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VOLATILE ORGANIC COMPOUNDS MEASUREMENT IN THE BOUNDARY OF WASTE TREATMENT FACILITIES

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Abstract : Concentrations of the principal volatile organic compounds, such as benzene, toluene, ethylbenzene, *m,p,o*-xylene, styrene, and chlorobenzene were measured at the solid waste treatment plants classified into four categories; municipal waste incinerator, municipal waste landfill site, industrial waste incinerator and industrial waste landfill site. The average concentration of VOCs in industrial waste treatment facilities was 33.43 ppb and was significantly higher than that measured at municipal waste treatment facilities (4.71 ppb). The average toluene concentrations measured at incinerators (13.05 ppb) were a little higher than those measured at landfill sites (11.54 ppb). The contribution of the waste treatment facilities to the concentration of benzene (0.35 ppb) and *o*-xylene (0.15 ppb) in the industrial area was relatively small. However, toluene measured in the industrial waste treatment facilities was the most abundant VOCs with the average concentration of 21.37 ppb. As a result of analyses of fingerprint, in cases of IISH and ILUS, a variety of compounds other than major VOCs were detected in high level. On the Pearson correlation analysis, the correlation was generally positive and some pairs of these VOCs were very strongly correlated (correlation coefficient > 0.75).

Key Words : *Volatile Organic Compounds, Incinerator, Landfill Site, Waste Treatment Facilities, Passive* Sampler

INTRODUCTION

Contamination of the environment with volatile organic compounds (VOCs) may cause risk on different scales, not only because of the toxicity of the chemicals to human and ecosystem in indoor and global environment but also because of the formation of photochemical reactants and malodorous in ambient, which affect the nearby inhabitants.[1-3] Recently, there has been growing environmental and public health-related concerns over the VOCs emission from the industrial plants and from transportation in the large cities.[4-10] The contribution of VOCs emitted from solid waste treatment plants such as waste incinerators and landfill sites to the local airborne environment would be also important.

The waste incineration for the municipal or industrial wastes was extensively employed as a waste disposal process in the last decades in Korea. Until now, general risk assessment have been primarily centered on the air contamination issues such as heavy metal deposition, malodors, and high-molecular weight combustion products, including polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins (PCDDs)

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and dibenzofurans (PCDFs). However, the occurrence, composition, and identity of the labile and short-lived VOCs, which are produced in the process of a variety of waste disposals, were comparatively little known.[11] A few studies were carried out to assess the emission characteristics of VOCs in the solid waste treatment plants like landfill facility in Korea.[8,12]

In this study, we classified the waste treatment plants into four categories, municipal waste incinerator, municipal waste landfill site, industrial waste incinerator, and industrial waste landfill site. For these facilities, we measured the concentrations of the principal volatile organic compounds, such as benzene, toluene, ethylbenzene, *m,p,o*-xylene, styrene and chlorobenzene, and investigated the emission characteristics of VOCs from the various waste treatment facilities to the local environment.

