Int. J. of GEOMATE, Dec. 2011, Vol. 1, No. 2 (Sl. No. 2), pp. 117-121
Geotec., Const. Mat. and Env., ISSN:2186-2982(P), 2186-2990(O), Japan

Determination of Organophosphoric Acid Tiesters from Different Landfill Sites and Sewage Plants in Japan

Haruki Shimazu
School of Science & Engineering, Kinki University, Japan

ABSTRACT: Seven organophosphoric acid triesters (OPEs) were measured in the water emissions from five active landfill sites and three closed inactive landfill sites. Many kinds of OPEs were detected and the highest concentration levels are 10,000ng/L orders of magnitude. The OPE concentration levels for the closed inactive landfill sites were almost same with those for the active landfill sites. It will be necessary for the closed inactive landfill sites to do continuous monitoring and further maintenance. The same OPEs were measured in the inlet waters and the outlet waters from two sewage plants. The OPE concentration levels in the inlet waters were almost same with those for the landfill sites. The OPE concentrations in the outlet waters were lower than those in the inlet waters. Some OPEs could be removed in the treatment process of sewage plants. It is probably effective for OPE reduction to introduce the treatment process into landfill sites.

Keywords: Organophophoric Acid Triesters, Active Landfill Site, Closed Inactive Landfill Site, Sewage Plant

1. INTRODUCTION

Organophosphoric acid triesters (OPEs) are ubiquitous environmental pollutants because OPEs have been used for plasticizer, flame retarder, antifoaming agent, surface active agent and so on [1]-[7]. Several OPEs have carcinogenic and/or neurotoxic properties [8]. Some reports indicate the elution from plastic products and the emissions from landfill sites [9], [10]. However, little is known about the occurrence and the emission characteristics of OPEs from landfill sites and sewage plants. The purposes of this paper are to measure OPEs from active landfill sites, closed inactive landfill sites, and sewage plants and to investigate the OPE emission characteristics from those sites and plants. It is determined that the water emissions from landfill sites and sewage plants have an influence on OPE pollution in aquatic environments.

2. METHODS AND MATERIALS

2.1 Landfill site description

This study focused on five active landfill sites shown in Table 1. The landfill areas were from 0.85-10.08 ha. Many kinds of wastes were disposed in Ⅱ landfill. The sampling point for Ⅱ landfill is shown in Fig. 1. When the waste water was drained from Ⅱ landfill, the water became muddy in brown and its putrid odor was strong. For Plastics were disposed in almost landfills. In 2007, the water emissions from Ⅰ, Ⅱ, Ⅲ landfill sites were taken three times on 11 November, 1 and 26 December. Furthermore, the water emissions from Ⅰ landfill site were taken five times on 20 November 2007 and six times on 6 January 2008 to investigate temporal change of OPE concentrations. In 2008, the water emissions from Ⅰ and Ⅱ landfill sites were taken three times on 29 July, 17 October and 21 November. The water emissions from Ⅲ landfill site were taken four times on 14 June, 29 July, 17 October and 21 November.

In 2009, the water emissions from Ⅰ and Ⅱ landfill sites were taken three times on 20 July, 25 August and 25 September. The water emissions from Ⅲ landfill site were taken five times on 20 June 18 July, 25 August, 25 September and 31 October. Furthermore, the water emissions from Ⅳ and Ⅴ landfill sites were taken one time on 25 August and 31 October, respectively.

This study focused on three closed inactive landfill sites shown in Table 2. Many kinds of wastes were disposed in Ⅶ landfill site.

Table 1. Active landfill sites monitored in this study

	Ⅰ	Ⅱ	Ⅲ	Ⅳ	Ⅴ
Opetation time	1995～	1991～	1990～	1989～	1982～
Landfill classification	Inert	Controlled	Inert	Inert	Inert
Area [ha]	1.34	6.47	10.08	1.15	0.85
Capacity [m^3]	135,404	874,850	1,302,908	104,270	35,098
Composition of waste	Glass, Metals, Plastics, Rubber.	Ash, Glass, Residue, Metals, Papers, Plastics, Rubber, Slag, Sludge, Textiles.	Glass, Metals, Plastics, Rubble.	Glass, Plastics, Rubble.	Rubble.

