

Detection, Distribution and toxicological effects of benzotriazole UV stabilizers

Lianjin Fang*

Inner Mongolia University, Hohhot

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)Is benzotriazole of a class has good UV absorption ability of Derivatives(Absorbable280~400 nmSpectral range in of ultraviolet)^[2]Often as an additive Breast milk, urine, and adipose tissue are also foundBusvssCheck out.Meanwhile, research suggestsBusvssPotentially endocrine disrupting

Effect, which may affect the aromatic receptor pathway in fish and human, althoughBusvssHowever, long-term exposure still poses potential risks to human health and ecological environment..Therefore, in the summaryBusvssOn the basis of environmental distribution and pollution level

BusvssResearch Progress of Toxicology and typicalBusvssIn order to predict the biological activityBusvssProvide theoretical basis and scientific basis for toxicity research and Risk Management.

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

1.1 busvssAnalysis 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 optimizeBusvssIt is conducive to research and obtain more accurate data information, and betterBusvssPollution levels in the environment,Distribution Law,Ecological Risk and other aspects of better

Land Assessment(Table1).

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

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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^[33]. 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.^[24] 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^[34] 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 59.8%~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^[27].

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.^[28] 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.^[29] 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.^[35] The relatively new pretreatment technology developed, Sbse 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

^[36]. 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.^[26] 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-MSWill 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.ZhangSuch.^[9]In research sediment and sludge inBuvssWhenGC-MSTechnology The monitoring detection limit0.1~0.5 ng in G⁻¹Recovery range in82%~106%.Xue Jianping^[37]WithGC-MSDetermination of textile inUV-320Of content detection limit up0.05 ng in G⁻¹Average recovery rate90.3%~103.0%.CarpinteiroSuch.^[6]TheSBSEAnd liquid desorption after Will samples a large number InjectionGC-MSThe analysis in ion monitoring(SIM)Mode Under determination sewage matrix in6OfBuvssQuantitative limit in4~15 ng in L⁻¹In the original sewage and processing after sewage respectively get29.3%~90.7%,24.6%~83.7%Of recovery rate.

1.1.2.2 High Performance Liquid Chromatography

HPLCIsNatural 20Century60Age 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,HPLCWith 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.

LiuWait.^[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-234AndUV-328This5.SeedBu-VSS, Concentration up37.1 ng · L⁻¹And improvedUV-328AndUV-Recovery Rate.And alsoRuanWait.^[11]WithHPLC-MS MSTechnology

Sludge samples from municipal sewage treatment plantsBusvssConduct inspections

Average93%The detection limit is0.15~0.77 ng · g⁻¹.The method is simple, practical and applicable to water samples.Busvss

Simultaneous Analysis and Monitoring.

Ultra Performance Liquid Chromatography(Ultra-high performance liquid chromatography, uhplc)Is by virtueHPLCThe 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 useUhplcCombined with tandem mass spectrometry to monitor fish^[14],Sewage Treatment Plant, sewage and seawater in coastal waters,Marine Deposition Things^[26, 38-39]InBusvss.

1.2 In environmental mediaBusvss

UV-P UV-234 UV-320 UV-326 UV-327 UV-328AndUV-329 (Table2)Detection concentrationNg in L⁻¹(OrNg in G⁻¹DW)Level.According to literature reports environment in is high concentrationBU-

VSSMain from sewage,Sludge and sediments in.BuvssIn sludge and sediments in detection rate was significantly higher than that of surface water someBuvssIn sludge and sediments in concentration up to number of tenMuG In G⁻¹DW (Table3).Compared under surface water inBuvssDetection rate low concentration in2.3~307.7 ng in L⁻¹.AlthoughBuvssOf water-soluble very low but by sewage emissions,Sediment Release and still constantly

BecauseBusvssHigh hydrophobicity(Logk_{ow}> 4.31, Table2)It is easier to adsorb to sludge and sediment in water environment.(Table3).KamedaWait.^[4]In an investigation into the waters of Saitama Prefecture, JapanBusvssFound in the sediment at the concentrationUV-234The average detectable concentration is362.75 ng · g⁻¹DWThe concentration in the water is lower than the detection limit..

In addition, high concentrations of sediment are found in many waters.UV-328This may be relatedUV-328High usage and highLogk_{ow}(7.22)About.Sediment in narakansett Bay, Rhode Island, United States

China UV-328 The concentration is as high as 74 000 ng/g DW. Meanwhile, in sludge and sediment, UV-P, UV-326, UV-327 and UV-328 are the highest detection rate and high concentration of several BUVSS. In the polluted water, the average concentration can reach thousands ng/g DW (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 are also the highest detection rate of several compounds concentration 2~85 ng/L (Table 3). And UV-234 and UV-329 are in recent years water environment especially in China's sewage samples in detection rate is high compounds. In sewage treatment plant sewage in BUVSS concentration low and in sludge

BUVSS The concentration is high. Ruan Such.^[11] Collection The China 33

A city of sewage treatment plant 60A sludge sample almost all-like

This in detection UV-234 and UV-329 (59/60) median concentration respectively 116 ng/g DW and 66.8 ng/g 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/L; 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/g DW.

1.3 Organisms in BUVSS

Because has height pro-fat, BUVSS easy to in biological in enrichment in recent years BUVSS. 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 exposure under, BCF value 1 380~10 000 and UV-320 similar, UV-

of BCF value 3 400~9 000^[2]. 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/g WW of BUVSS. 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 BUVSS 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 BUVSS (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/g 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 BUVSS the the research, 54% of sample in containing UV-234 concentration in 2. 70~2.750 ng/g¹ 31% of samples in monitoring UV-P concentration in 1.97~11.45 ng/g¹ UV-328 only in 2A sample in was monitoring to concentration respectively 8.05 and 106 ng/g¹.

