

Pollution Status and Research Progress of Azole Fungicides in Environment

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Abstract

Because of its broad spectrum, low toxicity and high efficiency, azole fungicides are widely used in various types of agricultural production, personal care products, medicines and material surface protection, which inevitably makes them enter various environmental media through surface runoff, rainfall, atmospheric volatilization and farmland irrigation, posing potential threats to the surrounding environment and human health. In rural areas, fungicides sprayed on crops are usually difficult to play a full role, most of which tend to enter the surface by wet sedimentation and other ways, and then directly into the environment through surface runoff. It is well known that China has been a big agricultural producer since ancient times, and the annual application amount of pesticides is as high as 500,000-600,000 tons, ranking first in the world. As an important part of pesticide products, the annual sales of fungicides account for about 25% of the total sales of pesticides, which makes a large number of fungicides into the environment, causing pollution to the surrounding environment. In urban areas, the population density is large, and the large use of all kinds of personal care products makes a considerable part of fungicides enter the municipal pipe network with domestic sewage. At the same time, the fungicides used to protect the urban vegetation landscape will also flow into the municipal pipe network with rainfall and eventually enter the sewage treatment plant. At present, most of the sewage treatment process design, whether domestic or foreign, considers the removal of conventional organic matter, and the removal rate of trace organic matter such as fungicides is often very low, which makes the residual fungicides in sewage eventually return to the environment.

Keywords

Pollution; Azole Fungicides; Algae.

1. Pollution Situation

In foreign countries, there have been many reports on the residue of fungicides in different environmental media. In different countries and regions, the residual amount of fungicides will vary with the difference in the level of development, such as the more developed areas, the residual level of fungicides is often high. However, in the same environmental medium, the order of magnitude of fungicide residues is mostly the same, mostly ng/L level in surface water

and domestic sewage, and mostly ng/g level in sediments and sewage plant sludge. Berenzen et al. examined water samples of azole fungicides in rivers and ditches in northern Germany and found that the highest concentration was 9.1 µg/L. In addition, azole fungicides have also been detected in wastewater from Lyon, France, and Marburg, Germany, with average concentrations between 5.8-43.3 ng/L and 50 ng/L, respectively. De Rossi et al. also found the presence of azole fungicides in the detection process of pesticides and polycyclic aromatic hydrocarbons in rainfall in Trier, Germany. The detected concentration was 5-187 ng/L, with a detection rate of 34%.

In China, Chen et al. investigated fungicides in aquatic environments in highly urbanized areas and found that the highest concentration of azole fungicides in the water body of Dongjiang River Basin was 264 ng/L, and the highest concentration in the sediment was 159 ng/L. Huang et al. conducted sampling surveys of azole fungicides in the Guangzhou reach of the Pearl River and the Pearl River Delta in 2010 and 2013 respectively, and found that they were not detected in the water body of the Guangzhou reach of the Pearl River, but the concentrations of clotrimazole and miconazole were nd-22 ng/L and 1-35 ng/L respectively in the sediments. The highest concentration of fluconazole was 110 ng/L in water, and the highest concentration of miconazole was 76.9 ng/L in sediment. Peng et al. studied the residues of azole fungicides in different treatment processes of different sewage treatment plants in China, and the results showed that the residual amount of azole fungicides in the activated sludge method was 190-398 ng/L, while in the A20 process, the residual amount of azole fungicides in the sludge was 1258-2547 ng/L.

2. Research Progress

2.1. Research Status of Single Toxicity of Azole Fungicides

In an ecosystem, microorganisms, plants and animals often do not exist in isolation, but interact with their surroundings to form an inseparable whole. The use of azole fungicides can not only control the target organisms, but also have different degrees of influence on the surrounding biological communities. Storck et al. evaluated the effects of tibuconazole, an azole fungicide, on the diversity and composition of soil bacterial community through field experiments, and the results showed that Tibuconazole could significantly reduce the diversity of soil bacterial community. N.kamar et al. used zebrafish embryo as a model to compare the relative biotoxicity of three azole fungicides (pentazolol, propionocyclozole, and nitrazole). According to the results of molecular biomarkers, Zebrafish can induce cell apoptosis and lipid peroxidation at concentrations (0.3 and 1 µg/L). Mitochondrial respiration analysis showed that the respiratory capacity of zebrafish was slightly reduced after 48h acute exposure to three azole fungicides at 1000 µg/L concentration. Clotrimazole is widely used in medical treatment as a 14-demethylase inhibitory fungicide and has been identified as a priority pollutant in the Marine environment. Tobias Porsbring et al. collected microalgae communities and exposed them to a series of concentrations of clotrimazole for 4 days. The results showed that the production of 14-demethylase was inhibited at 50 pmol·L⁻¹, the total sterol content decreased to 64% of the control level at 500 pmol·L⁻¹, and the growth of algae community decreased significantly at 10100 nmol·L⁻¹ and higher. Gilles Monod et al. [48] took rainbow trout as the research subject and discussed the in vitro effects of three pesticide azole fungicides imidazole, fluocyclazole and statin on the maturation of oocytes of rainbow trout. The results showed that all three fungicides could significantly promote and enhance the induction of gonadotropin on oocyte maturation in a dose-dependent manner.

2.2. Research Status of Mixed Toxicity of Azole Fungicides

The actual pollutants in the natural environment are usually in the form of mixtures rather than single substances. In the past half century, with the innovation of science and technology, the rapid development of industry and agriculture has been promoted, and the number of types of toxic pollution mixtures has been increasing, and the toxicity research of natural mixtures has also received much attention. Nong Qiongyuan et al. studied the combined toxicity of the mixture of antibiotics and azole fungicides in the test organism, and the results showed that there was a synergistic effect in the medium and low concentration area, and an antagonistic effect in the high concentration area. F.schmidt et al. took male rats as the research object to explore the combined effect of azole fungicides at different doses. By measuring the tissue residues of azole fungicides in liver, testis and kidney, the results showed that there was a significant difference in the residual amount of azole fungicides in various tissues after the use of a single substance and a mixed substance. Nong et al. used three common azole fungicides (nitriloxazole, propiconazole, and pentazotolol) to study the toxicity mechanism of their three-component mixtures to *Chlorella nucleosa* at environmental concentrations, taking superoxide dismutase, catalase, chlorophyll a and total protein as physiological indexes. The results showed that the growth of *Chlorella nucleata* was inhibited by promoting the activities of superoxide dismutase and catalase and inhibiting the production of chlorophyll a and total protein in the whole concentration range.

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