A COMPARISON OF VOC EMISSIONS FROM LANDFILLS BETWEEN JAPAN AND THAILAND

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揮発性有機化合物の日本とタイの廃棄物処分場からの排出

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ベンゼンなどの揮発性有機化合物(VOCs)は，その健康影響とともに光化学反応の核となりうることから，その規制が進められようとしている。廃棄物の処分場から発生するガスは，二酸化炭素とメタンを主成分とし，温暖化ガスの排出源として注目されているが，処分場ガスに含まれる VOCs についての報告はほとんどない。本研究では，タイとわが国の処分場について VOCs の濃度，種類を浸出水，処分場ガスなどについて調査した。さらに，VOCs の排出源として，ポリスチレンなどの廃棄物の処分層内での加熱の可能性を室内実験で検証した。その結果，実処分場でも，廃棄物の加熱によっても，検出される物質は，ベンゼン，トルエン，数種のキシレン，数種のトリメチルベンゼンに限られるが，廃棄物の加熱で生じるベンゼンの量では，浸出水や処分場ガス中のベンゼンの濃度を説明できないと考えられた。

1 Introduction

A growth of population and urbanization are largely responsible for the increase in solid waste, which is one of the problems being faced by many countries. Thailand produced nearly 22 million tons of waste annually (as of 2003), of which 67% were municipal solid waste (MSW). The major constituents of MSW were kitchen waste (51%) and plastic and foam (22%) [1]. In Japan, the total amount of waste was approximately 51 million tons of domestic waste per year in 1999 [2]. Landfill plays the most important role in the framework of solid waste disposal and various kinds of landfill gases, such as CH_4 and CO_2 some trace components like volatile organic compounds (VOCs), are generated inside landfill site.

VOCs, for example, benzene, toluene, xylene and ethylbenzene, are organic compounds that are more mobile and therefore more likely to be released to the environment. The presence of some VOCs in the atmosphere may pose a significant health risk, and they can lead to the formation of photochemical oxidants [3]. There are many studies on VOCs in various environments together with ambient atmosphere. Many aromatic and chlorinated hydrocarbons were observed in rainwater, rivers and lakes [4]-[7]. In coastal areas, high levels of aromatic hydrocarbons were attributed to anthropogenic emissions and discharges from shipping and oil-related activities [8]. In addition to industrial sources, many kinds of VOCs were produced by vehicle [9]. High levels of VOCs have been observed in ambient air in Asian countries. High traffic densities have been considered as their sources [10]. Automobiles were also the primary contributors of benzene, toluene, ethylbenzene and xylenes (BTEX) found in ambient atmosphere in Hongkong and in urban areas in US [11] [12].

Moreover, VOCs emissions from MSW in several environments have been investigated. Thirty most abundant VOCs were observed in remained uncollected waste in garbage containers [13]. Aromatic VOCs including toluene, ethylbenzene, and naphthalene were produced in the large amount during composting of simple MSW components, such as food wastes, yard wastes and mixed paper [14]. In landfill sites many aromatic compounds were present in leachates. [15]-[17]. VOCs have also been found in landfill gases and ambient air in landfill sites [18]-[21].

Although many of the previous studies were conducted to describe the presence of VOCs and their behavior in various source environments, few studies regarding VOCs in landfill sites have been published, especially in Thailand, to investigate the concentration levels and their compositions. Moreover, source attribution is also unclear, which is important for developing effective strategies to control VOC emissions.

This study presents the investigations of VOC concentrations in leachates and landfill gases including ambient air in landfill sites in Thailand and Japan. VOC emissions collected were used to determine a characteristic of VOC compositions in the landfill sites and finally some laboratory experiments were carried out to identify possible sources of VOCs found in the landfill sites.

2 Experiments

2.1 Site descriptions

In the present work, measurements of VOC concentrations at three solid waste disposal sites in Thailand, Sainoi open dump site, Nakornpatom sanitary landfill site and Pathumthanii landfill site, and a landfill site in Japan, have been undertaken during the field investigation period of 2004-2006.

Sainoi open dump site is a section of Solid Waste Disposal Center, Nonthaburi, Thailand. The Solid Waste Disposal Center is located in Sainoi district, Nonthaburi municipality. The center received wastes generated in this province, about 800 tons/day (2004). Without transfer station, all waste is transferred to this center directly. Raw leachate from open dumping area is sent through a pipe and then collected in deep stagnant pond and shallow stagnant pond directly without passing through any treatment process.

Pathumthani landfill, located in Pathumthani province is a closed site where receives no more solid wastes. Leachate in this site is collected in a trench around the landfill and then flowed into a nearby leachate collection pond.

Nakornpatom landfill site, covering a total of 281,600 m^2, is situated in Nakornpatom province. This engineered landfill site received approximately 110-130 ton of municipal waste a day (March 2005). A leachate treatment plant uses these processes in the order of anaerobic pond, aerobic pond1, aerobic pond2 and maturation pond.

The landfill sites on reclaimed land are the main final disposal sites for municipal solid waste generated from the target area in Japan. Three landfills have been established in the reclamation area: the older site, the main site, and the newer site. Leachate from the landfill site is temporarily collected in leachate collection wells around the landfill area and an equalization pond in the center of the main site, and then treated at leachate treatment plants. In addition, gas vents are installed through the final landfill cover extending down into the solid waste mass.

