

## Analysis of Benzotriazole UV Stabilizers in House Dust Using an UHPLC-MS/MS

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**Abstract**—Benzotriazole ultraviolet stabilizers (BUVVs) are used in a variety of consumer products, such as sunscreen products, plastic resin, paint, adhesive agent, coating material, some sports equipments and so on. Some BUVVs are categorized as potentially toxic, persistent and bioaccumulative in nature. This study analyzed BUVVs in house dust samples from Malate (residential site) and Payatas (municipal dumping site) in the Philippines. We also assessed the human exposure to these contaminants via house dust ingestion. UV-234 was the predominant contaminant detected in this study followed by UV-326 > UV-328 > UV-327 > UV-320. Significantly higher concentrations of UV-326 ( $p < 0.01$ ) and UV-327 ( $p < 0.05$ ) found in house dust samples from Malate than Payatas, suggesting that the household appliances are the major sources of the these contamination analytes. The estimated dietary intakes (EDIs) of BUVVs through the ingestion of house dust in the Philippines were two to four orders of magnitude lower than the guideline values (ranging from 600 to 210,000 ng/day for adults and from 150 to 52,500 ng/day for toddlers).

**Keywords:** BUVVs, house dust, risk assessment, Philippines

### INTRODUCTION

There is a rising concern on the occurrence, fate and potential for ecological effects of residues of pharmaceuticals and personal care products (PPCPs) as toxic substances in the aquatic environment (Jos *et al.*, 2003). Benzotriazole ultraviolet stabilizers (BUVVs) have been used in increasing amounts in sunscreen products, as well as building materials, plastic resins, paints, varnish, adhesive

agents, coating materials, film, air fresheners and some printing materials in many countries such as Taiwan, Ecuador, Korea, Poland, Switzerland, etc. (MEGJ, 2006a). According to MEGJ based on the hazard assessment, some BUVSs are categorized to potentially toxic, persistent and consequently bioaccumulative in nature. In Japan, 2-(2*H*-benzotriazol-2-yl)-4,6-di-*tert*-butylphenol (UV-320; CAS 3846-71-7) has been classified as a Class I Specified Chemical Substance, and its production, usage and import has been banned by Japanese government since 2007. UV-327 has also been regulated as a Class I Monitoring Chemical Substance since it shows high bioaccumulative characteristic similar to UV-320 (MEGJ, 2006b).

The present study investigated the distribution of BUVSs in house dust and their potential risk to human health through ingestion of house dust. House dust is a repository for various contaminants that are transported into the house from outside or originate from sources within the house itself, and is the subject of growing concern in recent years. Because BUVSs are not chemically bonded to the original material, these additives are easily released into the environment by abrasion and volatilization (Carpinteiro *et al.*, 2010). Then, they may remain in the vapor phase and/or adsorb on suspended particulate matter and settle in dust. Therefore, phenolic compounds such as BUVSs in indoor dust represent a potential risk for human health through oral ingestion and inhalation.

In the present study, the levels and distribution pattern of BUVSs were analyzed in house dust samples collected from residential homes with two different characteristics (one residential area in Malate having no specific industrial pollution sources, and the other Payatas a municipal dumping area) in the Philippines. In addition, we evaluated the role of house dust as a human non-dietary exposure route by comparing their daily intake with guideline standards for adults and toddlers, to determine the potential risk of BUVSs to human.

## MATERIALS AND METHODS

### *Sample collection*

House dust samples ( $n = 37$ ) were randomly collected in August, 2008 from two different locations in the Philippines, namely Malate ( $n = 17$ ) and Payatas ( $n = 20$ ). Floor dust samples were collected by vacuum cleaner bags used in each of the sampled house, which consist of dust from living room, kitchen, and bedrooms. The dust was sampled from the vacuum cleaner bag with a stainless steel spatula and transferred into clean aluminum foil. After collection the samples were stored at  $-25^{\circ}\text{C}$  in the Environmental Specimen Bank (*es*-BANK) of Ehime University (Tanabe, 2006) until further analysis. Characteristics of residence including floor area, number of computers/televisions, pieces of furniture and type of flooring were also documented at the time of sample collection.