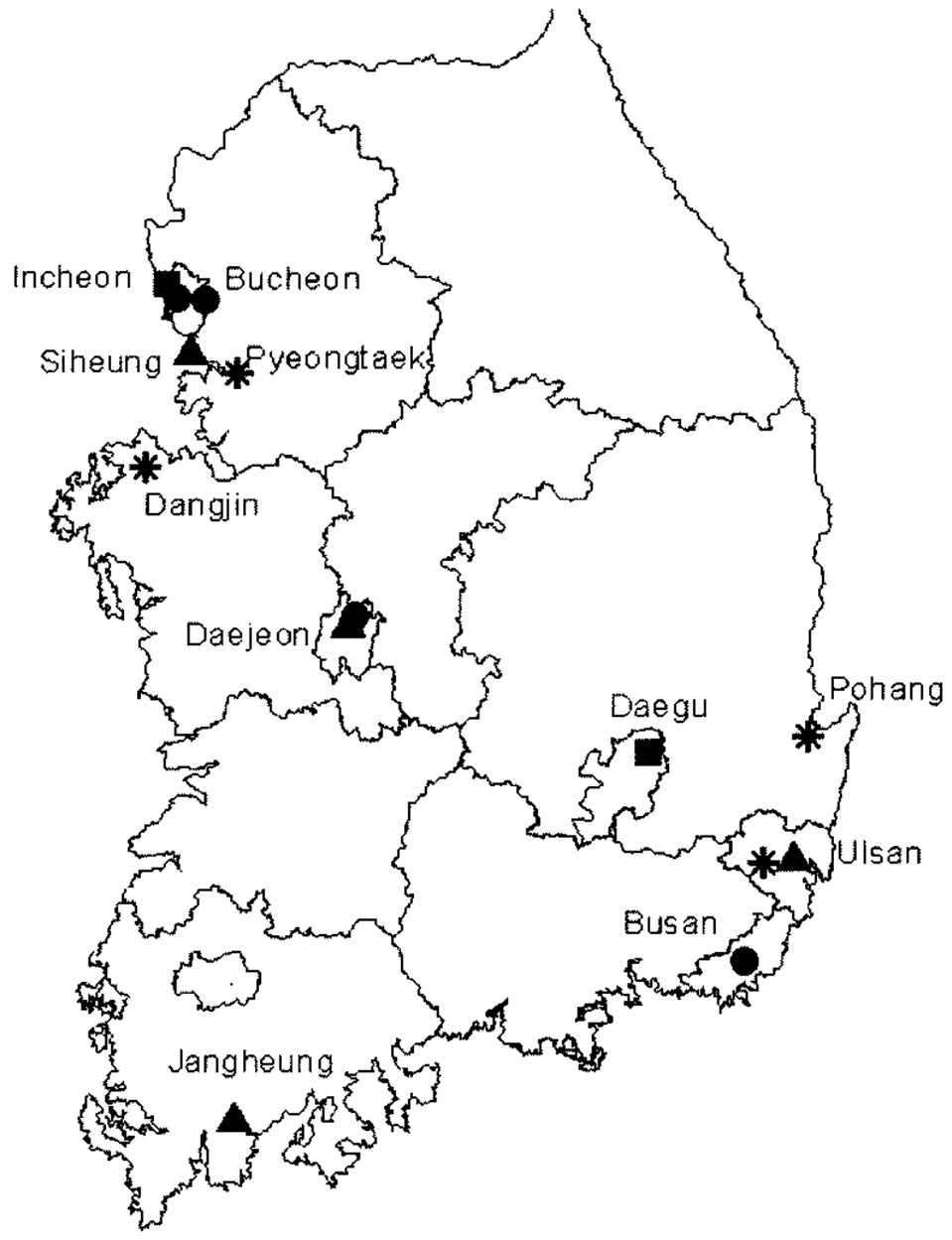

Figure 1. Location of the sampling sites. (●) Incinerator for municipal waste, (■) Landfill for municipal waste, (▲) Incinerator for industrial waste, (*) Landfill for industrial waste.

EXPERIMENTAL

Sites and Sampling Methods

As shown in Figure 1, VOCs measurement was performed at 14 sites (11 cities) in Korea and Table 1 shows the text descriptions about the sampling sites, including treatment capacity, landfill area, type of waste and sampling point. The specialized source categories as incineration and landfill for the industrial and municipal waste treatment were presented for each of the fourteen sites.

The final effect of each facility for the waste disposal on the neighboring residents would be different according to the size and distance of each source. For example, the effect would be

Table 1. Sampling sites description for the measurement of VOCs

Location code[a]	Location	Treatment capacity or landfill area	Type of waste[b]	Type of facility	Sampling point
MIIC	Incheon	500 ton/day	MSW	Incinerator	boundary and main gate
MIBC	Bucheon	300 ton/day	MSW	Incinerator	20 m and 50 m about from facility
MIBS	Busan	200 ton/day	MSW	Incinerator	southern and eastern main gate
MLIC	Incheon	9,024,834 m^2	MSW	Landfill	eastern boundary and main gate
MLDJ	Daejeon	602,429 m^2	MSW	Landfill	left and right boundary of landfill
MLDG	Daegu	596,764 m^2	MSW	Landfill	front and eastern boundary
IISH	Siheung	85 ton/day	SW	Incinerator	boundary
IIDJ	Daejeon	172 ton/day	SW	Incinerator	boundary and main gate
IIUS	Ulsan		SW	Incinerator	boundary
IIJH	Jangheung	8.4 ton/day	SW	Incinerator	boundary
ILPT	Pyungtaek	10,250 m^2	SW	Landfill	eastern and northern boundary
ILDA	Dangjin	37,000 m^2	SW	Landfill	main gate and eastern boundary
ILPH	Pohang	15,372 m^2 (61,360 m^2)	MSW (SW)	Landfill	western boundary
ILUS	Ulsan	16,850 m^2	SW	Landfill	boundary

[a]MSW = municipal solid waste, SW = specified waste.

smaller when the distance between an emission source and its boundary is long, even if the facility is emitting with larger VOCs emission rate. Furthermore, it would be impossible to evaluate accurately the effect of a source if we cannot measure the pollutants emitted from all the sources because there are a number of sources. In this study, therefore, VOCs concentration was measured at a boundary of each facility in terms of the evaluation of the direct effects of each facility on the neighboring residents.

