Detection, Distribution and toxicological effects of benzotriazole UV stabilizers

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Abstract: Benzotriazole ultraviolet stabilizers (busvss) are a class of widely-used chemicals in industrial and personal care products for their absorptive capacity in the full spectrum of UV-light. Due to their high production volume, wide distribution, persistence, bioaccumulation, and potential toxic effects, this paper re-viewed the analytic method, environmental concentrations and toxicological effects of busvss. In addition, toxicological bioactivities are predicted, and the future of studies on busvss in aquatic topology are proposed.

Keywords: Busvss; environmental concentrations; toxicological effects; toxicological bioactivity

The become a new pollutants[1]. Benzotriazole class UV Stabilizer (Benzotriazole ultraviolet stabilizers busvss), benzotriazole of a class has good UV absorption ability of Derivatives (Absorbable 280-400 nm Spectral range in of ultraviolet) [2]. Often as an additive Breast milk, urine, and adipose tissue are also found. Busvss Check out. Meanwhile, research suggests Busvss Potentially endocrine disrupting Effect, which may affect the aromatic receptor pathway in fish and human, although Busvss However, long-term exposure still poses potential risks to human health and ecological environment. Therefore, in the summary Busvss On the basis of environmental distribution and pollution level Busvss Research Progress of Toxicology and typical Busvss In order to predict the biological activity Busvss Provide the theoretical basis and scientific basis for toxicity research and Risk Management.

1. Environment Busvss Level of pollution (Pollution Level of busvss in Environment)

1.1 busvss Analysis Method

In environmental samples, due to the complex matrix and other reasons, it is difficult to detect pollutants directly. Therefore, it is usually necessary to carry out proper pretreatment before the determination, so as to eliminate the influence of matrix as much as possible and improve the accuracy of analysis. Currently, build and optimize Busvss It is conducive to research and obtain more accurate data information, and better Busvss Pollution levels in the environment, Distribution Law, Ecological Risk and other aspects of better Land Assessment (Table 1).

1.1.1 Pretreatment Method

1.1.1.1 Solid Phase Extraction

Solid Phase Extraction (Solid-phase extraction, SPE) It is the most commonly used pretreatment method for treating
target compounds in water samples, including physical extraction process of liquid and solid phases, the adsorbent was washed out with appropriate solvent and the retained interfering substance was purified. Concentrated isolate. SPE The performance is affected by a large number of variables, so often according to the different target compounds and sample matrix from the extraction column, Elution solvent, Elution volume, PH, Extraction cycle was optimized to obtain high recovery rate and improve the sensitivity of the analysis. Liu Wait. In the Assay 4. Benzotriazole (Benzotriazole, BT) and 6. Ultraviolet Absorbent, Will SPE As a pretreatment method for groundwater and sewage, regulating water samples PH to 2., Use HLB Column Extraction of water samples, and Dichloromethane (V: V = 50:50) The target compounds were obtained by elution. 70%~150% And 82%~127% Recovery Rate.

Wang Jincheng In the determination of benzotriazole and benzothiazole derivatives in surface water Oasis HLB For solid phase extraction column, 10% Methanol aqueous solution as leaching solvent, 20% The methanol solution of acetone was the elution solvent and the sample volume was 200, Adjust PH to 3.0, Won 59.6%~98.7% Recovery Rate. SPE While the technology is widely used in the field of environmental analysis, there are still some shortcomings, such as increasing the loss during sample processing and the need for large samples. SPE The technology automates routine procedures, reduces sample loss during preprocessing, minimizes contamination, and improves repeatability of analysis.

1.1.1.2 Liquid-liquid extraction

Liquid-liquid extraction (Liquid-liquid extraction, LLE) It is a technology to separate and purify samples using different solubilities of various components in a liquid mixture in a certain solvent. In simple terms, the extractant is added to the sample solution, fully mixed, different components into different phases, so as to achieve the purpose of separation of the target. Nakata Wait. Based on LLE Extraction of sewage treatment plant into and out of water Busvss Extraction Using hexane, obtained 98%~115% Recovery Rate.

1.1.1.3 Micro-Extraction Technology

In recent years, micro-extraction technology is developing, because of its simple operation, More and more applications in the extraction and analysis of compounds. Solid Phase Microextraction (Solid-phase microextraction, SPME) Is SPE The micro-extraction technology is also used for the determination of water samples. Busvss. SPME Usually in Fiber Coating, PH, Sample temperature and sample mode are optimized to improve monitoring efficiency. SPE And SPME While extracting valid samples, there is only medium or even no organic solvent consumption. With SPE By contrast, SPME The technical procedure is simpler, the solution consumption is less, and the sensitivity is higher.

