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Field dissipation and plant uptake of benzotriazole ultraviolet stabilizers in biosolid-amended soils†

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Benzotriazole ultraviolet stabilizers (BUVSs) have been commonly used in industrial and household product formulations, and have been detected in biosolids from wastewater treatment plants. However, little is known about their occurrence and dissipation behavior in the soil environment associated with biosolid application. This study investigated the occurrence and dissipation of five typical BUVSs (UV-326, UV-327, UV-328, UV-329 and UV-P) in biosolid-amended soils, and the uptake of these biocides by plants. The field trial includes two treatment groups: old groups with biosolid application at rates of 5, 10, 20 and 40 t ha^{-1} every year within 5 years, and new groups with only one biosolid application. The results showed that the five BUVSs could be detected in most biosolid-amended soils at a few to tens of ng g^{-1} levels, but not detected in the control soils. These chemicals were not found in the crop plants collected from the trial plots. Moreover, high biosolid application rates and repeated biosolid applications resulted in high accumulation of these BUVSs in soil. During one year monitoring, the five BUVSs were significantly dissipated in the biosolid-amended soils with their half-lives ranging from 79 to 223 days, which were comparable with the modeling results. The results from this study demonstrated the persistence of BUVSs in soil environments with quite slow dissipation rates.

Environmental impact

Benzotriazole ultraviolet stabilizers (BUVSs) are widely used as additives in paints, coatings, adhesives, polymeric surfaces, food packing films and construction materials. They have been detected in biosolids from wastewater treatment plants. With application of biosolid to agricultural land, these chemicals may contaminate the agricultural soils and thus affecting the terrestrial ecosystem and human health. BUVSs (UV-326, UV-327, UV-328, UV-329 and UV-P) could be detected in the biosolid-amended soils at a few to tens of ng g^{-1} levels. This one year monitoring study demonstrated slow dissipation of the BUVSs in soil environments.

Introduction

Benzotriazole ultraviolet stabilizers (BUVSs), which have a phenolic group attached to the benzotriazole structure, have excellent absorption capacity with a full spectrum of UV stabilizers.[1] BUVSs are widely used as additives in paints, coatings, adhesives, polymeric surfaces, food packing films and construction materials in order to improve the stability of industrial products and to prevent light-induced degradation reactions and yellowing due to ultraviolet radiation from sunlight.[2–4] In contrast to polar benzotriazole species, their phenolic derivatives show a medium to extremely high hydrophobic character, and thus potential to be accumulated in solid environmental matrices and even to be magnified through the food chain.[5] Recent studies have demonstrated the accumulation and persistence of several BUVSs such as UV-326, UV-327, UV-328, UV-329 and UV-P in sediments[6,7] and fish.[6,8,9] From the limited acute toxicity data available in the literature, except for dermatitis and skin irritation problems reported,[10] BUVSs have relatively low acute toxicity.[11] However, due to their significant bioaccumulative characteristics, BUVSs have potential toxic effects on biota.[12] A gender-related difference in the toxicity of UV-327 was observed in neonatal rats, which was markedly reduced by castration and absent in preweanling rats.[13] This *in vivo* study suggests that UV-327 is likely to be linked to alterations in sex hormones,[14] although these compounds did not exhibit estrogenic activities in *in vitro* studies.[13] Because of their wide presence and potential toxic impact, BUVSs have been considered as emerging contaminants.

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Most of the BUVSs were hydrophobic substances; therefore these compounds would adsorb onto sludge in wastewater treatment plants (WWTPs), as with other UV filters.[15,16] For example, UV-326 and UV-329 were detected at 88 ± 12 ng g^{-1} and 27 ± 0.1 ng g^{-1} in the biosolids of WWTPs, respectively.[17] The application of biosolids as fertilizers to agricultural land was one pathway for these chemicals to enter the environment, which may pose a potential risk to the soil ecosystem. The residue, dissipation and plant uptake of various contaminants in biosolid-amended soils have received increasing attention in recent years.[18–20] However, information about BUVSs in biosolid-amended soil is very limited.

The aims of this study were to examine the occurrence and fate of five typical BUVSs (UV-326, UV-327, UV-328, UV-329, and UV-P) in biosolid-amended soils. The field trials were performed in Shandong province, China with two different treatment groups: repeated biosolid applications every year (old group: OT); and one biosolid application (new group: NT). Following biosolid application at different rates, soils and grain crops grown in the treated plots as well as control plots with no biosolid application (CK) were collected for the assessment of contamination and dissipation of these three biocides.