2.2 Sampling points

(1) The field investigation in Thailand

Four field investigations were carried out on December 20, 2004, January 20, 2005, March 25, 2005 and August 9, 2005. Raw leachate, leachates from two leachate ponds in Sainoi dump site and water samples from nearby vegetable pad were collected. Water sampling locations in Pathumthani landfill site were leachate trench, shallow pond and nearby paddy field. At Nakornpatom landfill site, leachates in treatment process were collected. Air sampling was conducted at Sainoi open dump site and Pathumthani landfill site in January 2005. The samples were collected at landfill surface and at 50, 100 and 150 cm. below the landfill surface.

(2) The field investigation in Japan

The investigations were conducted totally six times on August 30, 2004, November 11, 2004, December 17, 2004, January 24, 2005, December 12, 2005 and January 10, 2005. Leachate samples were collected at 10 locations in the main site in every investigation. An influent, leachate in biological tank and leachate in coagulation tank in leachate treatment facility, leachate from well no.3 in the older site, well 10, 33, 20 and equalization pond in newer landfill site in Japan, and well no.A-1 and A-2 in the newer site were collected. Moreover, two locations of atmospheric air samples were observed in August 2004. One was near equalization pond inside the main landfill site and the latter was at the landfill office. Nine gas vents (gas vent A-I) in the main site area were investigated in November 2004. On other occasions, landfill gas samplings were conducted for checking purposes at only gas vents B, D and E.

2.3 Collection of water and air samples

Water samples were collected by using 10 ml pipette and added to screw-capped vial (15 ml) sealed with a polytetrafluoroethylene (PTFE)-lined silicone septum. Two kinds of air samplers, active sampler and passive sampler, were applied for the collection of air samples**.** High-performance passive sampler VOC-SD (Sigma-Aldrich Chemical Co.) was used. A collection time was about 3-4 hours for a sample, except for the investigation on August 30, 2004, which the collection time was 24 hours. In case of active sampler, samples were collected by drawing air through glass sampling tubes containing Carbosieve S-III (carbon based molecular sieve) adsorbent (ORBO 91, Supelco Inc.). For the field investigations in Thailand, the air was pumped through the adsorbent with a flow rate of 30 ml/min and a collecting time was 60 minutes. Instead of pump, 1000 cm^3 of air was drawn using a 200 cm^3 syringe in the investigations in Japan.

2.4 Samples for laboratory experiments

Screw-capped vials (15 ml) with 10 ml of milli-Q water were prepared. Ten kinds of materials were used in this study: new A4 paper, used disposable chopstick made of wood, cookie package made of polypropylene (PP), plastic bag made of polyethylene (PE), pure polystyrene (PS) beads, CD case made of PS, new disposable lunch box made of PS, new disposable food pack made of PS, used instant noodle cup made of PS, new noodle bowl made of PS (**Fig.1**). The materials were cut into 1 cm x 1cm pieces and added into the vials. The vials were then stored under room temperature (20°C) and heated at 60°C and 80°C for 1 day before VOC analysis. Moreover, after the analysis, the vials containing food pack and instant noodle cup were kept for another experiment. The materials were washed with milli-Q water and added into a new vial. They were then kept at 80°C for 5 days and analyzed for VOCs. After the analysis, the materials were processed again and analyzed 5 days later.

2.5 The analysis of VOC concentrations

Water samples were kept in a water bath at 40˚C for 30 minutes before a solid phase micro extraction (SPME). The extractions were carried out with a

100-µm poly dimethylsiloxane (PDMS) fiber assembly and a manual fiber holder from Supelco (Bellefonte, PA, USA). The SPME removed the compounds from the samples by adsorption and then gas chromatography mass spectrometry (GC-MS) was applied for VOC analysis. In case of air samples, an extraction by carbon disulfide was needed prior to the analysis by GCMS. GC-QP5000 (Shimadzu Corp., Japan) was used for VOC analysis. A GC column was Halomatics624 (0.25mmI.D.×30m×2.0µm.). A column temperature was programmed from 40°C (hold for 7 minutes) to 80°C at an increasing rate of 5°C /min, then to 200°C at 15°C/min (holds for 3 minutes). A flow rate of carrier gas, helium, was 1.0 ml/min with a pressure of 48.9 kPa. An interface temperature was 230°C, respectively. The mass spectrometer was operated in the SIM mode. Quantification was done using the total ion chromatogram (TIC). The type of target VOCs analyzed from this study amounts to a total of 41 compounds.

Fig.1 Materials used in laboratory experiment

3 Results and discussions

3.1 Validation of SPME method

In this study, solid phase extraction method was applied for VOC extractions. Several assumptions on chemical equilibrium and interference must be satisfied in the case of use of SPME technique in the analysis of highly contaminated aqueous samples like leachate. One of the assumptions is equilibrium between headspace and water after the samples were left in a water bath maintained at 40˚C for 30 minutes. Another thing to be confirmed is the effects of interanalyte displacement and competitive adsorption caused by contaminants in leachate. In order to validate an application of SPME for accurate quantitative analysis, therefore, two sets of samples were prepared: leachate samples and leachates added with 50 µg/l of the standard.

