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Simulation of the long-term transfer and fate of DDT in Lanzhou, China

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ABSTRACT

A level IV fugacity model is used to simulate the fate and transfer of DDT in the Lanzhou area over a 67-year period from their introduction into agricultural field until 2019. The established model is successfully applied to simulate the transfer processes and the concentration distribution of DDT in four environmental compartments: air, water, soil, and sediment in Lanzhou area under non-steady state assumptions. Furthermore, the calculated results agree well with monitoring data from the literature in same period of time. We assume 20% of the total usage of DDT enters into air and 80% enters the soils. The results indicate that the main source of DDT in the area is agricultural application, the biggest bulk sink is soil (accounting for 99.8% of total amount in the environment). Among all the transfer processes, the deposition from air to soil, deposition from air to water, soil erosion, and sedimentation from water to sediment are the primary processes, and the degradation in soil and air are the key process of DDT disappearance.

1. Introduction

The organochlorine pesticide DDT (dichlorodiphenyltrichloroethane) has been widely used since the 1940s for controlling agricultural pests and to combat vectors of insect-borne diseases, such as typhus or malaria (Schenker et al., 2009). DDT is resistant to biotic and abiotic degradation, which makes it very persistent in the environment. For this reason, significant level of DDT is still being detected worldwide in air, water, soil, plants and wildlife after large-scale agricultural usage has been banned. The DDT residues in the environment may have a high risk potential to the ecosystem and human healthy in China. DDT can do harm to nervous and reproductive systems and cause cancer (Beard, 2006). A number of case studies and small analytical studies undertaken in the early 1990s have also indicated that exposure to DDT may be one of the significant environmental risk factors for breast cancer (Falck et al., 1992; Wolff and Toniolo, 1995).

A large amount of dichlorodiphenyltrichloroethane (DDT) was applied to agricultural area in Lanzhou between 1952 and 1983. According to Guo and Wang's emission data (Guo and Wang, 1992), the consumption of DDT applied in agricultural land was estimated to be 7.05×10^4 mol a^{-1} between 1952 and 1983 (Guo and Wang, 1992). Due to agricultural application, subsequent dry or wet deposition, surface runoff, and leaching to soil, the environment is wide1y contaminated by DDT (Yao, 2009). Based on above reasons, production and agricultural application of DDT have been prohibited since 1984 in Lanzhou. However, recent studies on DDT pollution in Lanzhou area show that the pollution levels are still high. For example, in an investigation on the fate of persistent organic pollutants (POPs) in the Lanzhou Valley, the average concentrations of DDT in the soil samples were 22.6 ng g^{-1} (Gansu Environmental Protection Bureau, 2005). There are very interesting and pioneering studies of DDT concentration levels in soils from different regions in China and other countries. Compared with other regions in China and other countries, concentrations of DDT in soil of Lanzhou were higher than those data reported in some regions in china and other countries such as Taiwan (20 ng g^{-1}) (Thao et al., 1993), Tibet plateau (n.d.–2.83 ng g^{-1}) (Fu et al., 2001), Thailand (8.3 ng g^{-1}) (Thao et al., 1993), United States (9.63 ng g^{-1}) (Aigner et al., 1998), United Kingdom (0.1–10 ng g^{-1}) (Meijer et al., 2001), and South Korea (<3 ng g^{-1}) (Kim and Smith, 2001). However, the DDT concentrations in soil of Lanzhou were lower than those such as Beijing (140.79 ng g^{-1}) (Zhu et al., 2005), Vietnam (110 ng g^{-1}) (Thao et al., 1993), and Poland (4.3–2400 ng g^{-1}) (Falandysz et al., 2001). The DDT concentration in soil of Lanzhou is in a moderately polluted degree. So it is very important to deduce current ecological risk of DDT by evaluating the DDT residues in main environmental media of the Lanzhou area.

To assess the dynamic environmental fate and transfer of DDT, it is necessary to simulate the transfer flux and concentration of

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DDT in the multimedia environment. But the available monitoring data are very limited because we have few representative data in time and space from monitoring. Thus a level IV fugacity model provides a valuable overall description of the fate of DDT and has helped to further enhance our understanding of the processes controlling DDT concentrations in various environmental media such as air, water, soil and sediment (Mackay and Paterson, 1991; Cowan et al., 1995). A level IV fugacity model has been successfully used in a number of cases to simulate the fate of POPs. For example, it has been applied to simulate the transfer processes and fate of DDT in Hangzhou from 1953 to 2020 (Cao et al., 2007), and the fate of γ-HCH in Tianjin over a 68-year period (Tao et al., 2006).

In this study, a level IV fugacity model was used to simulate the transfer processes and the fate of DDT in the Lanzhou area before and after the ban of DDT use as pesticides. Distributions of DDT concentrations in air, water, soil, and sediment and transfer fluxes of DDT across these compartments were then estimated. Reliability of the model estimates was evaluated by various means including concentration validation and sensitivity analysis. The model results were also compared with the outcomes from Tianjin and Hangzhou, and the transfer process showed significant difference between Lanzhou and these regions. The possible causes of the various transfer processes were also analyzed.

