CHANGES OF HEXACHLOROCYCLOHEXANE (γHCH) CONCENTRATIONS IN VARIOUS MEDIA IN TIANJIN, CHINA FROM EARLY 1950's TO EARLY 1990's

Shu Tao and Hongyin Cao

Laboratory for Earth Surface Processes, Department of Urban and Environmental Sciences, Peking University, Beijing 100871, China

Introduction

HCHs have been widely used and dispersed in China, resulting in widespread environmental occurrence [1]. Extensive agricultural application of technical HCHs in China including Tianjin began in early 1950's and was banned in 1984 [2]. After the banning, lindane was used for another decade till early 1990's. In addition to the direct use of HCHs in agriculture, wastewater discharged from two chemical companies which had produced a very large quantity of HCHs over years had added a large amount of the pesticides to the local loadings [3,4]. Tianjin is, therefore, one of the most severely contaminated areas in terms of HCHs. The concentrations detected in soil samples recently collected from the area are still very high [5]. Dynamic changes of environmental concentrations and across-interface fluxes can be described using unsteady-state mass balance model formulated in terms of fugacity. The level IV fugacity model has been successfully used in a number of cases in simulating fate of POPs in a dynamic way [6]. The objective of this study was to characterize the building-up processes of γHCH in various media during a period of 40 years starting from early 1950's and to improve our understanding of dynamic changes of γHCH in the area.

Methodology

Four bulk compartments, namely air, water, soil, and sediment, were included in the model. Under unsteady-state condition, mass transfer between the compartments is a function of time. The concentration of γHCH in the compartments and the sub-compartments as well as the transfer fluxes between the adjacent compartments during a designed time span were modeled. The processes taken into consideration included: advective air and water flows from and to the outside of the area, pesticide application, wastewater discharge and irrigation, deposition from air to water and to soil as dry or wet deposition, diffusion between air and soil, air and water, and water and sediment, erosion from soil to water in either solid or aqueous phases, and degradation in air, water, soil, and sediment. For each compartment in concert, the change rate of fugacity equals to the difference between the input and output rates divided by a product of compartment volume and fugacity capacity. A differential mass balance equation with fugacities as variables can be assigned in this sense. For modeling purpose, fifty three parameters involving physical-chemical properties and transfer parameters of γHCH as well as environmental properties were used. The parameters were collected based on an in-depth literature review. The set of the four differential equations were solved using function ODE15S built in MATLAB. Zeros were assigned to the initial γHCH concentrations in all compartments as model boundary conditions. 20 years simulation was conducted as a preliminary modeling starting from 1953 in a hour-by-hour basis. Measured concentrations of γHCH in soil,

sediment, and water were collected from the literature for model validation.

The sensitivities of the modeled results to all input parameters except gas constant were tested. A sensitivity coefficient was defined for this purpose. Uncertainty analysis was conducted. For each selection of coefficient of variance (20%, 60%, or 100%), a set of input data with 3000 records was prepared. In the data set, the 17 key parameters, identified based on the results of the sensitivity analysis, were randomly generated from a log-normal distribution function with given means and standard deviations, while all the other non-key parameters remained constant. The model was then run for 3000 times using the input data set.

Results and Discussion,

The result of the dynamic modeling is presented in Fig. 1 as relative change of γHCH concentrations in four bulk media (Fig. 1). The model was initialized with zero concentrations in all media at 1953 and the unsteady-state responses of the contaminant levels in all bulk compartments to a continuous loading of the pesticide starting from 1953 are shown in Figure 1. Under assumed constant loading from both agricultural application and wastewater discharge, first-order shaped curves can be seen. In air and water, the responses of γHCH levels to the loading were much faster than those in soil and sediment, suggesting