Here, the leachates from two collection ponds, shallow and deep ponds in Sainoi dump site, were used. Each set of samples were then stored at room temperature and 80˚C for one day and the analysis results are shown in **Table 1**. Since there was some difficulty getting exact concentration of VOC standard, some samples with the standard did not give correct results, which are 50 µg/l for benzene, toluene and o-xylene and 100 µg/l for m-xylene plus p-xylene. There is a slight tendency of giving higher value in the measurement of heated samples at higher temperature. It may be due to equilibrium problem. However, these results are within acceptable limits.

3.2 Field investigations

(1) Occurrence of VOCs in leachates

The average VOC concentrations in leachates from Sainoi dump site and the main site in Japan is summarized in **Table 2**. Among 41 target compounds only 11 VOCs detected in all leachates in the investigations. Besides, they all were aromatic hydrocarbon compounds. The compounds found could be classified into 4 groups: benzene, toluene, xylenes consisting of ethyltoluene and m,p,o-xylene, and trimethyl benzenes (TMBs) including 3(or4)-ethyl toluene, 1,3,5-trimethylbenzene, 2-ethyl benzene, 1,2,4-trimethylbenzene, and 1,2,3-trimethylbenzene. The VOC concentration as high as 164 µg/l was found in raw leachate samples collected at Sainoi dump site in March 2005 (summer in Thailand: March-May). Among three investigations, the largest amount of total VOCs was observed in March 2004 since higher temperature and moisture content in summer tends to cause rapid biodegradation of organic matter. Additionally, raw leachate in Sainoi dump site gave relatively high VOC concentrations, while the concentrations in both leachate collection ponds were quite low. This could be subjected to an evaporation of VOCs from the leachate ponds. Groundwater samples collected at Sainoi dump site close to the dumping area was found at the level below groundwater standards in Thailand. Benzene, toluene, total xylenes and ethylebenzene shall not exceed 5, 1000, 10000 and 700 µg/l, respectively [22]. No significant level of VOC concentrations was identified in leachates from Pathumthani closed landfill site, water samples from the nearby vegetable pad and paddy field, and leachate samples from the treatment ponds in Nakornpatom sanitary landfill site.

In the main site in Japan, leachates from well No.10, 20 and 33 had the highest VOC concentration, which may be due to the pyrolysis of organic materials contained in wastes. The concentration of benzene was detected as high as 24 µg/l in leachate collection well no.20. However, low VOC concentrations were found in well no.A-1 and A-2 in the incineration ash disposal area as well as in well no.3 in the closed landfill area. The samples from leachate treatment plant contained high amount of VOCs in the influent and then it decreased to almost zero in biological tank and coagulation tank. The activated sludge process in wastewater treatment removes VOCs through stripping and biodegradation more than adsorption [23]. These two major mechanisms may cause the decrease in VOCs during the treatment process.

(2) Occurrence of VOCs in air samples

Only 11 kinds of VOCs, which are aromatic hydrocarbons, were detected in landfill gases and ambient air in the target landfill sites. **Table 3** presents level of VOC emissions in air samples collected at landfill surface and at different depths below landfill surface in Sainoi open dump site and Pathumthani landfill site. It is clear that the VOC emissions increased with depth below the landfill surface. Benzene was found as high as about 253 and 132 μg/m^3 at 150 cm. below Sainoi open dump site and Pathumthani landfill site respectively. Ambient air in both sited contained large amount of benzene, especially in Pathumthani landfill site which was found up to 38μg/m^3 (**Table 4**). So far benzene is not registered in air quality standards in Thailand, however, according to the standards issued by WHO benzene is a recognized carcinogen and exposure to 1μg/m^3 produces a lifetime of 4×10^{-6} for leukaemia. Site workers or neighboring residents, therefore, may have an exceptionally high risk of suffering an adverse health effect associated with exposure to such high level of benzene. VOC concentrations in ambient atmosphere at the main landfill site area are included in **Table 4**. According to the air quality standards in Japan, annual averaged benzene in air should not exceed 3 μg/m^3, while other target VOCs in this study have not been regulated yet [2]. Benzene levels do not exceed the standards. **Table 5** shows the results of VOC emission from nine gas vents at The main site. VOC concentrations from all gas vents measured in this study varied in a wide range. Gas vent G and H gave relatively low VOC concentrations compared to other gas vents. Among nine selected gas vents, gas vent B gave the most elevated amount of VOC emission and as high as 1.8×10^5 μg/m^3 of benzene was found in the investigation in November 2004. The features which may influence the measurement of VOCs were the location of the gas vents and categories of wastes buried at that area. Gas vent G and H gave relatively low VOC concentrations vents, gas vent B gave the most elevated amount of VOC emission and as high as 1.8×10^5 μg/m^3 of benzene was found in the investigation in November 2004. The features which may influence the measurement of VOCs were the location of the gas vents and categories of wastes buried at that area.

Table 1 Validation of SPME analytical analysis.