Sampling was conducted over approximately one week periods using a passive sampler (3M, 3500, USA). Passive samplers were designed as portable and noiseless devices without a power supply, it is especially very suitable for the purpose of our study to measure VOCs in a variety of industrial sources, because of its cost effectiveness.

Analysis

VOCs adsorbed in a passive sampler were extracted by adding 1.0 mL carbon disulfide (CS_2, low benzene content 99.9+%, Sigma-Aldrich, no peaks greater than 1 ppm benzene) for 30 min with continuous agitating of the sample. Then the extract was transferred to a 2-mL amber-vial for analysis, and 1 μm of extract was injected into gas chromatography. Desorption efficiencies were taken from 3M's literature on the sampler.[13)]

Ten main volatile organic compounds, such as benzene, toluene, stylene, *o*-xylene, *m,p*-xylene, chlorobenzene, ethylbenzene, 1,2-dichlorobenzene, 1,4-dichlorobenzene and 1,4-dichlorobenzene, were chosen for the quantification. Other compounds were analyzed nothing but were qualitatively evaluated by a fingerprint method related with their emission characteristics from a variety of sources.

VOCs were analyzed by gas chromatography (Fison 8340) using a flame ionized detector, and their spectra was carried out using a HP-1 capillary column (Agilent, 30 m, 0.53 mm I.D., 1.5 μm film thickness). High purity helium (> 99.999%) and nitrogen (> 99.999%) was used as a carrier gas and a reference gas, respectively. The gas chromatography oven was programmed to maintain the temperature at 40°C for 1 min, followed by heating at 4°C/min to 140°C, and finally heating at 30°C/min to 240°C when the temperature was held for 10 min.

A stock solution (Supelco, EPA 8020/8240 aromatic volatiles mix 100 μg/mL each in methanol, USA) containing ten standard compounds of our interest was prepared diluting original reagents with CS_2. For calibration of the quantitation analysis, 100 ppm (μg/mL) of standards was used to dilute an appropriate amount to 1, 2, 5, 10 and 20 ppm with CS_2. For each compound, calibration functions were determined based on the integrated area of the chromatogram. The VOCs masses adsorbed on a carbon filter in the sampler were determined from the integrated area by means of the calibration function. Finally, the average concentration of each component over the sampling interval was calculated according to the parameters, such as sampling period, the recovery coefficient, diffusion coefficient, and diffusion area.[13)]

The detection limits for the components were estimated as the three-fold standard deviation of five replicate measurements of blank samplers.[14)] The instrument detection limits regarding a sampling period of four weeks were 0.28 ppb for benzene and 0.12 ppb for toluene in ambient concentration, respectively. The precision for the retention time was shown by 0.58% for benzene and 0.38% for toluene in terms of % relative standard error. In addition, the precision for the retention area was 6.99% for benzene and 6.66% for toluene in terms of % relative standard error.

RESULTS AND DISCUSSION

VOCs were measured at each of the thirty sampling points during one week sampling period. Table 2 and 3 show the results of main VOCs concentrations measured at the municipal and industrial waste treatment facilities, respectively. The results of VOCs concentration measured at the incinerators and landfill sites for the treat-

Table 2. Results of VOCs measurements for the municipal waste treatment facilities (unit: ppb) [a]

Sites	Benzene	Toluene	Chloro benzene	Ethyl benzene	*m,p*-Xyrene	*o*-Xyrene	Syrene	Total VOCs
Incinerator								
MIIC 1	LOD	1.98	0.51	0.32	0.27	ND	ND	3.08
MIIC 2	LOD	1.71	0.57	0.23	0.23	ND	ND	2.74
MIBC 1	LOD	6.80	0.73	0.92	0.69	ND	0.52	9.66
MIBC 2	LOD	4.18	0.63	0.52	0.40	ND	0.31	6.04
MIBS 1	LOD	0.88	0.71	0.33	0.29	ND	ND	2.21
MIBS 2	LOD	0.75	0.69	ND	0.32	ND	ND	1.76
Average	-	2.72	0.64	0.39	0.37	-	0.14	4.25
SD	-	2.35	0.09	0.31	0.17	-	0.22	
Landfill								
MLIC 1	LOD	4.88	0.98	0.72	0.55	ND	0.38	7.51
MLIC 2	LOD	4.15	0.52	0.44	0.34	ND	0.26	5.71
MLDJ 1	ND	0.85	0.60	ND	ND	ND	ND	1.45
MLDJ 2	LOD	0.76	0.79	ND	0.12	ND	ND	1.67
MLDG 1	LOD	3.48	0.60	0.26	0.18	ND	ND	4.52
MLDG 2	LOD	8.24	0.73	0.45	0.44	ND	0.28	10.14
Average	-	3.73	0.70	0.31	0.27	-	0.15	5.16
SD	-	2.79	0.17	0.28	0.21	-	0.17	