2. Materials and methods

2.1. Study area

The Lanzhou Valley is located at the intersection of Qinghai–Tibet Plateau, the Inner Mongolian Plateau and the Loess Plateau (Fig. 1). It is 1631.6 km^2 with an east–west distance of 114 km and a maximum north–south width of proximately 35 km and is surrounded by mountains and hills that rise to 500–600 m. Approximately 2.0 million people live in four residential districts, including Xigu, Anning, Qilihe and Chengguan. Lanzhou City is on the upper reaches of the Yellow River. The Yellow River runs through the Lanzhou city from west to east, with mainstream 50 km long, the water surface area in Lanzhou reach of the Yellow River is equivalent to the water surface area of several large reservoirs. In addition, there are a large number of wetland widely distributing along the Lanzhou reach of Yellow River. Hence, the water area represents 10% of the surface area (Feng, 2009). The Lanzhou Valley has a continental climate of the north temperate zone, with an annual average temperature of 9.3 °C. The annual precipitation is 327.7 mm, of which 50% occurs during the July–September period. The monthly average of the surface wind speed is approximately 0.8 m s^{-1} (Ta et al., 2004).

2.2. Model framework

A level IV fugacity model was applied to simulate the changes of concentrations and transfer of DDT between 1952 and 2019. The framework of the model was similar to the one used for Tianjin in a previous study (Li et al., 2006), based on Mackay (Mackay and Paterson, 1991; Wania and Mackay, 1995). The study area was defined as four bulk compartments: air (gas and airborne particles), water (water and suspended solids, and fish), soil (air, water, and solids), and sediment (water and solids). The concentrations and the transfer fluxes of DDT between 1952 and 2002 were calculated by this model, and a further calculation was done to predict the future changing of DDT in the following 17 years according to the simulating results. The differential mass balance equations for the four compartment model are as follows:

$$V_1Z_1\frac{df_1}{dt} = E_1 + G_{A1}C_{B1} + f_2D_{21} + f_3D_{31} - f_1(D_{12} + D_{13} + D_{R1} + D_{A1}) \tag{1}$$

$$V_2Z_2\frac{df_2}{dt} = E_2 + G_{A2}C_{B2} + f_1D_{12} + f_3D_{32} + f_4D_{42} - f_2(D_{21} + D_{24} + D_{R2} + D_{A2}) \tag{2}$$

$$V_3Z_3\frac{df_3}{dt} = E_3 + f_1D_{13} - f_3(D_{31} + D_{32} + D_{R3}) \tag{3}$$

$$V_4Z_4\frac{df_4}{dt} = E_4 + f_2D_{24} - f_4(D_{42} + D_{R4} + D_{A4}) \tag{4}$$

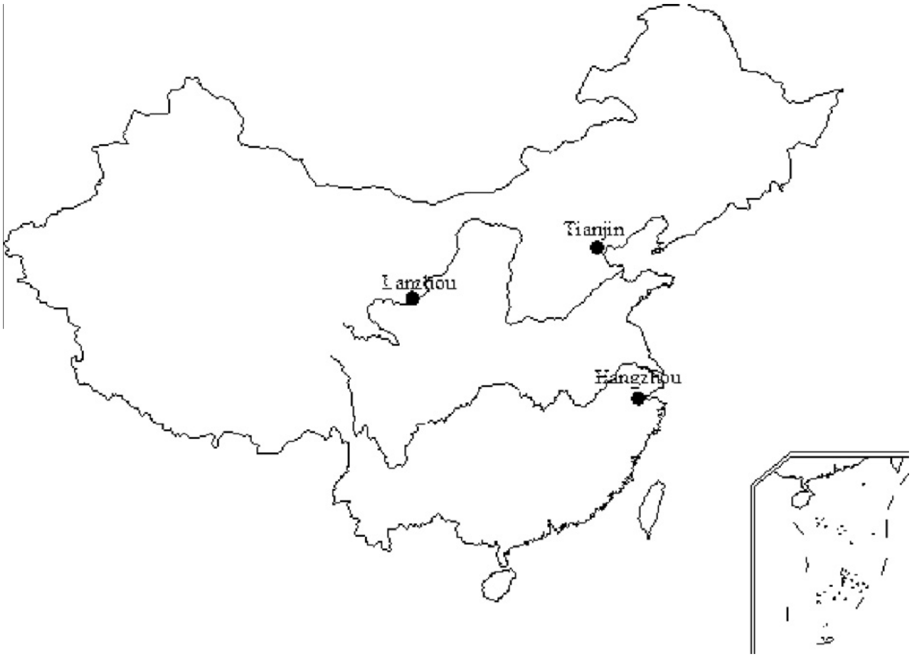

Fig. 1. Map of China showing the three study cities of Lanzhou, Tianjin, and Hangzhou.

where V_i is the volume of the compartment i, Z_i is fugacity capacity of the compartment i, f_i is the fugacity of the compartment i, E_i is emission rate into the compartment i, $G_{Ai}C_{Bi}$ is advection input to the compartment i, D_{ji} is the transfer coefficient from compartment j to compartment i. D_{Ri} and D_{Ai} represent degradation rate coefficient and advection flow rate coefficient of compartment i, respectively. A single subscript (1, 2, 3, or 4) represents bulk compartment of air, water, soil, or sediment, respectively.

2.3. Parameters

All parameters are collected from literatures or laboratory examinations. There are 62 parameters in this study, which include environmental properties, transfer processes, application rates of technical DDT, and physicochemical properties of DDT. The details of model parameters are presented in Supplementary material. (See Tables S1–S4.)

