-causing grades and quantities emitted. It was considered that benzene as a result of its cancer-causing grade, toluene in terms of the emission quantity, and chloroform and styrene with respect to both their grades and their emission quantities should be selected for priority measurements. Overall, these research findings can be utilized to establish measures to ensure the healthcare of the local residents.

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CONFLICT OF INTEREST

The authors have no conflict of interest to declare on this study.

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