We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

6,900
Open access books available

186,000
International authors and editors

200M
Downloads

154
Countries delivered to

Our authors are among the

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Endosulfan in China:
Usage, Emissions, and Residues

Hongliang Jia[1], Liyan Liu[2], Yeqing Sun[3] and Yi-Fan Li[4]

[1,3,4]*International Joint Research Center for Persistent Toxic Substances*
(IJRC-PTS), Dalian Maritime University
[2,4]*IJRC-PTS, State Key Laboratory for Urban Resources and Environment,*
Harbin Institute of Technology
[3]*Environmental System Biology Institute, Dalian Maritime University*
[4]*Science and Technology Branch, Environment Canada*
[1,2,3]*P. R. China*
[4]*Canada*

1. Introduction

Endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9a-hexahy-dro-6,9-methano-2,3,4-benzodioxyanthiepin-3-oxide), an organochlorine pesticide, was first introduced in the 1950s by Hoechst AG and FMC Corporation. As a non-systemic and ingested insecticide and miticide, endosulfan was extensively used for over 30 years on a wide variety of food crops, such as grains, tea, fruits, and vegetables, on non-food crops, such as tobacco and cotton, and also used as a wood preservative (Sutherland et al, 2000). The commercial technical endosulfan consists of 70% α-endosulfan and 30% β-endosulfan (Maier-Bode, 1968; Rice et al., 1997), which are with similar insecticidal properties but different physicochemical properties (Peterson & Batley, 1993; Schmidt et al., 1997). Main trade names of endosulfan are Beosit, Chlortiepin, Cyclodan, Devisulphan, Endocel, Endosol, Hildan, Insectophene, Malix, Rasayansulfan, Thifor, Thimul, Thiodan, Thionex, Thiosulfan. In the environment, the cyclic sulfite group of endosulfan can be hydrolyzed to form a less toxic endosulfan diol (Peterson & Batley, 1993) or oxidized to the corresponding endosulfan sulfate (Chandler & Scott, 1991; Miles & Pfeuffer, 1997). It has been reported that endosulfan is genotoxic in mammalian cells (Chaudhuri et al., 1999; ASTDR, 2000). Endosulfan is extremely toxic to fish and aquatic invertebrate (Verschureren, 1983; Sunderam et al., 1992) and it has been implicated increasingly in mammalian gonadal toxicity (Sinha et al., 1995), genotoxicity (Sutherland et al., 2002), and neuro toxicity (Southan & Kennedy, 1995). In India, the National Institute of Occupational Health conclusively proved that endosulfan was a causative factor in the incidence of all crippling illness in the Kasargode area of Kerela where this insecticide was sprayed aerially in the cashew plantations (Devakumar, 2002). α- and β-endosulfan, and their metabolize endosulfan sulfate are generally considered to be equally toxic and are classified by the US Environmental Protection Agency as priority pollutants (Keith & Telliard, 1979), and endosulfan was recently banned for use in the USA (Lubick, 2010).

Endosulfan was listed as a candidate for new persistent organic pollutants (POPs) under the Stockholm Convention (UNEP, 2007).

Endosulfan is still a widely-used insecticide in many countries. The World Health Organization estimated world wide annual production to be about 9.1 kt in the early 1980s (WHO, 1984), and the world average annual consumption was 10.5 kt for 1980-1989, and increased to 12.8 kt per year in 1990s (http://en.wikipedia.org/wiki/Endosulfan). India is the world's leading manufacturer of endosulfan, and third most produced pesticide in the country, with almost 81.6 kt being manufactured in 1999-2000 (Saiyed et al., 2003). Cumulative global use of endosulfan for crops was estimated to be 338 kt (Li & MacDonald, 2005), and the general trend of total global endosulfan use has increased continuously since the first year when this pesticide was applied, and the data for emissions of α-endosulfan show a large variance with a generally increasing trend at least up until the late 1990s (Li & MacDonald, 2005).

Widespread use and atmospheric transport of endosulfan account for its ubiquitous global distribution. High concentrations of endosulfan, as the total of α-endosulfan, β-endosulfan and endosulfan sulfate, have been detected in tree bark samples throughout the world, particularly in India and the Pacific Rim (Smimonich & Hites, 1995). Endosulfan also showed the highest levels of all the OCPs in air globally, in the range of tens to hundreds of pg/m^3. Very high air concentrations in the range of ng/m^3 were observed in Bahia Blanca in Argentina and Las Palmas on the Canary Islands (Pozo et al., 2006).

Endosulfan can be carried over long distances by atmospheric long-range transport (ALRT). A time trend of α-endosulfan air concentration at Canadian Alert Station, compiled from several sources (Patton et al., 1991; Halsall et al., 1998; Hung et al., 2002; Su et al., 2008), showed it to be one of the few OCPs that is still increasing in arctic air with a ranged from 3.3 to 4.7 pg/m^3 for 1987 – 1997 (Li & MacDonald, 2005), and the mean concentration of 4.3 pg/m^3 with a range of 0.12-25 pg/m^3 for 2000-2003 (Su et al., 2008).

In order to study the transport, fate and the impact to the health of humans and wildlives of chemicals on different scales, gridded emission inventories with reasonable accuracy evaluated by monitoring data are crucial input data for models to simulate the transport of chemicals and their behaviours in different environmental compartments (Li and Bidleman, 2003; Li et al., 2004a). The objective of this research presented in this Chapter is to develop Chinese inventories of air emissions and soil residues for endosulfan, and from which, inventories of air and soil concentrations for the chemical are created. The model results are compared with monitoring data across China to evaluate the quantities of the inventories.

This Chapter is divided into several sections. In Section 2 production of endosulfan in China is introduced, and Chinese inventories are presented for endosulfan usage in Section 3. Section 4 depicts the modeled emissions to air and residues in agricultural soil of endosulfan in China, while Section 5 discusses the monitoring results of endosulfan in Chinese air and soil, and also the air and soil concentrations of this insecticide. To evaluate the quantify of these modelled inventories, the comparisons between the monitoring results and the modeled data are presented in Section 6. Section 7 gives the conclusions to end the chapter.

2. Endosulfan production in China

China started to produce endosulfan in 1994, when it was used only on cotton (Peasant Daily, 2001). In 2001, there were two producers producing technical endosulfan and 36 formulators producing formulated endosulfan products in China (Chinese Network for

Public Science and Technology). The number of the companies increased to 43 at the end of 2005, three companies of which had become technical endosulfan producers and all others being formulators. All three producers of endosulfan in China in 2005 were located in Jiangsu province, while the location of formulators were mainly located in the east of China, especially in Shandong and Jiangsu provinces. The real production of endosulfan is not clear, but possibly because the domestic production of endosulfan could not meet the needs of the Chinese market so that the import of endosulfan has been necessary. Technical endosulfan has been imported from Germany, Israel, South Korea, and India to meet the needs of the domestic market in China (Peasant Daily, 2001).

3. Endosulfan usage in China

As an insecticide, endosulfan has been used only in agriculture in China. Endosulfan has been applied in china to control pests in cotton since 1994, and in wheat, tea, tobacco, apple and other fruits since 1998 (Jia et al., 2009a). According to Chinese pesticides registered, endosulfan was used on six crops, e.g., cotton, tea, tobacco, wheat, apples, and pears (Pesticide Electronic Handbook, 2006). In order to estimate the use of endosulfan in China, information of the application rates of endosulfan on lands of five crops, cotton, tea, tobacco, wheat, and apples, have been collected, and the total grow areas of these 5 crops in Chinese prefectures were used to estimate the endosulfan usage in each prefecture for each crop. The total endosulfan usage from 1994 to 2004 on cotton, wheat, tea, tobacco, and apples, were 14,600 t, 4000 t, 2900 t, 2300 t, and 1900 t, respectively. The total usage of endosulfan in China was estimated to be approximately 25,700 t between 1994 and 2004 (Jia et al., 2009a).
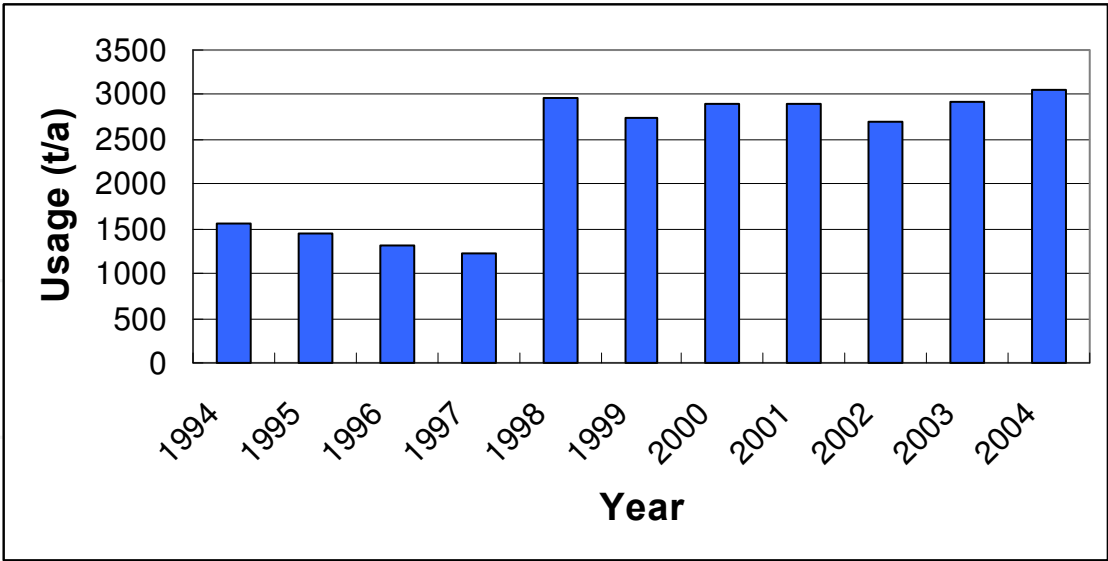

Fig. 1. Annual endosulfan usage in China from 1994 to 2004 (Jia et al., 2009a)