Materials and methods

Chemicals and materials

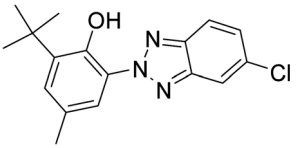
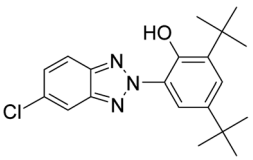
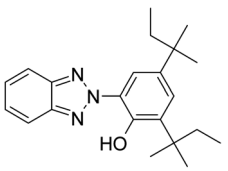
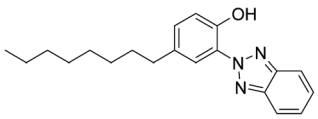
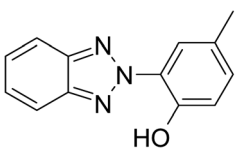
The standards of target compounds 2-(3-*t*-butyl-2-hydroxy-5-methylphenyl)-5-chlorobenzotriazole (UV-326, 98% purity), 2-(2′-hydroxy-3′,5′-di-*tert*-butylphenyl)-5-chlorobenzotriazole (UV-327, 98% purity), 2-(2-hydroxy-3,5-dipenryl-phenyl) benzotriazole (UV-328, 98% purity), 2-(2′-hydroxy-5′-octylphenyl) benzotriazole (UV-329, 98% purity) and (2′-hydroxy-5mg-methylphenyl) benzotriazole (UV-P, 99% purity) were purchased from J & K Chemical (Guangzhou, China). An internal standard chrysene-d12 (IS, 100%) and a surrogate standard benzyl cinnamate (SS, 99%) were obtained from Supelco (Bellefonte, USA) and Acros Organics (New Jersey, USA). The physicochemical properties of the target compounds are shown in Table 1. HPLC-grade methanol (MeOH) and dichloromethane (DCM) were purchased from Merck (Darmstadt, Germany) and CNW Technologies (Dusseldorf, Germany). Cellulose filters (30 mm) were purchased from Dionex (Sunnyvale, USA). Silica gel (80–100 mesh, Haiyang Chemical, Qingdao, China) and quartz sand (Qiangsheng Chemical, Suzhou, China) were successively hand-washed with methanol and dichloromethane each three times, and baked at 400 °C for four hours prior to use. Stock solutions (100 mg L^{-1}) of UV-326, UV-327, UV-328, UV-329, UV-P, chrysene-d12 and benzyl cinnamate were prepared in DCM and stored at −18 °C until use. Working standard solutions (1.0 mg L^{-1}) were prepared weekly. All glassware was hand-washed with tap water, rinsed with Milli-Q water and baked at 400 °C for at least 4 hours before use.

Field trials

Field trials of biosolid application on agricultural land were carried out in fluvo-aquic soil in the Dezhou Experimental Station, Chinese Academy of Agricultural Sciences (37° 20′ N, 116° 38′ E) located in Shandong, China. The biosolid (dewatered sludge) used in the trials was collected in May 2006 from the Beijing centralized sludge treatment plant, which treats 70% of sludge from domestic WWTPs in Beijing. Meanwhile, the dried biosolid was stockpiled in a warehouse before use and the same well-mixed biosolid was always applied in each treatment mentioned in this study. Biosolid samples were collected every year and stored in a fridge for chemical analysis. The field trial setup includes two treatment groups: an old group and a new group (Table 2). The old group includes six treatments: control with no biosolid application (CK1), control with 0.09 t ha^{-1} urea but no biosolid application (CK2), and treatments (OT1, OT2, OT3 and OT4) with repeated application of the biosolid at rates of 5, 10, 20 and 40 t ha^{-1} and with the same urea application rate of 0.09 t ha^{-1} every year. Each treatment of the old group had three replicate plots (8 × 5 m, each). For the old group, the biosolid was first applied on the 5th of October 2006, and then re-applied with the same rates on the 5th of October every year for 5 consecutive years. The new group includes four treatments: control with no biosolid application (CK3) and treatments (NT2, NT3 and NT4) with one biosolid application at rates of 10, 20 and 40 t ha^{-1}, respectively, on the 5th of October 2010. Each treatment of the new group had two replicate plots (2 × 2 m, each). In each treated plot, the biosolid was spread randomly over the fields and then mixed well using a hoe with the soil of 0–20 cm depth immediately following application. During the trials, the crops including wheat (*Triticum aestivum Linn*, October to next June) and corn (*Zea mays*, June to September) were planted in both old and new treatment plots. Only biosolid and urea were applied without any other organic material application. The flood irrigation was applied to the crops.

The field trials started in October 2006, but sampling campaign for organic contaminants was only conducted from the beginning of October 2010 to October 2011. Initial field trials paid attention to inorganic contaminants in the biosolid-amended soils.[20] Soil samples were collected in 1 L glass jars from each field plot at the depth of 0–20 cm from five points in each plot and then combined into one composite sample. First sampling was performed in Shandong on October 5th, 2010 before the re-application of the biosolid to the old group and after the first application of the biosolid to the new group, respectively. Moreover, the soil samples were sampled consecutively on the 5th of every month till October 2011. However, due to the frost period in Shandong, no soil samples were collected in January and February 2011. The collected soil samples and biosolid samples were freeze-dried, then sieved through a 0.90 mm mesh standard screen and then stored in the dark at 4 °C prior to extraction. In order to investigate the potential bioaccumulation of the BUVSs in crops, plant samples were collected from each new treatment plot during harvesting periods in June, 2011 for wheat and September, 2011 for corn. Wheat plant samples were divided into wheat grain and wheat stalk, while corn plant samples were separated into three parts: corn, corn stalk and corn cob. The collected plant samples were air-dried, then ground separately using a stainless steel grinder to pass through a 0.90 mm mesh sieve, and stored in the dark at 4 °C before extraction.

