AIR CONCENTRATION INVENTORIES OF ENDOSULFAN SULFATE IN CHINA

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Introduction

Endosulfan has been applied in China to control pests in cotton since 1994, and in wheat, tea, tobacco, apple and other fruits since 1998. The total usage of endosulfan in China was estimated to be approximately 25,700 t between 1994 and 2004[1]. The first Chinese gridded inventories of usage, emissions to air, and residues in soil inventories with a 1/4° longitude by 1/6° latitude resolution for α-, β-endosulfan and endosulfan sulfate were produced for 1994-2004[1, 2]. Air emissions were 7,400 t for α-endosulfan and 3,300 t for β-endosulfan between 1994 and 2004 (Jia et al., 2009b). Soil residues in application areas in 2004 varied largely for α-endosulfan, ranging from 1.7 to 365 t, but much less for β-endosulfan with a range from 119 to 263 t. Based on the emission and residue inventories, concentrations of α-, β-endosulfan and endosulfan sulfate in Chinese agricultural surface soil were further calculated for each grid cell[2, 3].

Endosulfan sulfate is the major metabolite product and is as persistent and toxic as its parent compounds[4]. Its concentrations were found higher than those of α-endosulfan and comparable to those of β-endosulfan in Chinese surface soil[3]. Therefore, study on environmental fate of endosulfan sulfate is equally important as endosulfan isomers.

Materials and methods

The modeled annual concentrations for α- and β-endosulfan were reported in an earlier study for Chinese air from 1995 to 2004 with 1/4 ° × 1/6 ° longitude and latitude resolution by using the Simplified Gridded Pesticide Emission and Residue Model (SGPERM)[2, 5]. Air concentrations for endosulfan sulfate were, however, not available because transformation mechanism from endosulfan isomers to endosulfan sulfate is not well understood. Significant and strong correlation between endosulfan sulfate and endosulfan isomers in Chinese soil provides an opportunity for us to compile soil concentration inventories for endosulfan sulfate based on the inventories of endosulfan isomers. Multiple linear regression was used to calculate endosulfan sulfate soil concentrations using soil concentrations for α- and β-endosulfan[3]. In present study, we try to use the same method to calculate air concentration inventories for endosulfan sulfate.

Table 1 Air concentration of endosulfan (pg/m3) in China during one year's study from 92 sampling sites

Compounds	GM (range) Period 1 (Jul. 2005 – Oct. 2005)	Period 2 (Oct. 2005 – Jan. 2006)	Period 3 (Jan. 2006 – Apr. 2006)	Period 4 (Apr. 2006 – Jul. 2006)	year (Jul. 2005 – Jul. 2006)
α-endosulfan	82 (3.7-8300)	1.7 (BDL-1200)	7.4 (BDL-1100)	23 (BDL-22000)	63 (2.3-8100)
β-endosulfan	5.1 (BDL-820)	0.54 (BDL-617)	2.1 (BDL-120)	1.6 (BDL-1100)	6.9 (BDL-630)
endosulfan sulfate	1.7 (BDL-230)	0.30 (BDL-79)	1.2 (BDL-57)	0.28 (BDL-320)	3.8 (0.13-170)
Total Endosulfan	98 (7.0-9300)	4.5 (BDL-1900)	13 (BDL-1300)	38 (BDL-23000)	78 (4.1-8900)

Results and discussion:

Air samples were set into four groups (period 1 to period 4) depending sampling time. Geometric mean (GM) of total endosulfan (α- + β-isomer + endosulfan sulfate) were observed in 98 pg/m3 and with a range of 7.0 to 9300 pg/m3 in period 1, 4.5 and BDL-1900 pg/m3 in period 2, 13 and BDL-1300 pg/m3 in period 3, 38 and BDL-23000 pg/m3 in period 4, 78 and 4.1-8900 pg/m^3 in the whole year.