3.1 Temporal trend of endosulfan usage
Annual endosulfan usage from 1994 to 2004 in China is shown in Fig. 1. The average annual usage was around 1,500 t from 1994 to 1997, and increased to almost 3,000 t/y from 1998 to 2004. Usage of endosulfan after 2004 were not estimated since the information was not available. It was reported that the usage of endosulfan was reduced, especially on tea.
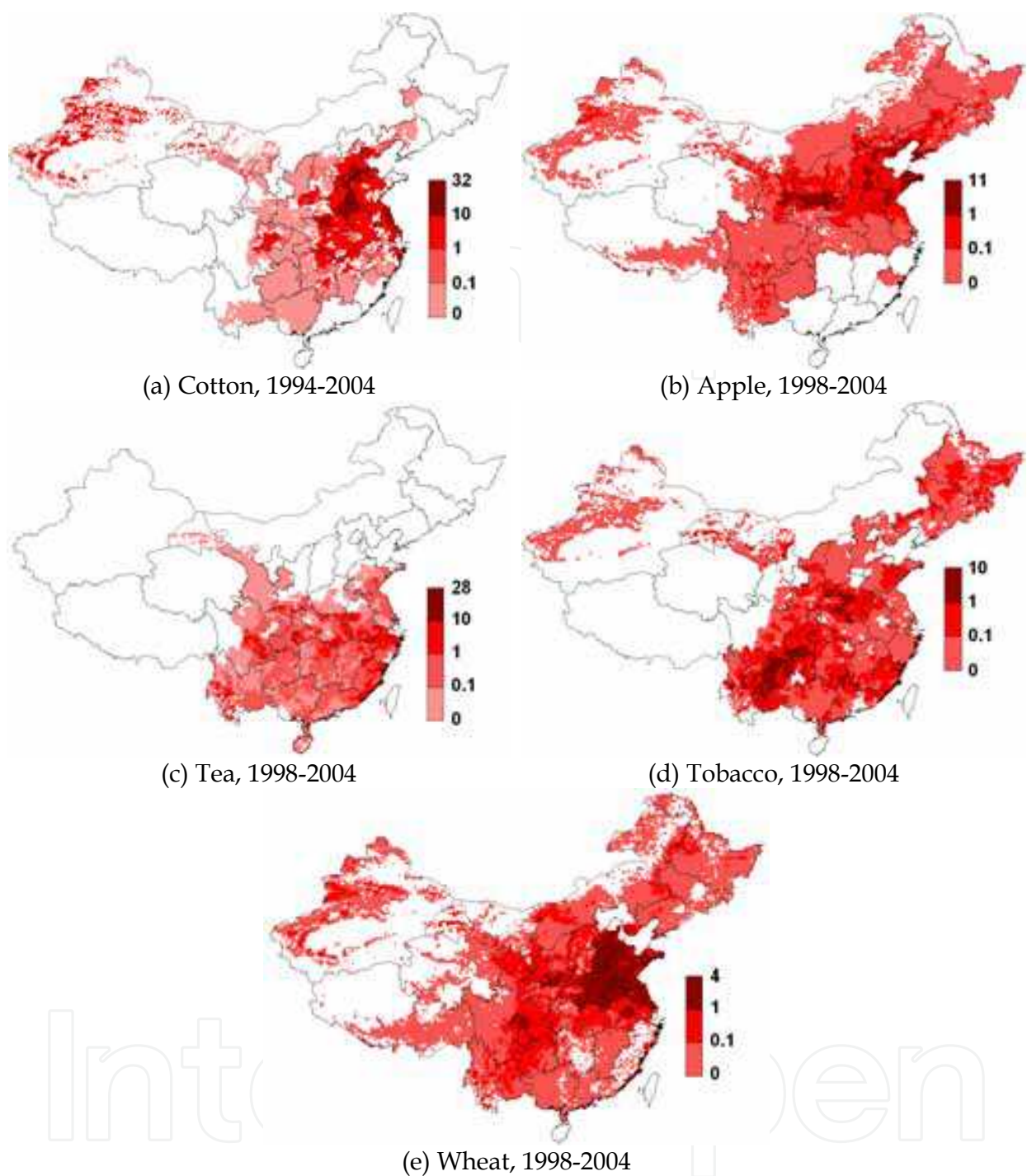
(a) Cotton, 1994-2004   (b) Apple, 1998-2004

(c) Tea, 1998-2004   (d) Tobacco, 1998-2004

(e) Wheat, 1998-2004

Fig. 2. Distribution of endosulfan usage in Chinese crops from 1994 to 2004 with 1/4° longitude by 1/6° latitude resolution (unit: t/cell).

3.2 Spatial endosulfan use distribution

In order to obtain a high resolution of spatial distribution of Chinese endosulfan usage, gridded lands with a 1/4° longitude by 1/6° latitude resolution for different crops (Li et al., 2001) was used to allocate the use of this insecticide, and the gridded Chinese endosulfan usage inventories with the same resolution were compiled (Jia et al., 2009a). These usage inventories were included endosulfan usage on cotton from 1994 to 2004 (Fig, 2 (a)),
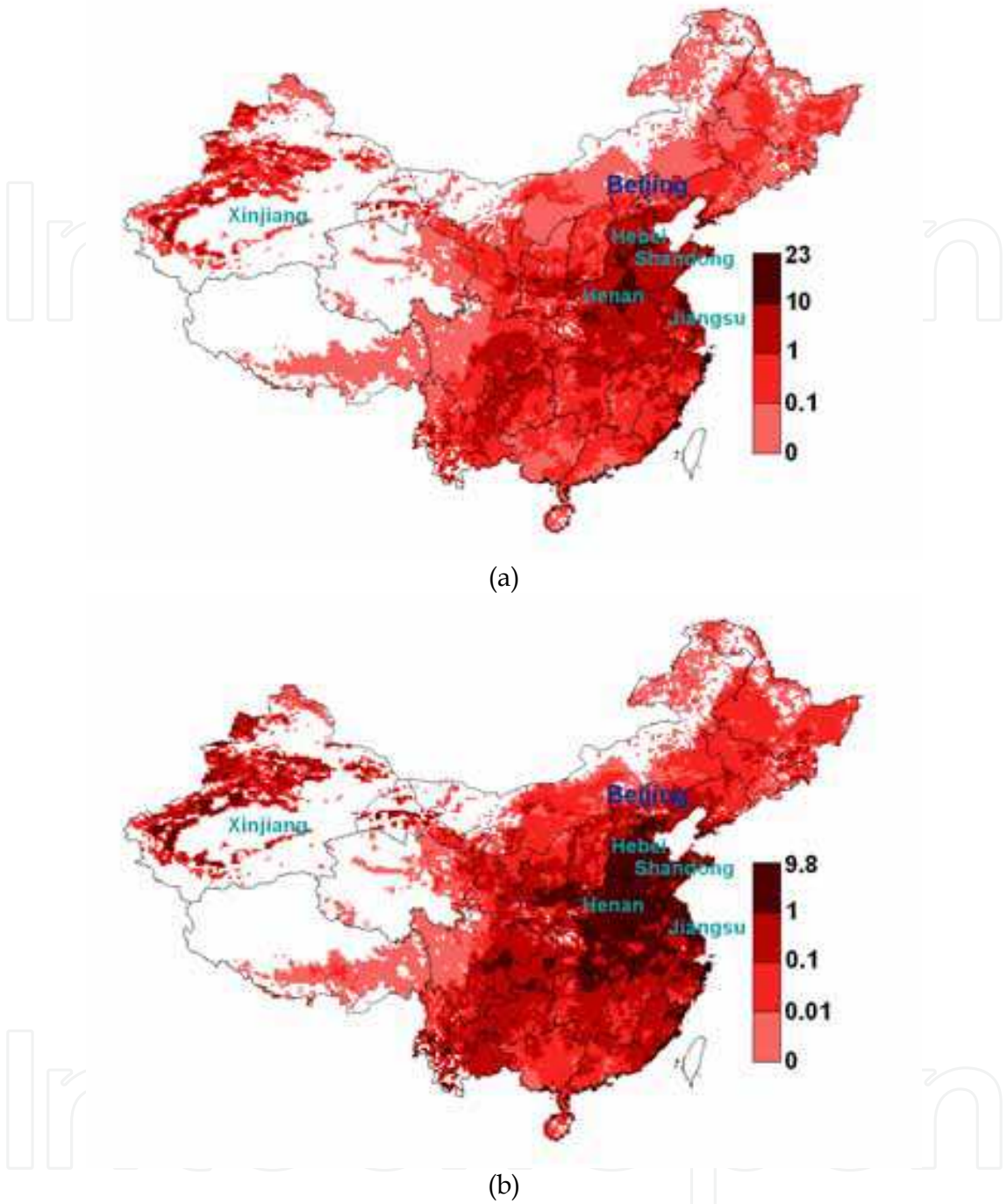
(a)

(b)

Fig. 3. Distribution of total α-endosulfan (a) and β-endosulfan (b) usage in China from 1994 to 2004 with 1/4° longitude by 1/6° latitude resolution (unit: t/cell).

endosulfan usage on apple, tea, tobacco, and wheat from 1998 to 2004 (Fig, 2 (b) – (e)). These maps show that the dense use of endosulfan on cotton in China was in the central east of China, including Provinces of Hebei, Henan, Shandong, and Jiangsu. The use of endosulfan on apple in China was also mainly in the central east of China, including provinces of Liaoning, Hebei, Henan, Shandong, Shaanxi, and Shanxi. The dense use of endosulfan on tea was in the south of China, and the dense use of endosulfan on tobacco in China was in Provinces of Yunnan, Guizhou, and Henan, where tobacco widely grows. The area of major

use of endosulfan on wheat in China was in the central east of China, including Provinces of Hebei, Henan, Shandong, Jiangsu, and Anhui.

3.3 Usage data for α- and β-endosulfan

Chinese technical endosulfan usage from 1994 to 2004 was estimated to be around 25700 t, as the proportion of α-endosulfan and β-endosulfan is 7: 3, the usage was 17990 t for α-endosulfan and 7710 t for β-endosulfan in this period. Gridded usage inventories for α-endosulfan and β-endosulfan on a 1/4° longitude by 1/6° latitude grid system are given in Fig. 3, which indicates that the most intensive use of endosulfan in China was in the south of Hebei Province, west of Shangdong Province, east of Henan Province, north of Anhui Province, east of Jiangsu Province, and some areas in Yunnan Province and Xinjiang Autonomous Region.

4. Modelling endosulfan in Chinese soil and air

4.1 Method

The simplified gridded pesticide emission and residue model (SGPERM) (Li et al., 2004b) has been used to estimate the emission and the residues for different pesticides in different areas, such as for toxaphene in the United States (Li et al., 2001), for α-HCH (Li et al., 2000) and β-HCH (Li et al., 2003) on a global scale. Details of the SGPERM can be found elsewhere (Li et al. 2004b; Jia et al., 2009b), and only a brief description is given here.

The model considers a single plant/harvest cycle in each year and two different emission scenarios for simplicity. The first one is a spraying event and the second is a tilling event. Both events were assumed to happen at the same time.

Considering two consecutive years, Year 1 and Year 2, we suppose that $U^{(1)}$ t of endosulfan is used in Year 1, and the emission in Year 1 will be (in the unit of t)

$$E_{sp}^{(1)} = U^{(1)}F_{sp} \qquad (1)$$

where F_{sp} is annual emission factor for spraying event. Soil is free of the pesticides considered before its use. After spray, the residue in soil becomes (in the unit of t)

$$R_1^{(1)} = U^{(1)} - E_{sp}^{(1)} \qquad (2)$$

The residues of all endosulfan applied are assumed to be mixed and stay in the soil until the next tilling event in the next year. In Year 2, the residue due to the previous year is given by

$$R_1^{(2)} = R_1^{(1)}e^{-\mu t} \qquad (3)$$

where μ is the degradation rate constant of endosulfan in soil (in the unit of year−1), and equal to $\ln 2/t_{1/2}$ with $t_{1/2}$ being the half-life of degradation (in year) for the pesticide in soil. t is the time period and equal to 1 year in our study.