[a]LOD = limit of detection, ND = not detected, SD = standard deviation.

Table 3. Results of VOCs measurements for the industrial waste treatment facilities (unit: ppb) [a]

Sites	Benzene	Toluene	Chloro benzene	Ethyl benzene	*m,p*-Xyrene	*o*-Xyrene	Syrene	Total VOCs
Incinerator								
IISH 1	LOD	30.26	1.06	2.39	2.00	1.14	1.52	38.37
IISH 2	1.01	39.33	1.40	2.92	2.26	0.43	1.74	49.09
IIDJ 1	LOD	3.28	1.10	1.45	1.13	ND	0.90	7.86
IIDJ 2	LOD	4.14	1.12	1.43	1.23	ND	0.84	8.76
IIDJ 3	1.46	63.65	1.45	5.80	4.88	ND	2.53	79.77
IIDJ 4	LOD	15.22	0.72	0.99	0.86	ND	0.54	18.33
IIUS 1	LOD	47.29	6.85	7.29	8.39	0.43	6.02	76.27
IIUS 2	LOD	27.18	5.52	5.11	5.96	0.47	4.27	48.51
IIJH 1	LOD	1.70	0.77	ND	ND	ND	ND	2.47
IIJH 2	LOD	1.77	0.74	ND	ND	ND	ND	2.51
Average	0.25	23.38	2.07	2.74	2.67	0.25	1.84	33.2
SD	0.53	21.83	2.20	2.52	2.81	0.38	1.95	
Landfill								
ILPT 1	LOD	5.78	0.78	0.19	0.21	ND	ND	6.96
ILPT 2	ND	4.63	ND	ND	0.19	ND	ND	4.82
ILDA 1	LOD	1.74	0.79	0.47	0.40	ND	0.33	3.73
ILDA 2	LOD	1.97	0.75	0.44	0.41	ND	0.27	3.84
ILPH 1	LOD	1.86	0.57	0.25	0.21	ND	ND	2.89
ILPH 2	LOD	1.74	0.68	0.40	0.31	ND	ND	3.13
ILUS 1	1.43	59.45	11.65	12.20	14.04	0.35	10.53	109.65
ILUS 2	1.03	64.04	5.53	12.15	14.38	ND	10.42	107.55
Average	0.35	19.35	2.85	3.70	4.28	0.05	3.08	33.66
SD	0.61	29.01	4.31	5.79	6.79	0.13	5.05	

[a]LOD = limit of detection, ND = not detected, SD = standard deviation.

ment of municipal waste are presented in Table 2. The highest average concentration among all quantified VOCs was found for toluene (3.73 ppb) measured at landfill sites for the treatment of municipal waste. The average concentration of toluene measured at landfill sites was higher than that measured at incinerators (2.72 ppb). On the measurement performed at the municipal waste treatment, benzene and *o*-xylene was not detected and below the limit of detection. The higher concentrations of total VOCs measured at incinerators and landfill sites for the treatment of municipal waste were observed at MIBC 1 (9.66 ppb) and MLDG 2 (10.14 ppb). Average concentrations of all other quantified VOCs at measured incinerators and landfill sites for municipal solid waste ranged from 0.14 ppb to 0.64 ppb and 0.16 ppb to 0.70 ppb, respectively.

