# Benzotriazole UV Stabilizers in Water and Atmosphere Environment of Hyogo Prefecture, Japan.

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## Introduction

Benzotriazole UV Stabilizers (BUVSs) are used in a variety of plastic products, such as building materials, automobile polymeric components, waxes, films to protect against UV-irradiation. Since a part of BUVSs has persistent and bioaccumulative property, it is widespread environmental pollutants. Recently, the occurrence of BUVSs has reported in marine organisms collected from Japanese coastal water. However, there is little information about the concentration level of BUVSs in environment of Hyogo prefecture. In this survey, BUVSs in water and atmosphere environment were investigated in Hyogo prefecture, Japan.

# Materials and methods

# Sampling points

The river water, river sediment, and air were sampled for 3 years from 2015 to 2017. Sampling points (River: 1-34, Air: A1-A5) were shown in Figure 1. River water sampling, river sediment sampling and air sampling were conducted in summer and winter.

# Analytical procedure of water sample

The target compounds on 1,000mL of water sample adjusted at pH2 with hydrochloric acid and added 30g sodium chloride were extracted by shaking with 50mL of dichloromethane. The extraction process was repeated two times. After extraction, lower layer of dichloromethane was concentrated under nitrogen stream to about 2mL.

The solvent of this concentrated solution was changed into 1mL of methanol under gentle nitrogen stream.

# Analytical procedure of sediment sample



Figure 1: Sampling points in Hyogo

After added 30mL of 30% ethylacetate/hexane, the target compounds on 5g of dry sediment sample were extracted by sonication for 10 min. After centrifuged for 10min at 3,000rpm, the extraction was transferred to new glass tube. The extraction process was repeated two times. The combined extraction was concentrated under gentle nitrogen stream to about 2mL. After this, the solution was applied with Florisil PR cartridge, and the cartridge was eluted with 5% ethyl acetate/hexane. The eluted solution was concentrated to about 2mL, again.

Then, the solution was applied with NH2 cartridge, and the cartridge was eluted with hexane. The eluted solution was concentrated to about 2mL, again. The solvent of this concentrated solution was changed into 1mL of methanol under gentle nitrogen stream.

# Sample collection of air

The air samples were collected by using a high volume air sampler (HV-700F, SIBATA) with sampling volume of approximate 1000 m and with flow rate of 700 L/min. Quartz micro fiber filters (QMF, QR-100, 203×254mm, ADVANTEC) and Poly-urethane foams (PUF, 90mm $\phi$ , SIBATA) were used for collection media.

# Analytical procedure of air sample

After added approximately 250mL of 30%ethylacetate/hexane, the target compounds on QMF and PUF were extracted by soxhlet extractor (B-811, BUCHI) for 60 cycles, respectively. After this, the procedure of the following cleanup was the same as sediment samples.

The measurement was performed by liquid chromatography (LC)-tandem mass spectrometer (MS/MS) using Xevo TQ (Waters) coupled with ACQUITY UPLC (Waters). Analysis was conducted using negative electrospray ionization with multiple reaction monitoring. 0.5mM ammonium acetate and methanol were used for LC mobile phase. Analytical column was GL Sustain C18 (C18, 2.1×150mm, 3µm, GL Sciences). The target compounds were 4 BUVSs : 2-(2H-1,2,3-Benzotriazol-2-yl)-4,6-di-tert-butylphenol (UV-320,CAS no:3846-71-7), 2-(tertbutyl)-4-mehtyl-6-(4-chloro-2H-1,2,3-Benzotriazole-2-vl)phenol (UV-326,CAS no;3896-11-5), 2,4-di-tert-butyl-6-(5-chloro-2H -1,2,3-Benzotriazol-2-yl) phenol (UV-327,CAS no:3864-99-1), 2- (2H-1,2,3-Benzotriazol-2-yl)-4,6-di-tert-phenylphenol (UV-328,CAS no:25973-55-1).

Table 1: Analysis condition of LC/MS/MS

LC conditions			MS condition		
Ins	trument : ACOUITY UPL	C(Waters)	Instrument		XEVO TO MS (Waters)
	Column ; GL sustain C18	(150mm,2.1mm,3µm)	Ionization mode	:	ESI(-)
Mobil	e phase : A : 0.5mM Amm	onium Acetate ag.	Source temp		150°C
	B: Methanol		Desolvation temp	÷	600°C
(	Gradient : 0.0→0.5min	B: 30→30%	Capillary voltage		2.7 kV
	: 0.5→1.5min	B: 30→95%	Cone gas flow	:	50 L/hr
	: 1.5→10min	B: 95→100%	Desolvation gas flow	÷	800 L/hr
	: 10→11min	B: 100→100%	Collision gas flow	:	0.15 mL/min
	: 11→11.5min	B: 100→30%	Monitor ion (m/z)	:	UV-320 = 322.2 / 306.1, UV-326 = 314.2 / 151.5
	: 11.5→13.5min	B: 30→30%			UV-327 = 356.3 / 305.3, UV-328 = 350.4 / 320.3
F	low rate : 0.3 mL/min		Cone voltage (V)		UV-320 = 64 / 36, UV-326 = 56 / 34
Colun	n temp. : 40°C		/ Collision voltage (V)		UV-327 = 62 / 31, UV-328 = 63 / 36
Injection	volume : 10uL				

