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Multimedia fate modeling and risk assessment of a commonly used azole fungicide climbazole at the river basin scale in China

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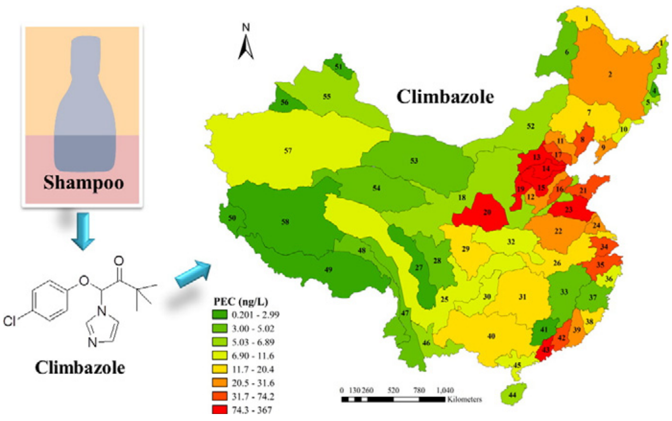
HIGHLIGHTS

- Emission of climbazole in the whole China was estimated based on market research data.
- Level-III fugacity model used to predict the fate of this chemical at the basin scale
- The mass inventory in the whole China: 294 t, with 6.79% in water and 83.7% in sediment
- High aquatic risks posed by climbazole expected in 2 out of 58 basins in China

GRAPHICAL ABSTRACT



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ABSTRACT

Climbazole is an antidandruff active ingredient commonly used in personal care products, but little is known about its environmental fate. The aim of this study was to evaluate the fate of climbazole in water, sediment, soil and air compartments of the whole China by using a level III multimedia fugacity model. The usage of climbazole was calculated to be 345 t in the whole China according to the market research data, and after wastewater treatment a total emission of 245 t was discharged into the receiving environment with approximately 93% into the water compartment and 7% into the soil compartment. The developed fugacity model was successfully applied to estimate the contamination levels and mass inventories of climbazole in various environmental compartments of the river basins in China. The predicted environmental concentration ranges of climbazole were: 0.20–367 ng/L in water, and 0.009–25.2 ng/g dry weight in sediment. The highest concentration was mainly found in Haihe River basin and the lowest was in basins of Tibet and Xinjiang regions. The mass inventory of climbazole in the whole China was estimated to be 294 t, with 6.79% in water, 83.7% in sediment, 9.49% in soil, and 0.002% in air. Preliminary risk assessment showed high risks in sediment posed by climbazole in 2 out of 58 basins in China. The medium risks in water and sediment were mostly concentrated in north China. To the best of our knowledge, it is the first report on the emissions and multimedia fate of climbazole in the river basins of the whole China.

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1. Introduction

Personal care products (PCPs), including moisturizers, lipsticks, shampoos, hair colors, deodorants and toothpastes, are widely used to improve the quality of human life (Boxall et al., 2012). A large variety of active ingredients in PCPs are considered as "emerging pollutants", and they are often high production volume chemicals (Daughton and Ternes, 1999; Boxall et al., 2012). After use, these chemicals are released directly or indirectly through wastewater treatment plants (WWTPs) into the receiving environments (Ternes et al., 2004). Therefore, it is essential to understand their fate and risks in the environment.

Climbazole is an azole fungicide used as an antidandruff ingredient in some household and personal care products such as shampoos, with its content up to a maximum concentration of 2.0% in formulations (SCCP, 2009). It is reported that the usage of this chemical in the European Union is in the range of 100 to 1000 tons per annum (Perez-Rivera et al., 2009). Due to incomplete removals in WWTPs (Wick et al., 2010; Chen et al., 2012), climbazole could enter into aquatic and terrestrial environments via sewage effluent discharge and sludge application. As the result, climbazole as well as other azole fungicides were detected in various environmental media such as effluent, sludge, surface water and sediment as well as soil (Kahle et al., 2008; Huang et al., 2010; Stamatis et al., 2010; Peng et al., 2012; Wick et al., 2010; Chen et al., 2012, 2014). Climbazole was reported to be quite toxic to aquatic organisms (Richter et al., 2013). In fact, azole fungicides showed potential endocrine disrupting effects to aquatic organisms due to their disturbing action on CYP450-regulated steroidogenesis (Kahle et al., 2008; Ankley et al., 2005; Kjærstad et al., 2010).