The results of VOCs concentration measured at the incinerator and landfill sites for the treatment of municipal waste are presented Table 3. The average concentration of toluene measured at landfill sites (23.38 ppb) was higher than that measured at incinerators (19.35 ppb). Toluene was the most abundant VOCs in this research and significantly varied with maximum concentration reaching 64.04 ppb. The concentration of benzene above 1 ppb was observed at four sampling sites, that is, IISH 2 (1.0 ppb), IIDJ 3 (1.5 ppb), ILUS 1 (1.4 ppb), and ILUS 2 (1.0 ppb). The very high concentration of toluene was observed at IIDJ 3 (63.7 ppb) and ILUS 2 (64.0 ppb). *o*-Xylene was only recorded at IISH 1 (1.14 ppb), IISH 2 (0.43 ppb), IIUS 1 (0.43 ppb), IIUS 2 (0.47 ppb) and ILUS 1 (0.35 ppb) with the low concentration. The higher concentrations of total VOCs measured at incinerators and landfill sites for the treatment of industrial waste were observed at IIDJ 3 (79.77 ppb) and ILUS 1 (109.65 ppb). The average concentrations of VOCs measured at the incinerators, except toluene, would be almost identical with those measured the landfill sites. Average concentrations of all other quantified VOCs at measured incinerators and landfill sites for industrial solid waste were in the range of 0.25 - 2.74 ppb and 0.05 - 4.28 ppb, respectively.

Figure 2 also compares average concentrations of the main VOCs measured at the municipal and industrial waste treatment facilities in this study. The average concentrations of VOCs at industrial waste treatment facilities (especially at the landfill sites for the disposal of industrial waste) were significantly higher than that measured at municipal waste treatment facilities. The average concentrations of these VOCs measured at the incinerators for the treatment of municipal waste were lowest. The measured VOCs concentrations exhibit the wide variation with a large deviation, especially on the results obtained from different sites for the treatment of industrial waste. Emission of VOCs from landfill sites would contribute to the VOCs concentrations in ambient air as one of the most significant sources.[15] The order of average concentrations obtained from each monitoring site was not entirely consistent with the treatment capacity or landfill size (see Table 1) of facilities investigated in this study. The emissions of air pollutants like VOCs from facilities for the treatment of industrial waste would have a strong effect in ambient air quality.

Figure 3 shows the analysis of a fingerprint for the VOCs concentration of several waste treatment facilities. The fingerprint was represented by the relative retention time of the chromatogram obtained from a gas chromatography analysis. The area of components, as

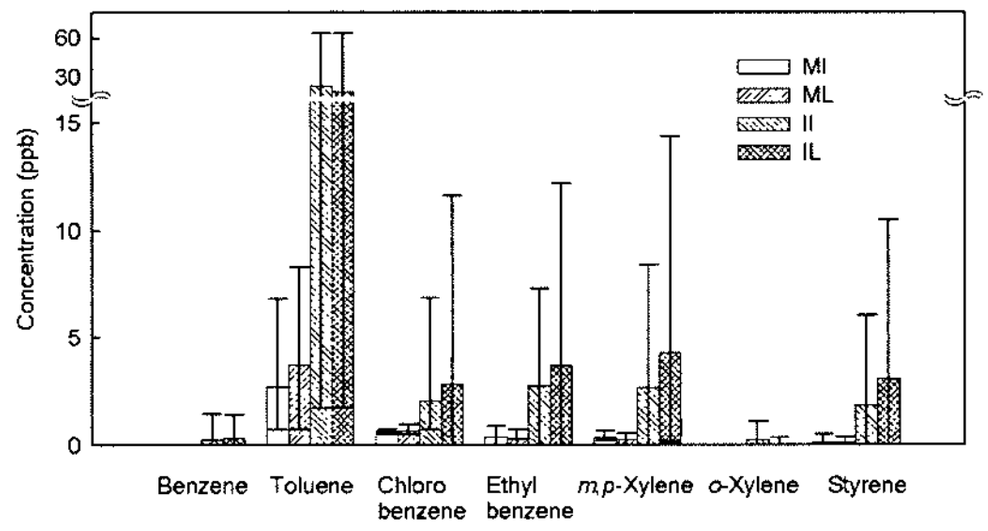

Figure 2. Comparison of average concentrations of the main VOCs measured at the municipal and industrial waste treatment facilities in this study. The whiskers in the bar plots are the maximum and minimum values of the VOCs concentrations.