The values of physicochemical properties of DDT including half-life derived from previous studies or most frequently used in the model calculation (Liu, 2005; Mackay et al., 2006). Degradation rate constants of DDT in different compartments were calculated from following formula (Mackay, 2001): $K_{Ri} = 0.693/t_{1/2}$. K_{Ri} is the degradation rate constants in compartment i, $t_{1/2}$ is the half-life in the corresponding compartment. The formula is from Mackay's book (Mackay, 2001). These values are summarized in Table S1.

Table S2 lists the volumes, areas, organic carbon contents, and other compartment parameters of the Lanzhou area. The volumes and areas of air, water, soil, and sediment were from Lanzhou Chorography (Editorial Committee of Lanzhou Chorography, 1998). Depth in air were from Mackay's book (Mackay, 2001), Depth in water were from Wang's work (Wang, 2006), Depth in soil and sediment were from Mackay and Paterson's work (Mackay and Paterson, 1991). Volume fraction of Air were from Mackay and Paterson (1991), volume fraction of solid in air were from Yang's work (Yang et al., 2005). Volume fraction of water were from Mackay and Paterson (1991), volume fraction of solid in water were from Lanzhou Chorography (Editorial Committee of Lanzhou Chorography, 1998), volume fraction of fish in water were from Mackay and Paterson (1991), fraction organic carbon of solids in water were from Qiou's work (Qiou, 1989). Volume fraction of air, water, and solid in soil were from Mackay and Paterson (1991), fraction organic carbon of solids in soil were from Lanzhou Chorography (Editorial Committee of Lanzhou Chorography, 1998). Volume fraction of water and solid in sediment were from Mackay and Paterson (1991), fraction organic carbon of solids in sediment were from Qiou's work (Qiou, 1989). In this study, agricultural application, air and water advection are the main inputs of DDT, the environmental processes considered include advection, reaction, and intermediate processes, such as diffusion, absorption, runoff, deposition, and so on. The route of DDT disappearance from study area includes degradation, air and water advection. All these processes are listed in Table S3. The coefficients of environmental transfer processes are listed in Table S4. These values are obtained from the literatures and the statistics information on the Lanzhou area (Mackay and Paterson, 1991; Mackay, 2001; Centre for Environmental Modelling and Chemistry (CEMC) http://www.trentu.ca/cemc, 2003; Gansu Environmental Protection Bureau; Liu, 2005; Zhang, 2005). Rain rate were from Gansu Environmental Protection Bureau. Dry deposition velocity were from Zhang's thesis recommended value for Lanzhou. Air-side mass transfer coefficient over water, water-side mass transfer Coefficient under air, soil–air phase diffusion mass transfer coefficient, and soil water phase diffusion mass transfer coefficient were calculated by Liu's method (Liu, 2005). All the calculated formula were modified by Liu. Liu's method was collected from following literature (Fuller et al., 1966; Hayduk and Laudie, 1974; Southworth, 1979). All the calculated formula were given in the Supplementary material. Water runoff rate from soil were calculated from following formula (Mackay and Paterson, 1991): $U_{EW} = 0.4U_R$. U_{EW} is water runoff rate from soil, U_R is rain rate in Lanzhou area. Air-side mass transfer coefficient over water, water-side mass transfer coefficient under air, soil–air phase diffusion mass transfer coefficient, soil water phase diffusion mass transfer coefficient, rain rate, dry deposition velocity, and water runoff rate from soil were specific to the Lanzhou area. These intermedia transport parameters differ from the one used by Mackay.

It is reported that during pesticide application event, up to 30–50% of the amount applied can be lost to air (Van den Berg et al., 1999). Li et al. (2006) assumed that the total rate of DDT application was divided into entry into soil (80%) and evaporation to atmosphere (20%). The low temperature and low precipitation in Lanzhou, China, can slow down the DDT volatilization. Therefore, Li's method has been adopted in this study. We presumed that 20% of the total usage of DDT entered into air and 80% into soil. No monitoring data were available for the inflow air advection concentrations of DDT in the upper-wind of the study area. The inflow air advection concentrations of DDT were neglected. Due to the lack of monitoring data about the inflow water concentrations of DDT, the inflow water concentrations were also neglected.

2.4. Model calculation

The modeling was performed using Matlab v.6.5 with the partial differential equations solved on an hourly basis. The concentrations of DDT in various compartments and sub-compartments, as well as the transfer fluxes between adjacent compartments can be calculated using fugacities and fugacity capacities. Measured concentrations of DDT in soil were collected from the literature.

Sensitivity analysis was also performed to evaluate the influence of input parameters to the model results, so as to determine the key input parameters in modeling. The sensitivity coefficient was defined as the radio of the relative variation of the estimated concentration to that of the input parameter (Li et al., 2006):

$$SC_i = \frac{\Delta Y_i/Y_i}{\Delta X_i/X_i} \qquad (5)$$

where SC_i represents the sensitivity coefficient of input parameter i. X_i and Y_i represent the input parameter i and corresponding calculated concentration, respectively.