Suppose $U^{(2)}$ of endosulfan are used in Year 2, and the emission due to spray in Year 2 will be

$$E_{sp}^{(2)} = U^{(2)}F_{sp} \qquad (4)$$

Emission due to the tilling is given by

$$E_{tl}^{(2)} = R_1^{(2)} F_{tl} \tag{5}$$

where F_{tl} is annual emission factor for tilling event. After both the events in Year 2, the emission is given by $E^{(2)} = E_{sp}^{(2)} + E_{tl}^{(2)}$ and the residue by

$$R_2^{(2)} = (U^{(2)} - E_{sp}^{(2)}) + (R_1^{(2)} - E_{tl}^{(2)}) \tag{6}$$

Therefore, in Year 2, there are two values for residues, $R_1^{(2)}$ and $R_2^{(2)}$. The former is the residues of endosulfan remaining in the soil from the previous year and the latter is residues of endosulfan remaining in the soil from the previous year plus the residues due to the current use of the pesticide. Obviously, $R_1^{(2)} - E_{tl}^{(2)}$ and $R_2^{(2)}$ are the minimum and maximum values of residue in the same year, respectively. The unit of all U, E, and R is in t, given total usage, emission, and residue in 1 year, respectively. The residue in soil decreases over time by degradation until the sudden increase in the next year due to application of the pesticide. Equations for Year 2 were used for any year after Year 2.

It appears that the calculation of emissions on a grid system covering the whole China requires considerable human and computer resources. The difficulty in undergoing such a large number of calculations is that some of the input data required for the calculations, such as the timing and mode of application and the degradation rates in the soil. Within the scope of the present study, a number of assumptions have been made for simplicity. In present study, only one plant/harvest cycle is assumed in a given year, and emission of endosulfan residues in the agricultural soil are assumed to start at the time of tilling in each year. The errors created by these assumptions are reduced since only annual emissions are considered here. But the re-emission by endosulfan deposition on soil and water transportation in the atmosphere has not been considered here, so in this case, only first-time emissions are estimated. Besides emission to the air, the residues of the pesticides in soil are lost over time by degradation.

To calculate the emission and residue of endosulfan, emission factors are crucial parameters in the SGPERM. Emission factors of the pesticides represent the emission potential of pesticides in a geographical area, and are used to calculate the emission. In present study, a simplified approach is taken for estimating the annual emission factor by considering two different emission factor scenarios: one is spraying event (F_{sp}) and the other is tilling event (F_{tl}). The definition of the emission factor is given as (Li et al., 2000)

$$F_k = \frac{E_k}{V_k} \tag{7}$$

where the subscript $k = s$ corresponds to a spraying event and $k = t$ corresponds to a tilling event. In the case of a spraying event, V_s is the current usage of pesticide as a spray, E_{sp} is the amount of pesticide emitted to the atmosphere due to the spraying event, and the emission factor (F_{sp}) is defined as the ratio of the emission (E_{sp}) to the usage (U_{sp}). In the case of a tilling event, U_t is the current usage of pesticide applied using a soil incorporation mode (if any) plus any pesticide residues remaining in the soil due to applications in previous years from all application modes. E_{tl} is the amount of pesticide emitted to the atmosphere, and the emission factor (F_{tl}) is defined as the ratio of the emission (E_{tl}) to the amount of current usage of pesticide applied by a soil treatment mode plus the residues in the soil. This definition is convenient for considering the emissions due to several consecutive years of pesticide application (Li et al., 2000).

The emission factors of organochlorine pesticides are a very complicated function of a large number of variables. They depend on a number of factors such as the physical and chemical properties of pesticides, application modes, the local meteorological conditions when they applied, the soil type, and the temperature (Li et al., 2000; Li et al., 2001).

Some prior researchers performed on emission of pesticides on a local scale (Baas & Huygen, 1992; Baas, 1994; Baart et al., 1995; Dörfler et al., 1991; Rüdel, 1997), and Rüdel (1997) concluded the volatilisaion rates of endosulfan were 50-70% from soil surfaces after this pesticide application. Further, Scholtz et al. tailed estimated emission factors for 20 pesticides for North America (1997) and on a global scale (1998). It had been realized that most pesticides emissions from soil residues happened due to high temperature (Harner et al., 2001). In this case, the emission factor (F_{tl}) defined as the ratio of annual emission (E_{tl}) to the amount of residues can be treated as the annual emission factor of endosulfan due to tilling or soil-air exchange. This will not create significant errors since only annual emissions are considered in this study.

Emission factors of endosulfan for China area are obtained from Scholtz et al. (1998), and were organized into a 1/6° x 1/4° grid system. The emission factors range from 0.41 to 0.55 for the spray mode are given in Fig. 4 (a) and at a tilling mode, the range is from 0.068 to 0.092 (Fig. 4 (b)). The areas with the highest emission factors are Xinjiang autonomous region, northwest of China, and Hainan province, the south of China.

It appears that the calculation of emissions on a grid system covering the whole China requires considerable human and computer resources. The difficulty in undergoing such a large number of calculations is that some of the input data required for the calculations, such as the timing and mode of application and the degradation rates in the soil. Within the scope of the present study, a number of assumptions have been made for simplicity. Emission and residue of endosulfan can be calculated by using the simplified gridded pesticide emission and residue model (SGPERM) (Li et al., 2004b), and in order to calculated the air/soil concentrations, a module were added to SGPERM. The detailed descriptions can be found elsewhere (Jia et al., 2009b). In present study, only one plant/harvest cycle is assumed in a given year, and emission of endosulfan residues in the agricultural soil are assumed to start at the time of tilling in each year. The errors created by these assumptions are reduced since only annual emissions are considered here. But the re-emission by
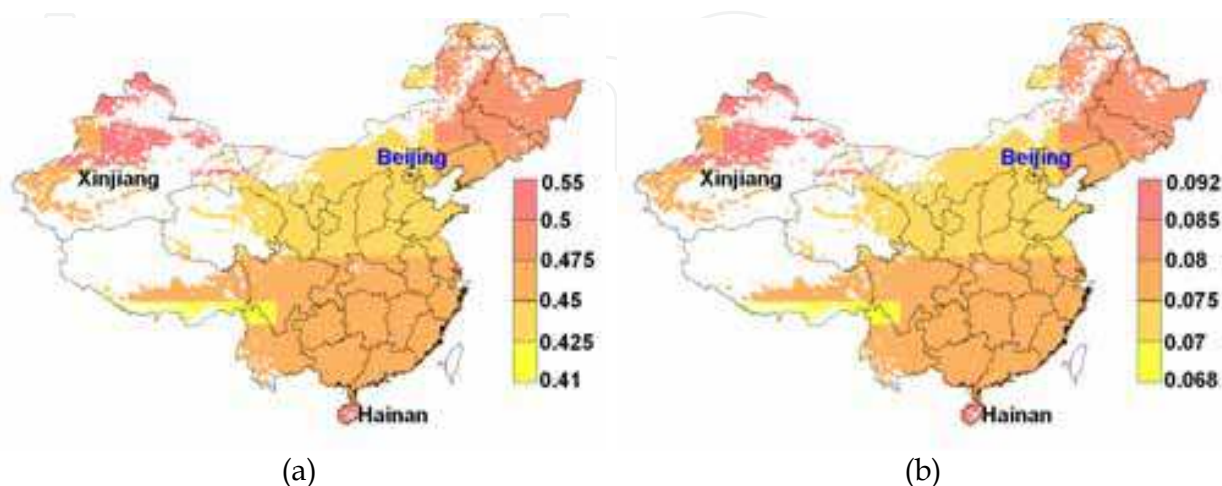

(a)   (b)

Fig. 4. Emission factors of endosulfan for (a) spray event, and (b) tilling event in China with 1/4° longitude by 1/6° latitude resolution.

endosulfan deposition on soil and water transportation in the atmosphere has not been considered here, so in this case, only first-time emissions are estimated. Besides emission to the air, the residues of the pesticides in soil are lost over time by degradation.

4.2 Temporal trends

Temporal trends of emissions to air and the highest and the lowest residues in Chinese agricultural soil for α- + β-endosulfan from 1994 to 2004 are given in Fig. 5. The annual emission were approximately 600 t from 1994 to 1997, 1,200 t for each year from 1998 to 2004, and the annual highest residue was approximately 629 t in 2004 with the lowest residue in the same year being approximately 120 t, around one fifth of the highest value. The highest residues of these 2 isomers appeared after the application of endosulfan, and the lowest residues occurred before the first application of this pesticide in the year.
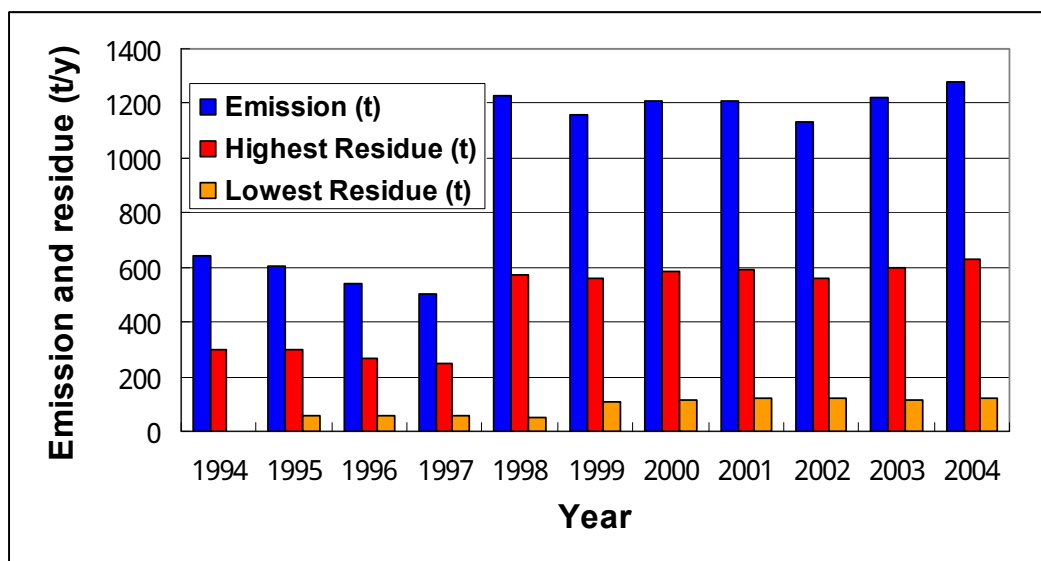
Fig. 5. Annual endosulfan emission and residue in China from 1994 to 2004 (Jia et al., 2009b)