Fig.1 γHCH in the bulk media as percentages of their steady-state concentrations

relatively more direct and faster transfer processes to and from air and water. Since the relative changes of γHCH concentrations in all media were extremely slow at the end of simulation period of 20 years, the concentrations at that time were taken as the steady-state levels. The time required for γHCH concentrations to reach such a steady-state in various compartments can be, therefore, quantified by defining a percentage of the steady-state concentrations. If 95% was chosen as the criteria for the approximation, the times for γHCH to reach the steady-state in air, water, soil, and sediment were 2, 2, 7, and 6 years, respectively.
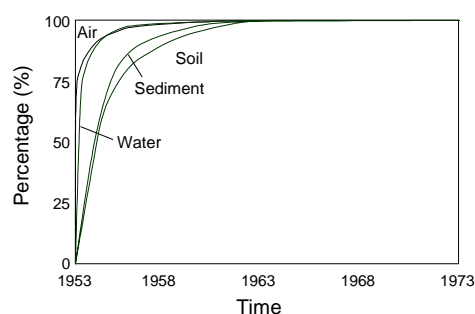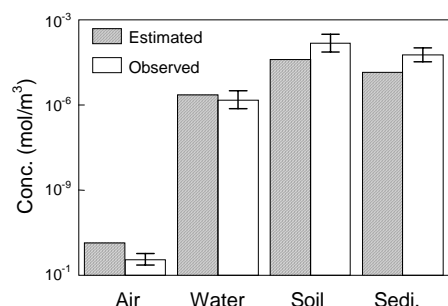

Fig.2 Comparison between the measured and the modeled γHCH concentrations

The only historical data available are those collected in later 1970's and early 1980's for soil, sediment, and water [3,7-10]. By that time, the steady-state levels of γHCH in various media were already reached. The calculated concentrations of γHCH in various compartments at 20 years were compared with the independently observed data as means ± one standard deviations in Fig. 2. The result of the comparison generally indicate a good agreement between the observed and the estimated γHCH concentrations. The difference between the observed and estimated mean concentrations in water is less than 0.15 log-units, the smallest among the four compartments. For soil and sediment, the differences between the estimates

and observes were more pronounced with log-transformed differences of 0.61 and 0.60, respectively. It appears that the model underestimated γHCH concentrations in these two media at steady-state. One explanation is that the observation was based on limited samples. Another possible reason is the uncertainty of the parameters, especially the degradation rate constants, adopted for the modeling. It is generally recognized that high levels of organic carbon in either soil or sediment can reduce significantly the bioavailability of organic chemicals to microbial attack, leading in turn to a slow degradation rate[11]. The organic matter contents in soil and sediment in Tianjin are pretty high with mean values of 1.9% and 7.9%, respectively. It is possible that a significant reduction of the degradation rate of γHCH in these media is caused to some extent by the presence of high levels of organic matter. One constrain of the modeling is that without relevant historical data, it is impossible to validate the model performance in terms of dynamic change prior to the steady-state. This limitation was partially compensated by sensitivity and uncertainty analyses.

While modeling the γHCH concentrations in various bulk compartments, fluxes of the pesticide into, within, and out of the area were also estimated. The estimated gain and loss fluxes and the γHCH quantity distribution among the bulk compartments at steady-state are presented in Fig. 3.
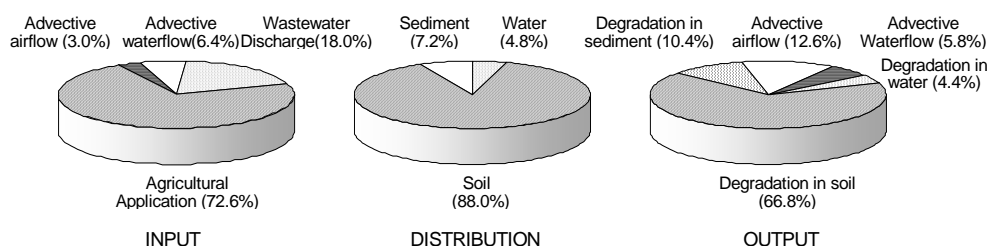

Fig. 3 Relative gain and loss fluxes and the quantity distribution of γHCH at steady-state.

Annual agricultural application of γHCH in Tianjin was as high as 15.9 tons during the modeled period, which accounted for more than 70% of total loading. Another important input was from industrial wastewater discharge. 18% of the total loading was directly from the wastewater. As a result, although advective air and water flows brought quite some γHCH into the area, more γHCH exported to the outside of Tianjin through out-flowing air (12.6%) and water (5.8%), indicating a fact that Tianjin was a source of γHCH in northern China. Degradation played a dominant role in loss mechanism of γHCH in the area and accounted for more than 80% of the total loss in soil (66.8%), sediment (10.4%), and water (4.4%). The primary sink of γHCH was soil which retained 88% of γHCH at steady-state.