3. Model results

3.1. Calculated concentration

The calculated concentrations of DDT in air, water, soil, and sediment from 1952 to 2019 in the Lanzhou area are shown in Fig. 2. The highly concentrated planned economy system were implemented from 1952 to 1983 in China. During the planned economy periods, the amount of DDT application in agriculture each year remain essentially unchanged. On the other hand, the frequent political movement starting from 1957 in China hinder normal growth in Chinese agriculture, which lead to the slowing growth rate of DDT use. When Cao et al. (2007) simulated the long-term transfer and fate of DDT in Hangzhou, Cao et al. (2007) assumed that the amount of DDT application maintained constant during 1952–1983. Hence, Cao' method were adopted in this study. We presumed that the amount of DDT application was held constant between 1952 and 1983, the concentration of DDT in all compartments have no change and maintain a relatively stable state in 31 years during the application of DDT from 1952. Due to the ban of DDT pesticides, a rapid decline in concentrations of DDT occurred in 1984, and the downward trend continued in the

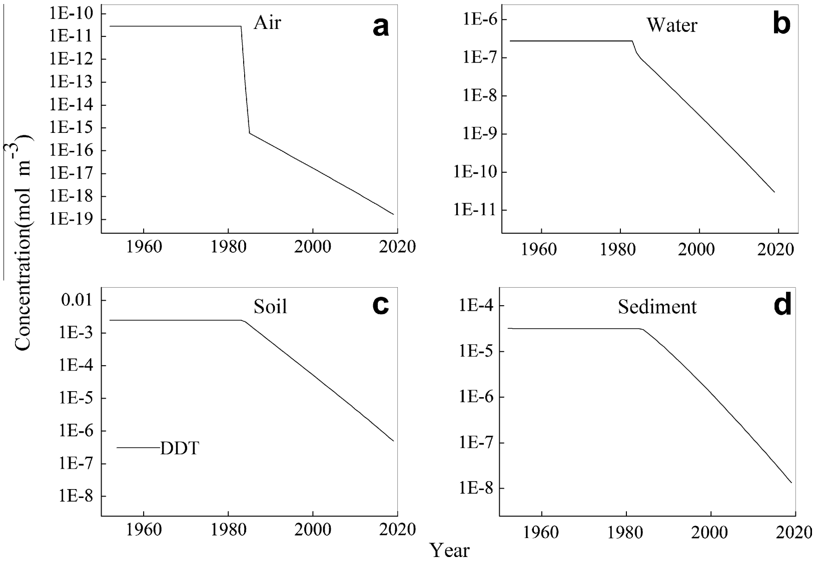

Fig. 2. Temporal trends of the concentration of DDT in various compartments from 1952 to 2019.

following years. As compared with 1983, concentrations of DDT in air, water, soil and sediment in 1984 reduced by about 99%, 49%, 10% and 6%, respectively. According to model result, only about 6.0×10^{-7}%, 0.01%, 0.02% and 0.04% of the concentrations in air, water, soil and sediment, respectively, will be left in 2019.

No measured data of DDT concentrations in Lanzhou air were found in the literature. The only measurements available are DDT concentrations in soil of Lanzhou. Table 1 listed DDT concentrations in soil calculated by Level IV model in comparison with measured ones in years around 1982 and 2004. The calculated DDT concentrations represent the averages of the whole study area, while observations are based on very limited samples collected in specific sites, which poorly represented general DDT pollution levels in Lanzhou. Hence, the comparison must be taken as indicative, in terms of orders of magnitude.

Table 1 displays that the calculated and measured concentrations agreed very well in 1982, and the residuals between calculated and measured values were less than 0.5 log unit in soil. In 2004, the residuals between calculated and measured concentrations were less than 1 log unit in soil.

3.2. Transfer fluxes

As the media concentrations change with time, so do the transfer fluxes. Analysis on the results has shown that environmental reservoir and transfer fluxes of DDT changed with time, which can be divided into two stages (see Fig. 3): (1) 1952–1983. Assuming that the amount of application was held constant each year, the transfer fluxes reached steady state in 20 years and continued to 1983. The consumption of DDT applied in agricultural land was estimated to be 7.05×10^4 mol a^{-1} during the period from 1952 to 1983. According to the calculation, the amounts of DDT that vanished from the study area through degradation, air, and water advection were 6.43×10^4, 7.33×10^3, and 7.84×10^2 mol a^{-1} respectively. The degradation was the main pathway for DDT to vanish from the study area, and degradation in soil was the major loss process, accounting for about 97% of the total degradation amount, followed by degradation in air. Local agricultural application of DDT was the only source emission in the Lanzhou area in the period when the pesticide DDT was used, while degradation in soil and air were the primary loss process. Transfer fluxes of air–soil deposition, air–water deposition, soil erosion were 5.30×10^3, 4.83×10^2, and 4.82×10^2 mol a^{-1} respectively, which account for 98.2% of total fluxes. (see Fig. 3). Total flux include seven interface transfer fluxes, which are transfer fluxes on the air–water surface, transfer fluxes on the air–soil surface, transfer fluxes from soil to water, and transfer fluxes on the water–sediment surface, respectively. Among the overall reserves, about 99.8% of DDT resided in the soil compartment. (2) 1984–2019. Assuming that the amount of application became zero, and a rapid decline of transfer fluxes and the environmental reservoir would followed. Dominant transfer processes for DDT changed considerably after 1983. Runoff from soil to water and sedimentation from water to sediment were the primary processes, and the following processes were resuspension and diffusion from sediment to water, diffusion from soil to air, etc. (see Fig. 3).

All the transfer fluxes of DDT in 2004 were less than 0.1% of those in 1983, and by 2019 they are expected to decrease to less than 0.002% of those in 1983. The distribution characteristic of DDT can be seen from Table 2. From 1984 to 2004, residue of DDT in the study area environment fell to less than 1.0% of that in 1983, and only about 0.02% will be left in 2019, according to the model prediction. Degradation in all compartments and main transfer fluxes of DDT in the study area in 1970 and 2000 can be seen from Fig. 4.