Figure 1 Waste water at the sampling point for Ⅱ landfill

Table 2. Closed inactive landfill sites monitored in this study

	Ⅵ	Ⅶ	Ⅷ
Opetation time	1986～approx.1990	1986～2007	-
Landfill classification	Inert	Controlled	Inert
Area [ha]	1.24	2.04	-
Capacity [m^3]	65,822	309,380	-
Composition of waste	Plastics, Metals, Glass, Rubber.	Ash, Glass, Residue, Metals, Papers, Plastics, Rubber, Slag, Sludge, Textiles.	-

Figure 2 Leachates at the sampling point for VI landfill

The sampling point for VI landfill is shown in Fig. 2. The leachates were always emitted from the pipe. The brown solid is included so much in the leachates. Their putrid and machine oil odors were strong.

In 2008, the leachates from VI landfill site were taken twice on 17 October and 21 November.

In 2009, the leachates from VI landfill were taken five times on 20 June, 18 July, 25 August, 25 September and 31 October. The leachates from Ⅶ landfill site were taken twice on 18 July and 31 October. Furthermore, the leachates from Ⅷ landfill site were taken four times on 18 July, 25 August, 25 September and 31 October.

For active landfill site, there were twenty, nine, twelve, one and one samples from Ⅰ, Ⅱ, Ⅲ, Ⅳ and Ⅴ landfill site, respectively. For closed inactive landfill site, there were seven, two and four samples from VI, Ⅶ and Ⅷ landfill site, respectively.

2.2 Sewage plant description

This study focused on two sewage plants shown in Table 3. The treatment capacities for Ⅸ and Ⅹ sewage plants were 75,000 m^3/d and 380,000 m^3/d, respectively. The treatment processes were anaerobic-anoxic-oxic process and step aeration process.

In 2009, the inlet water in Ⅸ sewage plant was taken one time on 19 October. The outlet waters in Ⅸ sewage plant were taken twice on 18 September and 19 October. Furthermore, the inlet waters in Ⅹ sewage plant were taken eight times on 29 September, 2 and 3 October to investigate temporal change of OPE concentrations. The outlet water in Ⅹ sewage plant was taken one time on 29 September. There were three and nine samples for Ⅸ and Ⅹ sewage plant, respectively.

Table 3. Sewage plants monitored in this study

	Ⅸ	Ⅹ
Opetation commencement	1986	1972
Service area [km^2]	28.81	72.13
Service population	163,209	651,737
Treatment capacity [m^3/d]	75,000	380,000
Treatment process	Anaerobic-anoxic-oxic process	Step aeration process

2.3 Analytical methods and instruments

Seven OPEs shown in Table 4 were measured. Those are object chemicals because many kinds of studies have been reported that they are fluently detected in aquatic and airborne environments [3]-[6].

Table 4. Measured OPEs in this study

Chemicals	CAS Number	abbr.	logKow
Tributyl phosphate	000126-73-8	TBP	4.00
Tri-2-butoxyethyl phosphate	000078-51-3	TBXP	3.75
Tri-2-chloroyethyl phosphate	000115-96-8	TCEP	1.44
Tris (1,3-dichloroisopropyl) phosphate	013674-87-8	TDCPP	3.65
Triethyl phosphate	000078-40-0	TEP	0.80
Tris (2-ethylhexyl) phosphate	000078-42-2	TEHP	4.23
Triphenyl phosphate	000115-86-6	TPP	4.59

* These abbreviations are used in this study.