1.1.1.4 Stirring bar adsorption Extraction

Stirring bar adsorption Extraction (Stir bar selection extraction, Sb-Se) Yes Baltussen Wait. The relatively new pretreatment technology developed, Sb- Se Based on and SPME Same of principle but compared SPME Has higher of polydimethylsiloxane (Polydimethylsiloxane PDMS) Phase volume so have better of sample capacity and extraction effect [26]. SBSE Is cost relative low of extraction technology suitable for on-site sampling can in don't has complex equipment of laboratory implementation, Montesdeoca-esponda Such. From water samples in Extraction Busvss For polarity strong Busvss Recovery rate high (68.4%~92.2%) And the polarity weak recovery rate is low (18.3%~47.0%).

1.1.2 Analysis Methods

At this stage for different of Environment Medium Determination Busvss The using of Methods main have gas chromatography-Mass Spectrometry (Gas Chromatography Mass spectrometry GC-MS) Gas Chromatography-String The Mass Spectrometry (Gas chromatography-Tandem Mass spectrometry GC-MS/MS) Performance Liquid Chromatography-Series Mass Spectrometry (Liquid Chromatography-tandem mass spectrometry LC-MS/MS) And high performance liquid chromatography method (High-Performance Liquid Chromatography
HPLC) Such Chromatography and Mass Spectrometry of combined with can Make its respectively play efficient of separation ability and specific of differential ability, In analysis monitoring field plays a more and more important of Role.

1.1.2.1 Gas Chromatography-Mass Spectrometry

GC-MS Will gas chromatography and Mass Spectrometry Combined with can at the same time organic matter quantitative and qualitative of analysis has been widely used in different ring

Environment Matrix (Water, Air, Soil and) In pollutants of monitoring. Zhang Such.[9] In research sediment and sludge in Buvs When GC-MS Technology The monitoring detection limit 0.1–0.5 ng in G⁻¹ Recovery range in 82%–106%. Xue Jianping[37] With GC-MS Determination of textile in UV-3200f content detection limit up 0.05 ng in G⁻¹ Average recovery rate 90.3%–103.0%. Carpinteiro Such.[10] The SBSE And liquid desorption after Will samples a large number Injection GC-MS The analysis in ion monitoring (SIM) Mode Under determination sewage matrix in ⁴ Of Buvs Quantitative limit in 4–15 ng in L⁻¹ In the original sewage and processing after sewage respectively get 29.3%–90.7%, 24.6%–83.7% Of recovery rate.

1.1.2.2 High Performance Liquid Chromatography

HPLC Is Natural 20 Century 60 Age at the end of the classic performance liquid chromatography method for foundation in gas phase chromatography of theory and test methods to liquid as an mobile phase of Chromatography Technology. And gas chromatography method compared, HPLC With the use of a wide range of separation efficiency high mobile phase select range wide analysis speed and fast advantages at this stage has been widely applied to environment samples in Organic Pollutants of analysis.

Liu Wait.[5] Using automatic online Solid Phase Extraction and High Performance Liquid Chromatography-Tandem Mass Spectrometry (MS) Water samples collected from different sewage treatment plants and rivers were analyzed. UV-P, UV-329, UV-350, UV-234 And UV-328 This. Seed Bu-VSS Concentration up 37.1 ng · L⁻¹ And improved UV-328 And UV-Recovery Rate. And also Ruan Wait.[11] With HPLC-MS MSTechnology Sludge samples from municipal sewage treatment plants Buvs Conduct inspections Average 93% The detection limit is 0.15–0.77 ng · g⁻¹. The method is simple, practical and applicable to water samples. Buvs

Simultaneous Analysis and Monitoring.

Ultra Performance Liquid Chromatography (Ultra-high performance liquid chromatography, uhplc) Is by virtue HPLC The principle of loading Stationary Phases on a chromatographic column, Ultrahigh Pressure infusion pump and other aspects of the improvement, to achieve a more rapid, Chromatographic techniques with high separation and high sensitivity. Have research use Uhplc Combined with tandem mass spectrometry to monitor fish[14], Sewage Treatment Plant, sewage and seawater in coastal waters, Marine Deposition Things[26, 38-39] In Buvs.