The sensitivities of the calculated concentrations of γHCH in air, water, soil, and sediment to all model input parameters were tested. This was done by changing the tested input parameters one at a time. To test the sensitivity conservatively, the selected varying range of the tested parameters was from 0.1 to 5.0, much larger than the actual variation ranges. Each parameter was multiplied by a factor of 0.1, 0.2, 0.3, ..., or 5.0, repeatedly. For each case, the changes in predicted concentrations in the four bulk compartments were calculated. A sensitivity coefficient (CS) was defined as the tangent slop of the curve at F=1 point normalized by concentration. The relative sensitivities of the four bulk compartments to all parameters were calculated and illustrated in Fig. 4.
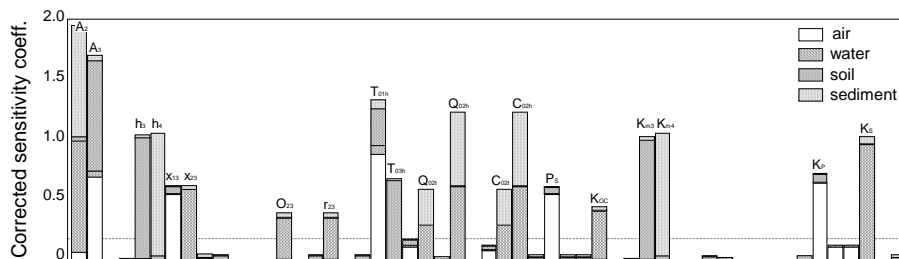
Fig. 4 Sensitivity coefficients of the 52 parameters used as the model inputs.

Of the 52 parameters evaluated, the accumulative sensitivity coefficients of 20 were above 0.2. Three out of the 20 parameters fall into the category of local perturbation [12]. The rest of 17 were identified as the key parameters which had a significant influences on model uncertainty in term the steady-state estimates of γHCH in one or more compartments.

Monte Carlo simulation was undertaken repeatedly for 3000 times with the values of the 17 key parameters randomly derived from log-normal distribution with given means and coefficients of variation. Fig. 5 presents the uncertainties of the estimated γHCH concentrations in sediment over 10 years starting from 1953 in terms of the estimated mean ± standard deviation as an example. For all four bulk compartments, the ranges of uncertainty fall in similar pattern increased gradually at beginning and reached constant values after the system reached the steady-state.
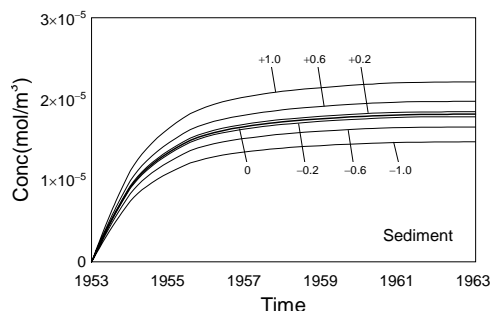

Fig. 5 Uncertainties of the calculated changes of γHCH concentrations in sediment

References.
1. Chen, S.P. and Chen, Z.W. (1986) Atlas of Environ. Qual. in Tianjin, Sci. Press, Beijing
2. Lin, Y. (1996) Management of Pesticides, 59, 30
3. Li, Q.S. (1986) Environ. Sci. 6, 5-14
4. Hua, X.M. and Shan, Z.J. (1996) Adv. Environ. Sci., 4, 33-45
5. Gong, Z.M., Cao, J., Zhu, X.M., Cui, Y.H., Guo, L.Q., Tao, S., Shen, W.R., Zhao, X.M., Han, L.X. (2002) Agr. Environ. Protection, 21, 459-461
6. Wania, F. and Mclachlan, M.S. (2001), Environ. Sci. Technol., 35, 582-590
7. Inst. Environ. Chem. (1983) Environ. Sci., 4, 12-15
8. Huang, Y.Y., Zhao, Z.X, Yi, C.G., and Pang, S.I. (1984) Acta Sci. Circumstantiae, 4, 60-63
9. TEPB (1987) Environ. Qual. Statement, Tianjin Environ. Protection Bureau
10. Zhao, L. and Ma, Y.J. (2001) Agri. Environ. Development, 67, 37-39
11. Robertson, B. and Alexander, M. (1988) Environ. Toxicol. Chem. 17,1038-1043

12. Lohman, R., Pai, P., Seigneur, C. and Levin, L. (2000) Sci. Total Environ. 259, 3-11