2. BUVSS of toxicity effect (Toxicological effects. BU-VSS)

2.1 Acute toxicity

With Buvss 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. -BT For reticulate (Ceriodaphnia Ceriodaphnia dubia) Of 48 h Half lethal concentration Relative-BT And other derivatives, Buvss 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

Of LC_{50} Respectively 6.35 And 2.59 mg in L^{-1} And other Buvss (UV-9 UV-234 UV-320 UV-326 UV-327 UV-328,

UV-329 UV-360) Of 24 h And 48 h LC_{50} Were > 10 mg in -1 [46]

LA the same time have reported prove UV 329 The large Daphnia 24 h EC_{50} For 15 mg in L^{-1} (U. S. environmental protection A-gency)^[47]. In addition study show that direct contact UV-PMay will cause dermatitis and other skin stimulation Problem^[48].

2.2 Chronic toxicity

Although Buvss 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-MeBT Can 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 rarus) 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 ($\log K_{ow} = 1.44$) Buvss 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 ($LC_{50} > 10$ 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 PPAR α) Of expression on male and female individual produce different of Effect. UV-320 For its biological cumulative and toxicity in Japanese has been listed I Class Specified Chemical Material, 2007 Years was Japanese Government^[32]. , -1 -Government bans, 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.^[56] And there are reports UV-327 Sex-related toxicity differences can lead^[57], These may be related Busvss Effect of enzyme activity on proliferation in vivo.

Recently, studies have shown that, BT And Busvss It has potential endocrine disrupting effect and has different Busvss The mechanism of toxicity is different. In vitro experiments (In vitro) China, Harris Wait.^[58] Report BT Has obvious anti-estrogen effect, while in vivo experiments (In vivo) China, BT Medaka of the ocean (Marine medaka, Oryzias melastigma)^[59] And rare minnow Crucian Carp (Rare minnow, gobiocypris rarus)^[60]

All showed estrogen interference effect; BT Cause marine medaka Vtg And Cyp19a 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, Busvss Activated aromatic hydrocarbon receptors in human and zebrafish (Aryl hydrogen receptor, AHR) Pathway, production^[21-23].

Significant anti-androgen activity, howeverBusvssTheir biological activity is also different..For example,LiangWait.^[61]Research shows thatBusvssSignificantly affect the Expression of Genes Related to the thyroid pathway in zebrafish embryos.BusvssDifferent Modes of Action.ZhuangWait.^[23]Reported.8.SeedBusvss

(BT, UV-P, UV-234, UV-326, UV-327, BT)InCYP3A4The enzyme has anti-androgen activity in the presence,UV-328JingCYP3A4Anti-androgen activity was significantly improved after enzyme metabolism, whileUV-PAfter metabolism, the anti-androgen activity is reduced.

3. BusvssPrediction of Biological Activity (Bioactivity prediction of busvss)

To investigate the different structuresBusvssThe toxic effect of using Typical in EnvironmentBusvss (UV-P, UV-234, UV-320, UV-326, UV-327AndUV-329)Predicted BIOLOGICAL ACTIVITY.Of the compoundsCanonical smilesInputPassPrediction procedure, we can get the corresponding biological activity prediction results.^[62-63] Results In the outputPa (probability "to be AC tive ")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,PaValues andPiThe potential biological activity of the corresponding compounds was obtained to predict

The results show that,UV-PAndUV-329There are many kinds of biological activity,Pa> 0.7The predicted biological activity was13.And23.And the otherBusvss Pa> 0.7Predictive biological activity only1~4.I(Table5).Compared the predicted biological activity of the compounds,UV-PStrong inhibition of aromatic transferase(Aspulvinone dimethylal-lyltransfer inhibitor), Alkyl monooxygenase Inhibition(Alkane 1-monooxygenase inhibitor)And decarboxylase Inhibition(Dehydro-L-gulonate decarboxylase inhibitor)Activity(Delta> 0.8, Table5);ButUV-329With strong inhibition of glycerol ether monooxygenase(Glyceryl-ether monooxygenase inhibitor), Sugar transferase(Undecaprenyl-phosphate mannosyltransferase inhibi-tor)And Ubiquinone cytochromeCReductase Inhibition(Ubiquinol-cyto-chrome-C reductase inhibitor)Activity(Delta> 0.9, Table5).

UV-234Outside, allBusvssAll have Ubiquinone cytochromeCReductase Inhibition(Ubiquinol-Cytochrome-C reductase inhibitor)Activity(Table5)The enzyme is an important component of the mitochondrial respiratory electron transport chain.^[67]This shows thatBusvssIt is very likely to act on mitochondria, inhibit mitochondrial respiration, and produce toxic effects.

4. Outlook (Future Prospects)

BusvssThe toxicity data are still very limited.BusvssThe toxicity may be different. Therefore

BusvssThe Study of toxic effects and toxic pathways is helpful to elucidate the mechanism of toxic effects on human and other organisms..

AccordingPassThe results of the prediction,BusvssMay act on mitochondria and produce toxic effects, but there is no relevant report, because

Further DevelopmentBusvssThe Study of mitochondrial function can provide a new perspective for exploring the toxic mode of such compounds..

Despite the current toxicity data andPassPrediction shows

BusvssMay have toxic effects on humans and other organisms, but the currentBusvssThe potential ecological risk and health risk are still relatively small..RecentlyMolins-DelgadoWait.^[68]Application risk Broker(Hazard quote, HQs)Towards the waters near Barcelona, Spain

BTAndMEBT)Risk assessment, the results show thatBTAndMEBTOfHQs> 1Water ecological environment has certain risks.BusvssEcological Risk Research has not been reported yet..

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