Chemosphere 74 (2009) 370–376

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Application of a level IV fugacity model to simulate the long-term fate of hexachlorocyclohexane isomers in the lower reach of Yellow River basin, China

Jiangting Ao, Jingwen Chen *, Fulin Tian, Xiyun Cai

Key Laboratory of Industrial Ecology and Environmental Engineering (MOE), Department of Environmental Science and Technology, Dalian University of Technology, Linggong Road 2, Dalian 116024, China

ARTICLE INFO

Article history:
Received 4 July 2008
Received in revised form 30 August 2008
Accepted 29 September 2008
Available online 8 November 2008

Keywords:
Fugacity model
Environmental fate
Yellow River
HCHs

ABSTRACT

A level IV multimedia fugacity model was established to simulate the fate and transfer of hexachlorocyclohexane (HCH) isomers in the lower reach of the Yellow River basin, China, during 1952–2010. The predicted concentrations of HCHs are in good agreement with the observed ones, as indicated by the residual errors being generally lower than 0.5 logarithmic units. The effects of extensive agricultural application and subsequent prohibition of HCHs are reflected by the temporal variation of HCHs predicted by the model. It is predicted that only 1.8 tons of HCHs will be left in 2010, less than 0.06% of the highest contents (in 1983) in the study area, and about 99% of HCHs remain in soil. The proportions of HCH isomers in the environment also changed with time due to their different physicochemical properties. Although β-HCH is not the main component of the technical HCHs, it has become the most abundant isomer in the environment because of its persistence. The dominant transfer processes between the adjacent compartments were deposition from air to soil, air diffusion through the air–water interface and runoff from soil to water. Sensitivity analysis showed that degradation rate in soil, parameters related to major sources, and thickness of soils had the strongest influence on the model result. Results of Monte Carlo simulation indicated the overall uncertainty of model predictions, and the coefficients of variation of the estimated concentrations of HCHs in all the compartments ranged from 0.5 to 5.8.

1. Introduction

Organochlorine pesticides, such as hexachlorocyclohexane (HCH), have been recognized as one of the major classes of environmental pollutants (Bidleman and Olney, 1974; Tanabe and Tatsukawa, 1980; Atlas and Giam, 1981). Technical HCHs contain only 10–12% of the active isomer γ-HCH and are predominantly composed of non-insecticidal α-isomer (60–70%), β-isomer (5–12%) and δ-isomer (6–10%) (Iwata et al., 1993). Although only γ-HCH exhibits significant insecticidal activity, all the isomers are acutely and chronically toxic (Metcalf, 1955). β-HCH isomer may be the most toxicologically significant HCH due to it's high persistence and estrogenic effects (Willett et al., 1998). Exposure to HCHs could be one of the significant risk factors for human beings.

HCHs were used extensively in China for many decades, because it is both effective and inexpensive. Technical HCHs were first introduced for use as pesticide in 1952, and on April 1, 1983, the Chinese government banned the production and use of HCHs (Chinese Ministry of Agriculture, 1989). The total amount of technical HCHs produced in China was about 4.46 million tons from 1952 to 1983. During the 1970s and early 1980s, China was the largest producer and user of technical HCHs in the world (Li et al., 1998). In China, HCHs were mainly used in agriculture, although a small portion was also used in forestry and public health (Cai et al., 1992). The lower reach of the Yellow River basin is one of the major agricultural production bases in China, and thus was also one of the agricultural areas with the highest usage of HCHs in history (Li et al., 1998).

To date, information on the dynamic environmental fate and transfer of HCH isomers has not been available in the Yellow River basin. The methodology of multimedia environmental fugacity model was proven to be effective in simulating the fate of persistent organic pollutants in different spatial scales (Mackay and Paterson, 1991; Hertwich, 2001; Mackay, 2001), and a level IV fugacity model can be used for dynamic modeling addressing the changes in the past and predicting environmental fate of a pollutant in the future.

In this study, the dynamic changes of HCH isomers concentrations and transfer fluxes between adjacent compartments were simulated in the lower reach of the Yellow River basin during 1952–2010, by establishing a level IV fugacity model. Distribution

* Corresponding author. Tel./fax: +86 411 8470 6269.
E-mail address: jwchen@dlut.edu.cn (J. Chen).

0045-6535/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2008.09.085

of HCHs concentrations in the air, water, soil, and sediment was estimated. Model validation, sensitivity analysis and uncertainty analysis were performed to estimate the reliability of the model outputs. The results of the modeling can be used to assess the environmental quality of the lower reach of the Yellow River basin, and provide fundamental data to assess the potential ecotoxicological effects.

2. Methodology

2.1. Study area

The Yellow River is the second largest river in China, with a total length of 5464 km. The lower reach of the Yellow River extends 786 km from Huayuankou through the flat alluvial plains of Henan and Shandong provinces to the river mouth, with a basin area of 2.261×10^4 km^2 (Liu et al., 1997; He, 2000; Wang et al., 2007), accounting for 3% of the whole area of the Yellow River basin. The lower basin is a humid area, with annual average temperature of 12–14 °C, and annual average precipitation of 670 mm (Wang et al., 2007). The light and heat resources are very abundant in the basin, and the natural conditions make it an agriculturally fertile area for many kinds of crops.

2.2. Model framework and calculation

A level IV fugacity model based on a non-steady-state assumption was applied to simulate the temporal trends of concentrations and inter-compartmental transfer fluxes of HCHs from 1952 to 2010. Air (pure air and particulates), water (pure water and suspended solids), soil (air, water and solids), and sediment (water and solids) were the four bulk compartments included in the fugacity model. The processes taken into consideration in the model for HCHs included agricultural application, advection air/water flow in/out of area, exchange between inter-compartment, and degradation in the four bulk compartments.