4.3 Residues in soil and soil concentrations

The annual average soil concentrations of endosulfan in agricultural soil of each cell can be determined by using its residue inventories, given by

$$C_{soil} = R / (ALD) \tag{8}$$

where A is the area of the agricultural land in a grid cell, L is the depth of the soil (assuming that endosulfan residues in each grid cell are contained in the top 15-cm layer of cropland soil), and D is the density of the soil. The gridded soil density with 1/4° longitude by 1/6° latitude resolution was interpolated from a soil density dataset with 1° longitude by 1° latitude resolution, available at http://islscp2.sesda.com/ISLSCP2_1/data/hydrology_soils/islscp2soils-1deg. The soil densities in the model domain are from 0.53 to 1.79 g/cm^3.
R is either $R_1^{(2)}$ or $R_2^{(2)}$, but with a unit of ng in this equation. The unit for C soil is usually given in ng/g dry weight (dw). There are also two values for C soil, the lowest value when R = $R_1^{(2)}$ and the highest when R = $R_2^{(2)}$.
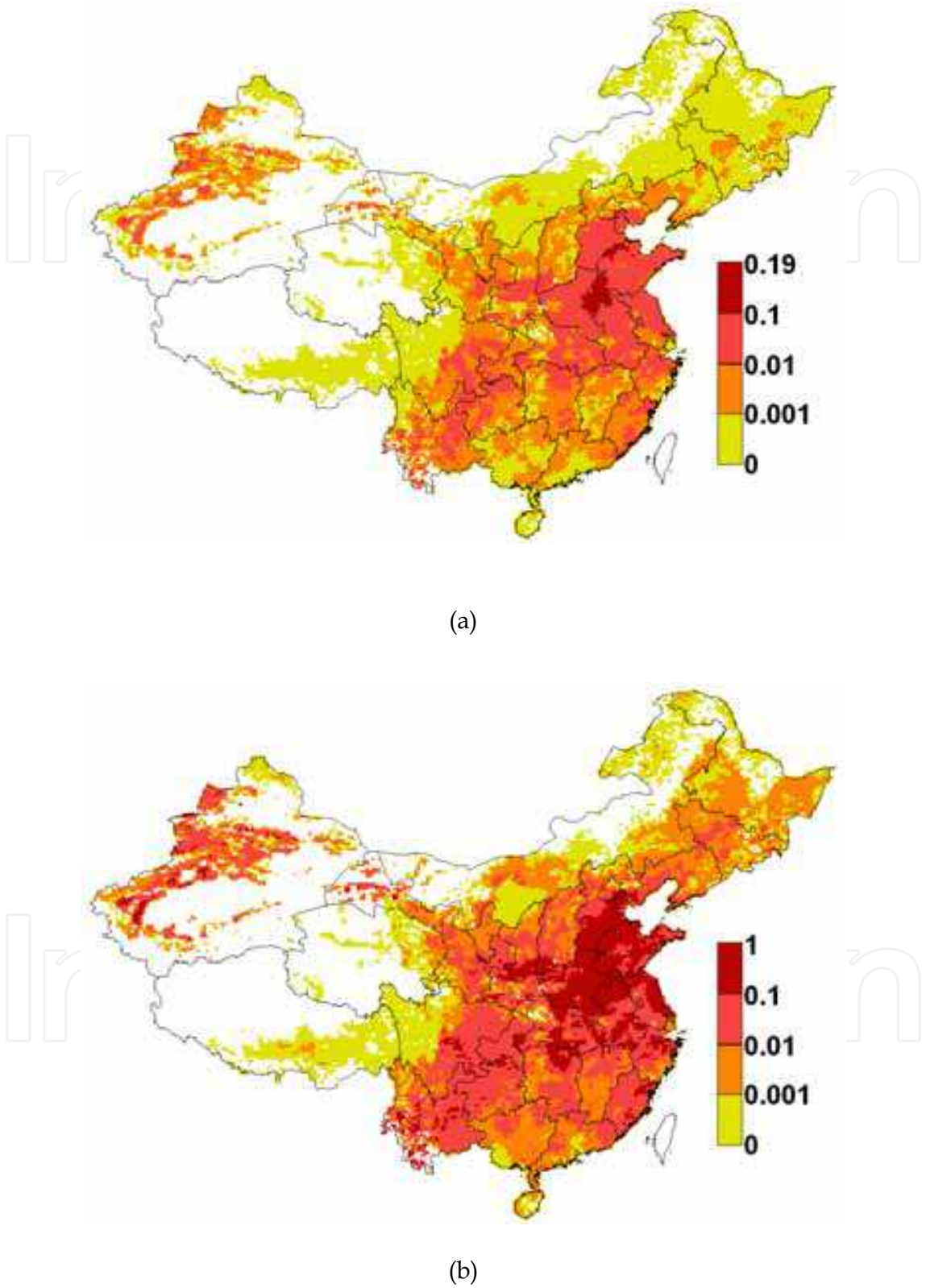
(a)

(b)

Fig. 6. Distribution of (a) the lowest and (b) the highest residuest of endosulfan in Chinese agricultural soil in 2004 with 1/4° longitude by 1/6° latitude resolution. (unit: t/cell)

Distribution of the lowest and the highest residues of endosulfan (α- + β-isomer) in Chinese agricultural soil in 2004 with $1/4°$ x $1/6°$ longitude and latitude resolution are shown in Fig. 6, which indicating heavier residues of these 2 isomers located in the central east China, including Henan, Shandong, Anhui provinces, and the south of Hebei, north and east Jiangsu, parts of Hubei, Hunan provinces. In 2004 the lowest and the highest residues endosulfan were 120 and 629 t, respectively in Chinese cropland where endosulfan had been applied.

Fig. 7 and Fig. 8 depicts the gridded lowest and highest concentration of α-endosulfan and β-endosulfan in Chinese agricultural soil in 2004 with $1/4°$ x $1/6°$ longitude and latitude resolution, respectively. The densest concentrations of endosulfan in Chinese agricultural soil were in Yunnan Province, where tobacco planning is a common agricultural practice. Other regions with dense soil concentrations included northern Gansu, southern Anhui, north of Fujian, and parts of Xinjiang Autonomous Region. As shown in Fig. 7 and Fig. 8, while the highest concentration is only several times higher than the lowest concentration for β-endosulfan, the difference between the lowest and the highest concentration for α-endosulfan in agricultural soil is very large, reaching as high as 2-3 orders of magnitude. The much longer (135 days) half-life for β-endosulfan than α-endosulfan (35 days) leads to a more stable soil concentration in soil for β-endosulfan.

4.4 Emissions to air and air concentrations

The annual average concentration of endosulfan in air can be calculated by using a simplified Gaussian formula (Jiang & Wu, 1990).

$$C_{air} = E / (ut\Delta l\Delta h) \qquad (9)$$

where C air is air concentration in each grid cell (in unit pg/m^3), E is annual emission in the grid cell ($=E_{sp} + E_{tl}$) (t before, but needs to be transferred to pg here), t is the time period, and equal to 1 year here, Δl is the dimension of the grid cell (24 km used here), Δh the height of the boundary layer, which is assumed to be 1,000 m in this study, and u is the annual mean wind speed (in m/year), which was obtained from the National Centers for Environmental Prediction (NCEP) reanalysis at standard atmospheric pressure levels (Kalnay et al. 1996). The annual wind speeds (in m/s) in the model domain were from 2.7 to 8.0. It is worthwhile to point out first that the air concentration estimated using our model is an annual average, and actual air concentration will vary from season to season. Secondly, our model does not consider the transport of the insecticide in the atmosphere, which could be very important in some areas.

Emissions of α- and β-endosulfan on a $1/4°$ longitude by $1/6°$ latitude resolution in 2004 are shown in Fig. 9. Total emissions of α- and β-endosulfan in 2004 were estimated to be 890 t and 390 t, respectively, and the highest emissions per each grid cell were 1.45 t for α-endosulfan and 0.64 t for β-endosulfan.

Distribution of air concentrations for these 2 isomers in 2004 with $1/4°$ x $1/6°$ longitude and latitude resolution are shown in Fig. 10. The highest α-endosulfan concentrations in air were in the Shandong, Henan, Shanxi, and Shaanxi provinces, which are the wheat and cotton growing area.
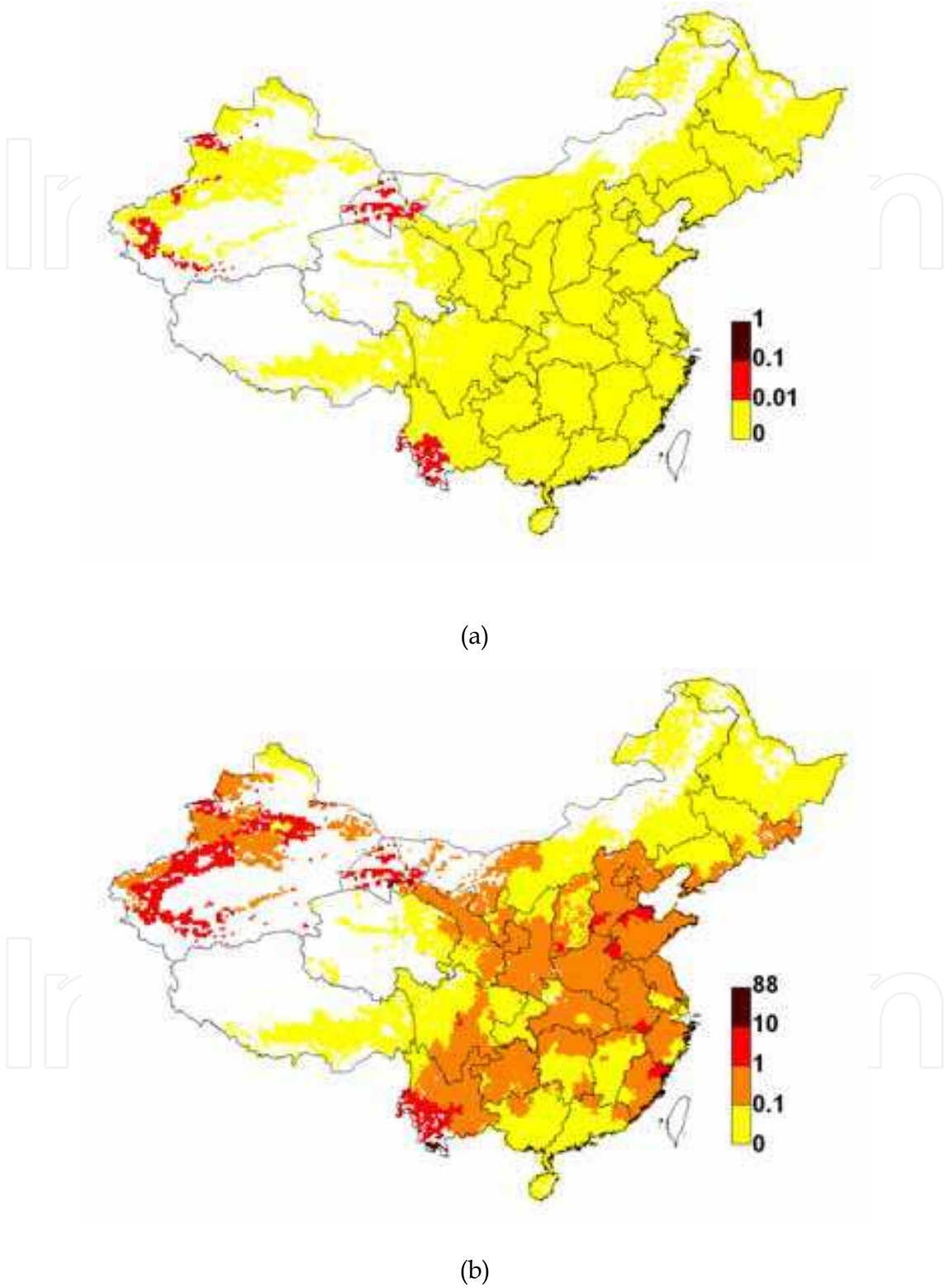
(a)

(b)