We also compared the model results with model results from Tianjin and Hangzhou sites. It can be found that the transfer processes between Lanzhou and these regions were obvious different. Firstly, the emission sources in the Lanzhou region differed with those in Tianjin and Hangzhou. The major source of DDT in the Lanzhou region was attributed to agricultural application of pesticides, while the leading inputs of *p,p′*-DDT in Tianjin and Hangzhou were from local agricultural use, waste water discharge from the

Table 1
Comparison between the observed and calculated concentrations of DDT in soil between1982 and 2004 (unit: mol m^{-3}).

	DDT	
	1982	2004
Obs	2.24×10^{-3} $(6.35 \times 10^{-5}–1.19 \times 10^{-2})$[a]	9.54×10^{-5} $(1.69 \times 10^{-6}–1.89 \times 10^{-4})$[a]
Cal	2.47×10^{-3}	2.00×10^{-5}

Notes: Observed concentrations were collected from Guo and Wang (1992) and Gansu Environmental Protection Bureau (2005).

[a] The range (min–max) and the average of measured data are given in here.

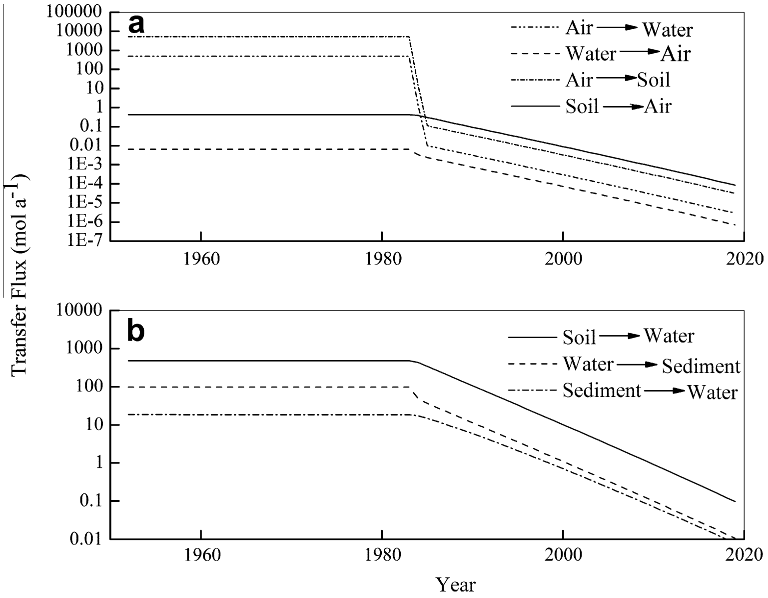

Fig. 3. Transfer fluxes of DDT between 1952 and 2019 in all the compartments. (a) Transfer fluxes on the air–water surface and air–soil surface. (b) Transfer fluxes from soil to water and on the water–sediment surface.

Table 2
Changing of environmental reservoirs of DDT in bulk compartments in the Lanzhou region (units: mol).

Phase	Air	Water	Soil	Sediment
1983	3.34×10^1	8.96×10^1	2.75×10^5	3.15×10^2
2004	8.02×10^{-6}	3.90×10^{-1}	2.20×10^3	4.89×10^0
2019	1.99×10^{-7}	9.75×10^{-3}	5.46×10^1	1.33×10^{-1}

pesticide factory. Secondly, the arrangement order of the transfer fluxes in the Lanzhou region was different from those in Tianjin and Hangzhou. As far as Lanzhou is concerned, deposition from air to soil/water, runoff from soil to water, and sedimentation from water to sediment were the dominant processes before 1983, Since 1984, soil erosion, sedimentation from water to sediment, resuspension and diffusion from sediment to water, and soil–air diffusion have become the main transfer processes. For *p,p′*-DDT in the Tianjin area, air deposition and the diffusion through the water–air interface were the dominant transfer processes, while the sedimentation from water to bottom sediment and soil or water runoff contributed significantly to the fate of *p,p′*-DDT over a long time period. The diffusion direction is therefore from water to air and from water to sediment. On the air–soil surface, the diffusion direction is from soil to air except for the first beginning when the pesticide DDT was applied (Li et al., 2006). The transfer processes in Hangzhou can also be divided into two stages. Between 1952 and 1983, the transfer fluxes of DDT in Hangzhou decreased in the order of deposition from air to soil, sedimentation from water to sediment, deposition from air to water, runoff from soil to water, diffusion from water/soil to air in the same time. From 1984 to now, runoff from soil to water and sedimentation from water to sediment were the most important processes in Hangzhou, and the other processes were diffusion from soil to air, resuspension and diffusion from sediment to water (Cao et al., 2007).