Table 1 Physicochemical properties of BUVSs in this study

		Properties[a]					
Compound	CAS number	Molecular formula	M_W[b]	K_{oc}[c] (L kg^{-1})	pK_a	pK_{ow}	Structure
2-(3-*t*-Butyl-2-hydroxy-5-methylphenyl)-5-chlorobenzotriazole (UV-326)	3896-11-5	$C_{17}H_{18}ClN_3O$	315.5	3.9×10^4	9.5	5.55	
2-(2′-Hydroxy-3′,5′-di-*tert*-butylphenyl)-5-chlorobenzotriazole (UV-327)	3864-99-1	$C_{20}H_{24}ClN_3O$	357.89	9.7×10^4	NA[d]	6.91	
2-(2-Hydroxy-3,5-dipenryl-phenyl) benzotriazole (UV-328)	25973-55-1	$C_{22}H_{29}N_{3O}$	351.5	1.5×10^5	NA	7.25	
2-(2′-Hydroxy-5′-octylphenyl)-benzotriazole (UV-329)	3147-75-9	$C_{20}H_{25}N_3O$	323	1.1×10^5	NA	6.21	
(2′-Hydroxy-5mg-methylphenyl) benzotriazole (UV-P)	2440-22-4	$C_{13}H_{11}N_3O$	225.25	3539	NA	4.31	

[a] Source: http://www.syrres.com/what-we-do//databaseforms.aspx?id=386; EPI suite, US EPA. [b] M_W, molecular weight. [c] Estimated by using EPIWEB 4.0 (KOCWIN), US EPA. [d] NA, not available.

The site information including soil properties and application rates is given in Table 2. The soil type and soil texture was fluvo-aquic soil and clay loam, with a field moisture capacity of 23%. The average annual temperature was 12.9 °C, while the average annual rainfall was 522 mm. Soil pH was measured with 0.01 M $CaCl_2$ (soil to solution ratio of 1 : 5) using a pH meter. Soil organic carbon was determined using a LECO carbon and nitrogen analyzer, while soil particle size distribution was analyzed by using the pipette method.[21]

Table 2 Information of the field trial sites and treatments

Group	Treatment	pH[a]	Soil organic carbon (%)	Clay (<0.002 mm) (%)	Biosolid application (t ha^{-1})	Urea application (t ha^{-1})
Old group	CK1	7.7 ± 0.1	0.67 ± 0.01	23.6 ± 11.3	0	0
	CK2	7.5 ± 0.1	0.68 ± 0.04	16.5 ± 3.6	0	0.09
	OT1	7.7 ± 0.0	0.78 ± 0.09	23.3 ± 2.3	5 every year	0.09
	OT2	7.7 ± 0.1	0.78 ± 0.08	30.9 ± 2.4	10 every year	0.09
	OT3	7.7 ± 0.1	0.93 ± 0.06	28.6 ± 2.8	20 every year	0.09
	OT4	7.6 ± 0.1	1.35 ± 0.18	28.2 ± 0.2	40 every year	0.09
New group	CK3	7.7 ± 0.0	0.74 ± 0.07	31.8 ± 14.2	0	0
	NT2	7.6 ± 0.1	0.81 ± 0.21	19.8 ± 3.0	10 once	0
	NT3	7.6 ± 0.0	0.93 ± 0.04	20.7 ± 2.4	20 once	0
	NT4	7.7 ± 0.1	0.70 ± 0.20	17.9 ± 0.9	40 once	0

[a] Mean ± standard deviation ($n = 3$ for the old group and $n = 2$ for the new group). All the pH, soil organic carbon and clay content values were detected in the samples collected in October 2010.

Chemical analysis

Freeze-dried solid samples (5.0 g for each soil sample; 1.0 g for each sludge sample mixed with 4.0 g quartz sand; and 2.0 g for each plant sample) were extracted using a pressurized liquid extractor (ASE 300 accelerated solvent extraction system, Dionex, Sunnyvale, CA, USA), equipped with 34 mL capacity stainless-steel cells. A cellulose filter was placed at the bottom of each stainless-steel cell followed by 2.0 g silica gel as an in-cell clean-up sorbent. After loading the samples individually, 100 μL 1 mg L^{-1} surrogate standard solution (benzyl cinnamate) was added. Then 5.0 g quartz sand was added, and another cellulose filter was placed on the top finally. Methanol–dichloromethane (50 : 50, v/v) was used as the extraction solvent, while the extraction temperature was 120 °C, and extraction time was 5 min with 2 cycles. Each extract was evaporated to dryness under a rotary evaporator (Buchi, Sweden), re-dissolved in 1 mL methanol, and then filtered through a 0.22 μm membrane filter (Anpel, Shanghai, China) into a 2 mL amber glass vial (Agilent, USA). For analysis by gas chromatography-mass spectrometry (GC-MS), 100 μL of the final extract was put into a 250 μL glass insert (Agilent, USA), solvent exchanged into 100 μL of dichloromethane spiked with 10 ng of internal standard (chrysene-d12).