** logKow values are obtained from reference [11], [12].

In the preparation, the water sample is filtered with glass fiber prefilter (MILLIPORE AP40, nominal pore size 0.7 μm). OPEs in the filtered water are given as the solved OPEs. OPEs in the suspended matter on the glass fiber are given as the suspended OPEs.

Each 1000 ml filtered sample is passed into the solid phase extraction column (WATERS PS-2) at the rate of 20 ml/min. The column is dried with air by means of sanction pump. The chemicals are eluted by passing 5 ml of dichloromethane through the column. The extract is concentrated to 0.1 ml under a N_2 flow. Hexane is added to the extract until 2 ml.

Each glass fiber prefilter sample is dried in a dark place over night and put into a vial with 15ml of dichloromethane. The chemicals are extracted with ultrasonic waves. The extract is filtered and concentrated to 0.1 ml under a N_2 flow. Hexane is added to the extract until 2 ml. The chemicals in these extracts are determined with gas chromatograph with mass spectrometer (Agilent technologies, 5975B inert XL E/CI MSD).

The operation condition for GC/MS (gas chromatograph with mass spectrometer) is shown in Table 5. After qualifying by three typical SIM mass, each OPE is quantified by the largest SIM mass. The detection limits were calculated from threefold values of signal-noise ratio in the baseline of chromatogram. The recoveries and the variation coefficients for solved OPEs in this analysis ranged from 70% to 120% and from 7% to 20%, respectively.

Table 5. Operation condition for GC/MS in this study

5975B inert XL E/CI MSD (Agilent Technologies)	
Column	HP-5MS(30m×0.25mmf, 0.25μm)
Oven temperature	50℃(1.5min)→20℃/min→180℃→ 5℃/min→280℃(2min)
Injection temperature	250℃
Injection method	Splitless, 2μL
Carrier gas	He
Detector temperature	230℃
SIM mass	TBP : 99, 151, 211 TBXP : 125, 199, 227 TCEP : 249, 205, 251 TDCPP : 191, 209, 193 TEP : 155, 99, 127 TEHP : 99, 113, 211 TPP : 326, 325, 215

3 RESULTS AND DISCUSSION

3.1 OPEs from active landfill sites

Seven OPEs were measured in the water emissions from five active landfill sites. The solved OPEs and PAHs in the water emissions from the active landfill sites are shown in Table 6.

Table 6. OPE concentrations in the water emissions from the active landfills

	Solved OPEs		Suspended OPEs	
	[ng/L]*	DR**	[ng/L]*	DR**
TBP	337(49.0-2670)	39/43	61.4(9.22-1340)	43/43
TBXP	1250(49.2-6110)	26/43	755(456-834)	5/43
TCEP	926(47.4-3850)	31/43	252(8.12-713)	18/43
TDCPP	51.9(20.6-83.1)	2/43	204(41.3-366)	2/43
TEP	1400(43.1-20900)	40/43	18.4(4.32-415)	36/43
TEHP	31.0(3.9-58.1)	2/43	8.77(1.17-29.0)	18/43
TPP	58.7(15.0-329)	13/43	49.1(18.1-204)	5/43

* Median(min-max)

** Detection rate

For active landfill sites, the solved OPEs for the high detected frequencies were TBP, TBXP, TCEP, and TEP. The suspended OPEs for the high detected frequencies were TBP and TEP. The highest concentrations of the solved OPEs and the suspended OPEs were 20,900 ng/L for TEP and 1340 ng/L for TBP.

The total concentrations and the component ratios of OPEs in water emissions from active landfill sites were shown in Fig.3. The concentrations and component ratios were different in each landfill site. The total of solved OPEs and suspended OPEs from Ⅱ landfill site were lower than those from the other landfill sites because many kinds of wastes were disposed. However, the OPE concentrations for Ⅰ and Ⅲ landfill sites were high. It may be due to plastic wastes because typical OPEs containing plastic products such as TBXP, TCEP, and TEP were so high [1], [13].