VOC	Shallow collection pond				Deep collection pond			
	Leachate		Leachate with standard		Leachate		Leachate with standard	
	20˚C	80˚C	20˚C	80˚C	20˚C	80˚C	20˚C	80˚C
Benzene	0.49	2.8	45.61	74.23	0.51	0.65	60.59	54.61
Toluene	0.94	1.61	49.45	68.46	1.1	1.05	31.29	50.52
m,p-Xylene	0.09	0.28	101.58	107.56	0.13	0.27	79.57	82.58
o-Xylene	0.08	0.14	51.78	54.35	0.1	0.11	61.67	47.62

Table 2 Comparison of VOC concentrations (μg/L) in leachates between this study and others

VOC	The main site in Japan		Sainoi dump site		8 landfill sites in Japan [16]		10 Danish landfill sites [15]	
	Mean conc.[a)]	Conc. range	Mean conc.[b)]	Conc.range	Mean conc.	Conc. range	Mean conc.	Conc. range
Benzene	3.81	N.D.-24.34	0.98	N.D-1.50	0.105	0.065-0.400	11.08	N.D.-38.9
8Toluene	7.96	0.15-61.49	3.77	0.39-6.34	0.066	0.010-0.180	31.42	1.4-241
ethyl benzene	5.07	N.D.-44.30	0.31	0.01-0.73	-	-	33.79	2.5-150
m-Xylene, p-Xylene	6.14	N.D.-64.53	1.26	0.09-2.79	0.010	0.010-0.150	56.90[c)]	5.4-2220
o-Xylene	2.62	N.D.-13.55	0.72	0.05-1.81	0.062	0.060,0.064	16.94	2.0-53.2
3 or 4 ethyl toluene	0.11	N.D.-0.54	0.04	0.01-0.10	-	-	18.36	5.1-69.8
1,3,5 trimethyl benzene	0.33	N.D-2.96	0.65	0.09-1.55	-	-	11.01	4.3-36.8
2 Ethyl Toluene	0.07	N.D.-0.49	0.12	0.02-0.30	-	-	13.29	4.5-26.1
1,2,4 trimethyl benzene	0.33	N.D.-2.60	0.73	0.09-1.91	0.008	0.007, 0.009	38.46	5.3-152
1,2,3-trimethyl benzene	0.13	N.D.-0.54	0.23	0.02-0.80	0.004	0.003-0.005	19.05	5.1-67.7

[a)] Averaged value from six leachate collection wells and equalization pond
[b)] Averaged value from deep pond and shallow pond
[c)] Averaged value from nine landfill sites excluding the extraordinarily high value (2220 μg/l)

Table 3 VOC concentrations (μg/m^3) in air samples collected at different depths below landfill surface

VOC	Sainoi open dump site				Pathumthani landfill site			
	Depth below landfill surface (cm)				Depth below landfill surface (cm)			
	0	50	100	150	0	50	100	150
benzene	11	23	202	253	38	57	N.D.	132
toluene	B.Q.L	106	106	25914	B.Q.L	252	259	4252
Ethylbenzene	N.D.	6	193	859	51	14	2	258
m,p-xylene	5	13	193	4881	34	21	6	1760
o-xylene	N.D.	N.D.	31	768	7	9	N.D.	320
3 or 4 ethyl toluene	N.D.	N.D.	41	309	6	5	N.D.	30
1,3,5-trimethylbenzene	N.D.	6	78	1667	9	21	N.D.	279
2 ethyl toluene	N.D.	N.D.	10	222	N.D.	10	N.D.	46
1,2,4-trimethylbenzene	N.D.	N.D.	34	1116	4	N.D.	N.D.	150
1,2,3-trimethylbenzene	N.D.	N.D.	14	1198	N.D.	N.D.	N.D.	58

Considering a comparison between these three landfill sites, the main site gave the lowest VOC levels in ambient air. Apart from meteorological conditions, including temperature, wind speed and humidity as well as the waste compositions, leachate collection system may cause the increase in VOC levels [19]. Sainoi open dump site and Pathumthani landfill site have no well-designed leachate collection system. Also, there is no leachate treatment process and the collection ponds are just left uncontrolled.

(3) Comparisons of VOC concentrations in leachates between the results in this study and others

Mean VOC concentrations and concentration ranges in leachats collected from the collection wells in The main site and Sainoi open dump site, eight landfill sites in Japan, and 10 Danish municipal solid waste landfill sites are shown in **Table 4.** The average levels of VOCs in these landfill sites were found to vary greatly. This was particularly the leachates in the main site in this study and the eight landfill sites in Japan [16]. The VOC concentrations in Central breakwater site are remarkably higher than those in 8 landfill sites in Japan. VOCs found in leachates from Danish landfill sites [15] gave higher concentrations than that in this study. Compared the concentrations in Sainoi dump site to 8 landfill sites in Japan, VOCs detected in this study were much higher excluding benzene, which almost the same level of concentration was found. Both landfill sites in this study gave small VOC concentrations compared to those in the Danish landfill sites. VOC compositions in leachates in these landfill sites are categorized into four groups, which are benzene, toluene, xylenes and trimethylbenzenes (TMBs) Xylenes and toluene are predominant in leachates from the main site and Sainoi dump site. However, 41% of benzene contained in leachates from 8 landfill sites in Japan. Almost the same percentage of trimethylbenzenes and xylenes are predominant in leachates from 10 Danish landfill sites.