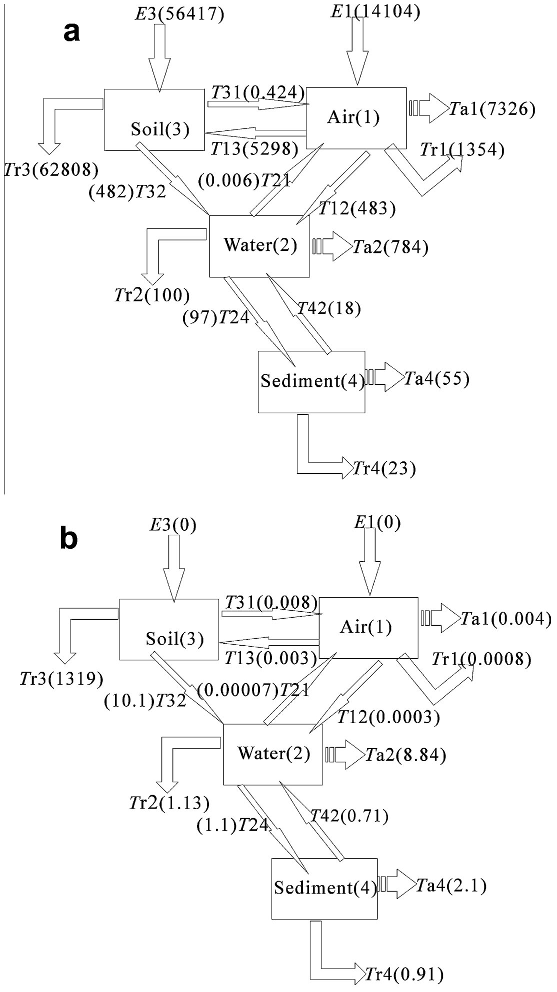

Fig. 4. Degradation in all compartments and main transfer fluxes of DDT in the study area (mol a^{-1}) in (a) 1970 and (b) 2000.

3.3. Sensitivity analysis

Because the conceptual model could not reflect the real world exactly and there are always inherent variability and uncertainty in the parameters (McKone, 1996). Hence, a sensitivity analysis was conducted for identifying the most influential parameters in the model. Method for calculating the sensitivity coefficients has been described and given in Section 2. In this model, the sensitivity coefficients of input parameters to the concentration of DDT in four bulk compartments were calculated.

Results of sensitivity analysis indicate that the emission rate, degradation rate in soil, air advection residence time, air depth, dry deposition velocity, and rain rate have a direct impact on the simulated DDT concentrations. As an input parameter, molecular weight was used to calculate air-side mass transfer coefficient over water, water-side mass transfer coefficient under air, and soil–air phase diffusion mass transfer coefficient. When molecular weight have changed, air-side mass transfer coefficient over water, water-side mass transfer coefficient under air, and soil–air phase diffusion mass transfer coefficient also have changed at the same time, the relative variation of the input parameter (molecular weight) will lead to relative variation of the calculated concentration. So, the input parameter (molecular weight) have an influence on the simulated DDT concentrations. The influences of model input parameters on the simulated DDT concentrations in different compartments were greatly different. For example, air was sensitive to air advection residence time and air depth, while soil was strongly affected by degradation rate in soil. The sensitivity of most input parameters also changed with time, the variability of some parameters such as the degradation rate in soil were relatively higher because fluctuation of sensitivity coefficients increased after the ban.

In summary, the emission rate and degradation rate in soil have a strong impact on calculated concentrations of DDT due to their high variability in this study. The calculated results in this study could be improved if more accurate input data were available. For example, the real degradation rate and more detailed emission data in study area could be obtained from the experiments or investigations in the study area.

4. Discussion

Fig. 2 suggests that the evolution of concentrations of DDT varied greatly among different compartments. It can be seen from the figure that the DDT concentrations in air changed more drastically than in other compartments. There are two possible reasons that can explain this modeled result. Firstly, Lanzhou city is located in the intermountain basin with complicated and changeable meteorological conditions, which make the air mobility higher than other three compartments. Secondly, degradation and advective removal processes from atmosphere are fast. The storage capacity of the atmosphere is very weak for POPs, and that the combination of a fast removal process and a low storage capacity results in an efficient removal of DDT from the atmosphere after its ban. The concentrations of DDT in soil and sediment changed and decreased slowly after the ban, due to their slow response time (large fugacity capacity, and slow evaporation and degradation). The variation of DDT concentrations in water was between that of air and soil. A much higher concentration of DDT was found in soil before 1983. After the ban in agriculture, the concentration of DDT also maintained a relative high level in soil. It was reported that detection rate of DDT in agricultural products ranged from 89% to 100% in the polluted soil of Lanzhou area (Guo and Wang, 1992). As a typical persistent chemical, DDT degrades very slowly in natural environment and may easily be enriched in food and living organisms. Therefore, DDT residues in the soil may become a threat to people's health in the Lanzhou area.

A large portion of the DDT found in air was sorbed on particles. The mean concentrations estimated in the gas and solid phases were 1.66×10^{-13} and 2.88×10^{-2} mol m^{-3}, respectively. Almost all of the DDT found in air was bound to the solid phase (99.9%) with only a negligible the amount in the gas phase (0.1%). Some researches have pointed out that the particulate air pollution in Lanzhou is more serious than other regions in China. Concentrations of total suspended particles (TSP) and PM_{10} in Lanzhou, China can keep a relative high level in spring and winter, because of the dust events and burning coal for heating. As the possible carcinogen, the high particulate fraction of DDT in Lanzhou air may have an adverse effect on human health. In water compartment, the mean concentration of DDT in fish was 5.48×10^{-4} mol m^{-3}, while that for water phase was 1.85×10^{-9} mol m^{-3}. The former was much higher than the latter, indicating a tendency for bioaccumulation.