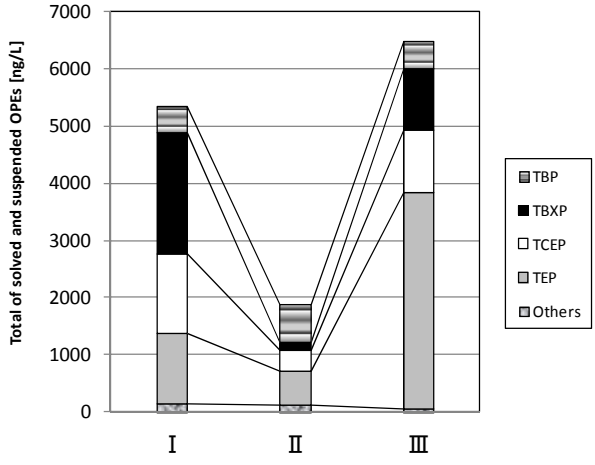

Figure 3 Total concentrations and component ratios of OPEs in the water emissions from the active landfill sites

The temporal changes of OPEs in the water emissions from Ⅰ landfill site on 20 November 2007 were shown in Fig.4. TBP, TBXP, TCEP, and TEP ranged from approximately 1000 ng/L to 2000 ng/L. The specific trends of OPE concentrations were not observed. The trends of OPE concentrations on 6 January 2008 were almost same. It probably indicates that these OPEs were gradually dissolved from plastic wastes and/or contaminated soils and emitted to the environment [1].

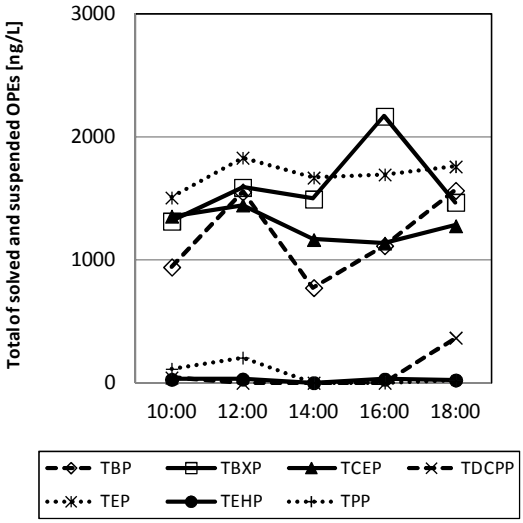

Figure 4 Temporal changes of OPEs in the water emissions from Ⅰ landfill site (Nov.2007)

3.2 OPEs from closed inactive landfill sites

Seven OPEs were measured in the water emissions from three closed inactive landfill sites. The solved OPEs and PAHs in the water emissions from the closed inactive landfill sites are shown in Table 7.

For closed inactive landfill sites, the solved OPEs for the high detected frequencies were TBP, TBXP, TDCPP, and TEP. The suspended OPEs for the high detected frequencies were TBP, TEP, and TEHP. The highest concentrations of the solved OPEs and the suspended OPEs were 6870 ng/L for TBP and 3780 ng/L for TBP. The OPE concentration levels for the closed inactive landfill sites were almost same with those for the active landfill sites. In spite of the closed inactive landfill sites, the OPE concentration levels were high. It shows that the closed inactive landfill sites need continuous monitoring and further maintenance.

Table 7. OPE concentrations in the water emissions from the closed inactive landfills

	Solved OPEs		Suspended OPEs	
	[ng/L]*	DR**	[ng/L]*	DR**
TBP	1490(321-6870)	13/13	50.4(4.05-3780)	13/13
TBXP	628(210-4230)	8/13	6.21	1/13
TCEP	89.3	1/13	29.2	1/13
TDCPP	52.5(37.0-277)	7/13	ND	0/13
TEP	1360(30.9-4290)	13/13	15.8(2.05-503)	10/13
TEHP	3.00	1/13	6.59(3.36-17.8)	10/13
TPP	ND	0/13	ND	0/13

* Median(min-max)

** Detection rate

*** ND means Not detected.

3.3 Effects of water temperature and rainfall on OPE emissions from landfill sites

Effects of water temperature and rainfall on OPE emissions from landfill sites were investigated. Figure 5 shows the relationship between OPE concentrations in the water emissions from the landfill sites and water temperature. The correlation coefficient for the active landfill sites is so low because wastes are continuously disposed in the active landfill sites. However, the relationship between OPE emissions and water temperature for the closed inactive landfill sites is a little significant. The disposed wastes containing OPEs were so closed for a long time that water temperature could depend on the elution characteristics for OPEs.

