

POPS RELEASE IN THE DICOFOL PRODUCTION PROCESS

Li S¹, Tian Y², Zhu Q², Shang Y², Yao W², Liu W^{1*}

¹Research Center for Eco-Environmental Sciences, Chinese Academy Sciences, Beijing, 100085 China;
²Ministry of Environmental Protection of the People's Republic of China, Beijing, 100035 China

Abstract

Some samples were collected and analyzed in a closed-system dicofol production process using DDT as the intermediate. The highest level of Σ DDT in the waste waters and waste acids was 4.13 mg/L. The contents of PCDD/Fs in the wastewaters were lower than in the waste acids. PCDD/Fs were also detected in the dicofol product and the WHO-TEQ value was up to 84 pg/g.

Introduction

Polychlorinated dibenzo-p-dioxins, dibenzofurans (PCDD/Fs) and 1,1,1-trichloro-2,2-bis (p-chlorophenyl) ethane (DDT) are among the persistent organic pollutants (POPs) targeted for international source reduction by the Stockholm Convention. Exposure to these POPs is of great concern because of their toxicity, which would induce hormone-dependent cancers and reproductive effects in humans and wildlife.

Dicofol (2,2,2-trichloro-1,1-bis(4-chlorophenyl)ethanol) is an organic chlorine acaricide which has broad spectrum control and high activity for pests, while low toxicity for natural enemies and crops. Currently it is widely used to prevent acarid pest in cotton, fruit, sugarcane, hawthorn, pawpaw and flowers production. Dicofol may contain high impurity of DDT-related compounds, and therefore becomes an important source of DDT in China (J. Li et al., 2006). PCDD/Fs can be produced as impurities during several chemical productions and the use of elemental chlorine in the pulp and paper industry (UNEP, 2005). During the production of dicofol, chlorine is used as an important materials and the production process maybe fulfill the reaction situation of PCDD/Fs, however, no any data about the PCDD/Fs in the dicofol production are given.

As closed system dicofol production will be lasted for several years in China, it's significant to study the DDT and PCDD/Fs pollution in the dicofol production. It will be helpful to estimate the environmental risk of the production and use of dicofol and protect the human health and environment.

Materials and Methods

A typical dicofol plant was selected in this study and DDT and PCDD/Fs residues were analyzed. Dicofol is produced from trichloroacetaldehyde (CCl_3CHO) and chlorobenzene ($\text{C}_6\text{H}_5\text{Cl}$) through condensation, alkalization, chlorination and hydrolyzation. First of all, condensation reaction of CCl_3CHO and $\text{C}_6\text{H}_5\text{Cl}$ yields DDT in the presence of sulfuric acid. Then, DDE is produced in the alkalization process from the intermediate DDT and transferred into chlorination kettle and mixed with chlorine. Afterwards, the chloridized DDT is put into hydrolyzation kettle and reacts with H_2O to produce dicofol. After being purified, the dicofol is packed and sold in markets.

In this process, DDT only presents in the reaction kettle, which fulfill the requirements of the closed system dicofol production process. During the production process, waste acid 1 (mainly H_2SO_4 from the condensation kettle), waste water 1 (from the alkalization kettle), waste acid 2 (sulfonic acid from the hydrolyzation kettle) and waste water 2 (from the hydrolyzation kettle) are released. So these samples were collected to estimate POPs release in the wastes. The dicofol product was also collected for analyzing POPs contamination.

Results and Discussion

DDT related compounds may release to the environment via waste acid and waste water. Fig. 1 presents DDT distribution in the waste water and waste acid samples.

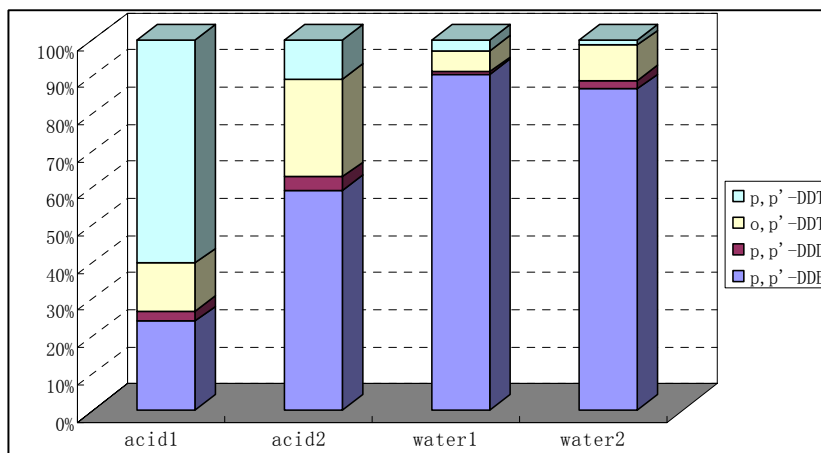


Fig.1 DDT distribution in the samples

o,p'-DDT, one of the two main isomers in the raw material DDT, is hardly to be chlorinated. Another isomer, *p,p'*-DDT can be transformed into dicofol. So during the dicofol production, *p,p'*-DDT level decreased more rapidly than *o,p'*-DDT. The contents of PCDD/Fs were shown in Fig. 2.

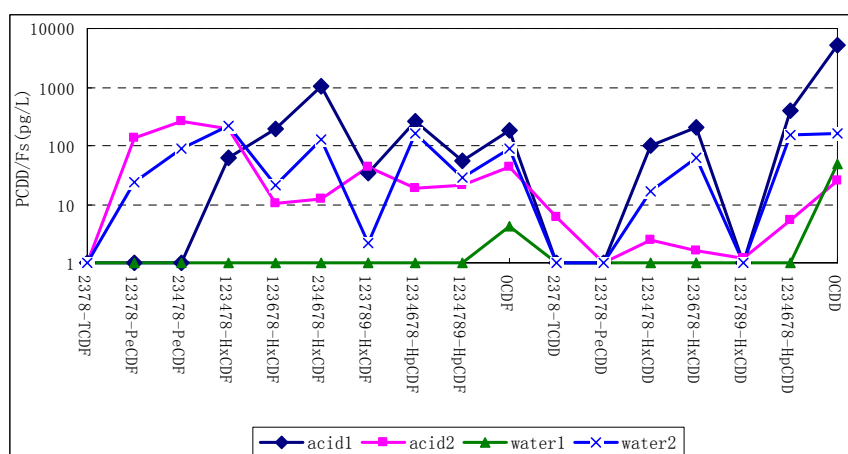


Fig. 2 PCDD/Fs in the dicofol production process

The contents of PCDD/Fs in the wastewaters were lower than in the waste acids. PCDD/Fs in the waste acid samples were higher than 0.17 ng/L. PCDD/Fs were also detected in the dicofol product and the WHO-TEQ value was up to 84 pg/g, while they spread in the air and water environment when dicofol is used as the acaricide in agricultural sector.

Acknowledgements

The funding of this study was provided by the Foreign Economic Communication Office of the Ministry of Environmental Protection of the People's Republic of China.

References

1. UNEP, 2005. Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases.
2. J. Li, et al., Science of the Total Environment 2006, 372: 215–224.