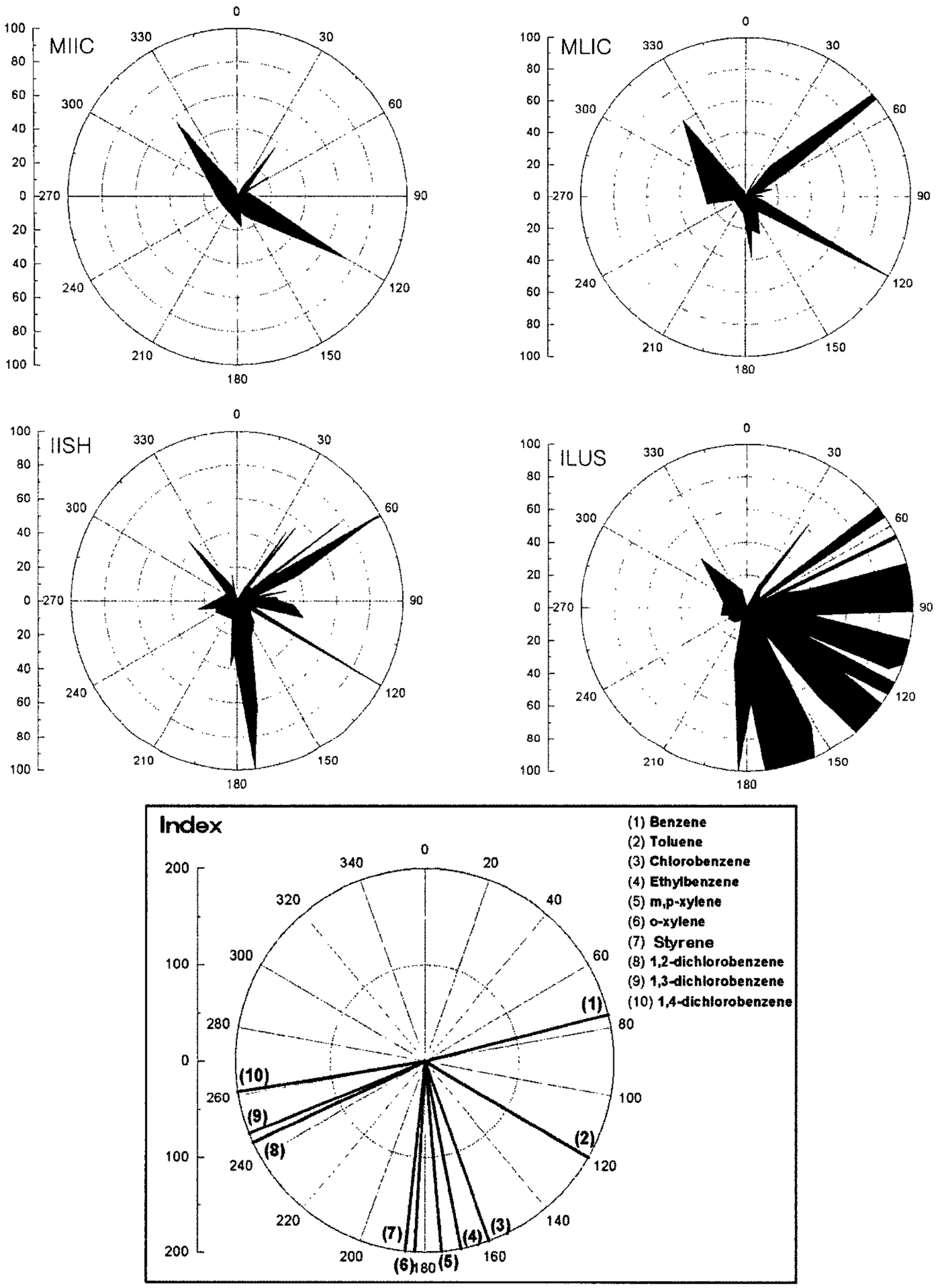

Figure 3. Fingerprint analyses for the VOCs concentration of several waste treatment facilities.

shown in y axis, was standardized to completely represent the VOCs with small peak area in a chromatogram. The result of standard fingerprint described by considering the retention time of major VOCs was expressed in index in Figure 3. VOCs characteristic for representative four waste treatment facilities (e.g., MIIC, MLIC, IISH and ILUS) was presented by the fingerprint. The levels and species of compounds emitted from municipal waste treatment facilities, such as MIIC and MLIC were relatively lower and less than those emitted from the industrial waste treatment facilities, such as IISH and ILUS. In cases of IISH and ILUS, a variety of compounds other than major VOCs were detected with high level. Especially in the case of ILUS, the emission levels of compounds with the retention time between benzene (76 degree) and

chlorobenzene (160 degree) were high, compared with other cases. The emission of several compounds with comparatively low level above 330 degree and below 70 degree was confirmed by the fingerprint. The detection of isometric xylene was one of the emission characteristics observed from the analyses of fingerprint for industrial waste treatment facilities.

Pearson correlation coefficient (r) is available for determination of an important relationship between two variables. In this study, the Pearson correlation coefficient was used to evaluate the degree of association between two variables. Values of the coefficient are taken in the range of -1 to 1. The absolute value of the coefficient represents the strength of the degree of correlation between the variables. The sign of the correlation coefficient indicates the direction of the relationship such as negative (-) and positive (+).