Fig. 7. Distribution of of (a) the lowest and (b) the highest concentration (ng/g dw) of α-endosulfan in Chinese agricultural soil in 2004 with 1/4° longitude by 1/6° latitude resolution.
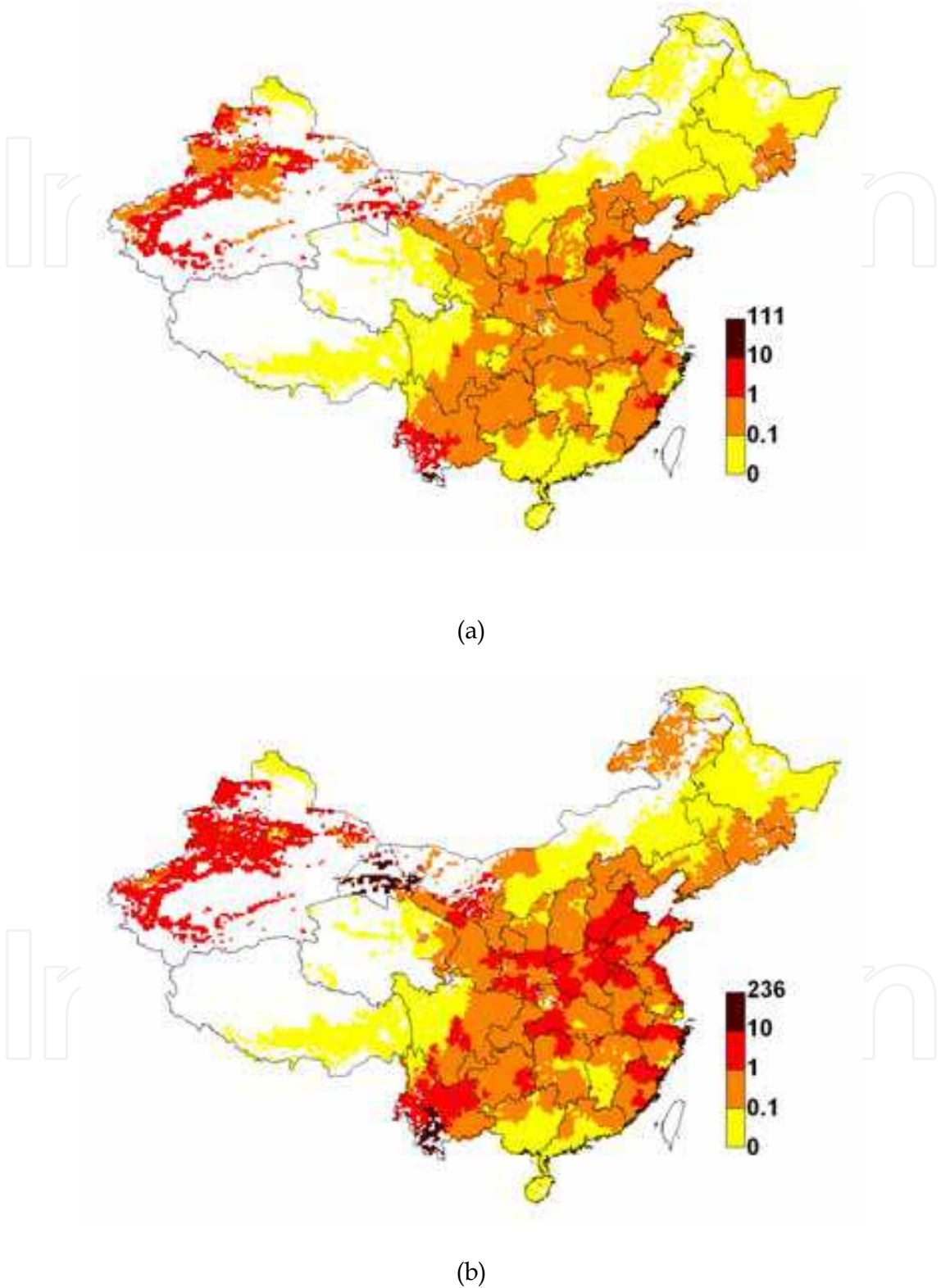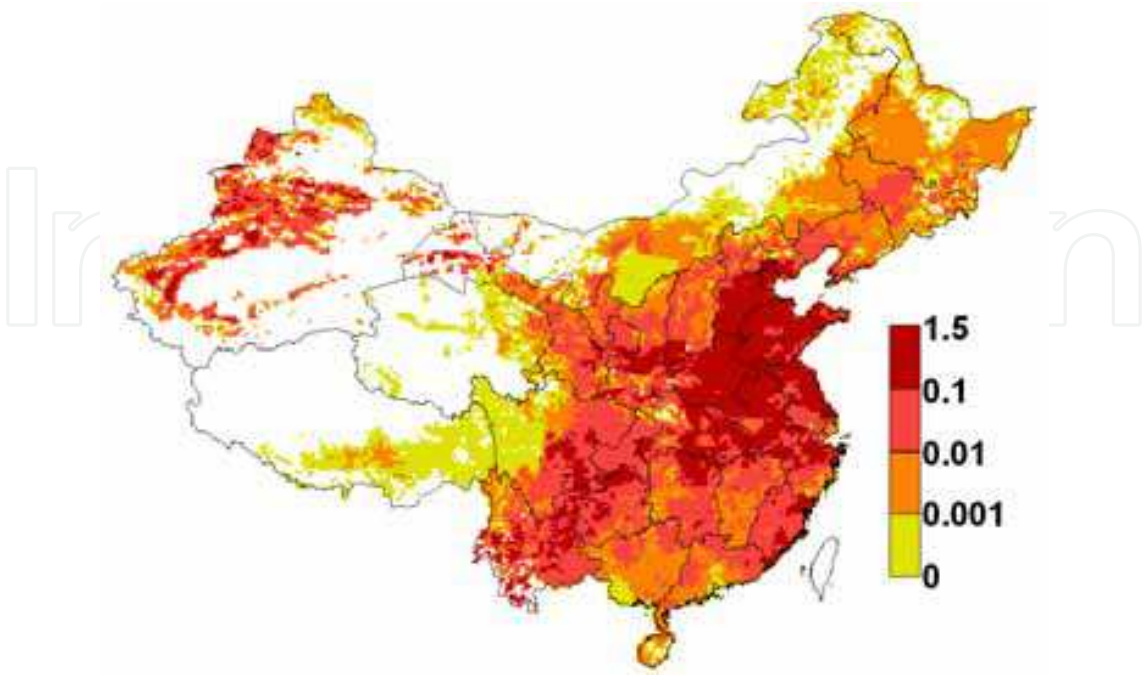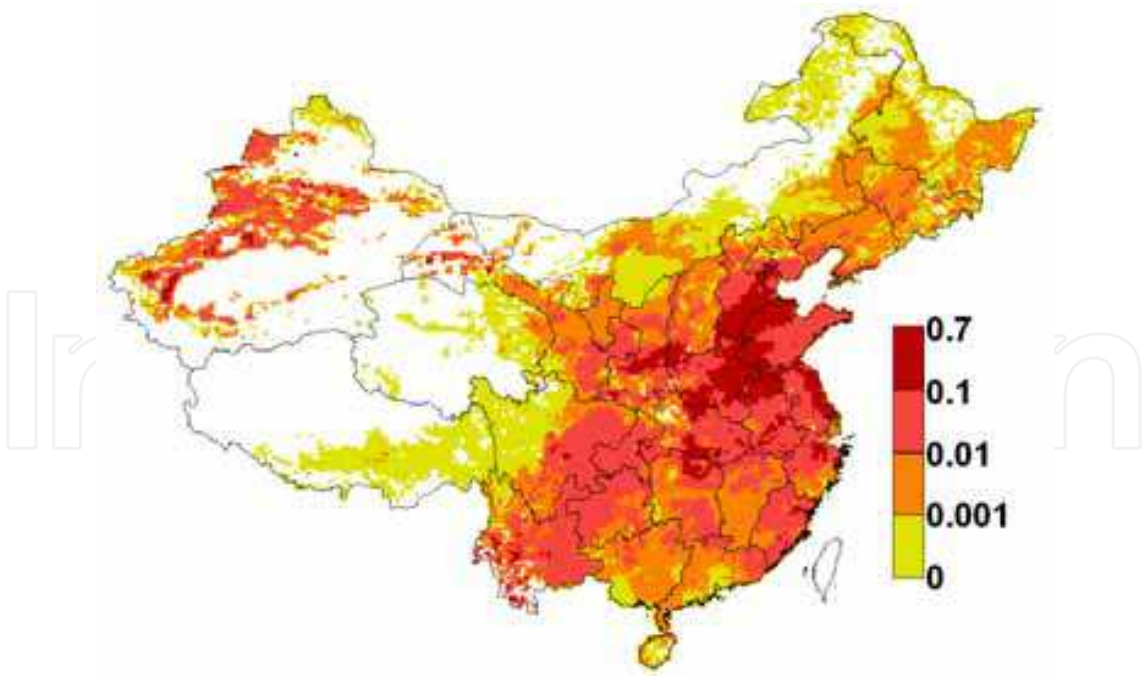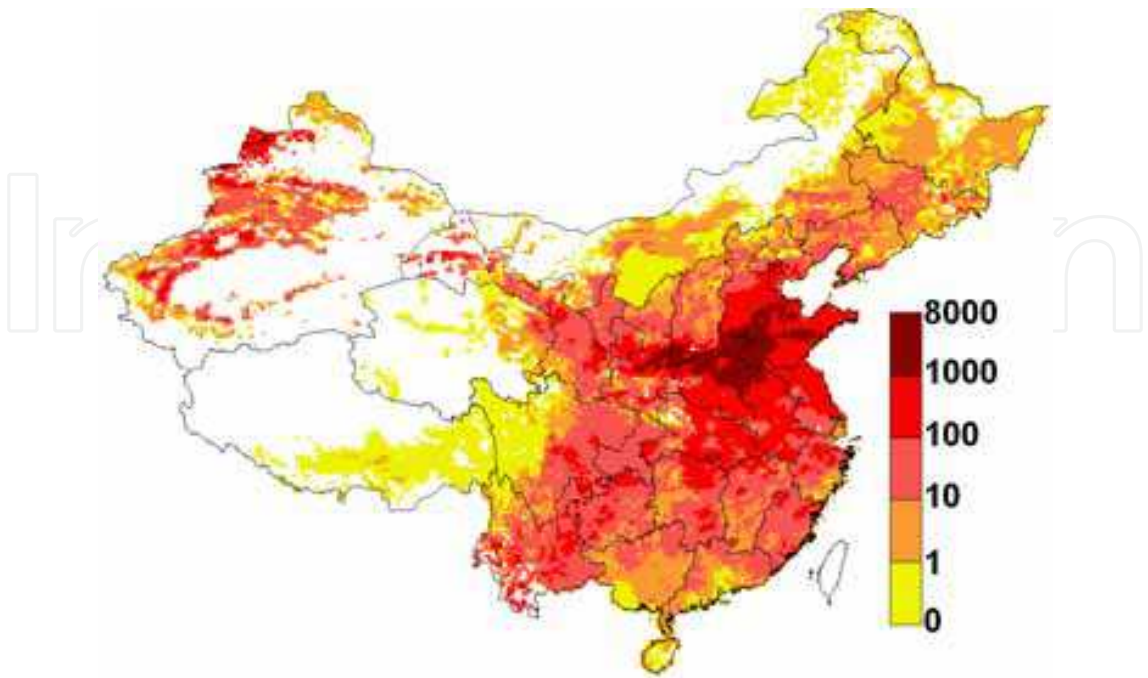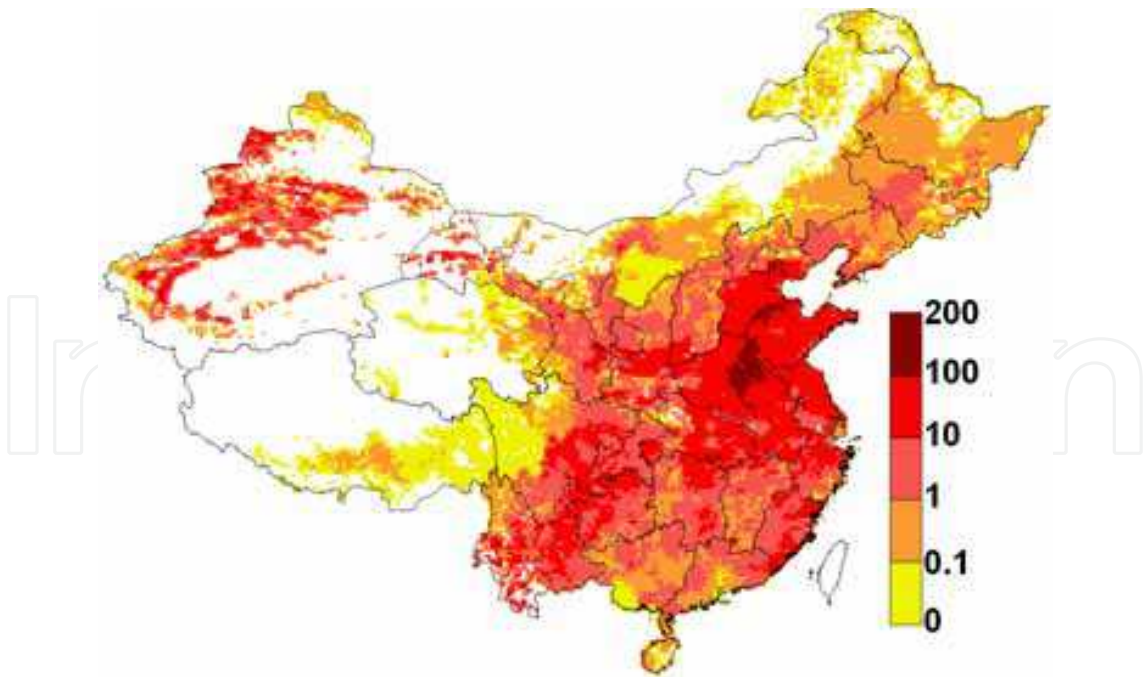
(a)