Generally, air concentrations of endosulfan were obviously higher in period 1 and 4 than that of period 2 and 3 ($p < 0.05$), which indicating that endosulfan were mainly used in period 1 and 4. However, much lower air concentration of endosulfan was observed in period 2, which was according with the lack of agriculture activity in China during this period. It is not obviously different of air concentration of endosulfan in GM between rural and urban samples, but large concentration ranges were observed in rural ones, which were likely depending usage density of endosulfan in rural sites, contributed from primary sources[3]. However, urban samples were observed much uniform (compared to rural ones), which seemed to be created from secondary sources [3].

Pearson correlation of log-transformed concentrations between endosulfan sulfate and endosulfan isomers were found statistically significant in 4 period. Elevated endosulfan sulfate was found at sites where concentrations of α- and β-endosulfan were high as well (Table 2). It suggests that endosulfan sulfate is likely from historical application of endosulfan and consequent degradation.

Table 2 Pearson correlation (P value) of log-transformed concentrations between endosulfan sulfate and endosulfan isomers

	Period 1	Period 2	Period 3	Period 4	Year's mean
α-endosulfan	0.64 ($p < 0.0001$)	0.69 ($p < 0.0001$)	0.80 ($p < 0.0001$)	0.66 ($p < 0.0001$)	0.82 ($p < 0.0001$)
β-endosulfan	0.55 ($p < 0.0001$)	0.66 ($p < 0.0001$)	0.85 ($p < 0.0001$)	0.75 ($p < 0.0001$)	0.74 ($p < 0.0001$)

Multiple linear regression was used in this study to calculate endosulfan sulfate air concentrations using air concentrations for α- and β-endosulfan. Measured air logarithm concentrations of endosulfan sulfate at 141 sampling sites were treated as dependent variables, whereas those of α- and β-endosulfan were set as two independent variables. The multilinear regression was performed with SPSS V.10.0, and the coefficients of regression were found statistically significant ($R = 0.83$, $p < 0.0001$) as shown in eq (1)

$$y = 0.645x_1 + 0.192x_2 + 0.749 \qquad (1)$$

where y, x_1, and x_2 are measured air concentrations of endosulfan sulfate, α-endosulfan, and β-endosulfan, respectively.

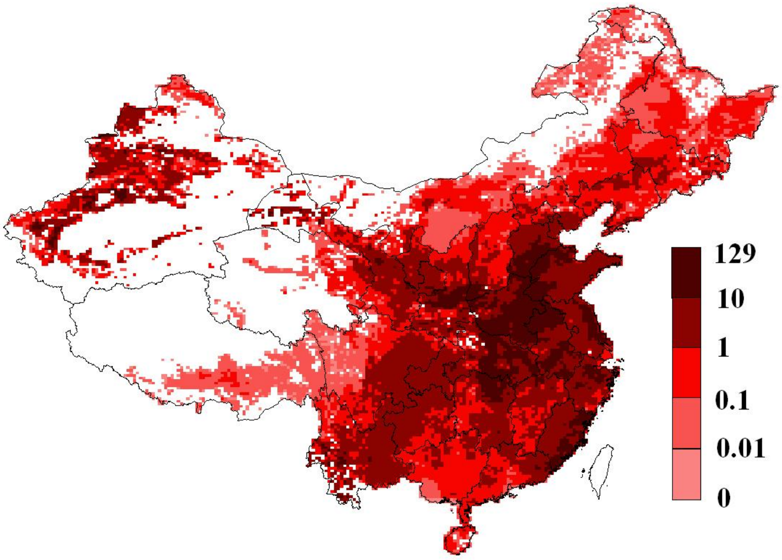

Figure 1 Annual mean concentrations of endosulfan sulfate in Chinese air in 2004 with a 1/4 ° × 1/6 ° longitude and latitude resolution.

Gridded air concentrations of endosulfan sulfate were calculated by using eq 1 using the modeled air concentrations of α- and β-isomer[2]. Figure 1 depicts annual mean concentrations of endosulfan sulfate in Chinese air in 2004 with a 1/4° × 1/6° longitude and latitude resolution. The highest concentrations of endosulfan sulfate in Chinese air were in central and east China, where cotton cultivation is common. Other regions with high air concentrations included southern Fujian, northern of Zhejiang, and parts of Xinjiang Autonomous Region. To our knowledge, this is the first air concentration inventories for endosulfan sulfate, which paves the way for further study on its environmental fate and pathways.