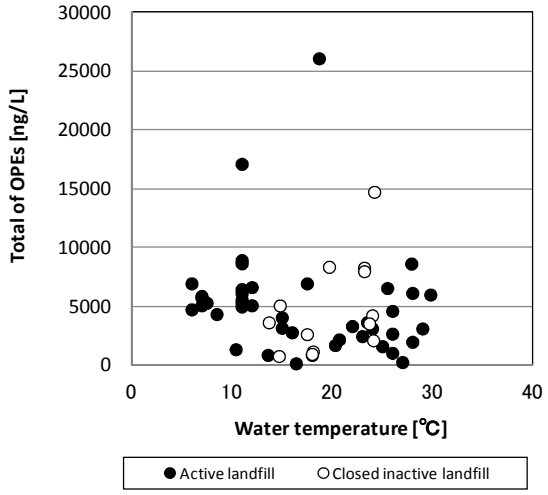

Figure 5 Relationship between OPEs in the water emissions from landfill sites and water temperature

Figure 6 shows the relationship between OPE concentrations in the water emissions from the landfill sites and rainfall. For both active landfill sites and closed inactive landfill sites, the significant relationship between OPE emissions and rainfall were not observed.

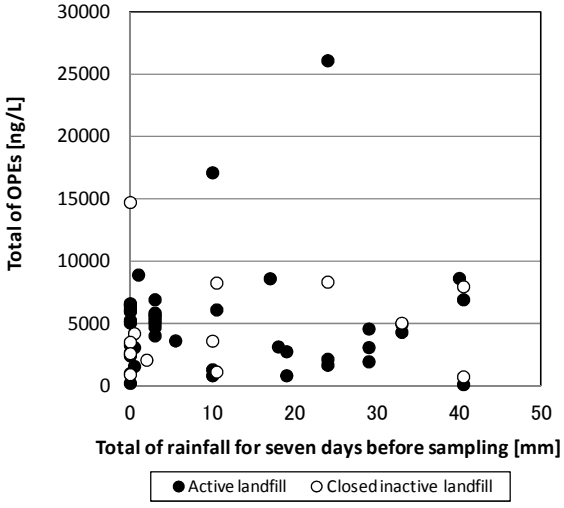

Figure 6 Relationship between OPEs in the water emissions from landfill sites and rainfall

The quantity of water emissions is not related with total of rainfall for seven days before sampling. It could be due to the complex mechanism of rainfall elution from landfill sites.

3.4 OPE partition characteristics in water emission from active landfill sites

Suspended OPEs / solved OPEs partition coefficients (Ksw) in water emissions from active landfill sites are shown in Fig. 7. The shown OPEs were detected both filtered water and suspended matter. Each dot means the median value of Ksw. Each Ksw range means from minimum value to maximum value. TEP is the most hydrophilic and TPP is the most hydrophobic, as shown in Table 4. The trend indicates that logKsw would be higher for hydrophobic OPEs.