(b)

Fig. 8. Distribution of of (a) the lowest and (b) the highest concentration (ng/g dw) of β-endosulfan in Chinese agricultural soil in 2004 with 1/4° longitude by 1/6° latitude resolution.

(a)

(b)

Fig. 9. Distribution of endosulfan emissions in China in 2004 with 1/4° longitude by 1/6° latitude resolution. (unit: t/cell)

(a)

(b)

Fig. 10. Distribution of annual mean concentration of endosulfan (pg/m³) in Chinese air in 2004 with 1/4° longitude by 1/6° latitude resolution.

5. Monitoring endosulfan in Chinese soil and air

5.1 Concentrations of endosulfan in Chinese soils

A survey of endosulfan in Chinese soil was carried out by *the International Joint Research Center for Persistent Toxic Substances* (IJRC-PTS) in 2005 as part of a Chinese persistent toxic substances (PTSs) Soil and Air Monitoring Program, Phase I (SAMP-I), in which concentrations of endosulfan were monitored from 141 Chinese surface soil (Jia et al. 2010). Endosulfan was found ubiquitous in Chinese surface soil. Occurrence frequencies (OFs) were high in the 141 soil samples, and 83%, 96%, and 91% for α-endosulfan, β-endosulfan and endosulfan sulfate, respectively. Concentrations of total endosulfan ranged from BDL (below detection limit) to 19,000 pg/g dry weight (dw) with GM = 120 pg/g dw. Spatial distribution of soil concentration for endosulfan isomers and endosulfan sulfate is shown in Fig. 11. It is clear that endosulfan sulfate had highest concentration in Chinese soil, followed by β-endosulfan. The concentration of α-endosulfan in Chinese soil was the lowest although its usage was much higher than that for β-endosulfan (Fig. 3). The highest total endosulfan (sum of α-endosulfan, β-endosulfan and endosulfan sulfate) concentration (19,000 pg/g dw) was found at a rural site in Yancheng, Jiangsu Province, which is located in an agricultural area where endosulfan was extensively used. High concentrations (>4000 pg/g dw) of total endosulfan were also found at some other rural sites which were also laid on agricultural area. Among urban sites, high concentrations of total endosulfans were found in Xizang Autonomous Region (Tibet), and the other two in Fujian Province.
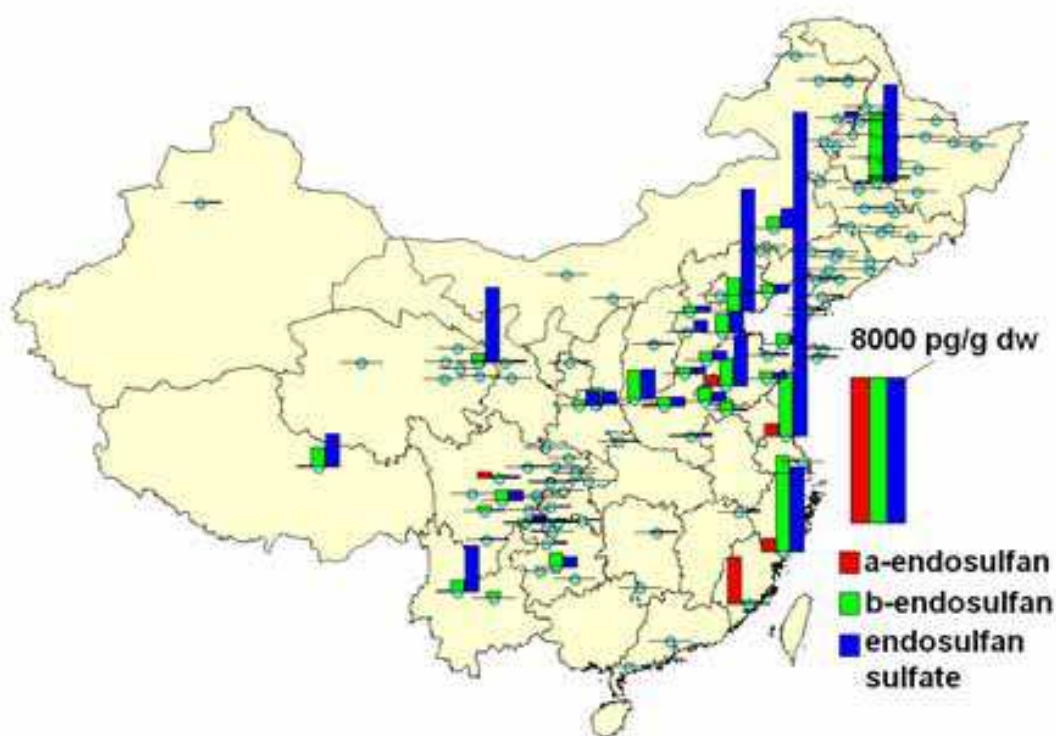

Fig. 11. Distribution of α-, β-endosulfan and endosulfan sulfate in Chinese surface soil from 141 sites, among which 6 are background sites (blue), 95 are rural sites (green) and 40 are urban sites (red).

5.2 Concentrations of endosulfan in Chinese air

Chinese air concentrations of endosulfan from thirty seven cities and three background stations were measured in the former study (Liu et al., 2009) in 2005. Endosulfan concentrations for α-isomer were ranged 0-340 pg/m³ and 0-121 pg/m³ for β-isomer, which were generally lower than those reported for North America, South America, Europe, and Africa by the GAPS study (Pozo et al., 2006; 2009), and also lower than that reported for India (Zhang et al., 2008). The high concentrations of total endosulfan occurred in the cotton production areas in thiry seven Chinese cities were also reported by Liu et al. (2009), which is according with that endosulfan was mainly used for controlling cotton bollworm in China.
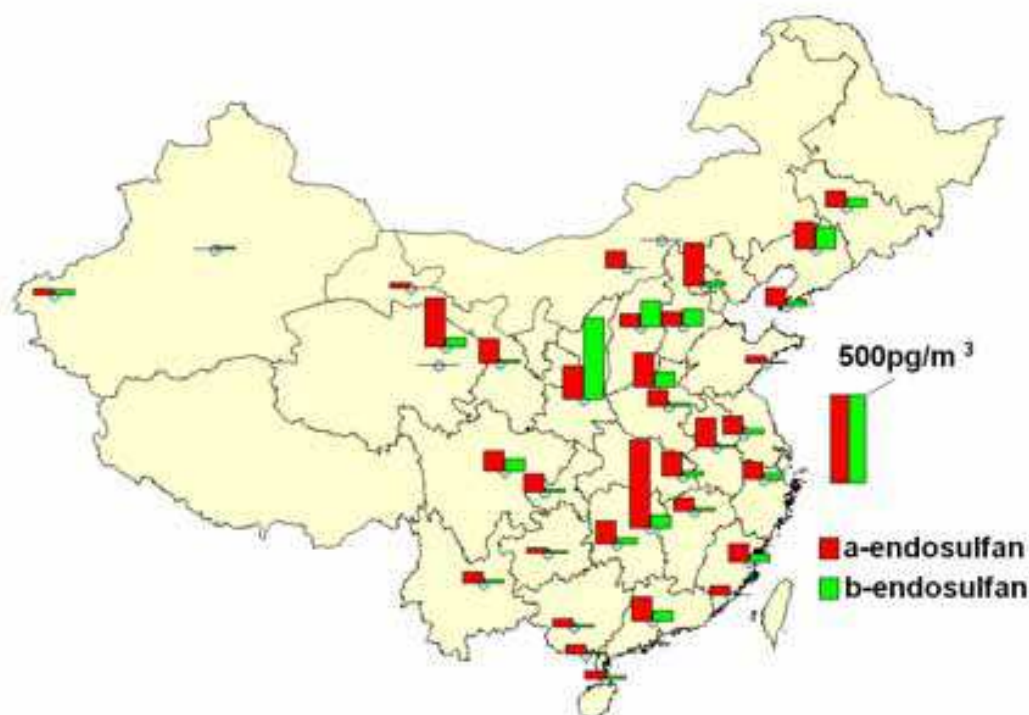

Fig. 12. Distribution of α-endosulfan (red) and β-endosulfan (green) in Chinese air from 37 urban sites and 3 background sites (Liu et al., 2009).

6. Comparison between monitoring and modeling results

6.1 Comparison of concentrations in soils

The lowest (pre-application) and highest (post-application) concentrations for α- and β-endosulfan were calculated in this study in Chinese agricultural soil between 1994 and 2004 in 1/4° × 1/6° longitude and latitude resolution. Our modeling work indicated that, before the pesticide application, the soils had the lowest residues caused by endosulfan remaining in the soil from the previous year, and after application, the soils had the highest residues due to endosulfan remaining in the soil from the previous year plus the residues from the current use of the pesticide. In order to further assess the differences between modeled and monitored data, annual average soil concentrations of endosulfan were also calculated for China in this study.