1.2 In environmental media Buvs

UV-P UV-234 UV-320 UV-326 UV-327 UV-328 And UV-329 (Table2) Detection concentration Ng in L⁻¹ (Or Ng in G⁻¹ DW) Level. According to literature reports environment in is high concentration Bu-

VSS Main from sewage, Sludge and sediments in Buvs In sludge and sediments in detection rate was significantly higher than that of surface water some Buvs In sludge and sediments in concentration up to number of ten MuG In G⁻¹ DW (Table3). Compared under surface water in Buvs Detection rate low concentration in 2.3–307.7 ng in L⁻¹. Although Buvs Of water-soluble very low but by sewage emissions, Sediment Release and still constantly

Because Buvs High hydrophobicity (Log kow > 4.31, Table2) It is easier to adsorb to sludge and sediment in water environment. (Table3). Kameda Wait.[14] In an investigation into the waters of Saitama Prefecture, Japan Buvs Found in the sediment at the concentration UV-234 The average detectable concentration is 362.75 ng · g⁻¹ DW The concentration in the water is lower than the detection limit..

In addition, high concentrations of sediment are found in many waters. UV-328 This may be related UV-328 High usage and high Log kow (7.22) About. Sediment in narakansett Bay, Rhode Island, United States
China UV-328. The concentration is as high as 74,000 ng g\(^{-1}\)DW. Meanwhile, in sludge and sediment, UV-P, UV-326, UV-327, and UV-328 is the highest detection rate and high concentration of several Buvs. In the polluted water, the average concentration can reach thousands. Ng \(\cdot\) g\(^{-1}\) DW above (Table 3). Studies show that in Sediments UV-326, UV-327, and UV-328, there is a significant correlation between the concentrations [2, 4, 11]. It indicates that the source may be similar or similar to the Environmental Fate.

In the sewage, UV-P, UV-326, UV-327, and UV-328 is also the highest detection rate of several compounds concentration 2~85 ng in L\(^{-1}\) (Table 3). And UV-234 and UV-329 is in recent years environment especially in China's sewage samples in detection rate is high. Compounds. In Sewage Treatment Plant Sewage in Buvs Concentration low and in sludge

Buvs: The concentration is high. Ruan Such. [13] Collection The China 33 A city of Sewage Treatment Plant 60 A sludge sample almost all-like

This in detection UV-234 And UV-329 (59/60) Median concentration respectively 116 ng in G\(^{-1}\) DW And 66.8 ng in G\(^{-1}\) DW. Reported in Harbin a sewage treatment plant of sewage samples in UV-234 And UV-329 Of detection rate respectively 98% And 100%. Water average concentration 37.8 And 38.9 ng in L\(^{-1}\) And in sludge samples UV-234 And UV-329 Of detection rate are 100% And by different process processing after sludge in concentration respectively 297~303.4 And 130.6~166.8 ng in G\(^{-1}\) DW.

1.3 Organisms in Buvs

Because has height pro-fat, Buvs Easy to in biological in enrichment in recent years Buvs In marine invertebrates, Fish and birds and many kinds of biological in detection (Table 3).

UV-320 And UV-327 Of biological enrichment coefficient (Bioconcentration factor BCF) Relative is high carp in UV-320 Of Exposure under, BCF Value 1 380~10 000 And UV-320 Similar, UV-320 Of BCF Value 3 400~9 000. For Japanese ariake sea of finless porpoise (Finless porpoises neophocaena phocaenoides)

UV-327 Of BCF Value up to 33 300 Than same regional in the fish (3 250) High about a order of magnitude [32]. Based on different of exposure, UV-326 And UV-328 Of BCF Value relative low 54~2 700 [2]. Nakata Such. [2] Reports the in Japanese ariake sea of no spine dynamic

Of such as square clams, Oyster and gastropods in detection 0.30~80 ng in G\(^{-1}\) WW. In Philippines Manila Bay around market fish body in UV-328 UV-P UV-320 UV-234 Of detection rate respectively 88%, 86%, 79% And 55% Which UV-328 Of average concentration In ~1 [3].