(4) Comparisons of VOC levels in ambient atmosphere between the target landfill sites in this study and others

Table 5 compares the results of VOC levels from this study (The main site, Sainoi open dump site and Pathumthani landfill site) and those reported for a number of other studies, including Ireland landfill site, with and without leachate collection [19], together with Datianshan landfill site [20].The lowest level of VOCs was detected in ambient air in The main site (mostly 1-2 orders of magnitude lower other sites). Benzene levels investigated in both Thailand landfill sites were relatively lower than those in Ireland landfill site with leachate collection and China landfill site investigated in summer. At The main site VOC levels in ambient air observed in summer 2004 were not much different from those observed at Datianshan landfill site in China in winter, except for toluene. The report from China showed that the concentrations in winter were less than those in summer due to higher biology degradation. Therefore, not only temperature but also some other factors, such as the waste compositions and the stage reached in the decomposition process, also contribute to levels of VOC emissions.

(5) Characteristic of leachates and landfill gases

Eleven VOCs detected in this study are categorized into two groups according to their molecular weight: light VOCs (Benzene and Toluene) and heavy VOCs (m,p,o-xylenes ethylbenzene, ethyltoluene, and trimethybenzene). Raw leachates in Sainoi dump site comprised chiefly heavy VOCs, whereas the ratios of benzene and toluene became larger in both leachate collection ponds. Light VOCs were mainly found in leachate trench and leachate collection pond in Pathumthani landfill site as well. The collection ponds in both landfill sites in Thailand contained chiefly light VOCs. This may perhaps be the results of volatilization and/or biological biodegradation.

At The main site, light VOCs mainly presented in influent, and percentages of heavy

VOCs became larger in the biological and coagulation tanks in the treatment plant. Leachates from well no.3 in Inner breakwater landfill site, which is a closed landfill site, contained mainly heavy VOCs. Well no.33 and 20 also contained mainly heavy VOCs. On the other hand, well no.10, well no.A-1, well no.A-2 and equalization pond gave higher proportions of light VOCs. Almost all of landfill gas samples from gas vent B, D and E in Japan landfill site consisted of heavy VOCs for the most part. In landfill gases in both Thailand sites, the light compounds were a significant fraction, excepting the gases at 100 cm. below Sainoi dump site, where heavy VOC was hardly observed

Table 4 Comparison of levels of VOC (μg/m^3) in atmospheric air in landfills between this study and others

VOC	Central breakwater landfill	Sainoi open dump site	Pathumthani landfill	Ireland landfill site [19]		Datianshan landfill site [20]	
				Cell A[b)]	Cell B[c)]	Winter	Summer
benzene	1.88	11	38	0.3	165.5	7.3	73
toluene	2.41	B.Q.L	B.Q.L	15.9	308	12	113
ethyl benzene	0.60	N.D.	51	0.8	47.6	1.8	24
M,p-xylene	0.48	5	34	2.3	50	3.7	42
o-xylene	0.46	N.D.	7	0.5	36	2.5	33
3 or 4 ethyl toluene	-[a)]	N.D.	6	19.8	26.7	-	-
1,3,5-trimethylbenzene	-	N.D.	9	-	-	3.4	37
2 ethyl toluene	-	N.D.	N.D.	-	-	-	-
1,2,4-trimethylbenzene	-	N.D.	4	-	-	3.6	188
1,2,3-trimethylbenzene	-	N.D.	N.D.	-	-	1.2	89

[a)] Not a target compound in the study
[b)] Cell A-site with no leachate collection
[c)] Cell B-site with leachate collection

Table 5 VOC emissions (μg/m^3) from ten selected gas vents in The main site

GAS VENT	A	B	C	D	E	F	G	H	I
benzene	625	57110	6508	8173	3609	907	12	33	4814
toluene	62	3351	2339	23611	9829	B.Q.L	B.Q.L	B.Q.L	2852
ethylbenzene	271	27286	13449	40726	32451	22	3	21	4690
m,p-xylene	105	12794	5207	23783	14703	14	3	11	2422
o-xylene	50	5570	2327	8643	6246	3	1	4	1289
3 or 4 ethyltoluene	-	35286	-	4854	3251	-	-	-	-
1,3,5 trimethylbenzene	-	7905	-	12719	10995	-	-	-	-
2-ethyltoluene	-	5544	-	1245	1064	-	-	-	-
1,2,4 trimethylbenzene	-	4172	-	9134	7918	-	-	-	-
1,2,3 trimethylbenzene	-	760	-	1825	1984	-	-	-	-

3.3 Laboratory experiments

There is evidence that the polymeric materials such as plastics, which are major components of incombustible wastes, can produce a wide range of hydrocarbons by the thermal degradation of the wastes in the absence of oxygen/air, or called a pyrolysis process [24]-[26]. The decomposition of the organic content of disposed waste results in production of landfill gases and heat. Therefore, the VOC emissions from landfill site may be occurred under this pyrolysis process, however, the aromatic hydrobarbons can be also biodegraded by some microorganisms. Toluene is the most readily degraded aromatic hydrocarbon under various anaerobic conditions [27]. Benzene degradation may be competitively inhibited by the presence of more readily degraded compounds such as toluene [28].

In order to clarify the possible sources of VOCs in the landfill sites, laboratory experiments were conducted based on the principle of pyrolysis process.