Correlations between monitored and the annual mean modeled results (log-scale) in all soil samples were found significant for both isomers ($P < 0.0001$) with the correlation coefficient R = 0.48 for α-endosulfan and R = 0.80 for β-endosulfan (Fig. 13). Better agreement for β-

endosulfan indicated their longer half-life in soil for β-endosulfan than α-endosulfan in soil. Besides, Paired-Sample T test was made to address the possible difference between monitoring and modeling data for both α- and β-endosulfan separately, and the results show that, at the 0.05 level, no significantly differences were found between modeled and monitoring results.
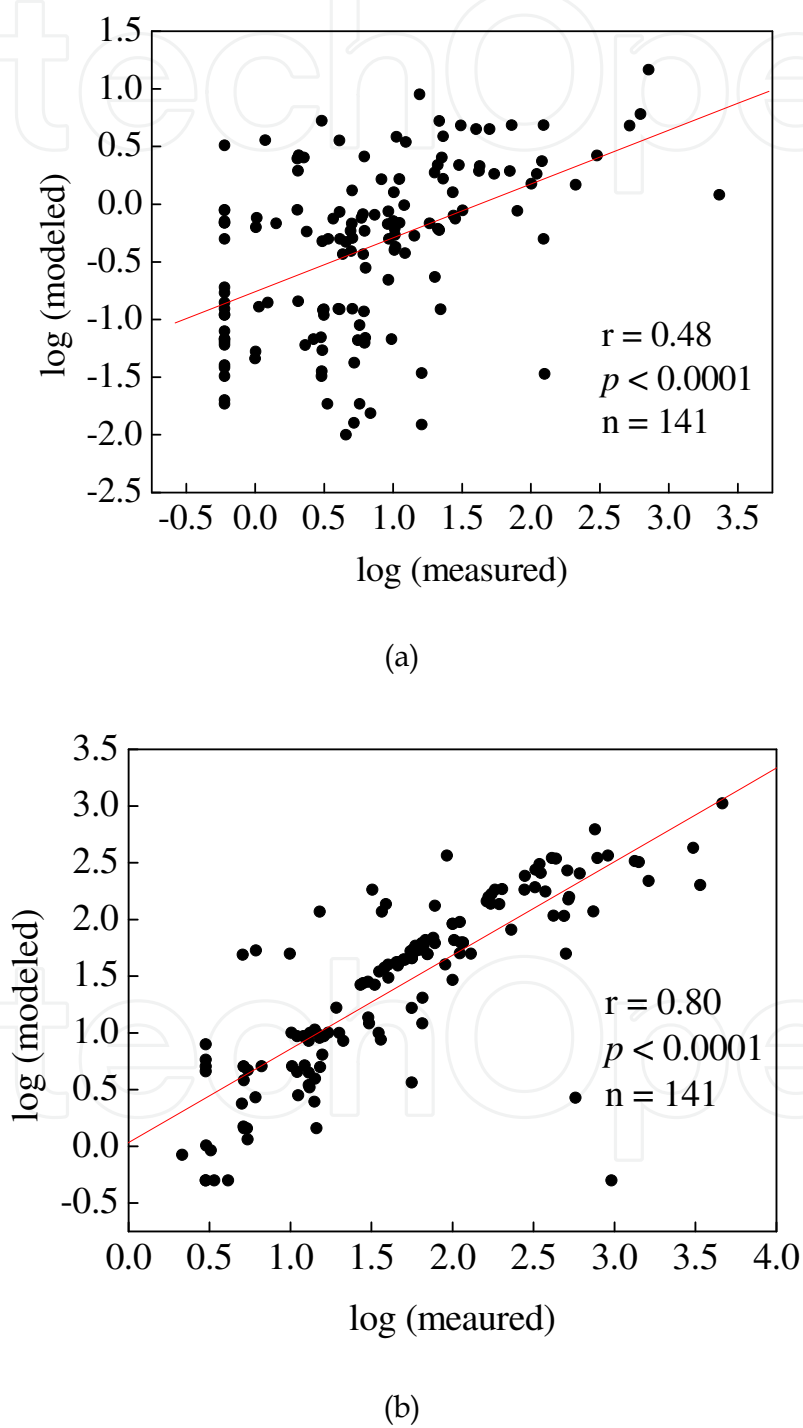

(a)

(b)

Fig. 13. Comparison between monitoring soil concentrations in 2005 and modeling data in 2004 for (a) α-endosulfan, (b) β-endosulfan. The monitoring data were from Liu et al (2009).
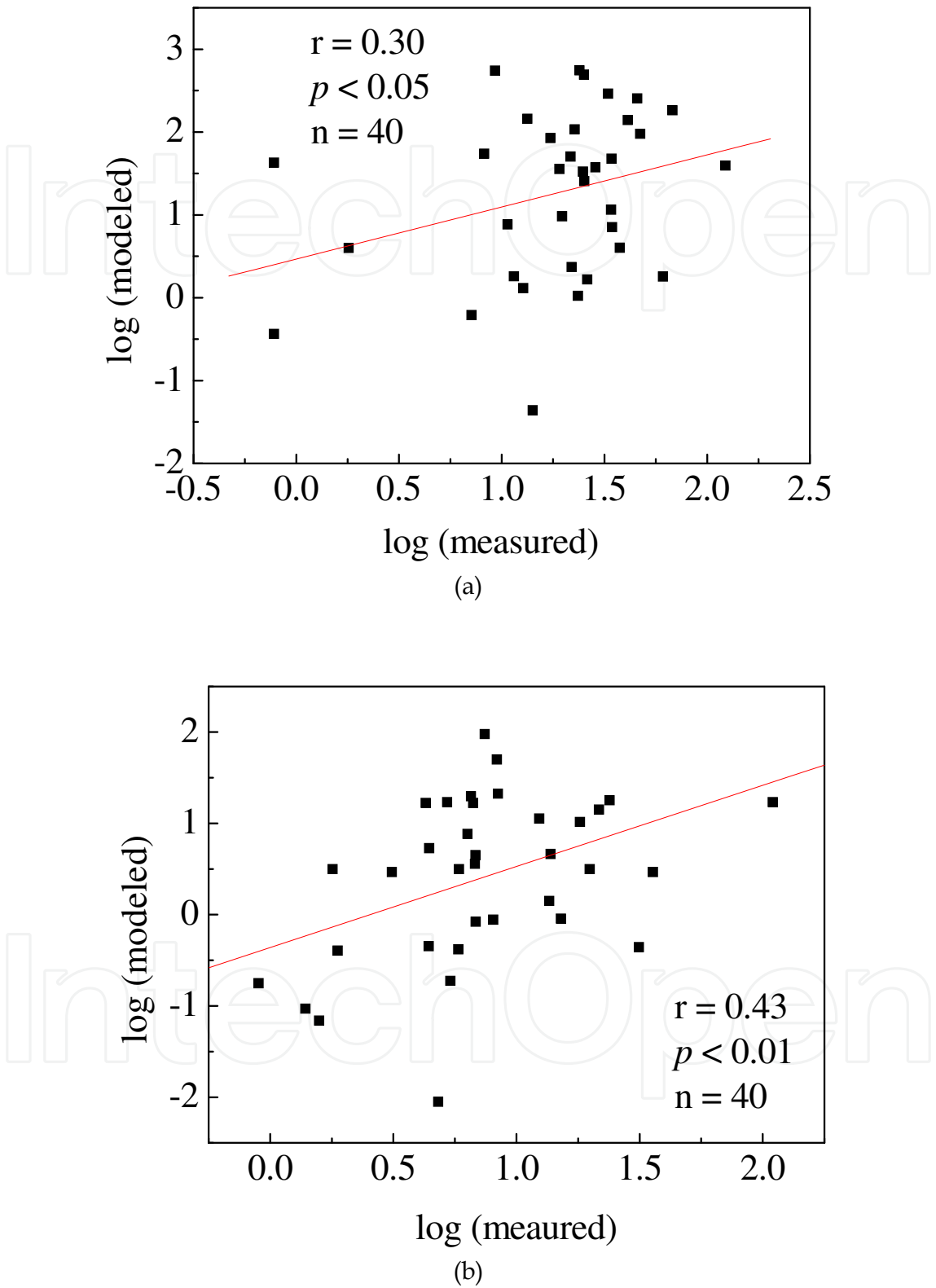
Fig. 14. Comparison between monitoring air concentrations in 2005 (Liu et al. 2009) and modeling data in 2004 for (a) α-endosulfan, (b) β-endosulfan.

6.2 Comparison between concentrations in air

Fig. 14. depicts correlation between modeling and monitoring concentrations (log-scal) in air across China. The measured soil concentration data for α- and β-endosulfan at the 40 monitoring sites in 2005 (Liu et al. 2009). were compared to their corresponding modeled concentration data in 2004 and a good consistence was found. Firstly, Paired-Sample T test was made to address the possible difference between monitoring and modeling data for both α- and β-endosulfan separately, and the results show that, at the 0.05 level, no significantly differences were found between modeled and monitoring results. Secondly, regression analysis between the monitoring and modeled data indicated a weak correlations with R = 0.30 for α-endosulfan and R = 0.43 for β-endosulfan. Besides, GM of measured air concentration of α-endosulfan from 40 sampling site was 18 pg/m³, which is the same as our modeling results (18 pg/m³), and for β-endosulfan, GM of measured concentration was 7 pg/m³, which is also close to the modeled data (3 pg/m³).

7. Conclusion and future work

The following conclusions were derived from this chapter:

- Chinese endosulfan usage inventories were developed with a high resolution of 1/4° longitude by 1/6° latitude, which localized the source of this pesticide in China.
- Chinese endosulfan inventories for emissions to air and residues in soil were calculated for both α- and β-endosulfan by using the SGPERM, and the inventories for air and soil concentrations were also compiled for these two isomers.
- Soil and air samples were collected from 141 and 40 sites over China, respectively, for α- and β-endosulfan and their concentrations in these two media were measured. The results gave general spatial trends of the occurrence of these two isomers in Chinese air and soil.
- Comparison between the measured and modeled results for both α- and β-endosulfan led to a good consistence between them, indicating the accuracy of the developed inventories.

This research has paved the way for further research for endosulfan in future, which includes development of inventories of emissions to air, residues in soil, and air and soil concentrations for endosulfan sulfate, the metabolize of both α- and β-endosulfan, the transport and the fate of endosulfan in Chinese environment, and risk assessment of this pesticide to the health of humans and wild lives. This work is also beneficial to the study of endosulfan on a global scale, including development of global gridded emission/residue inventories for this pesticide.

8. References

ASTDR. (2000). Toxicological Profile for Endosulfan. US Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, Atlanta, Ga., USA.

Baart, A.; Berdowski, J. & van Jaarsveld, J. (1995). The calculation of atmospheric deposition of contaminants on the North Sea (in Dutch), Rep. TNO-MW-R95-138, TNO Inst. of Environ. Sci., Delft, The Netherlands.

Baas, J. (1994). Emission of pesticides from orchards to the atmosphere (in Dutch), Rep. IMWTNO R 94-040a, TNO Lnst. of Environ. Sci., Delft, The Netherlands.

Bass, J. & Huygen, C. (1992) Emission of pesticides from greenhouses to the atmosphere (in Dutch), Rep. IMW-TNO R 920304, TNO Inst. of Environ. Sci., Delft, The Netherlands.

Chandler, G. & Scott, G. (1991). Effects of sediment-bound endosulfan on survival reproduction and larval settlement of meiobenthic polychaetes and copepods, *Environ Toxicol Chem* 10: 375-382.

Chaudhuri, K.; Selvaraj, S. & Pal, A. (1999). Studies on the genotoxicity of endosulfan in bacterial systems, *Mutat Res* 439: 63–67.