Nevertheless, measured concentrations of climbazole and other azole fungicides in the environment are still very limited worldwide. There are 58 basins in China with more than 1500 rivers (Statistical Yearbook of China in 2011). Monitoring campaigns for climbazole, however, have only been conducted in three rivers with a few samplings (Chen et al., 2014; Heeb et al., 2012; Qi et al., 2014). Modeling approach can provide an alternate method to estimate the environmental concentrations of this chemical. And it can be a time-saving and less expensive operation for a large scale assessment. Some studies have demonstrated that by coupling of chemical usage data, population, removal rate in WWTPs, and a parameterized multimedia model describing the fate of chemicals, the environmental exposure concentrations of ingredients used in PCPs can be predicted (Keller et al., 2007; Price et al., 2009, 2010a, 2010b; Whelan et al., 2012). Multimedia fugacity models are well established, well documented and widely used for predicting the environmental fate of chemicals at various scales by numerous researchers (single river scale, regional scale, and global scale) (Cao et al., 2004; Mackay, 2001; Prevedouros et al., 2004; Tan et al., 2007; Tao et al., 2003; Wang et al., 2012). In addition, successful modeling was reported for some PCPs such as triclosan based on their chemical usage data and level III fugacity model in our previous studies (Zhang et al., 2013; Zhao et al., 2013), as well as for natural steroids in all basins of the whole China (Zhang et al., 2014).

The aim of this study was to predict and evaluate the environmental concentrations and multimedia fate of climbazole at the river basin scale in the whole China using a level III multimedia fugacity model. Market research data was collected for the estimation of climbazole usage. A sensitivity analysis was performed to identify the most influential parameters and processes responsible for the fate of chemicals, while an uncertainty analysis with Monte Carlo calculation was used to estimate the total variance associated with the model outcome. Environmental risks were also assessed based on the simulated concentrations and literature ecotoxicity data by using the risk quotient (RQ) approach. The results can help to understand the contamination profiles of climbazole and mitigation of its potential risks in Chinese riverine environments.

2. Methodology

2.1. Basic basin unit in China

According to the Industry Standard of China (ISC, 2000), the whole China is divided into 58 basins (all the secondary rivers are included). To simplify the model description, an ID was allocated to each basin (Fig. 1) and the detailed basin information is displayed in Table S1 (Supplementary information). The geographic information layers of the basin system and administrative region of China are both available at the National Geomatics Center of China (http://sms.webmap.cn/). The map of China basins was created by ArcGIS 9.3 software. Details about administrative areas contained in each basin are displayed in the Supplementary information (SI-A). And the national wide multimedia modeling for climbazole was conducted in the unit of each basin.

2.2. Estimation of climbazole emissions

Climbazole is widely used as an antidandruff active ingredient in hair care formulations with a maximum concentration of 2.0% (SCCP, 2009). The method used to estimate consumption of climbazole was based on the market sales data for hair care products taken from Euromonitor (www.euromonitor.com). Meanwhile, the Mintel's Global New Products Database (GNPD) (www.gnpd.com) provided the ingredient lists associated with shampoo products released to the Chinese market in 2011. Consequently, with the information of market research data and ingredient list of hair care products and the inclusion level defined for climbazole in hair care formulations, we were able to estimate the total amount of climbazole consumed in the whole China. As some studies available in literature have demonstrated that the emission of chemical ingredients included in the personal care products in a region corresponded well with the *per capita* chemical consumption (PCC) estimate (mg/cap/yr) inputs and populations (Holt et al., 1998; Price et al., 2009; Whelan et al., 2012), we assumed that climbazole was uniformly distributed based on the population in China. The emission rate for each of the 58 basins was calculated according to the average consumption data *per capita* and the populations in the region. The detailed data sets of the populations for all of the 58 basins are available in the Supplementary information (SI-A).

After use, the chemical ingredient associated with the products is discharged directly or indirectly into the environment. But for the climbazole from urban population, the chemical mass is partly removed in WWTPs before discharge into the receiving environments in China (Chen et al., 2012), while for that from rural population, it is mostly discharged directly into the environment due to the low sewage treatment rate in majority of rural areas in China (GOSC, 2012). The climbazole emissions from the urban population were calculated based on the local wastewater treatment rate (SI-A), the removal efficiency of the target chemical in WWTPs (Table 2) and the corresponding usage of climbazole from the urban population. And for the emissions from the rural population, the usage of climbazole equals to the emission to the receiving environment. Thus, the emission to the receiving environment includes three parts: emission from the rural population, emission from the urban population without WWTPs (direct discharge), and emission from WWTPs (indirect discharge). Wastewaters whether treated or untreated are mainly received by the aquatic environment. In addition, sewage irrigation and sludge application are other pathways for the chemical to reach the soil environment. But in China, disposal of sewage sludge on agricultural land is still prohibited (Chen et al., 2013). The ratio of sewage irrigation area to the whole agricultural land was 6.65% according to the second national survey of sewage irrigation (Fang, 2011). Assuming that the irrigation water amount per unit area of the agricultural land was the same, the chemical emission into the soil compartment via sewage irrigation can be estimated by the ratio of the sewage irrigation volume to the sewage wastewater discharge volume multiplied by the chemical emission from the sewage wastewater. The detailed equations for the