Fig.2 shows total VOC concentrations in leachates from two ponds in Sainoi dump site stored at 20˚C and 80˚C. Temperature did not provide clear evidence on VOC production. However, the heated shallow pond

leachates gave higher benzene concentrations than those at 20˚C, whereas the concentrations of other compounds did not have a significant change. The production of benzenes might be caused by some substance containing in the leachates.

Heating materials could produce VOCs and the results clearly indicates that heating polystyrene products gave outstandingly high amount of VOCs, especially noodle cup producing up to 40 mg VOCs per kg-dry material (**Fig.3**). However, heated pure PS beads did not give VOCs. Heated plastics at lower temperature (60°C), also gave VOC productions (**Fig.4**). PS gave higher VOC productions as heating temperature increased. A production of VOCs possibly attributes to a pyrolysis, degradation, desorption or a combination of these mechanisms under high temperature. A roughness of the surface might have an effect on an adsorption of VOCs on to plastic surface; therefore, used noodle cup, which has the highest roughness in this study, gave a substantial VOC production after heating. Some plastic additives used in the manufacturing process of polystyrene products and/or some adsorption of VOCs on to the plastic surface may lead to an inconsistency in sorts of VOCs produced.

Fig. 5 shows the VOC productions on the 1st, 6th, 11th day from heated noodle cup and food pack. It can be concluded that the production rates of VOCs by heating used noodle cup and food pack had decreased exponentially, when time elapsed. The VOC desorption from plastic surface might bring about this high concentration during the first period.

3.4 Comparisons of VOC compositions

Toluene was a major compound in raw leachates, leachates from both collection ponds including the air samples in Sainoi open dump site (**Fig.6(a)-(d)**). Among xylene group, m,p-xylene was mainly found in the air samples, whereas in the raw leachates, of xylene groups 65 percent was o-xylene. Small amount of benzene was observed in the raw leachates and the air samples from Sainoi open dump site. However, approximately 10 percent of benzene was detected in the leachates from shallow ponds and deep ponds. An amount of benzene in both ponds did not increase compared to that in raw leachates, but many times a decrease in toluene concentrations in the ponds occurred. This could be considered as a volatilization and/or a biodegradation of toluene in the ponds. m,p-Xylene,1,2,4-trimethylbenzene and 1,3,5-trimethyl benzene were the main proportions of xylene group and trimethybenzene group (TMBs) in leachates from both ponds. The patterns of VOC compositions in leachates from the both ponds were quite similar not only in the compounds detected but also a percentage of each VOC containing in the leachate.

Major parts of VOCs found in influent and landfill gases from The main site were xylenes (**Fig.6(e)-(f)**). In influent, xylenes mainly consisted of m,p-xylene and ethylbenzene, while ethylbenzene was solely predominant in landfill gases. The composition of TMBs in the landfill gases is relatively close to that in the influent.

Regarding VOC compositions in heated materials in **Fig.6(g)-(o)**, roughly 90 % of VOC production from heated PP was toluene. Heated paper and wood also gave mainly toluene, followed by xylenes, and TMBs. The ratios of benzene:toluene:xylenes:TMBs in heated paper are fairly close to those of wood. Heated PE produced almost identical pattern of VOC compositions with that of heated paper. In cases of polystyrene, VOC productions from heated PS products composed of mostly toluene and xylenes. In xylenes group, ethylbenzene was predominantly detected. In addition, benzene was obtained only 1-2 percent from heating foam bowl and noodle cup including CD case. About 7 percent of VOC productions from heating CD case was TMBs, whereas very little proportion of TMBs gained from heating other PS materials.

Considering the field investigation results together with the laboratory experiments, the pattern of VOC compositions in the raw leachates from Sainoi dump site is quite similar to the VOC compositions of heated paper. Further discussion is needed because paper did not produce VOCs in high quantities in the experiment, even though, certainly, paper is one of the major wastes transferred to the municipal solid waste disposal sites including Sainoi open dump site.