There are five possible reasons that can explain these disagreements between model results and field data: (1) Emission data of DDT used in the model were with large uncertainties, which may lead to incorrect results. The real variance of agriculture application rate in various types of cropland and in various regions of Lanzhou was very large. For instance, the unit application rate in vegetables was usually far higher than that in other crop. We believe that this might be the major reason for the deviation of DDT in the Lanzhou region. (2) Observations were based on very limited samples collected from Anning and Chengguan, which were not uniformly distributed in four residential districts. The measured data poorly represent the average of the whole study area. (3) The use of the pesticide dicofol, containing up to 12% of DDT as impurity, could also contribute to the additional emission of DDT, besides the possible illegal use of DDT in agriculture. (4) The uncertainty of the input parameters, such as the degradation rate that was from the literature instead of specific measurements for the purpose of modeling, may lead to prediction errors. (5) The uncertainty of land use type was relatively higher, the model results may be affected especially by urban construction and planning.

The geological and meteorological characteristics in Lanzhou are different from those in Tianjin and Hangzhou, which render the characteristics of DDT transfer processes different from those in these regions. Because Lanzhou is a typical valley-basin city, the Yellow River runs across the Lanzhou city from the west to the east, and the South Mountains and the North Mountains stand separately along the banks of the Yellow River. Lanzhou is located in the west of the loess plateau, most areas of Lanzhou belong to semiarid regions, where precipitation are low. The Special topographic characteristics of the Lanzhou area feature the special meteorological conditions (low dry and wet deposition rate). Zhang (2005) evaluated the fate of Phenanthrene in Lanzhou using a non-steady-state multimedia fugacity model. Zhang's study showed that 10.8 is more appropriate value for dry deposition rate in Lanzhou. Therefore, Zhang's recommended dry deposition rate has been adopted in this study.

Table 3 listed dry deposition velocity and rain rate in Lanzhou, Tianjin, and Hangzhou. It can be seen from Table 3 that dry deposition velocity and rain rate in Lanzhou are obviously lower than those in Tianjin and Hangzhou. In addition, Table 3 displayed that volume fraction of solid in air is much higher than that of Tianjin and Hangzhou. These meteorological conditions contribute to slowing the transfer flux through dry, wet and dissolved deposition

Table 3
The comparison of environment parameters in different regions in China.

Parameter	Lanzhou	Tianjin[a]	Hangzhou[b]
Rain rate (m h^{-1})	3.74×10^{-5}	6.3×10^{-5}	1.57×10^{-4}
Dry deposition velocity (m h^{-1})	10.8	50	112
Volume fraction of solid in air	4.5×10^{-10}	1.1×10^{-10}	6.17×10^{-11}

[a] Tianjin's parameters were obtained from Li's article (Li et al., 2006).

[b] Hangzhou's parameters were obtained from Cao's thesis (Cao, 2005).

from air to soil. The deposition air–soil in Lanzhou is lower than those in Tianjin and Hangzhou.

5. Conclusions

In the study area, the main source of DDT is agricultural application between 1952 and 1983, and it is estimated that $7.05 \times 10^4\ \mathrm{mol\ a^{-1}}$ were applied to air and soil compartments. Based on Level IV model calculation, the degradation was the main pathway for DDT to vanish from the study area, and degradation in soil was the major loss process, accounting for about 97% of the total degradation amount, followed by degradation in air. Among the overall reserves, about 99.8% of DDT resided in the soil compartment. The concentrations of DDT maintained a relatively steady state in the 1980s, and then decreased quickly since the ban of DDT use as pesticide in 1983. A small amount of DDT has been left till now, according to the model prediction. Therefore, the environmentally ecological risk of DDT pesticide should not be neglected. The calculated transfer fluxes also indicate that the most important transfer processes influencing the fate of DDT are the deposition from air to soil, deposition from air to water, soil erosion, and sedimentation from water to sediment.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2010.07.035.

References

Aigner, E.J., Leone, A.D., Falconer, R.L., 1998. Concentrations and enantiomeric ratios of organochlorine pesticides in soils from the US Corn Belt. Environ. Sci. Technol. 32, 1162–1168.

Beard, J., 2006. DDT and human health. Sci. Total Environ. 355, 78–89.

Cao, H.Y., 2005. Studying the Area Differentiation of Transfer and Fate of Persistent Organic Pollutants using Modeling Method. Thesis (Postdoctoral), The Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences (in Chinese).

Cao, H.Y., Liang, T., Tao, S., Zhang, C.S., 2007. Simulating the temporal changes of OCP pollution in Hangzhou, China. Chemosphere 67, 1335–1345.

Cowan, C.E., Mackay, D., Feijtel, T.C.J., van de Meent, D., Di Guardo, A., Davies, J., Mackay, N., 1995. The Multi-media Fate Model: A Vital Tool for Predicting the Fate of Chemicals. SETAC Press, Penascola, FL. p. 78.

Editorial Committee of Lanzhou Chorography, 1998. Lanzhou Chorography, vols. 1 and 18. Lanzhou University Press, Lanzhou (in Chinese).

Falandysz, J., Brudnowska, B., Kawano, M., Wakimoto, T., 2001. Polychlorinated biphenyls and organochlorine pesticides in soils from the southern part of Poland. Arch. Environ. Contam. Toxicol. 40, 173–178.

Falck, F.J., Ricci, A.J., Wolff, M.S., Godbold, J., Deckers, P., 1992. Pesticides and polychlorinated biphenyl residues in human breast lipids and their relation to breast cancer. Arch. Environ. Health. 47, 143–146.

Feng, R., 2009. To treasure the yellow river wetland—a dewy green leaf: a survey on wetland along the Lanzhou Section of Yellow River and a strategy for protection. Wetland Sci. Manage. 5, 51–53 (in Chinese).

