Environmental Modelling & Software 49 (2013) 129–140

Contents lists available at ScienceDirect

Environmental Modelling & Software

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

Application of a combined sensitivity analysis approach on a pesticide environmental risk indicator

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ARTICLE INFO

Article history:
Received 11 January 2013
Received in revised form
13 August 2013
Accepted 20 August 2013
Available online

Keywords:
Sensitivity analysis
Correlation
Sobol' method
Importance measurement
Pesticide risk

ABSTRACT

Sensitivity analysis aims to characterize factors (i.e., model inputs) accounting for the amount of uncertainty in model output. Input factors are usually assumed to be independent, which may lead to incorrect conclusions. In this study, a combined sensitivity analysis approach, composed of the Sobol' and Importance Measurement (IM) methods, is applied on a pesticide environmental risk indicator (called PURE), where main, interaction, and correlation effects (i.e., the effects of factor correlations on sensitivity indices) are all addressed. PURE calculates pesticide risk scores for air, soil, groundwater, and surface water based on pesticide properties and surrounding environmental conditions. The Sobol' method calculates the first-order sensitivity index (S_i) and the total-effect sensitivity index (S_{Ti}) in noncorrelated-factor setting to address the main and interaction effects; while the IM method calculates S_i in both noncorrelated-factor and correlated-factor settings to show the correlation effects. In the tested case, the S_i estimations in noncorrelated-factor setting by the Sobol' and IM methods are very similar, which not only cross-validates the main effect estimations by the two different methods, but also provides the common ground for combining the two methods to address both interaction and correlation effects. In addition, the S_i estimations in correlated-factor setting are relatively different from the ones in noncorrelated-factor setting, which demonstrates that it is cautious to assume all factors are independent in sensitivity analysis. Take the soil risk evaluation as an example, the positive correlation between the chronic no-observed-effect concentration and acute 50%-lethal concentration to earthworms largely increases the S_i of the latter factor. The results of S_i estimations show that the risk scores for air, soil, groundwater, and surface water are most sensitive to the application rate of pesticide product, the application rate of pesticide active ingredient, the organic carbon sorption constant, and the monthly maximum daily water input, respectively. In summary, while this study enhances the understanding of PURE, it also provides an option for investigating both interaction and correlation effects, and hence promotes sensitivity analysis with factor-correlation structures in environmental modeling.

1. Introduction

Pesticide use, along with fertilizer, newly bred crop cultivars, and machinery, assures that agricultural production keeps pace with global population growth. However, many pesticides are toxic, persistent, and mobile. A large portion of the pesticides don't reach their targets but were transported or emitted to the environment, posing risks to ecosystems and human health (Bolognesi, 2003). Stakeholders seek available tools for assessing pesticide risk and choosing appropriate low risk pest management practices. Pesticide risk is determined by pesticide exposure to nontargeted organisms and the caused effects, but the risk value is difficult to measure. Therefore, an indicator approach, providing information on variables that are difficult to access (Bockstaller et al., 2008), is appropriate for pesticide risk assessment. In a broad sense, pesticide environmental risk indicators are also a group of environmental models. Numerous pesticide risk indicators have been developed around the world (Bockstaller et al., 2009), such as the Environmental Impact Quotient (EIQ) based on simple combinations of important variables (Kovach et al., 1992) and the Environmental Potential Risk Indicator for Pesticides (EPRIP) derived from simple simulation models for predicting pesticide concentrations (Trevisan et al., 2009). Whether employing complex (*e.g.*, Šimůnek et al., 2003) or simple simulation models in developing pesticide risk indicators depends on data availability and temporal–spatial scales of assessment. While various types of pesticide

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http://dx.doi.org/10.1016/j.envsoft.2013.08.005

environmental risk indicators exist, only one of 20 reviewed indicators since year 2000 has been evaluated with sensitivity analysis. Nevertheless, sensitivity analysis is an essential step in environmental model development (Jakeman et al., 2006) and one of the important methods for analyzing uncertainty in the environmental modelling process (Refsgaard et al., 2007).