Determination of the five target compounds was performed by gas chromatography-mass spectrometry (GC-MS, Agilent 6890N/5975B). The target compounds were separated on an Agilent DB-5MS column (30.0 m × 250 μm, 0.25 μm thickness) with helium as carrier gas at a flow rate of 1.0 mL min^{-1}. The GC oven temperature was programmed from 80 °C (hold 1 min) to 230 °C (25 °C min^{-1}, hold 1 min), then increased to 260 °C (15 °C min^{-1}, hold 1 min) and finally increased to 310 °C (20 °C min^{-1}, hold 8 min). Post run was performed for 8 min at 300 °C. The injection port, ionization source, mass analyzer, and transfer line temperatures were set at 280, 250, 150 and 280 °C, respectively. The injection volume was 2.0 μL. The injection was performed in splitless mode, and the splitless time and split flow were set at 1 min and 100 mL min^{-1}. The mass spectrometer was operated in electron impact (EI) mode at 70 eV and in the selected ion mode (SIM) for quantification purposes. The retention times and ions monitored for each compound are summarized in Table S1 (ESI†).

Quality control

The target compounds were identified by comparing the retention times and the ratios of three selected ions with those of the standards. Quantification of the target compounds was obtained using the internal standard method. The recoveries, matrix effects, limits of detection (LODs) and limits of quantitation (LOQs) are given in Table S2.† The recoveries of the five target compounds ranged between 80.1% and 117% in soil, between 70.9% and 112% in the biosolid, and between 71.4% and 97.0% in plants, respectively. The LOQs of most targets for soil samples were lower than 1 ng g^{-1}, and the highest LOQ was 1.23 ng g^{-1} for UV-P. The LOQs of the five target compounds ranged between 3.76 ng g^{-1} and 11.6 ng g^{-1} for biosolid samples, and between 1.34 ng g^{-1} and 5.59 ng g^{-1} for plant samples.

All data obtained from the analysis were subject to strict quality control procedures. For each batch of samples to be analyzed, a solvent blank, a standard solution (100 μg L^{-1}) and a method blank were run in sequence to check for background contamination and instrument performance. The recoveries of the surrogate standard benzyl cinnamate in all samples ranged between 77.6% and 133%.

Data analysis

Statistical analysis and dynamic curve fitting were performed using the software SPSS 19.0 and Sigma Plot 10.0, respectively. One-way ANOVA and Duncan's multiple range tests were performed to determine significant differences ($p < 0.05$) among the concentration data of the target compounds in different treatments of the old group and the new group respectively. Linear regression analysis was performed to determine the relationships between the BUVS concentrations and soil organic carbon (%) of soil samples in the trials. Prior to all nonlinear regression fitting, the concentration data were converted to normalized concentration as a ratio of the initial concentration (C/C_0). C_0 represented the average concentration of each compound in the biosolid-amended soils in October 2010. A standard first-order exponential decay model (eqn (1)) was applied to fit the concentration data (C/C_0) and the time t (days). The time to dissipate 50% of a chemical (DT50) (half-life, days) was calculated by eqn (2).

$$C = C_0 e^{-kt} \quad (1)$$

$$\mathrm{DT50} = (\ln 2)/k \quad (2)$$

where k is the first-order rate constant ($month^{-1}$).

Results and discussion

Occurrence of BUVSs in the biosolid and biosolid-amended soils

Five target compounds had been detected in the biosolid applied to the field. In the biosolid, UV-329 had the highest concentration of 389 ± 13.7 ng g^{-1}, followed by UV-328 and UV-P with concentrations of 108 ± 2.6 ng g^{-1} and 102 ± 1.5 ng g^{-1}, and the lowest concentrations were found for UV-326 and UV-327 at 47.0 ± 0.2 ng g^{-1} and 28.3 ± 1.2 ng g^{-1}, respectively. Due to the hydrophobicity of BUVSs, the target compounds tended to adsorb onto sludge during the wastewater treatment processes in WWTPs. In fact, these BUVSs have been reported to be detected in the biosolid (or sludge) in the present study and previous studies, meanwhile the usage of UV-P, UV-329, UV-326 and UV-328 was considered to be extensive in China due to their high detection rates in sludge samples.[16,17]

The concentrations of BUVSs in biosolid-amended soil samples collected from the trial fields in Shandong are summarized in Tables S3 and S4.† The five target compounds were detected in all biosolid-amended plots (OT1, OT2, OT3, OT4, NT2, NT3 and NT4), but they were not found in the soils of

control plots without biosolid application (CK1, CK2 and CK3). This result suggests that the target compounds detected in the soils of biosolid applied plots originated from biosolid application. Most of the target compounds were found in the biosolid-amended soils at a few to tens of ng g^{-1} levels, except for UV-329 with the concentrations of 108 ± 12.9 ng g^{-1} in December 2010 and 166 ± 9.1 ng g^{-1} in April 2011. The concentrations of different treatments were markedly different. Comparing the concentration data of each treatment in October 2011, it was found that UV-329 showed significantly higher concentrations than the other BUVSs for each treatment, with the following decreasing order: UV-329 > UV-328 > UV-P > UV-327 > UV-326. For each compound, the concentrations in plot soils were generally in the following decreasing trend: OT4, OT3, OT2 and OT1 for the old group; NT4, NT3 and NT2 for the new group. This is consistent with the biosolid application rates in both old group and new groups. For the treatments with the same biosolid application rates, the concentrations of the target compounds in the soils with repeated biosolid applications (old group) were higher than those in the soils with only single biosolid application (new group) (OT2 > NT2, OT3 > NT3 and OT4 >NT4). These results suggest that chemical residues in the soils of the old treatment group were accumulated from previous applications. Moreover, high biosolid application rates and repeated biosolid applications resulted in higher accumulation of these BUVSs in soil. It is clear that biosolid application on agricultural land is a pollution pathway for BUVSs to the terrestrial environment.