### *Chemical analysis*

Analysis of BUVSs was performed following the procedure of Stapleton *et*

*al.* (2009) with slight modification. Briefly, 0.1 g of house dust sample was accurately weighted and homogenized with anhydrous sodium sulfate, spiked with 10 ng of internal standard TnBP-*d*<sub>27</sub> as surrogate, and extracted using high speed solvent extractor (SE-100; Mitsubishi Chemicals, Japan) with a mixture of acetone and hexane (1:1 v/v) at 30°C at 10 mL/min flow rate for 30 min. After extraction, the extract was concentrated to 10 mL using a rotary evaporator (EYELA, Japan). Then the extracts were purified by using a glass column (200 × 10 mm i.d.) containing 4 g of 6% deactivated alumina and the analytes were eluted with 50 mL of dichloromethane. The dichloromethane fraction was then evaporated using a rotary evaporator until about 1 mL, and transferred into a 2 mL glass vial and dried under a gentle stream of nitrogen gas. After complete solvent evaporation, the analytes were reconstituted in 1 mL of methanol and 1 ng of TPhP-*d*<sub>15</sub> was added as a syringe standard, and analyzed by using ultra high performance liquid chromatography coupled with tandem mass spectrometry (UHPLC-MS/MS). Parallel to the samples, a blank was processed as described above for each batch of 7 house dust samples.

Seven BUVSs were identified and quantified using an UHPLC (UHPLC-XR, Shimadzu Corporation, Japan) coupled with an Applied Biosystems API 5500 electrospray triple-quadrupole mass spectrometer (ESI-MS/MS) (Applied Biosystems/MDS Sciex, Foster City, CA, USA). A 10 µL aliquot of the extract was injected onto a Asentis Express C<sub>18</sub> analytical column (2.7 µm, 100 × 2.1 mm; Supelco, Bellefonte, USA) with 0.1% (v/v) formic acid in Milli-Q water (A) and 10 mM ammonium acetate in methanol (B) at a flow rate of 0.2 mL/min. The gradient conditions in positive mode were as follows: (A) 80%, (B) 20% as initial conditions and held for 2 min, (A) 5%, (B) 95% at 3 min and held for 8 min, (A) 0%, (B) 100% at 9 min and held for 13 min. The MS/MS parameters optimized for individual analytes were given in our previous paper (Kim *et al.*, 2011).

## RESULTS AND DISCUSSION

### *BUVSs levels in house dust*

UV-234 was the predominant contaminant detected in this study followed by UV-326 > UV-328 > UV-327 > UV-320 (Fig. 1). These results indicate the ubiquitous contamination of BUVSs (except for UV-P and UV-9) in the Philippines house environment. Furthermore, higher concentration of UV-234 might be due to their high affinity to absorption on particles, large scale usage in the past and continuous release into the indoor environment. The presence of UV-P, UV-326, UV-327 and UV-328 in indoor dust was found in a private house, a public building and car cabin in Spain (Carpinteiro *et al.*, 2010). Generally, levels of BUVSs including UV-326, UV-327 and UV-328 in dust from the Philippines are comparable to or lower than those reported in Spain. Concentrations of UV-P in dust from private house in Spain was in the range of 77 ± 5–657 ± 27 ng/g, but not detected in the present study. Although the usage and production of this compound in the Philippines was unknown, these results indicate considerably low consumption of UV-P in this country. Furthermore, concentrations of UV-