Fuller, E.N., Schettler, P.D., Giddings, J.C., 1966. A new method for prediction of binary gas–phase diffusion coefficients. Ind. Eng. Chem. 58, 18–27.

Fu, S., Chu, S., Xu, X., 2001. Organochlorine pesticide residue in soils from Tibet, China. Bull. Environ. Contam. Toxicol. 66, 171–177.

Guo, X.J., Wang, S.Y., 1992. Study on detection of organophosphorus and organochlorine pesticide residues in vegetable, Lanzhou. Gansu. Environ. Study Monitor. 18, 24–27 (in Chinese).

Gansu Environmental Protection Bureau, 2005. Environmental Quality Statement, 2000–2005 (in Chinese).

Hayduk, W., Laudie, H., 1974. Predictions of diffusion coefficients for non-electrolysis in dilute aqueous solution. AIChE J. 20, 611–615.

Kim, J.H., Smith, A., 2001. Distribution of organochlorine pesticides in soils from South Korea. Chemosphere 43, 137–140.

Li, Q.L., Zhu, T., Qiu, X.H., Hu, J.X., Vighi, M., 2006. Evaluating the fate of *p,p′*-DDT in Tianjin, China using a non-steady-state multimedia fugacity model. Ecotoxicol. Environ. Saf. 63, 196–203.

Liu, Z.Y., 2005. Multimedia Environment Modeling of Polychlorinated Organic Compounds (PCOCs) in Liao-he River Watershed. Thesis (Ph.D.), Dalian University of Technology (in Chinese).

Mackay, D., Paterson, S., 1991. Evaluating the multimedia fate of organic chemicals: a level III fugacity model. Environ. Sci. Technol. 25, 427–436.

Mackay, D., 2001. Multimedia Environmental Models: The Fugacity Approach, second ed. Lewis, Boca Raton.

Mackay, D., Shiu, W.Y., Ma, K.C., Lee, S.C., 2006. Handbook of Physical–Chemical Properties and Environmental Fate for Organic Chemicals, second ed. CRC Press.

McKone, T.E., 1996. Alternative modeling approaches for contaminant fate in soils: uncertainty, variability, and reliability. Reliab. Eng. Syst. Saf. 54, 165–181.

Meijer, S.N., Halsall, C.J., Harner, T., Peters, A.J., Ockenden, W.A., Johnston, A.E., Jones, K.C., 2001. Organochlorine pesticides residues in archived UK soil. Environ. Sci. Technol. 35, 1989–1995.

Qiou, R.J., 1989. Characteristics of colloid chemistry in water body of Lanzhou reach of Yellow River. Gansu. Environ. Study Monitor. 1, 46–50 (in Chinese).

Schenker, U., Scheringer, M., Sohn, M.D., Maddalena, R.L., McKone, T.E., Hungerbühler, K., 2009. Using information on uncertainty to improve environmental fate modeling: a case study on DDT. Environ. Sci. Technol. 43, 128–134.

Southworth, G.R., 1979. The role of volatilization in removing polycyclic aromatic hydrocarbons from aquatic environments. Bull. Environ. Contam. Toxicol. 21, 507–514.

Ta, W.Q., Wang, T., Xiao, H.L., Zhu, X.Y., Xiao, Z., 2004. Gaseous and particulate air pollution in the Lanzhou Valley, China. Sci. Total Environ. 320, 163–176.

Tao, S., Yang, Y., Cao, H.Y., Liu, W.X., Coveney, R.M., Xu, F.L., Cao, J., Li, B.G., Wang, X.J., Hu, J.Y., Fang, J.Y., 2006. Modeling the dynamic changes in concentrations of γ-HCH in Tianjin, China from 1953 to 2020. Environ. Pollut. 139, 183–193.

Thao, V.D., Kawano, M., Tatsukawa, R., 1993. Persistent organochlorine residues in soils from tropical and subtropical Asian countries. Environ. Pollut. 81, 61–71.

Van den Berg, F., Kubiak, R., Benjey, W.G., 1999. Emission of pesticides into the air. Water Air Soil Pollut. 115, 195–218.

Wania, F., Mackay, D., 1995. A global distribution model for persistent organic-chemicals. Sci. Total Environ. 160 (161), 211–232.

Wang, Y.L., Zhang, J.K., Sun, Y.H., Zhou, Z.F., 2006. The study of sediment characteristics and water quality prediction in Lanzhou reach of the Yellow River, Gansu. Sci. Technol. 22, 69 (in Chinese).

Wolff, M.S., Toniolo, P.G., 1995. Environmental organochlorine exposure as a potential etiologic factor in breast cancer. Environ. Health Perspect. 103, 141–145.

Yang, M., Ding, R.Q., Wang, S.G., Shang, K.Z., 2005. The Characteristics of aerosols over Lanzhou City and their influence on respiratory disease. Arid Meteorol. 23, 54–57 (in Chinese).

Yao, H.J., 2009. Modelling Multimedia Environmental Behavior and Ecological Risk of Persistent Organic Pollutants using Fugacity Models – Take the Study of Semi-arid Lanzhou Area as an Example. Thesis (MA.SC), Lanzhou University (in Chinese).

Zhang, L., 2005. Research on Multimedia Environmental Fate Model. Thesis (Ph.D.), Nankai University (in Chinese).

Zhu, Y.F., Liu, H., Xi, Z.Q., Cheng, H.X., Xu, X.B., 2005. Organochlorine pesticides (DDTs and HCHs) in soils from the outskirts of Beijing, China. Chemosphere 60, 770–778.