Chinese Network for Public Science and Technology. http://database.cpst.net.cn/

Devakumar, C. (2002). Endosulfan aerial spray controversy in Kerela. *Pestic Res* J 14: 343–344.

Dörfler, U.; Adler-Körler, R.; Schneider, P.; Scheunert, I. & Korte, F. (1991). A laboratory model system for determing the volatility of pesticides from soil and plant surfaces, *Chemosphere* 23: 484-496.

Halsall, C.; Bailey, R.; Stern, G.; Barrie, L.; Fellin, P. & Muir, D. (1998). Multi-year observations of organohalogenated pesticides in the Arctic atmosphere, *Environ Pollut* 102: 51–62.

Harner, T.; Bidleman, T.; Jantunen, L. & Mackay, D. (2001). Soil- air exchange models of persistent pesticides in the U. S. Cotton Belt, *Environ Toxicol Chem* 20: 1612-1621.

Hung, H.; Halsall, C.; Blanchard, P.; Li, H.; Fellin, P. & Stern, G. (2002). Temporal trends of organochlorine pesticides in the Canadian Arctic atmosphere, *Environ. Sci. Technol* 36: 862–868.

Jia, H.; Li, Y.; Wang, D.; Cai, D.; Yang, M.; Ma, J. & Hu, J. (2009a). Endosulfan in China 1-gridded usage inventories, *Environ Sci Pollut Res* 16: 295-301.

Jia, H.; Liu, L.; Sun, Y.; Sun, B.; Wang, D.; Su, Y.; Kannan, K. & Li, Y. (2010). Monitoring and modeling endosulfan in Chinese surface soil, *Environ Sci Technol* 44: 9279-9284.

Jia, H.; Sun, Y.; Li, Y.; Tian, C.; Wang, D.; Yang, M.; Ding, Y. & Ma, J. (2009b). Endosulfan in China 2-emissions and residues, *Environ Sci Pollut Res* 16: 302-311.

Jiang, W. & Wu, X. (1990). A linked three-dimensional PBL and dispersion model in coastal regions, *Bound-lay Meteorol* 53: 43-62.

Kalnay, E.; Kanamitsu, M.; Kistler, R.; Collins, W.; Deaven, D.; Gandin, L.; Iredell, M.; Saha, S.; White, G.; Woollen, J.; Zhu, Y.; Leetmaa, A.; Reynolds, B.; Chellia, M.; Ebisuzaki, W.; Higgins, W.; Janowiak, J.; Mo, K.; Ropelewski, C.; Wang, J.; Jenne, R.; & Joseph, D. (1996). The NCEP/NCAR reanalysis project, *Bull Am Meteorol Soc* 77: 437-471.

Keith, L.; & Telliard, W. (1979). Priority pollutants: I-a perspective view, *Environ. Sci. Technol* 13: 416-423.

Li, Y. & Bidleman, T. (2003). Correlation between global emissions of α-hexachlorocyclohexane and its concentrations in the arctic air, *JEnviron Informatics* 1: 52-57.

Li, Y.; & MacDonald, R. (2005). Sources and pathways of selected organochlorine pesticides to the Arctic and the effect of pathway divergence on HCH trends in biota: A review, *Sci Total Environ* 342: 87-106.

Li, Y.; Bidleman, T. & Barrie, L. (2001). Toxaphene in the United States: (2) Emissions and Residues, *JGeophys Res* 106(D16): 17,929-17,938.

Li, Y.; Macdonald, R.; Ma, J.; Hung, H. & Venkatesh, S. (2004a). α-HCH Budget in the Arctic Ocean: The Arctic Mass Balance Box Model (AMBBM), *Sci Total Environ* 324: 115-139.

Li, Y.; Scholtz, M. & Heyst, B. (2003). Global gridded emission inventory of β-hexachlorocyclohexane, *Environ Sci Technol* 37: 3493-3498.

Li, Y.; Scholtz, M. & Van-Heyst, B. (2000). Global gridded emission inventory of α-hexachlorocyclohexane, *JGeophys Res* 105: 6621-6632.

Li, Y.; Venkatesh, S. & Li D. (2004b). Modeling global emissions and residues of pesticides, *Environ Model Assess* 9: 237-243.

Liu, X.; Zhang, G.; Li, J.; Yu, L.; Xu, Y.; Li, X.; Kobara, Y. & Jones, K. (2009). Seasonal patterns and current source of DDTs, chlordanes, hexachlorobenzene, and endosulfan in the atmosphere of 37 Chinese cities, *Environ Sci Technol* 43: 1316-1321.

Lubick, N. (2010). Endosulfan's exit: U. S. EPA pesticide review leads to ban, *Science* 328: 1466.

Maier-Bode, H. (1968). Properties, effect, residues and analytics of the insecticide endosulfan, *Residue Rev* 22: 1-44.

Miles, C. & Pfeuffer, R. (1997). Pesticides in Canals of south Florida, *Arch Environ Contam Toxicol* 32: 337-345.

Patton, G.; Walla, M.; Bidleman, T. & Barrie, L. (1991). Polycyclic aromatic and organochlorine compounds in the atmosphere of northern Ellesmere Island, Canada, *JGeophys Res* 96: 10867–10877.

Peasant Daily. (2001). June 8th, 2001, in Chinese.

Pesticide Electronic Handbook. (2006). http://www.chinapesticide.gov.cn/

Peterson, S. & Batley, G. (1993). The fate of endosulfan in aquatic ecosystems, *Environ Pollut* 82: 143-152.

Pozo, K.; Harner, T.; Lee, S.; Wania, F.; Muir, D. & Jones, K. (2009). Seasonally resolved concentrations of persistent organic pollutants in the global atmosphere from the first year of the GAPS study, *Environ Sci Technol* 43: 796-803.

Pozo, K.; Harner, T.; Wania, F.; Muir, D.; Jones, K. & Barrie, L. (2006). Towards a global network for persistent organic pollutants in air: Results from the GAPS Study, *Environ Sci Technol* 40: 4867-4873.

Rice, C.; Chernyak, S. & McConnell, L. (1997). Henry's Law Constants for Pesticides Measured as a Function of Temperature and Salinity, *JAgric Food Chem* 45: 2291-2298.

Rüdel, H. (1997). Volatilisation of pesticides from soil and plant surfaces, *Chemosphere* 35: 143-152.

Saiyed, H.; Dewan, A. & Bhatnagar, V. (2003). Effect of endosulfan on male reproductive development, *Environ Health Perspect* 111: 1958-1962.

Schmidt, W.; Hapeman, C.; Fettinger, J.; Rice, C. & Bilboulian, S. (1997): Structure and asymmetry in the isomeric conversion of β- to α-endosulfan, *J Agric Food Chem* 26: 1101-1106.

Scholtz, M.; McMillan, A.; Li, Y.; Ting, N.; Taylor, A. & Van Heyst, B. (1998). Global pesticide emissions: Development of pesticide emission factors on a global 1°×1° longitude-latitude grid and global emissions of Hexachlorocyclohexane, Final Rep. CGEIC-1998-2, pp. 1-89, Can. Global Interpretation Cent, Toronto, Ont.

Scholtz, M.; McMillan, A.; Slama, C.; Li, Y.; Ting, N. & Davidson, K. (1997). Pesticide emissions modeling: development of a north American pesticide emissions inventory, Rep. CGEIC-1997-1, pp. 1-242, Can. Global Interpretation Cent., Toronto, Ont.

Sinha, N.; Narayan, R.; Shanker, R. & Saxena, D. (1995). Endosulfan induced biochemical changes in the testis of rats, *Vet Hum Toxicol* 37: 547-551.

Smimonich, S. & Hites, R. (1995). Global distribution of persistent organochlorine compounds, *Science* 269: 1851-1854.

Southan, S.; & Kennedy, I. (1995). Dissipation of the pesticide endosulfan from cotton field run-off water using an improved apparatus for the simulation of field conditions. In *Proceedings of the 4th RACI Environmental Chemistry Conference* (pp. 104-109). Darwin, Australia.

Su, Y.; Hung, H.; Blanchard, P.; Patton, G.; Kallenborn, R.; Konoplev, A.; Fellin, P.; Li, H.; Geen, G.; Stern, G.; Rosenberg, B. & Barrie, L. (2008). A circumpolar perspective of atmospheric organochlorine pesticides (OCPs): Results from six Arctic monitoring stations in 2000-2003, *Atmos Environ* 42: 4682-4698.

Sunderam, R.; Cheng, D. & Thomson, G. (1992). Toxicity of endosulfan to native and introduced fish in Australia, *Environ Toxicol Chem* 11: 1469-1476.

Sutherland, T.; Horne, I.; Lacey, M.; Harcourt, R.; Russel, R. & Oakeshott, J. (2000). Enrichment of an endosulfan-degrading mixed bacterial culture, *Appl Environ Microbiol* 66: 2822–2828.

Sutherland, T.; Weir, K.; Lacey, M.; Horne, I. & Russel, R. (2002). Gene cloning and molecular characterization of a two enzyme system catalyzing the oxidative detoxification of β-endosulfan. *J Appl Microbiol* 92: 541-548.

UNEP (United Nations Environment Programme). (2007). Guidance on the Global Monitoring Plan for Persistent Organic Pollutants, Preliminary Version February 2007. Amended in May 2007. Stockholm Convention Secretariat, Geneva, pp 147.

Verschureren, K. (1983). Endosulfan. In *Handbook of environmental data on organic chemicals* (pp. 604-607). New York : Van Nostrand Reinhold.

WHO. (1984). World Health Organization, Environmental Health Criteria 40.

Zhang, G.; Chakraborty, P.; Li, J.; Sampathkumar, P.; Balasubramanian, T.; Kathiresan, K.; Takahashi, S.; Subramanian, A.; Tanabe, S. & Jones, K. (2008). Passive atemospheric sampling of organochlorine pesticides, polychlorinated biphenyls, and polybrominated diphenyl ethers in urban, rural, and wetland sites along the coastal length of India, *Environ Sci Technol* 42: 8218-8223.
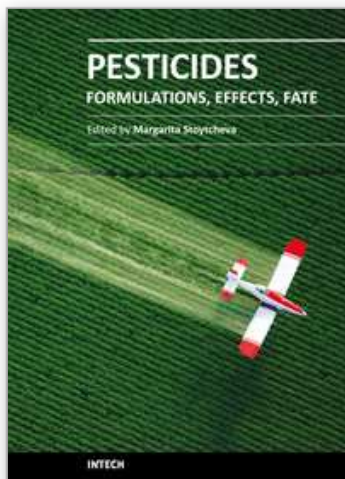
Pesticides - Formulations, Effects, Fate

Edited by Prof. Margarita Stoytcheva

ISBN 978-953-307-532-7

Hard cover, 808 pages

Publisher InTech

Published online 21, January, 2011

Published in print edition January, 2011

This book provides an overview on a large variety of pesticide-related topics, organized in three sections. The first part is dedicated to the "safer" pesticides derived from natural materials, the design and the optimization of pesticides formulations, and the techniques for pesticides application. The second part is intended to demonstrate the agricultural products, environmental and biota pesticides contamination and the impacts of the pesticides presence on the ecosystems. The third part presents current investigations of the naturally occurring pesticides degradation phenomena, the environmental effects of the break down products, and different approaches to pesticides residues treatment. Written by leading experts in their respective areas, the book is highly recommended to the professionals, interested in pesticides issues.

INTECH
open science | open minds