Sensitivity analysis serves to characterize factors (*i.e.*, model input variables) accounting for the amount of uncertainty in model output (Saltelli and Annoni, 2010), and the sensitivity analysis results are valuable to model diagnosis, interpretation, and parameterization, and prioritizing data collection (Berthiaume et al., 2010; Confalonieri et al., 2010; Nossent et al., 2011; Pannell, 1997). Sensitivity analysis methods can be classified into local and global sensitivity analyses based on the techniques for exploring the input factor space. Local sensitivity analysis exploits the factor space around a specific point to study the effect of small variations of factors on model output, and the result can be highly biased for nonlinear models (Yang, 2011). On the contrary, global sensitivity analysis exploits the entire factor space by simultaneously varying all factors (Jacques et al., 2006; Lilburne and Tarantola, 2009). Global sensitivity analysis techniques include (1) regression or correlation based techniques, such as standardized regression coefficients and Spearman rank correlation coefficients; (2) elementary effect methods, including Morris (Campolongo et al., 2007; Morris, 1991; Pujol, 2009), Latin Hypercube-OAT (van Griensven et al., 2006), and winding stairs (Jansen, 1999), etc.; (3) metamodeling (emulation-based), such as high dimensional model representation (HDMR) (Li et al., 2006, 2002; Rabitz et al., 1999) and Gaussian emulators (Oakley and O'Hagan, 2004); and (4) variance-based techniques, such as the Sobol' method (Saltelli, 2002; Sobol', 1993; Tarantola et al., 2006), Fourier amplitude sensitivity test (FAST) (Cukier et al., 1973, 1975; McRae et al., 1982; Saltelli et al., 1999), and the importance measurement (IM) method (McKay, 1995). Variance-based sensitivity analysis techniques are popular in environmental modeling (*e.g.*, Nossent et al., 2011; Yang, 2011). In spite of the high computational expenses, variance-based techniques are model independent, provide easy-interpretable sensitivity indices, can capture interaction effects among factors, and can handle qualitative and quantitative factors. Saltelli and Annoni (2010) suggested using the Sobol' method when input factors are noncorrelated. Nevertheless, pesticide environmental fate models, which are usually computational expensive, tended to employ one-at-a-time sensitivity analysis methods (*e.g.*, Dubus et al., 2003; Ma et al., 2004).

Both interaction and correlation among input factors can affect sensitivity analysis results. Interaction is a property of the model while correlation is a property of input factors (Saltelli and Tarantola, 2002). Interaction, or nonlinear effect, means that a factor would act nonlinearly on the model output when its interacted factors are at different values. In a case when factors are correlated, fixing a factor would restrict the distributions of its correlated factors, and hence the effect of the studied factor would be carried over, which is referred to as the correlation effect hereafter. While interaction effects are usually studied, correlation effects are often ignored due to expensive computation cost (*e.g.*, Nossent et al., 2011; Vezzaro and Mikkelsen, 2012). Nevertheless, correlation commonly exists in real cases and may considerably impact sensitivity analysis results (Saltelli and Tarantola, 2002). Specifically in pesticide risk assessment, ignoring the existence of correlation between input factors may have a significant effect on the results of exposure assessments. Yet, to the authors' knowledge, none of the sensitivity analysis studies on pesticide risk assessment or fate modelling have taken factor correlations into account, except the regression-based sensitivity analysis study on three pesticide leaching models (Soutter and Musy, 1999). A few methods were developed for sensitivity analysis on correlated factors, such as the IM method mentioned above (McKay, 1995), which was employed by Saltelli and Tarantola (2002) and recommended by Saltelli and Annoni (2010). In addition, sensitivity analysis with correlated input factors may also be analyzed by emulation-based methods, such as the local polynomial technique (Da Veiga et al., 2009), the State Dependent Parameter (SDP) method (Ratto et al., 2007), and the Bayesian approach (Oakley and O'Hagan, 2004); nevertheless, they are more difficult to implement.

This study aims to enhance the understanding of the PURE (Pesticide Use Risk Evaluation) indicator (Zhan and Zhang, 2012) and to draw more attention to correlated factors in sensitivity analysis of environmental models by applying a combined variance-based sensitivity analysis approach. PURE is able to evaluate site-specific risk to air, soil, groundwater, and surface water from agricultural pesticide use. It employs the risk ratio approach (*i.e.*, the ratio of the predicted environmental concentration to the toxicity) under worst case scenarios, which is also applied by the European Union System for the Evaluation of Substances (EUSES) suited for initial and refined risk assessments on industrial chemicals and pesticides (Vermeire et al., 2005). PURE considers the short- and long-term exposure levels, rather than the environmental fate at equilibrium status that for example is evaluated by the Equilibrium Concentration (EQC) model (Mackay et al., 1996a, b, c).

The combined sensitivity analysis approach is composed of two parts. The first part uses the Sobol' method (Saltelli, 2002; Sobol', 1993) to estimate the first-order sensitivity index or main effect (S_i) and the total sensitivity index or total effect (S_{Ti}) in noncorrelated-factor setting. The second part uses the IM method (McKay, 1995) to estimate S_i in both noncorrelated-factor and correlated-factor settings. The specific objectives of this study are (1) to identify sensitive factors in PURE, with associated interaction or correlation effects; (2) to compare S_i estimations and convergence between the Sobol' and the IM methods in noncorrelated-factor setting; and (3) to investigate the applicability of the combined approach to evaluating interaction and the correlation effects. The results and conclusions of this study are anticipated to improve the confidence in the PURE risk scores and to promote sensitivity analysis with correlated input factors in environmental modeling.