# **Results and discussion**

#### *River* water

The recovery rates were between 103-110%. Limit of detection (LOD) was ranged from 0.38 to 0.54ng/L. Table 2 shows the concentrations of BUVSs in river water samples. UV-320, UV-327, UV-328 were not detected in water samples at any sampling points, only UV-326 was detected in 4 points (point 23,24,33,34) in Hokkesantanigawa-River system. The maximum concentration detected was 2,800ng/L at point 24 located most upstream part of 4 points in Hokkesantanigawa-River system, and the concentration was low as to be located downstream in other 3 points. This indicates the presence of the source of UV-326 in the upstream part of Araigawa-River (River under the Hokkesantanigawa-River system which joins the Hokkesantanigawa-River left bank.).

Table 2:	Concentrations	of BUVSs in	river water	(ng/L)
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Sample No	River	Location			Summer			Winter						
			year	UV-320	UV-326	UV-327	UV-328	year	UV-320	UV-326	UV-327	UV-328		
1-22,25-32	-	Rivers of Hyogo pref, Japan	2015-2017	ND	ND	ND	ND	2015-2017	ND	ND	ND	ND		
23	Hokkesanntanigawa	Chidorio Bridge	2017	ND	<loq< td=""><td>ND</td><td>ND</td><td>2016</td><td>ND</td><td>4.1</td><td>ND</td><td>ND</td></loq<>	ND	ND	2016	ND	4.1	ND	ND		
24	Arawaigawa	Araigawa River 1	2017	ND	2,800	ND	ND	2016	ND	88	ND	ND		
33	Arawaigawa	Araigawa River 2	2017	ND	140	ND	ND	-	-	-	-	-		
34	Hokkesanntanigawa	Tanigawa Bridge	2017	ND	3.8	ND	ND	-	-	-	-	-		
LOD			-	0.38	0.52	0.54	0.42	-	0.38	0.52	0.54	0.42		
LOQ			-	0.96	1.3	1.4	1.1	-	0.96	1.3	1.4	1.1		
Unit: ng/L		24,33,34,23 oder from ups	tream	ND: Not de	etected ( <lo< td=""><td>DD)</td><td></td><td></td><td></td><td></td><td></td><td></td></lo<>	DD)								

LOQ: limits of quantification

#### River sediment

The recovery rates were between 91-102%. Limit of detection (LOD) was ranged from 0.08 to 0.14ng/g-dry. Table 3 shows the concentrations of BUVSs in river sediment samples. Though BUVSs were not detected in most water samples analyzed, they were detected in most sediment samples analyzed. Since BUVSs have a strong hydrophobic property, it seems that they were easy to accumulate in sediment than in water. The range of  $\Sigma BUVSs$ concentration was from ND to 1,700 ng /g-dry. High concentration levels of BUVSs (SBUVSs; 8.0-1,300 ng /gdry) were detected in Hokkesantanigawa-River system (point 23, 24, 33, 34) and Kanzakigawa-River (point 4, 5). Those were relatively higher in Hyogo prefecture, and higher than those in other areas of Japan (maximum of ΣBUVSs: 720ng /g-dry) (Nakata et al, 2009). The maximum UV-326 concentration detected was at point 24, like water sample (1,300 ng /g-dry, 2,800ng/L, respectively). This result indicates that the source of the UV-326 outbreak is located the upstream part of Araigawa-River. Point 5 and Point 9 are in another river and located in the upper stream of Point 4( $\Sigma$ BUVSs; 1,700 ng/g-dry). Though high concentrations of BUVSs were detected at point 5 (SBUVSs; 1,300 ng /g-dry), low concentration of BUVSs were detected at point 9 (SBUVSs; 38 ng /g-dry). This result indicates that the presence of sources of BUVSs in the upstream part from point 5 in Kanzakigawa-River. In most sampling points detected high concentrations of BUVSs, the organic carbon contents in sediment

were high compared with them in the sampling points detected low concentrations of BUVSs. But, in point 24, 33, the correlation of the levels of BUVSs and organic carbon content was small. Because the concentrations of BUVSs in water at point 24, 33 were too high, the concentrations of sediments were high regardless organic carbon content.