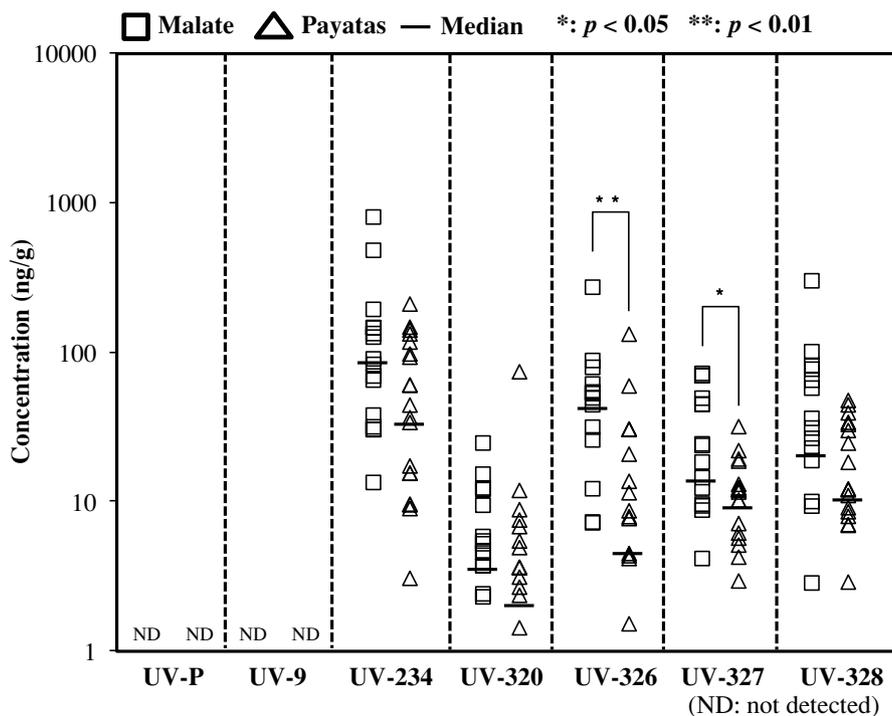


Fig. 1. Concentrations of benzotriazole UV stabilizers in house dust from Malate and Payatas in the Philippines.

327 and UV-328 in private house of Spain were ranged from  $22 \pm 1$  to  $101 \pm 13$  ng/g and from  $46 \pm 3$  to  $149 \pm 4$  ng/g, respectively. The relatively low levels of BUVSs in the present study as compared to Spain could be due to lesser usage of these compounds in the Philippines.

Associations between concentrations of BUVSs in house dust from Malate and Payatas were explored using Mann-Whitney U test. Concentrations of UV-326 and UV-327 were significantly higher in Malate than in Payatas ( $p < 0.05$ ). Higher concentrations of most of the BUVSs in Malate than in Payatas may be suggestive of differences in the specific applications of these compounds in Malate. Further information on the application patterns and/or rate of consumption of these compounds in household products is necessary to arrive a solid conclusion on their distribution.

Relationship between the BUVSs were shown in Fig. 2. Statistically significant correlations ( $p < 0.05$ ) were found between UV-234, and other two compounds, UV-327 and UV-328. The high correlation values observed among the BUVSs in house dust samples in the present study indicate that these compounds might have similar sources and exposure routes. Similarly, Nakata *et*

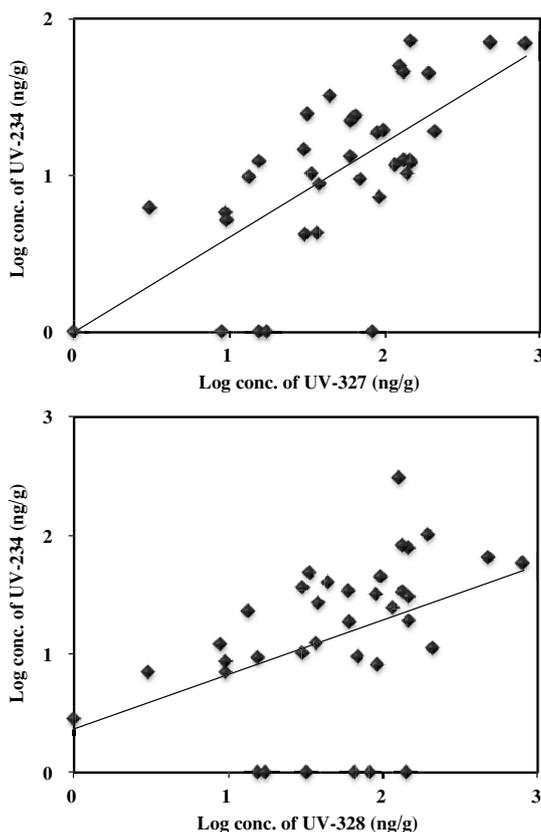


Fig. 2. Relationship among BUVSs in house dust samples from the Philippines.