Of 34.2 ng g LW In Asia-Pacific area and American coastal waters mussels samples in UV-326 UV-327 And UV-328 According to sampling points of different compounds concentration and a great of difference reflect Buvs Of Usage, Source and release way of difference [13]. UV-326 UV-327 And UV-328 Height pro-fat high trophic level species biological in cumulative mode similar this show that they In marine food chain in has is strong of persistent and biological accumulation

Recent have reports show that in human breast milk also have Buvs (UV-P UV-9 UV-320 UV-326 UV-327 UV-328, UV-329) The existence of total concentration range in<LOQ~2 172 (Median 64.7) ng in G\(^{-1}\) LW Cumulative mode and high trophic level species biological similar [17]. In addition Clothing Textile also may is human by skin contact exposure in harmful chemicals of way one is also by washing release to family wastewater in potential Environment Pollution Source. Avagyan Such. [15]

The retail market of clothing (26A sample) In Buvs The the research, 54% Of sample in containing UV-234 Concentration in2. 70~2.750 ng in G\(^{-1}\) LW Of samples in monitoring UV-P Concentration in 1.97~11.45 ng in G\(^{-1}\) UV-328 Only in 2A sample in was monitoring to concentration respectively 8.05 And 106 ng in G\(^{-1}\).

2. Buvs Of toxicity effect (Toxicological effects, BU-VSS)

2.1 Acute toxicity
With BUSS In environment and object in constantly was detected its potential of Health Effect and Ecological Toxicology effect caused by the widely of attention (Table 4). At present has been more a study reported the on benzotriazole and Its Derivatives of aquatic biological of acute toxicity study show that its acute In -1 . [43] Toxicity low Mg L Level Pillard And reported-BTFor reticulate (Ceriodaphnia Ceriodaphnia dubia) Of 48 h Half lethal concentration Relative-BTAnd other derivatives, BUSS In toxicology of information also few has been reported show that its acute toxicity low (Mg IN L -1 Level). In freshwater crustaceans animal of acute toxicity experiment In, UV-571 The flea-Daphnia (Daphnia pulex) Exposure 24 h and 48 Or LCS0 Respectively 6.35 And 2.59 mg in L -1 And other BUSS (UV-9 UV-234 UV-320 UV-326 UV-327 UV-328, UV-329 UV-360) Of 24 h and 48 h IC50 Were> 10 mg in -1 [46]. L At the same time have reported prove UV 329 The large Daphnia 24 h EC50 For 15 mg in L -1 (U. S. environmental protection A-gency) [47]. In addition study show that direct contact UV-P May will cause dermatitis and other skin stimulation Problem [48].

2.2 Chronic toxicity

Although BUSS Of acute toxicity low but study show that BU-VSS Has potential of chronic toxicity long-term exposure still may be the human. Health and ecological environment adverse influence.-BT With plant toxicity and the salmonella and Escherichia coli of has mutation (Health Council. Netherlands 2000) [49]. In long-term exposure under, -BT And 5-MeBi The aquatic plants and aquatic invertebrates breeding period and the toxicity and Growth Suppression [45]. In addition,-BT Can interference rare minnow Crucian Carp (Rare minnow gobiocypris rar us) Brain tissue of cells respiratory, Signal Conduction and cells apoptosis pathway has potential of neural Toxicity Effect [50]. At the same time by long-term exposure,-BT Can influence rare minnow crucian carp liver protein group of expression interference Oxidation stress, Apoptosis and translation and biological process and, due to the injury produce liver toxicity [51].

Compared-BT (log k ow = 1.44) BUSS Of pro-fat of stronger (Log k ow > 4.31) Are more likely to in biological in Accumulation. For example although UV-320 The flea-Daphnia of acute toxicity don't high (LC50 = 10 mg in -1 [46] - L) But rats UV 320 28 Days and 52 Weeks of long-term exposure liver, Kidney, Thyroid and spleen of Blood Index and organization pathology [52-53].

Were significant change and Its Toxicity Effect and gender related- [54-55] Hirata Koizumi And prove that this a kind of gender difference is due UV-320 Has liver peroxide of enzyme proliferation of activity by influence peroxidase body proliferation of activation Receptor (Peroxisome proliferator-activated receptor PPARα) Of expression on male and female individual produce different of Effect. UV-320 For its biological cumulative and toxicity in Japanese has been listed IClass Specified Chemical Material, 2007 Years was Japanese Government [32] , -1 -Government hans, in addition, male rats in 25 mg kg UV 327 After repeated dose exposure, the serum albumin and white blood cell ratio increased significantly, and the proportion of liver increased significantly, and there are reports UV-327 Sex-related toxicity differences can lead [57]. These may be related BUSS Effect of enzyme activity on proliferation in vivo.