Due to their hydrophobic properties, BUVSs have a tendency to adsorb onto the solid phase; meanwhile the properties of soils and sludge would influence the distribution of organic contaminants. In fact, previous studies showed significant linear correlations between the concentrations of BUVSs (UV-328, UV-329 and UV-P) and soil organic carbon in the sludge samples.[16] In the present study, the five BUVSs also showed strong significant correlations with soil organic carbon of the biosolid-amended soils ($R^2 = 0.6372–0.7859$, $p < 0.0001$) (Fig. 1). This implies that soil organic matter can influence the fate of BUVSs in the terrestrial environment.

Field dissipation of BUVSs in biosolid-amended soils

The dissipation of five BUVSs (UV-326, UV-327, UV-328, UV-329 and UV-P) in the biosolid-amended soils was assessed for the old group (OT1, OT2, OT3 and OT4) and the new group (NT2, NT3 and NT4) from October 2010 to October 2011 (Fig. 2, 3 and S1–S5†). For all treatments of both the old group and the new group, considerable variations in their concentrations were observed during the one year monitoring period, with the concentrations of each compound being found increasing slightly from October 2010 to March 2011 and then decreasing from March 2011 to October 2011. This phenomenon has been observed in previous studies.[19,22] Besides the difficulties in getting homogeneous samples, this phenomenon might also be partly due to the rapid carbon turnover and release of the five relatively hydrophobic target compounds from sludge. Therefore, dynamic curve fitting was performed for the concentration data obtained for the period of March 2011 to October 2011. Significant dissipation ($p < 0.05$) was found for the five chemicals under each treatment of both the old group (OT1, OT2, OT3 and OT4) and the new group (NT2, NT3 and NT4). Based on the first-order reaction model, dissipation kinetic parameters for each chemical were obtained and are given in Table 3. The dissipation half-lives for UV-326, UV-327, UV-328, UV-329 and UV-P in the field trials were 81–135 days, 120–173 days, 99–223 days, 79–155 days and 85–157 days, respectively.

UV-326, UV-327, UV-328, UV-329 and UV-P are the derivatives of 2-hydroxyphenyl benzotriazole, and they have similar molecular structures which only differ by substituents (Table 1).

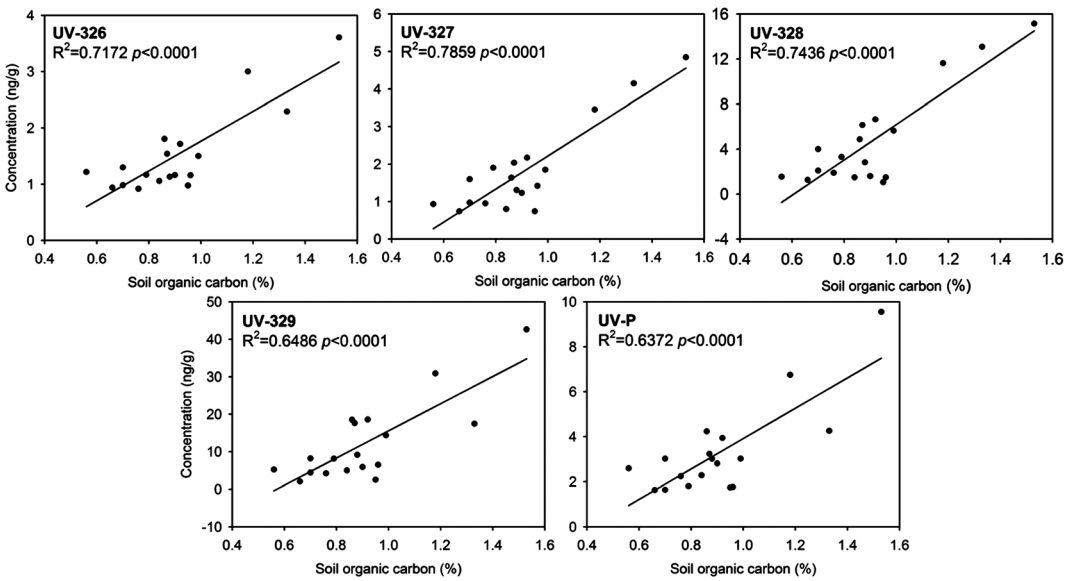


Fig. 1 Correlations between concentrations of UV-326, UV-327, UV-328, UV-329 and UV-P and soil organic carbon in the biosolid-amended soils from both old and new treatment groups in October 2010 ($n = 18$).