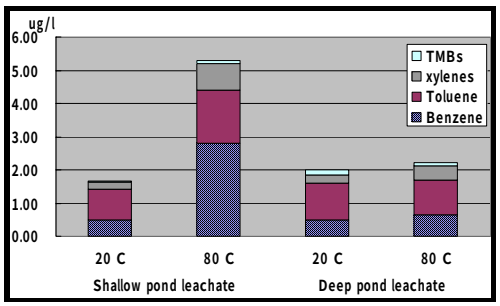


Fig.2 VOC productions on heating leachates

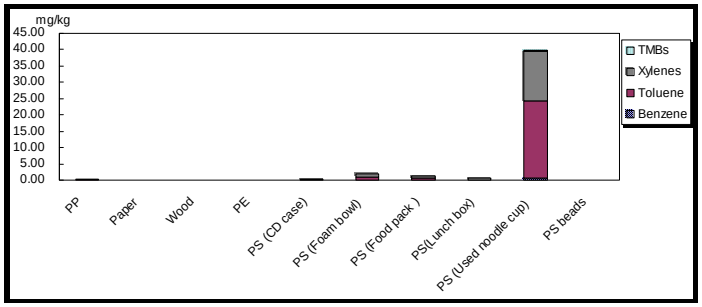
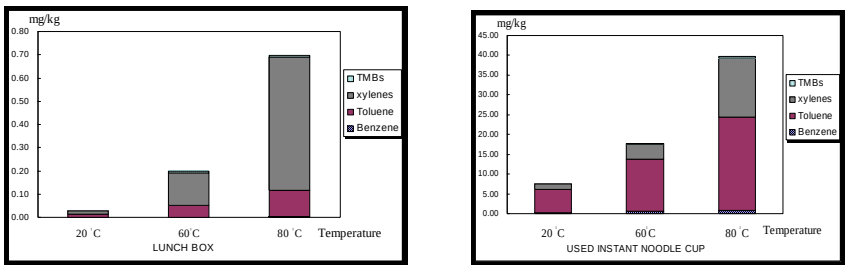
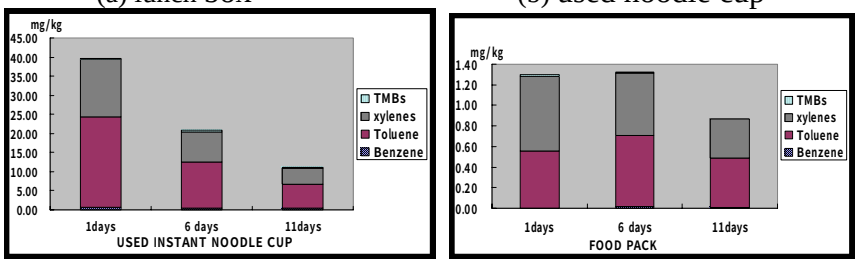


Fig.3 VOC productions from heating various types of materials



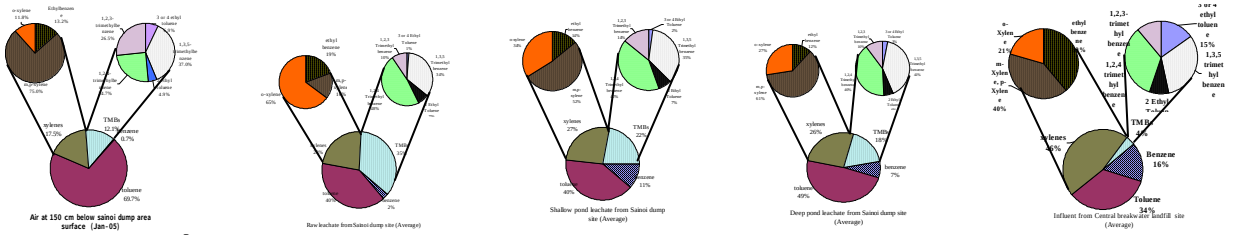
(a) lunch box (b) used noodle cup

Fig.4 VOC productions from heating several polystyrene products at different temperature



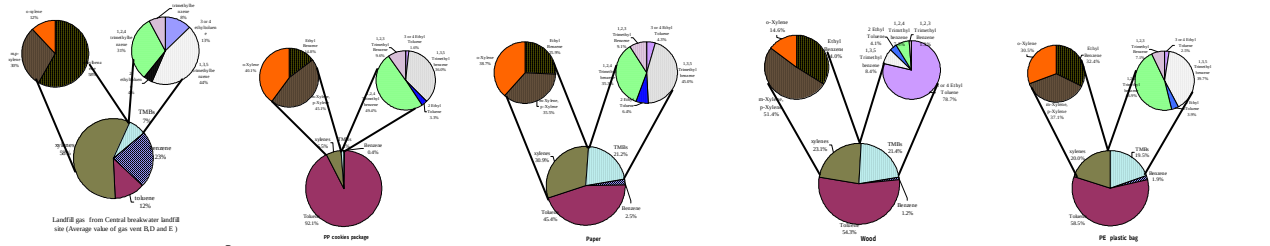
(a) used instant noodle cup (b) food pack

Fig.5 Time dependent production of VOCs by heating PS products



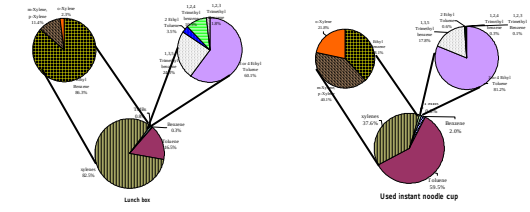
(Avg. VOCs=37 mg/m^3) (Avg. VOCs=106 μg/l) (Avg. VOCs=11 μg/l) (Avg. VOCs=6μg/l) (Avg. VOCs=30μg/l)

(a)Air at 150 cm below surface (b)Raw leachate (c)Shallow pond leachate (d)Deep pond leachate (e)Influent in Japan site



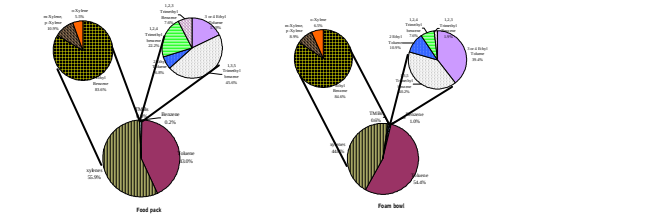
Avg. VOCs=129 mg/m^3 Avg.VOCs=0.25mg/kg Avg.VOCs=0.05mg/kg Avg.VOCs=0.14mg/kg Avg.VOCs=0.14mg/kg