Figure 4 shows a frequency data of correlation coefficients between VOCs measured different facilities for the treatment of municipal and industrial wastes. The Pearson correlation coefficients were computed from pairs of the measured VOCs data. The correlation of pairs of these data was mostly positive and pairs of 52% were strongly correlated with values of correlation coefficient greater than 0.75 (white vertical bar in Figure 4). The Pearson correlation coefficients that were calculated from the concentration data for pairs of VOCs measured at each waste treatment facility, were almost positive and some pairs of these VOCs were very strongly correlated (r > 0.75). Especially, the strong correlation (r > 0.75) between VOCs data obtained from the industrial landfill was observed with the frequency of Pearson coefficients of approximately 81%. Among the correlations between waste treatment facilities, the pairs of municipal and industrial landfill have also the most significant correlation.

On the other hand, the Pearson correlation coefficients calculated from VOCs measured industrial incinerator and measured between municipal and industrial incinerator (MI and II) were only observed between -0.25 and 0, a range indicating negatively correlated data.

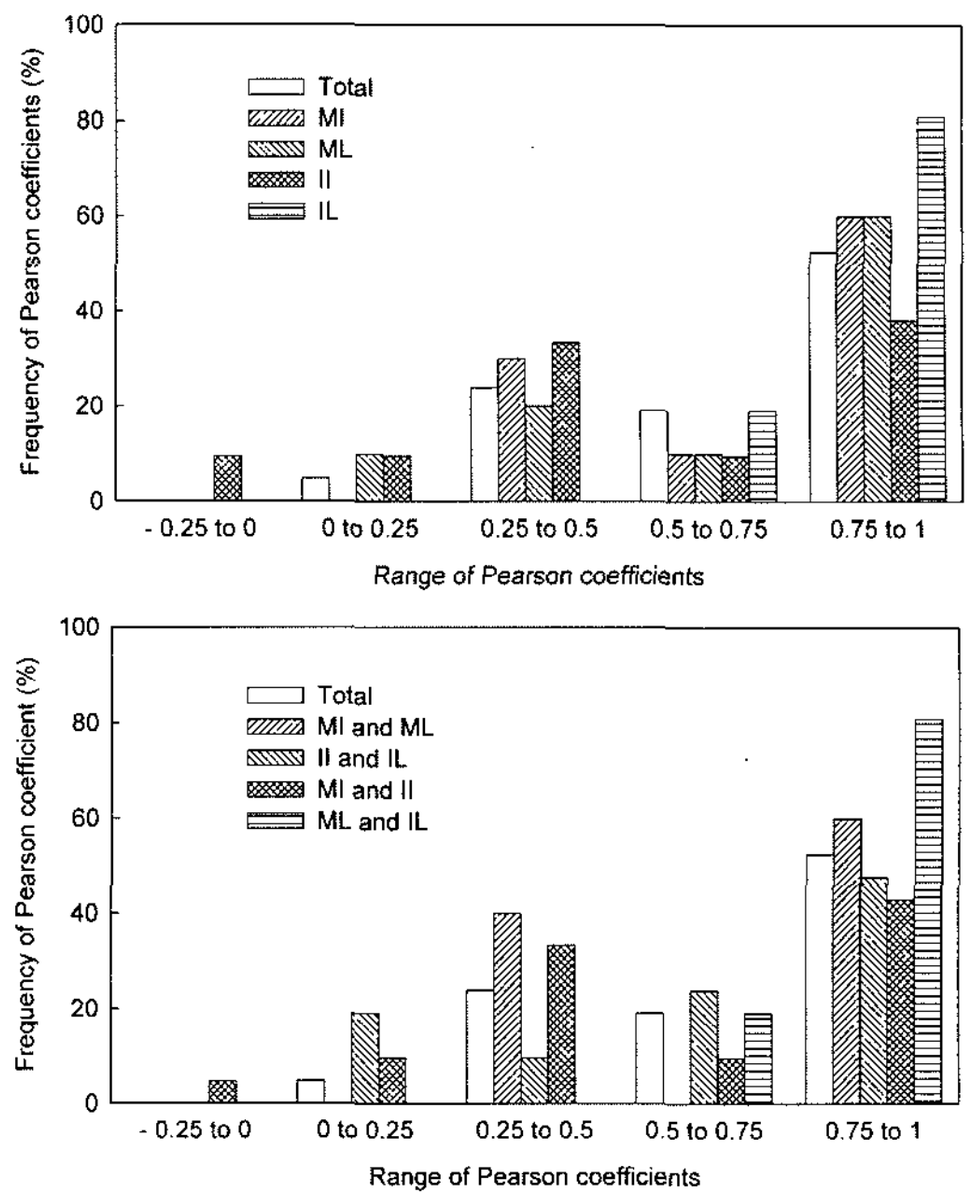

Figure 4. Correlations between VOCs measured different facilities for the treatment of municipal and industrial wastes.