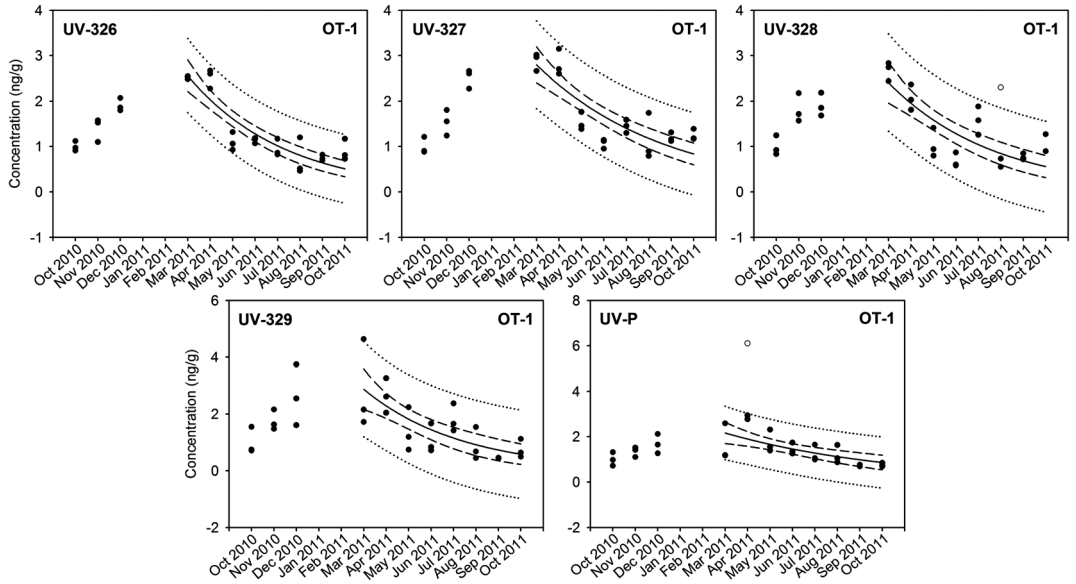


Fig. 2 Field dissipation of UV-326, UV-327, UV-328, UV-329 and UV-P in the biosolid-amended soils of OT1 within one year (October 2010 to October 2011). OT1: 5 t ha^{-1} of biosolid applied to the plots every year since first application in October 2006. Data points with empty symbols are treated as outliers during data fitting since the points are not included between the two 95% prediction bands. The nonlinear regression fits for the first-order kinetic model, 95% confidence band and 95% prediction band are represented by the solid line, dashed line and dotted line, respectively.

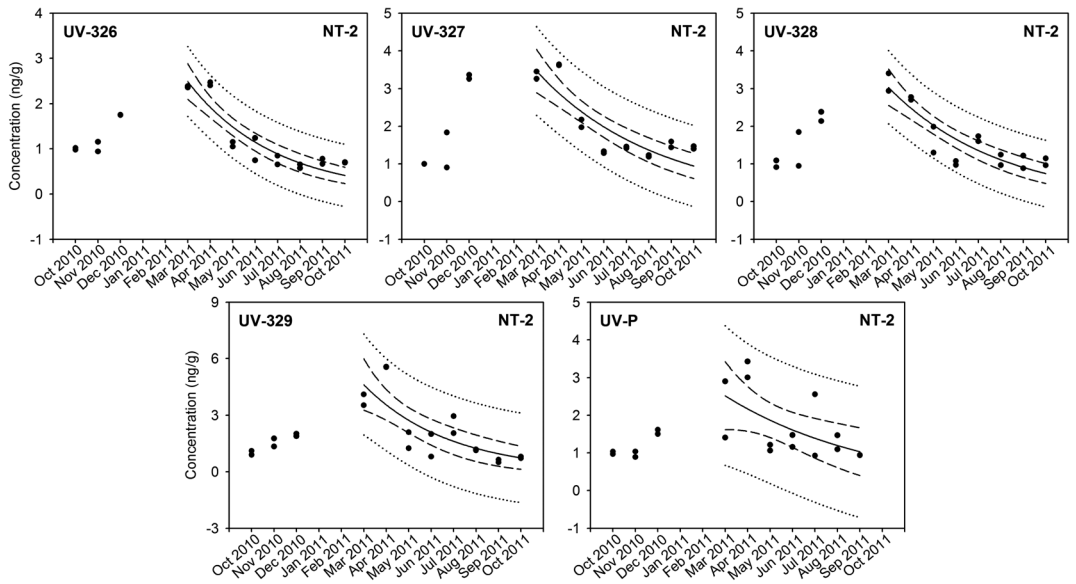


Fig. 3 Field dissipation of UV-326, UV-327, UV-328, UV-329 and UV-P in the biosolid-amended soils of NT2 within one year (October 2010 to October 2011). NT2: 10 t ha^{-1} of biosolid applied once in October 2010.

Their hydrophobic properties, transport behaviors and dissipation potential may be quite similar. The similar dissipation half-lives of these five compounds observed in the present study proved the above-mentioned prediction. Ruan *et al.*[16] had applied the US EPA EPI Suite V4.1, the University of Minnesota Pathway Prediction System (UM-PPS), and OECD overall persistence and long-range transport potential fugacity screening tool (Pov-LRTP tool) respectively to predict potential transformation pathways and total persistency of the these BUVS compounds in a multimedia evaluative environment. The predicted half-lives of the five BUVSs (UV-326, UV-327, UV-328, UV-329 and UV-P) in soil calculated by EPI Suite V4.1 ranged between 75 and 120 days, while those predicted by the Pov-LRTP tool ranged between 108 and 173 days (Table 4). These predicted results were generally comparable with those obtained from the field trials in the present study. UM-PPS is a well-established microbial catabolic reaction database that recognizes the substructure of a chemical and predicts transformation