Recently, studies have shown that BT And BUSS Islt has potential endocrine disrupting effect and has different BUSS The mechanism of toxicity is different. In vitro experiments (In vitro) China, Harris Wait [38] Report BT Has obvious anti-estrogen effect, while in vivo experiments (In vivo) China, BT Medaka of the ocean (Marine medaka, Oryzias melastigma-Ma) [58] And rare minnow Crucian Carp (Rare minnow, gobiocypris rarus) [60].

All showed estrogen interference effect; BT Cause marine medaka Vtg And Cyp 19 A Ji, Yin's table, Daxian, Shang, tune, at the same time, suppression, System CYP1A1 Expression [59]. In the exposure to rare minnow crucian carp, BT By interfering with the rare minnow Crucian Carp HPG Axis receptor pathway, affect the level of estrogen in the blood, produce endocrine Interference Effect on it, cause liver and gonad damage [60]. In addition, BUSS Activated aromatic hydrocarbon receptors in human and zebrafish (Aryl hydrogen receptor, AHR) Pathway, production [21-23].
Significant anti-androgen activity, however, is different. For example, research shows that Busvss significantly affect the expression of genes related to the thyroid pathway in zebrafish embryos. Busvss different modes of action. Zhuang et al. reported.8. Seed Busvss (BT, UV-P, UV-234, UV-326, UV-327, BT) In CYP3A4, the enzyme has anti-androgen activity in the presence. UV-328 Jin CYP3A4, anti-androgen activity was significantly improved after enzyme metabolism, while UV-P after metabolism, the anti-androgen activity is reduced.

3. Busvss prediction of biological activity (Bioactivity prediction of busvss)

To investigate the different structures Busvss, the toxic effect of using typical in environment Busvss (UV-P, UV-234, UV-326, UV-327, UV-329) predicted biological activity. Of the compounds, Canonical smiles input prediction procedure, we can get the corresponding biological activity prediction results. Results in the output Pa (probability "to be active") indicating the possibility of predicting the activity of the compound, Pi (probability "to be inactive") indicates the possibility that the predicted compound does not have this activity. Pa and Pi The potential biological activity of the corresponding compounds was obtained to predict.

The results show that UV-P and UV-329 there are many kinds of biological activity, Pa > 0.7. The predicted biological activity was 13. And 23. And the other Busvss Pa > 0.7. Predictive biological activity only 1-4. (Table 5). Compared to the predicted biological activity of the compounds, UV-P strong inhibition of aromatic transferase (Aspulvinone dimethylal-lyltransfer inhibitor), Alkyl monoxygenase inhibition (Alkane 1-monooxygenase inhibitor) and decarboxylase inhibition (Dehydro-L-gulonate decarboxylase inhibitor) activity (Delta > 0.8, Table 5). But UV-329 With strong inhibition of glycerol ether monoxygenase (Glycerol-ether monoxygenase inhibitor), Sugar transferase (Undecaprenyl-phosphate mannosyltransferase inhibitor) and Ubiquinone cytochrome C reductase inhibition (Ubiquinol-cytochrome-C reductase inhibitor) activity (Delta > 0.9, Table 5).

UV-234 outside, all Busvss All have Ubiquinone cytochrome C reductase inhibition (Ubiquinol-Cytochrome-C reductase inhibitor) activity (Table 5). The enzyme is an important component of the mitochondrial respiratory electron transport chain. This shows that Busvss In is very likely to act on mitochondria, inhibit mitochondrial respiration, and produce toxic effects.

4. Outlook (Future Prospects)

Busvss The toxicity data are still very limited. Busvss The toxicity may be different. Therefore, Busvss The study of toxic effects and toxic pathways is helpful to elucidate the mechanism of toxic effects on human and other organisms.

According to the results of the prediction, Busvss May act on mitochondria and produce toxic effects, but there is no relevant report, because

Further development of Busvss The study of mitochondrial function can provide a new perspective for exploring the toxic mode of such compounds.

Despite the current toxicity data and prediction shows Busvss May have toxic effects on humans and other organisms, but the current Busvss The potential ecological risk and health risk are still relatively small. Recently, Molins-Delgado Wait. Application risk Broker (Hazard quote, HQs) Towards the waters near Barcelona, Spain

BT And MEBT) Risk assessment, the results show that BT And MEBT HQs > 1 Water ecological environment has certain risks. Busvss Ecological Risk Research has not been reported yet..

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