The comprehensive and detailed descriptions of the fugacity model are available in the monograph of Mackay (2001). By considering all the above processes, the non-steady-state mass balance of HCH isomers in the four compartments was described with the following system of linear differential equations:

$$V_A Z_A \frac{df_A}{dt} = E_A + G_A C_A + D_{W-A} f_W + D_{S-A} f_S - (D_{A-W} + D_{A-S} + D_{A(A)} + D_{R(A)}) f_A \quad (1)$$

$$V_W Z_W \frac{df_W}{dt} = G_W C_W + D_{A-W} f_A + D_{S-W} f_S + D_{Sed-W} f_{Sed} - (D_{W-A} + D_{W-Sed} + D_{A(W)} + D_{R(W)}) f_W \quad (2)$$

$$V_S Z_S \frac{df_S}{dt} = E_S + D_{A-S} f_A - (D_{S-A} + D_{S-W} + D_{R(S)}) f_S \quad (3)$$

$$V_{Sed} Z_{Sed} \frac{df_{Sed}}{dt} = D_{W-Sed} f_W - (D_{Sed-W} + D_{R(Sed)}) f_{Sed} \quad (4)$$

where the subscript i = A, W, S and Sed, represents bulk compartment of air, water, soil and sediment, respectively. V_i is the volume of the compartment i, Z_i is fugacity capacity of the compartment i. E_i is the emission rate into the compartment i. G_i is advection flow rate of compartment i. C_i is background inflow concentration of adjacent region in compartment i. D_{ij} is transfer rate coefficient from compartment i to compartment j. $D_{A(i)}$ and $D_{R(i)}$ represent advection flow rate coefficient and degradation rate coefficient of compartment i, respectively.

The model was programmed using Matlab 7.0, and the system of the linear differential equations was solved at hourly time steps. The initial values of the fugacity were set at zero in 1952, and the calculated values of fugacity from previous phase served as the initial values for the succeeding phase. For each value of t, the values of the fugacities $f_i = f_i(t)$ are multiplied by the capacity of fugacity Z_i to determine the value of concentration $C_i = C_i(t)$ of HCH isomers in the bulk compartment. Consequently, the transfer fluxes between the adjacent compartments can also be calculated using the values of fugacity and transfer rate coefficient.

2.3. Model parameters

The input parameters to the model comprised environmental parameters describing compartment composition, inter-compartment exchange rates, etc., physicochemical properties of HCH isomers and emission data. Since the parameter values usually span a wide range, geometric means and standard deviations could be derived. For the parameters with only a single value available, their coefficients of variation (CV) were artificially assigned (Cao et al., 2004). The geometric means and standard deviations were used for model calculation and uncertainty analysis.

As many parameters as possible that represent the environmental characteristics of the study area were collected from literatures (Wu et al., 1999; He, 2000; Cao et al., 2005a; Liu et al., 2004; Shi et al., 2005; Zhao et al., 2005). Default values were taken from Mackay and Paterson (1991) and Mackay (2001) in absence of reliable literature data. These values of relevant environmental parameters are listed in Table 1. The values of physicochemical properties of HCH isomers used here were the mean values derived from previous studies or most frequently used in the model calculation (Mackay et al., 1997; Mackay, 2001; Cao et al., 2005a, 2007), and these values are summarized in Table 2.

Few anabranch and sewage merged into the lower reach of the Yellow River (Dong, 1992). Therefore, the impact of this factor on the concentration of HCHs can be neglected. The inputs of HCHs into the environment of the study area were from agricultural use and air/water advection. Emission data are not always easily accessible or largely uncertain, and have to be estimated (Scheringer and Wania, 2003; Li et al., 2006). The amount of HCHs used in the local agriculture is estimated by the annual average usage of HCHs in the Shandong and Henan provinces, and the agriculture area in the basin (Dong, 1992; Hua and Shan, 1996; Li et al., 1998, 2001). The agricultural use of HCHs increased since 1970s in the basin and reached a peak in 1980, decreased thereafter to zero in 1984 (Li et al., 2001). Therefore, the historical agricultural use of HCHs in the basin could be roughly divided into three phase: (1) during 1952–1969, the estimated HCHs agricultural use was about 530 tons per year; (2) 1470 tons per year during 1970–1983; and (3) none since 1984.

According to Li et al. (2003), the amount of β-HCH emitted to the atmosphere due to the spraying event was 30% of the total application. Considering the vapor pressures of the other isomers are higher than that of β-HCH, we presumed that 40% of the total use of the other isomers entered into air and 60% entered into the soil. No monitoring data were available for the air advection flow concentrations of HCH isomers in the upper-wind of the study area. The air advection flow concentrations (C_a) of HCH isomers before 1983 were estimated from concentrations of pine needle HCHs in North China in early 1980s, by assuming equilibrium between the air and pine needles phases (Ockenden et al., 1998; Xu et al., 2002), and C_a after 1983 were estimated from the monitoring results about HCHs in 1996 and 2002 in North China (Wu et al., 2003; Cao et al., 2005a). Due to the lack of monitoring data about the inflow water concentrations of HCH isomers before 1983, the inflow water concentrations were estimated from the measurement of HCHs concentrations in up-stream of the lower reach of the Yellow River in 1986–1987 (Bao et al., 1991), according to the variation of water concentrations derived from the model results, as also did by Cao et al. (2005b).