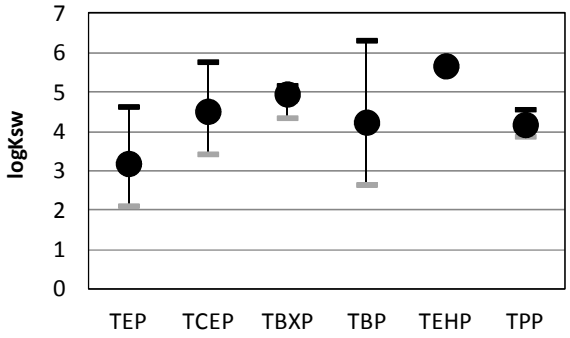

Figure 7 Median and range of Ksw for detected OPEs both filtered water and suspended matter

3.5 OPEs from sewage plants

Seven OPEs were measured in the inlet waters and outlet waters for two sewage plants. The solved OPEs and PAHs in the inlet waters and the outlet waters for the sewage plants are shown in Table 8 and 9.

In the inlet waters, the solved OPEs for the high detected frequencies were TBP, TDCPP, TEP, TEHP, and TPP. The suspended OPEs for the high detected frequencies were TBP and TEHP. The highest concentrations of the solved OPEs and the suspended OPEs were 36,200 ng/L for TBXP and 842 ng/L for TBP. The temporal changes of OPEs in the inlet waters from IX sewage plant were investigated. The specific trends of OPE concentrations were not observed as those for I landfill site shown in Fig.2. In the outlet waters, the highest concentrations of the solved OPEs

Table 8. OPE concentrations in the inlet waters for the sewage plants

	Solved OPEs		Suspended OPEs	
	[ng/L]*	DR**	[ng/L]*	DR**
TBP	764(441-14,700)	9/9	159(40.3-842)	9/9
TBXP	6920(1530-36200)	9/9	140	1/9
TCEP	3150(1320-4500)	4/9	ND	0/9
TDCPP	190(106-404)	7/9	ND	0/9
TEP	129(86.3-357)	9/9	36.1	1/9
TEHP	76.4(28.7-115)	9/9	266(118-508)	9/9
TPP	79.4(61.2-108)	9/9	ND	0/9

* Median(min-max)

** Detection rate

*** ND means Not detected.

Table 9. OPE concentrations in the outlet waters for the sewage plants

	Solved OPEs		Suspended OPEs	
	[ng/L]*	DR**	[ng/L]*	DR**
TBP	1050(133-2690)	3/3	25.0(5.60-71.0)	3/3
TBXP	871(564-1400)	3/3	50.7	1/3
TCEP	1810(1600-2170)	3/3	ND	0/3
TDCPP	109(106-138)	3/3	20.8	1/3
TEP	143(103-203)	3/3	5.64(2.14-9.14)	2/3
TEHP	5.30(1.89-8.72)	2/3	15.6(8.77-22.5)	2/3
TPP	16.5	1/3	ND	0/3

* Median(min-max)

** Detection rate

*** ND means Not detected.

and the suspended OPEs were 2690 ng/L for TBP and 71.0 ng/L for TBP. The concentration levels for TBXP, TEHP, and TPP in the outlet waters were lower than those in the inlet waters. Some OPEs could be removed in the treatment process of sewage plants.

4 CONCLUSION

Seven OPEs were measured in the water emissions from five active landfill sites and three closed inactive landfill sites. The same OPEs were measured in the inlet waters and the outlet waters in two sewage plants.

For active landfill sites, the solved OPEs for the high detected frequencies were TBP, TBXP, TCEP, and TEP. The suspended OPEs for the high detected frequencies were TBP and TEP. The highest concentrations of the solved OPEs and the suspended OPEs were 20,900 ng/L for TEP and 1340 ng/L for TBP.

For closed inactive landfill sites, the solved OPEs for the high detected frequencies were TBP, TBXP, TDCPP, and TEP. The suspended OPEs for the high detected frequencies were TBP, TEP, and TEHP. The highest concentrations of the solved OPEs and the suspended OPEs were 6870 ng/L for TBP and 3780 ng/L for TBP. The OPE concentration levels for the closed inactive landfill sites were almost same with those for the active landfill sites. It will be necessary for the closed inactive landfill sites to do continuous monitoring and further maintenance.