Figure 2 depicts correlation between modeling[2] and monitoring concentrations (this study) in air across China. The measured air concentration data for α- and β-endosulfan at the 63 monitoring sites from July 2005 to June 2006 were compared to their corresponding modeled concentration data for 2004 and a good consistence was found. Firstly, one-way analysis (ANOVA) was made to address the possible difference between monitoring and modeling data for both α-, β-endosulfan, and endosulfan sulfate respectively, and the results show that, at the 0.05 level, no significantly differences were found between them. Secondly, regression analysis between the monitoring and modeled data indicated the good correlations with r = 0.81 for α-endosulfan, r = 0.78 for β-endosulfan, and r = 0.66 for endosulfan sulfate. Good agreement indicates that the air concentrations from both monitoring and inventory works have similar spatial trends.

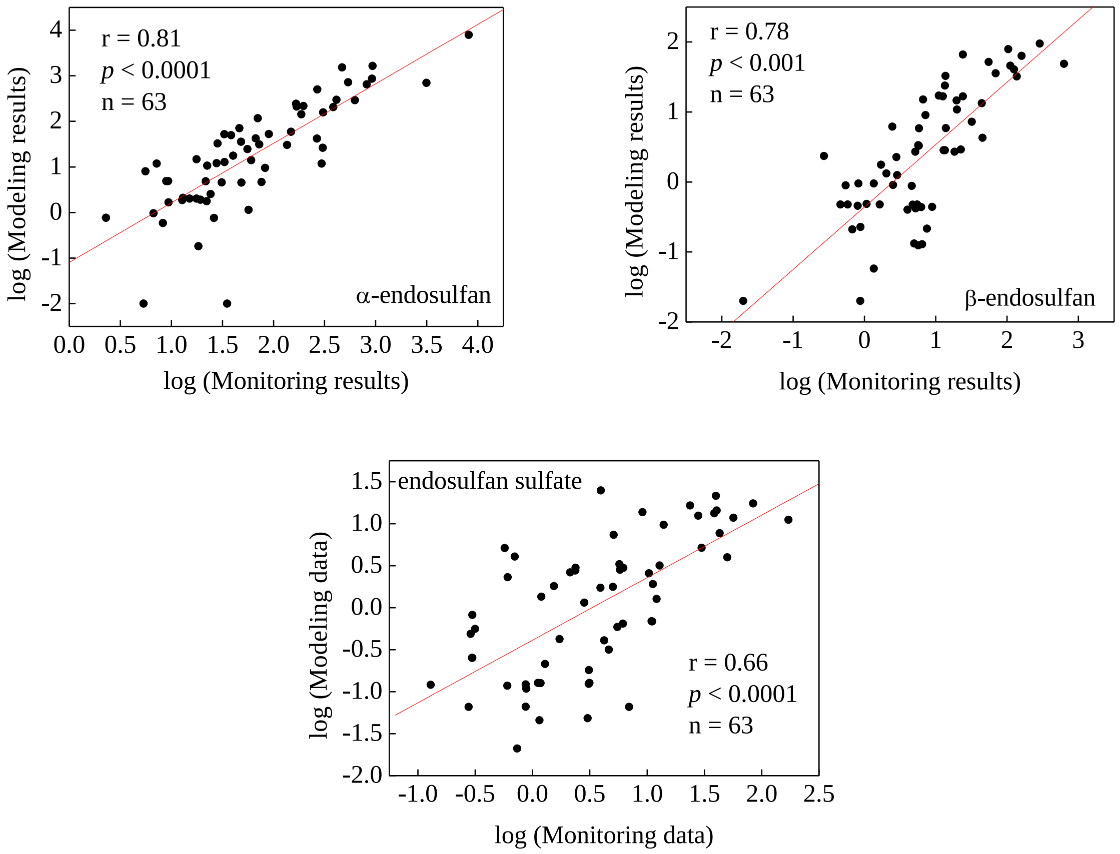

Figure 2 Correlations between monitoring and modeling results of endosulfan isomers.

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