Table 3 Summary of the dissipation information for the selected BUVSs in biosolid-amended soils based on the first-order model

Compound	Calculation	OT1	OT2	OT3	OT4	NT2	NT3	NT4
UV-326	Fitting formula	$Y = 10.2531 \times \exp(-0.2311 \times X)$	$Y = 7.7686 \times \exp(-0.2175 \times X)$	$Y = 6.0395 \times \exp(-0.1627 \times X)$	$Y = 5.8713 \times \exp(-0.1711 \times X)$	$Y = 11.6580 \times \exp(-0.2574 \times X)$	$Y = 6.2183 \times \exp(-0.1732 \times X)$	$Y = 6.8586 \times \exp(-0.1535 \times X)$
	R^{2a}	0.7777	0.6892	0.6459	0.6099	0.8343	0.8342	0.7065
	p-value[b]	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
	k (error)[c]	0.2311 (0.0288)	0.2175 (0.0345)	0.1627 (0.0271)	0.1711 (0.0321)	0.2574 (0.0349)	0.1732 (0.0225)	0.1535 (0.0284)
	DT50 (error)[d]	90 (11)	96 (16)	128 (22)	122 (24)	81 (11)	120 (16)	135 (26)
UV-327	Fitting formula	$Y = 7.8875 \times \exp(-0.1726 \times X)$	$Y = 5.9128 \times \exp(-0.1662 \times X)$	$Y = 5.0718 \times \exp(-0.1357 \times X)$	$Y = 4.0218 \times \exp(-0.1203 \times X)$	$Y = 10.5639 \times \exp(-0.1858 \times X)$	$Y = 4.2520 \times \exp(-0.1369 \times X)$	$Y = 7.7246 \times \exp(-0.1346 \times X)$
	R^2	0.6874	0.5994	0.5096	0.4276	0.7520	0.7147	0.7169
	p-value	<0.0001	<0.0001	0.0003	0.0010	<0.0001	<0.0001	<0.0001
	k (error)	0.1726 (0.0253)	0.1662 (0.0308)	0.1357 (0.0287)	0.1203 (0.0315)	0.1858 (0.0298)	0.1369 (0.0235)	0.1346 (0.0235)
	DT50 (error)	120 (18)	125 (24)	153 (34)	173 (49)	112 (18)	152 (27)	154 (28)
UV-328	Fitting formula	$Y = 8.4369 \times \exp(-0.2090 \times X)$	$Y = 5.7531 \times \exp(-0.1837 \times X)$	$Y = 3.5090 \times \exp(-0.1130 \times X)$	$Y = 3.5856 \times \exp(-0.1118 \times X)$	$Y = 10.1413 \times \exp(-0.2011 \times X)$	$Y = 6.2503 \times \exp(-0.1379 \times X)$	$Y = 5.9346 \times \exp(-0.0933 \times X)$
	R^2	0.6070	0.5066	0.3062	0.3325	0.7875	0.7266	0.4020
	p-value	<0.0001	0.0002	0.0093	0.0050	<0.0001	<0.0001	0.0111
	k (error)	0.2090 (0.0373)	0.1837 (0.0414)	0.1130 (0.0358)	0.1118 (0.0356)	0.2011 (0.0296)	0.1379 (0.0247)	0.0933 (0.0326)
	DT50 (error)	99 (18)	113 (22)	184 (65)	186 (66)	103 (16)	151 (28)	223 (89)
UV-329	Fitting formula	$Y = 11.3644 \times \exp(-0.2290 \times X)$	$Y = 10.0401 \times \exp(-0.2244 \times X)$	$Y = 10.3489 \times \exp(-0.2129 \times X)$	$Y = 13.8256 \times \exp(-0.2201 \times X)$	$Y = 22.4301 \times \exp(-0.2631 \times X)$	$Y = 10.3784 \times \exp(-0.1953 \times X)$	$Y = 12.8841 \times \exp(-0.1339 \times X)$
	R^2	0.5295	0.3266	0.5867	0.4071	0.6270	0.5803	0.3066
	p-value	<0.0001	0.0055	<0.0001	0.0014	0.0003	<0.0001	0.0261
	k (error)	0.2290 (0.0525)	0.2244 (0.0833)	0.2129 (0.0424)	0.2201 (0.0710)	0.2631 (0.0661)	0.1953 (0.0527)	0.1339 (0.0623)
	DT50 (error)	91 (22)	93 (40)	97 (20)	94 (34)	79 (21)	106 (31)	155 (92)
UV-P	Fitting formula	$Y = 4.7761 \times \exp(-0.1321 \times X)$	$Y = 12.7100 \times \exp(-0.2403 \times X)$	$Y = 9.2638 \times \exp(-0.1562 \times X)$	$Y = 16.1827 \times \exp(-0.2452 \times X)$	$Y = 6.1504 \times \exp(-0.1488 \times X)$	$Y = 10.0476 \times \exp(-0.2041 \times X)$	$Y = 15.3737 \times \exp(-0.2106 \times X)$
	R^2	0.4461	0.5704	0.3586	0.4930	0.3423	0.7455	0.5533
	p-value	0.0007	<0.0001	0.0032	0.0004	0.0280	<0.0001	0.0010
	k (error)	0.1321 (0.0346)	0.2403 (0.0527)	0.1562 (0.0488)	0.2452 (0.0657)	0.1488 (0.0629)	0.2041 (0.0387)	0.2106 (0.0593)
	DT50 (error)	157 (44)	87 (20)	101 (32)	85 (24)	149 (72)	102 (20)	99 (30)

[a] The correlation coefficient of the first-order reaction kinetic model. [b] Significance of the first-order reaction kinetic model. [c] Rate constant of the first-order reaction kinetic model. [d] The dissipation half-life (days) determined using the first-order reaction kinetic model under the treatments (OT1, OT2, OT3, OT4, NT2, NT3 and NT4). It should be noted that the time unit is month in the kinetic equation.