In the inlet waters for sewage plants, the solved OPEs for the high detected frequencies were TBP, TDCPP, TEP, TEHP, and TPP. The suspended OPEs for the high detected frequencies were TBP and TEHP. The highest concentrations of the solved OPEs and the suspended OPEs were 36,200 ng/L for TBXP and 842 ng/L for TBP.

In the outlet waters for sewage plants, the highest concentrations of the solved OPEs and the suspended OPEs were 2690 ng/L for TBP and 71.0 ng/L for TBP.The concentration levels for TBXP, TEHP, and TPP in the outlet waters were lower than those in the inlet waters. Some OPEs could be removed in the treatment process of sewage plants. It is probably effective for OPE reduction to introduce the treatment process into landfill sites.

5 REFERENCES

[1] Cho K. J., Inoue Y., Hirakawa T., Mukai T., Takimoto K. and Okada M., "Variations and sources of TCP (tricresyl phosphate) isomers in the Kurose river basin in Higashi-Hiroshima city" *J. Japan Society on Water Environment*, Vol.19, No.12,1996, pp.986-994.

[2] Haraguchi K., Yamashita T. and Shigemori N., "Sampling and analysis of phosphoric acid triesters in ambient air", *J. Japan Society for Atmospheric Environment*, Vol.20, No.6, 1985, pp.407-415.

[3] Nakasugi O., "Organophosphoric acid triesters ; production, use and release to aquatic environment", *J. Japan Society on Water Environment*, Vol.19, No.9,1996, pp.686-691.

[4] Saito I., Okuni A. and Seto H., "Determination of organic phosphate triesters in indoor and outdoor air", *Aerosol Kenkyu*, Vol.16, No.3,2001, pp.209-216.

[5] Shimazu H., Okada J., Ozaki N., Fukushima T. and Takeshita Y. "Behavior and modeling of organophosphoric acid triesters in the Kurose river basin", *Environmental Engineering Research*, Vol.38, 2001, pp.227-237.

[6] Shimazu H., "Polycyclic aromatic hydrocarbons and organophosphoric triesters in air and atmospheric deposition", *Doboku Gakkai Ronbunsyuu G*, Vol.67, No.7, 2011, pp.Ⅲ-741-Ⅲ-747.

[7] Takahashi Y. and Morita M., "Studies on organic compounds in water (3) Organochlorine herbicides, organophosphorus pesticides and organophosphate triesters in raw and finished water", *J. Japan Society on Water Environment*, Vol.11, No.3, 1988, pp.161-168.

[8] Hirose A., "Effects of organophosphoric acid triesters on human health", *J. Japan Society on Water Environment*, Vol.19, No.9,1996, pp.708-712.

[9] Nagase M., Toba M., Kondo H., Yasuhara A. and Hasebe K., "Estimation of organophosphoric acid triesters in soft polyurethane foam using a concentrated sulfuric acid dissolution technique and gas chromatography with flame photometric detection", *Analytical Sciences*, Vol.19, 2003, pp.1617-1620.

[10] Kawagoshi Y., Fujiwara Y., Fukunaga I. and Itoh H., "Change of organophosphoric acid triesters concentration at sea-based solid waste disposal site", *J. Japan Society on Water Environment*, Vol.20, No.3,1997, pp.166-174.

[11] Interactive PhysProp Database Demo, http://www.syrres.com/what-we-do/databaseforms.aspx?id=386

[12] Kanagawa Environmental Research Center, http://www.k-erc.pref.kanagawa.jp/kisnet/

[13] Yasuhara A, "Elution of tris(2-chloroethyl) phosphate from waste plastics into water", *J.Environmental Chemistry*, Vol.6, No.1, 1996, pp.43-47.

International Journal of GEOMATE, Dec. 2011, Vol. 1, No.2 (Sl. No. 2) MS No. 2g received Aug. 30 2011, and reviewed under GEOMATE publication policies.

Corresponding Author: Haruki Shimazu