Table 4 compares concentration of benzene and toluene measured by this study and determined from different study sites. The concentrations of benzene observed at this study sites were notably than those monitored in other industrial sites and the ambient air lower (i.e., in this study, benzene mean concentration measured at industrial waste treatment facilities was 0.35 ppb). It seems likely that the contribution of the waste treatment facilities to the concentration of benzene in the industrial area was relatively small, although the rainfall during the sampling period was considerably increased. The benzene concentration measured at the treatment plants of municipal waste in Southampton, UK was 41.14 $\mu g/m^3$. The industrial area of Mumbai, India showed highest benzene concentration (201.58 $\mu g/m^3$). The concentration of toluene measured at the municipal waste treatment facilities was lower than that observed from other industrial area and landfill sites (i.e., in this study, toluene mean concentration measured at industrial waste treatment facilities was 19.35 ppb). But, the results obtained from the industrial waste treatment facilities in

Table 4. Comparison with benzene and toluene concentrations measured in other sampling sites

Sampling site	Sampling period	Benzene	Toluene	Reference
Municipal Industrial	April-May 2004	- 0.35	3.73 ppb 19.35 ppb	This study
Southampton [a)] (UK)	1996-1997	41.14 μg/m^3	65.37 μg/m^3	11)
Ulsan [b)] (Korea)	Nov 1996-Mar 1997	2.1 ppb	3.9 ppb	10)
Seoul [c)] (Korea)	Aug 1998-July 1999	1.0 ppb	6.4 ppb	9)
Nanjido [d)] (Korea)	Mar-Oct 2000	1.65 ppb	9.62 ppb	12)
Guangzhou [e)] (China)	Jan 1998 (winter) Sep 1998 (summer)	7.3 μg/m^3 73 μg/m^3	12 μg/m^3 113 μg/m^3	15)
Mumbai [f)] (India)	May 2001-Apr 2002	201.58 μg/m^3	79.64 μg/m^3	16)

[a)] This sampling sites circumscribed a juxtaposed municipal incinerator, waste collection and processing center and sewage treatment plant.
[b)] This city has become one of the largest industrial areas in Korea. Sampling time is 24 h.
[c)] This data is annual mean concentration.
[d)] Najido is abandoned landfill located near the Hangang (river) that traverses the center of the metropolitan Seoul, Korea.
[e)] This site is landfill permitted to receive commercial and municipal solid waste.
[f)] Mumbai is hub of commercial and industrial activity. This data is annual mean concentration.

this study were somewhat higher than those measured at industrial sites (3.9 ppb) and landfill site (9.62 ppb) in Korea. The concentration of toluene measured during the summer period at the industrial area in China was 113 μg/m^3 and was higher than those obtained from other sampling sites.

CONCLUSIONS

The research was conducted in the boundary of municipal and industrial waste treatment facilities, such as incinerator and landfill site in order to measure the concentrations of major VOCs and to investigate the emission characteristics of VOC. The average concentration of VOCs in industrial waste treatment facilities (33.43 ppb) was significantly higher than that measured at municipal waste treatment facilities (4.71 ppb). The emissions of air pollutants from the industrial waste treatment facilities would have a strong effect in ambient air quality. The contribution of the waste treatment facilities to the concentration of benzene (0.35 ppb) and o-xylene (0.15 ppb) in the industrial area was relatively small. However, toluene measured in the industrial waste treatment facilities was the most abundant VOCs with the average concentration of 21.37 ppb. The concentration of VOCs measured at the incinerators, except toluene, was almost identical with that measured the landfill sites.

As a result of analyses of fingerprint, in cases of IISH and ILUS, a variety of compounds other than major VOCs were detected with high level. The Pearson correlation coefficients that were calculated from the concentration data for pairs of VOCs measured at each waste treatment facility, were generally positive and some pairs of these VOCs were very strongly correlated (correlation coefficient > 0.75). These results would be useful data to work out the management strategic of VOCs in the waste treatment plants, although the limited number of samples was taken in each waste treatment facilities.

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