Table 4 Comparison of the predicted and measured half-lives of BUVSs in biosolid-amended soils

Compound		UV-326	UV-327	UV-328	UV-329	UV-P
Predicted	EPI Suite[a]	120	120	120	120	75
	Pov-LRTP tool[b]	173	173	173	173	108
Measured	OT1	90	120	99	91	157
	OT2	96	125	113	93	87
	OT3	128	153	184	97	101
	OT4	122	173	186	94	85
	NT2	81	112	103	79	149
	NT3	120	152	151	106	102
	NT4	135	154	223	155	99

[a] The half-lives of the five BUVSs in soil calculated by EPI Suite V4.1.[16] [b] The overall persistent half-lives predicted by the Pov-LRTP tool.[16]

products by matching biotransformation rules. The results predicted by UM-PPS showed that hydrolysis was the major reaction for the five BUVSs of the transformation, but different branched-chain substituents of the five BUVSs led to distinct plausible transformation pathways for each compound. In the present study, the five BUVSs displayed diverse dissipation behaviors in biosolid-amended soils at various application rates. For example, UV-329 had remarkably similar half-lives ranging from 91 to 97 days for the old treatments, while those for the new treatments half-lives increased (ranging from 79 to 155 days) with the increasing application rates. The results showed that the dissipation potential of UV-329 in repeated biosolid-amended soils was quite similar at various application rates, but for single biosolid application treatments, a higher application rate would slow the dissipation of UV-329. However, different results for UV-P were observed in the trials that higher application rates promoted the dissipation of UV-P approximately for both single biosolid application treatments (half-lives ranging from 85 to 157 days) and repeated application treatments (half-lives ranging from 99 to 147 days). For UV-326, UV-327 and UV-328, higher application rates significantly slowed the dissipation of these three compounds for both single and repeated application treatments while the results were opposite for UV-P. Similar dissipation behaviors of UV-326, UV-327 and UV-328 in biosolid-amended soils observed in the present study might be due to their similar molecular structures (Table 1). Being different from the compounds with one aliphatic substituent (UV-329 and UV-P), UV-326, UV-327 and UV-328 with two aliphatic branched-chain substituents at the phenolic group showed similar properties and degradation potential. However, other chemical mechanisms, such as planar-like configuration and adsorption, could also affect the field dissipation capability and further studies are needed to investigate degradation patterns of BUVSs.

Uptake of BUVSs in crop plants

None of the target BUVSs were found in the crop plant samples (wheat grain, wheat stalk, corn, corn stalk and corn cob) collected from the new treatment plots. This result showed that no plant uptake or bioaccumulation of the five BUVSs was found in the present study, although uptake of some organic contaminants such as PPCPs and veterinary medicines in various crop plants (carrot, lettuce and soybean) was observed in previous studies.[18,23] This could be explained by compound properties and experimental conditions such as the sludge application rate. In previous studies, biosolids were spiked with the mixed standard solution or applied at high rates, thus the concentrations of target compounds in soil were much higher than those in the present study.[18,23] Moreover, hydrophobic properties and soil sorption potential could also affect the plant uptake potential of these compounds. The research reported by Wu *et al.*[23] showed that increased sorption of ionized compounds will reduce their uptake potential. Therefore, the high K_{ow} and relatively strong sorption capability of BUVSs led to their limited uptake in plants. However, considering their persistence in soil environments, BUVSs might pose potential risks to soil organisms. Due to the limited terrestrial toxicological data of BUVSs, risk assessment could not be performed at the current stage. Therefore, further work is needed to explore the potential negative effects on soil organisms.

Conclusions

The results demonstrated the accumulation and persistence of the five BUVSs (UV-326, UV-327, UV-328, UV-329 and UV-P) in the biosolid-amended soils of the field trials. Moreover, repeated biosolid applications resulted in higher accumulation of these BUVSs in soil. One year monitoring showed significant dissipation of these five BUVSs in the biosolid-amended soils under both single and repeated biosolid treatments at various application rates, with their half-lives ranging from 79 to 223 days. Increased biosolid application rates would slow the dissipation of UV-326, UV-327 and UV-328 in both two treatment groups, which was different from the results obtained from UV-329 and UV-P. This phenomenon might be due their different chemical structures, which can affect their transformation pathways in the soil environment. Moreover, no uptake or bioaccumulation of the five BUVSs was found in the crop plants from the plots with biosolid application. This could be explained by their hydrophobic properties, soil sorption potential and experimental conditions. Therefore, no risks from these chemicals would be expected from consumption of these crop products from the biosolid applied plots.

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