Sample No	River	Location	Summer						Winter							
			year	C%	UV-320	UV-326	UV-327	UV-328	ΣBUVSs	year	C%	UV-320	UV-326	UV27	UV-328	ΣBUVSs
1-3,6-8,10-22,25-31	-	Rivers of Hyogo pref, Japan	2015-2017	0.48-2.6	ND	ND-4.0	ND-2.2	ND-1.4	ND-8.0	2015-2017	0.62-5.9	ND-0.84	ND-7.8	ND-14	ND-15	1.2-22
		Left bank of Kanzaki Bridge	2015	11	53	810	680	170	1700	2015	13	10	150	69	66	300
4	Kanzakigawa	Mddle of Kanzaki Bridge	2015	1.4	<loq< td=""><td>5.3</td><td>1.5</td><td>2.2</td><td>9.0</td><td>2015</td><td>8.1</td><td>5.6</td><td>77</td><td>22</td><td>38</td><td>140</td></loq<>	5.3	1.5	2.2	9.0	2015	8.1	5.6	77	22	38	140
		Right bank of Kanzaki Bridge	2015	5.3	3.6	71	39	68	180	2015	9.7	2.0	50	19	30	100
5	Kanzakigawa	Ootoyo Bridge	2015	9.0	53	420	680	170	1300	2015	12	18	130	240	46	430
9	Inagawa	Mogawa Bridge	-	-		-	-	-	-	2015	6.6	ND	17	5.7	15	38
23	Hokkesanntanigawa	Left bank of Chidorio Bridge	2017	0.92	<loq< td=""><td>6.2</td><td>ND</td><td><loq< td=""><td>8.0</td><td>2016</td><td></td><td>ND</td><td></td><td>2.7</td><td></td><td>22</td></loq<></td></loq<>	6.2	ND	<loq< td=""><td>8.0</td><td>2016</td><td></td><td>ND</td><td></td><td>2.7</td><td></td><td>22</td></loq<>	8.0	2016		ND		2.7		22
	Hokkesanntanigawa	Right bank of Chidorio Bridge	2017	2.5	ND	120	2.2	8.4	130	Chidorio	2.2	ND	11	2.7	8.0	22
24	Arawaigawa	Araigawa river 1	2017	0.17	ND	1300	1.0	7.4	1300	2016	1.4	ND	460	1.7	11	470
33	Arawaigawa	Araigawa river 2	2017	1.1	ND	330	1.0	7.6	340		-	-	-	-	-	-
34	Hokkesanntanigawa	Left bank of Tanigawa Bridge	2017	22	ND	1100	9.5	40	1100	-	-	-	-	-	-	-
	Hokkesanntanigawa	Right bank of Tanigawa Bridge	2017	5.5	0.71	260	5.4	14	280		-	-	-	-	-	-
LOD			-	-	0.14	0.14	0.08	0.14	-	-	-	0.14	0.14	0.08	0.14	-
LOQ			-		0.36	0.35	0.2	0.34				0.36	0.35	0.2	0.34	
Unit: ng/g-dry		24,33,34,23 oder from upstrea	m		ND: Not d	etected ( <l0< td=""><td>DD)</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></l0<>	DD)									

LOD: limits of detection LOQ: limits of quantification

C%: carbon % in sediment

#### *Atmosphere*

The recovery rates of QMF and PUF were between 92-113%, 89-138%, respectively. Limit of detection (LOD) of QMF and PUF was ranged from 0.098 to 1.9 pg/m<sup>2</sup>, 0.33 to 24pg/m<sup>2</sup>, respectively. Fig.2 shows the results of the target compounds distribution in atmosphere at sampling point. In this study, the compounds collected by QMF were assumed to be in the particle phase, and the compounds collected by PUF were assumed to be in the gas phase. BUVSs were detected in all samples analyzed, and UV-326 was the dominant compound, like water and sediment samples. These results imply a large amount of production and usage of UV-326 compared with other BUVSs in Hyogo. Whereas the concentration of gas phase UV-326 was higher than particle phase in summer, it was the reverse in winter. The difference in concentrations and phase of UV-326 can be attributed to temperature. On the other hand, about UV-328, particle phase was higher than gas phase in both seasons, and it seems that it was easy to be distributed in particle phase than in gas phase regardless of temperature. Since the molecular weight of UV-328 (351.5) is higher than UV-326 (315.8), and the octanol / water partition coefficient (Log Pow) of UV-328 (8.28) is larger than UV-326 (6.58), it seems that UV-328 was easy to be distributed in particle phase than UV-326. To our knowledge, this is the first study of 4 BUVSs in the atmosphere.

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Figure 2: Gas phase and Particle phase distribution of BUVSs in atmospheric samples collected on the sampling points