*al.* (2009) observed good correlations between UV-326 and UV-327, UV-326 and UV-328, and UV-327 and UV-328 in sediment from the Ariake Sea, wherein a common source such as plastic materials was suggested.

#### *Human exposure to BUVSs via dust ingestion*

Ingestion of house dust could be an important pathway of human exposure, however, the primary route of human exposure to persistent BUVSs is still unclear. In this study, to determine the human health risk the measured concentration of BUVSs was used. The estimated exposure amounts were then divided by typical body weight of 60 kg for an adult and 15 kg for toddler (2–5 year old) (CDC, 2002). Klepeis *et al.* (2001) reported that a typical human activity pattern in home as 64% for adults and 86% for toddlers. Mean dust ingestion of 20 and 50 mg/day and high dust ingestion of 50 and 200 mg/day were used for adult and toddler, respectively. Furthermore, data on chronic effects such as no

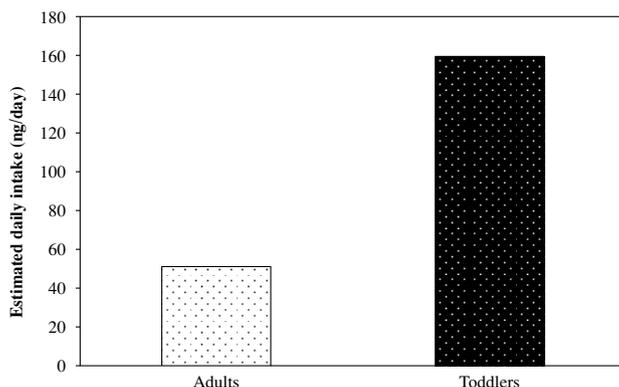


Fig. 3. Estimated daily intakes (ng/day) of BUVSs from house dust exposure pathway for adults and toddlers in Malate from the Philippines.

observed effect level (NOEL) values of UV-P (35 mg/kg/day for dog) and UV-328 (15 mg/kg/day for rat), with increased liver enzyme reported at higher dose levels (U.S. EPA, 2006) and no observed adverse effect level (NOAEL) value of UV-320 (0.1 mg/kg/day for male rat) (Hirata-Koizumi *et al.*, 2009) were used to estimate reference dose value (RfD). RfD of UV-P, UV-320 and UV-328 were calculated by dividing chronic NOEL or NOAEL by a safety factor of 10,000 as described in Van den Eede *et al.* (2011) to minimize the toxicological risks. The guideline values calculated from RfDs were: 210,000 ng/day for UV-P (U.S. EPA, 2006), 600 ng/day for UV-320 (Hirata-Koizumi *et al.*, 2009) and 90,000 ng/day for UV-328 (U.S. EPA, 2006). The calculated intakes of BUVSs were 2–4 orders of magnitude lower than guideline values. However, the estimated daily intakes (EDIs) of total BUVSs in Malate were 160 ng/day for toddlers and 51 ng/day for adults when high dust ingestion were applied (Fig. 3). This result implies that toddlers may be at higher risk of exposure to BUVSs compared to adults, considering their sensitivity to potential human health effect during the developmental stage.

### CONCLUSIONS

This is the first report of BUVSs in house dust in the Philippines. The results clearly showed that BUVSs are ubiquitously found in the home environments of these two study sites in the Philippines. Remarkably high concentrations of BUVSs, particularly UV-234 were found in the Philippines at higher frequency. The estimates of the Philippines resident's exposure to BUVSs via dust ingestion were found to be below the guideline values (ranging from 600 to 210,000 ng/day for adults and from 150 to 52,500 ng/day for toddlers). However, intake of total BUVSs by toddler was 5 times higher than adults, suggesting potential risk for toddlers if those BUVSs are continuously used in household products.

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