(f) Landfill gases in Japan site (g) PP (h) Paper (i) Wood (j) PE



Avg.VOCs=0.70mg/kg Avg.VOCs=40 mg/kg

(k) PS lunch box (l) PS noodle cup



Avg.VOCs=1.30 mg/kg Avg.VOCs=1.80 mg/kg Avg.VOCs=0.33 mg/kg

(m) PS food pack (n) PS foam bowl (o) PS CD case

Fig.6 Compositions of VOCs in leachates, landfill gases and heated materials

The patterns of VOC composition of PS, which produced the greatest amount of VOCs in the laboratory experiments, are not similar to any of the investigation results. However, polystyrene might be one source of VOCs in landfill sites. Moreover, the leachates and landfill gases in The main site contained relatively much amount of benzene, but there was no benzene

The largest source of benzene emissions into the atmosphere is from gasoline. Consequently, the VOC composition in gasoline and that in landfill gases from The main site was compared. The VOC composition in gasoline in Japan observed in 1986 [29]. Gasoline consists toluene 41%, benzene 38%, m,p-xylene 13%, o-xylene 4% and ethylbenzene 4%. A pattern of VOC compositions is not similar to that of the landfill gases and the influent from The main site. No evidence shows clear similarity in VOC compositions in gasoline and those of landfill gases as well as those of leachates from the main site. A VOC composition pattern in rainwater observed in Yokohama [4] is very close to that of the influent, but the concentrations of VOCs in rainwater was relatively low compared to those in influent. In addition, the VOC compositions in urban air in Yokohama [4] are not similar to those in ambient air in The main site. This supports that there are some other sources of VOCs in landfill site excepting rainwater.

4 Conclusions

The field investigations were conducted in this study at the municipal solid waste disposal sites in Thailand and Japan. Sainoi open dump site, Pathumthani landfill site and Nakornpatom landfill site in Thailand as well as The main site in Japan were the target sites. Volatile organic compounds (VOCs) in leachates were analyzed by a combination of solid phase micro extraction (SPME) and gas chromatography mass spectrometry (GC-MS). Carbon-based active and passive gas samplers were applied for gas sampling. Laboratory experiments were carried out to study VOC sources found in the landfill sites. The results have been summarized as follows:

1) Among 41 target compounds, only 11 compounds in four groups of aromatic hydrocarbons, which are categorized into benzene, toluene, xylenes and trimethylbenzenes, were found in leachate and landfill gas samples collected in the target landfill sites. In other words, there was no organochlorine compound observed in the field investigations in this study.

2) The VOC concentration in leachates and landfill sites collected at Sainoi open dump site and The main site, varied greatly. On the other hand, whilst the VOC concentrations in Pathumthani landfill site and Nakornpaatom landfill site were observed at negligible level.

3) Toluene is predominant in leachates and air at 150 cm. below landfill suface at Sainoi open dump site, but xylenes are mainly found in leachates and landfill gases from gas vents in The main site. High concentrations of benzene were detected in The main site, but relatively small amount of benzene was found in the landfill sites in Thailand. Total VOC concentrations in gas vents in The main site were also very high, especially in the case of benzene. Benzene was thousands times higher than benzene regulated in air quality standards in Japan, and the benzene level was found as high as 100 mg/m^3.

4) VOC emissions inside landfill sites increased with depth below the landfill surface. High concentrations of VOCs in gases were observed at 150 cm. below the landfill surface of Sainoi open dump site as well as Pathumthani landfill site.

5) Light VOCs, benzene and toluene, seem to be predominant in gases and leachate collection ponds in landfill sites in Thailand, whereas heavy VOCs, xylenes and trimethylbenzenes, were mainly found in raw leachate from Sainoi dump site. In The main site, heavy VOCs are chiefly observed in landfill gases including most of leachate collection ponds.

6) Heating PS products, such as foam bowl, noodle cup, food pack, disposable lunch box and CD case, gave high concentration of VOCs, which mainly are xylenes and toluene. The compositions of heated PS are not similar to those of leachates and landfill gases investigated in this study; however, heated PS is surely one of the sources of xylenes and toluene in landfill sites. Moreover, the similarities in VOC compositions were obtained from heated paper and leachate collection ponds in Sainoi open dump site. Further discussion is needed because heating paper did not produce high VOC in quantity, even though, certainly, paper is one of the major wastes in municipal solid waste disposal sites.

7) Gasoline may not be the sole source of benzene in landfill sites because of the differences in VOC compositions from leachates and landfill gases in The main site. Benzene and trimethylbenzene sources are still unclear and needed further study.

Further studies are suggested to be conducted in order to clarify the main sources of benzene, which is listed as a carcinogen and has been registered in air quality standard in Japan. Gasoline under the new standards should be investigated for VOC compositions. Though SPME method gives compositions of VOCs, there is a limitation on quantitative evaluation of VOCs in SPME method. In further study, more quantitative method should be applied, such as purge-and-trap method to clarify mass balance of VOCs in the landfill site. Chemical equilibrium between water and air in landfill site, transport of VOCs to air and water in landfill site, heat balance in landfill site, and reaction kinetics, such as aerobic or anaerobic biodegradation inside landfill site, are suggested to investigate in the further study. In addition, it is desirable that experiment be conducted on large scale amount of waste, performed with real municipal solid wastes, including benzene-based municipal solid wastes.

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