2. Materials and methods

2.1. Model description

The PURE indicator (Zhan and Zhang, 2012) is composed of four submodels, including air, soil, groundwater, and surface water, with outputs of risk scores R_A, R_S, R_G, and R_W, respectively. A stepwise procedure is employed for each submodel except for the air (Fig. A.1). First, R_A is based on the multiplication of the pesticide application rate (*RATE*), the emission potential (*EP*) that is a pesticide product property for estimating potential volatile organic compound (VOC) emissions by the California Department of Pesticide Regulation (CEPA, 2007), and the application method adjustment factor (*AMAF*). Second, R_S is the maximum of the short-term and long-term risk scores for soil, which are derived from the ratios of the predicted short-term (PEC_{SS}) and long-term (PEC_{SL}) pesticide concentrations in topsoil to the acute and chronic pesticide toxicities to earthworms, respectively. PEC_{SS} is contributed by the amount of the pesticide reaching ground right after the pesticide application, while PEC_{SL} is the average concentration in topsoil considering the decay of PEC_{SS} during 21 days (the typical period for measuring the chronic toxicity) after the application. Third, R_G is based on the ratio of the predicted pesticide concentration leaching to groundwater (PEC_G) to the acceptable daily intake (*ADI*). PEC_G is calculated by using an adapted version of the attenuation factor

(*AF*) method, which was originally proposed by Rao et al. (1985) to indicate pesticide degradation, convection, and dispersion processes in soil. Finally, R_W, similar to R_S, is the maximum of the short-term and long-term risk scores for surface water, which are based on the ratios of the predicted short-term (PEC_{WS}) and long-term (PEC_{WL}) pesticide concentrations loaded to surface water to the maximum acute and chronic pesticide toxicities to aquatic organisms (including fish, *Daphnia*, and algae), respectively. PEC_{WS} is contributed by the pesticide drift and runoff processes. The drift process is modeled using the Drift Calculator (FOCUS, 2001), while the runoff calculation relies on the SCS curve number method (SCS, 1972). PEC_{WL} is the average concentration during 21 days after the application. In this study, sensitivity analysis is performed on each submodel separately, and for preserving the output integrity the risk scores are not truncated to [0, 100] (the truncation is a post-processing step in PURE to make the results more intuitive) (Zhan and Zhang, 2012).

2.2. Factors for sensitivity analysis

The distribution parameters (Table A.1) and the correlation coefficients (Table A.2) of the input factors for each submodel are summarized from the built-in database in PURE, which was developed to evaluate agricultural pesticide risk in California (one of the world's most agricultural productive regions). This database contains the properties of registered pesticides and the environmental conditions of agricultural areas in California from 1990 to 2010 (detailed information can be found in Appendix A). The correlation between *EP* and *RATE* ($\rho = -0.175$) is not listed in Table A.2a to simplify the table layout. The hydrological group (*HG*), crop type (*CT*), the application month (*AM*), and the application method adjustment factor (*AMAF*) are discrete variables, and all other factors are continuous variables. The majority of factors are log-normal distributed, and the rest of the factors are of normal, exponential, or uniform distributions. The factor ranges are utilized in truncated sampling. More realistic samples would be obtained through considering factor ranges and correlation structures (Beulke et al., 2006).

2.3. Sensitivity analysis

Variance-based sensitivity analysis technique is employed to perform sensitivity analysis on each submodel of PURE. This technique outputs sensitivity indices ranging from 0 to 1, where a larger value means higher sensitivity. While various types of sensitivity indices can be calculated by this technique, the first order sensitivity index or main effect (S_i) and the total sensitivity index or total effect (S_{Ti}) are the most important and commonly referred (Yang, 2011). S_i denotes the effect of a factor X_i alone, while S_{Ti} denotes the effects of X_i and all its interactions; consequently ($S_{Ti} - S_i$) indicates the interaction effects of X_i with other factors in the model. Intuitively, S_i is the expected reduction in variance proportion when X_i is fixed (so-called the Factors Prioritization setting), and S_{Ti} is the expected remaining variance proportion when all the factors but X_i are fixed (so-called the Factors Fixing setting) (Saltelli, 2004; Saltelli and Annoni, 2010). In this study, a factor whose S_i is higher than 0.05 (intuitively accounting for more than 5% model variability) is considered sensitive.

For a function $Y = f(x_1,\ldots,x_k)$, S_i is defined as follows (Saltelli and Annoni, 2010):

$$S_i = \frac{V[E[Y|X_i]]}{V[Y]} \tag{1}$$

where $V[Y]$ is the unconditional total variance (Eq. (2)), and $V[E[Y|X_i]]$ is the variance of conditional expectation on X_i (Eq. (5)), which requires an inner multi-dimensional integral to calculate $E[Y|X_i]$ followed by an outer one-dimensional integral to calculate the variance.

$$V[Y] = E\left[Y^2\right] - E^2[Y] \tag{2}$$

where $E[Y]$ is the unconditional expectation (Eq. (3)), and $E[Y^2]$ is calculated by Eq. (4).

$$E[Y] = \int \cdots \int f(x_1,\ldots,x_k)p(x_1,\ldots,x_k)\prod_{j=1}^{k} dx_j \tag{3}$$

where $p(x_1,\ldots,x_k)$ is the joint probability density of the factors.

$$E\left[Y^2\right] = \int \cdots \int f^2(x_1,\ldots,x_k)p(x_1,\ldots,x_k)\prod_{j=1}^{k} dx_j \tag{4}$$

$$V[E[Y|X_i]] = \int \left\{ \int \cdots \int f\left(x_1,\ldots,x_{i-1},x_i^*,x_{i+1},\ldots,x_k\right) p\left(x_1,\ldots,x_{i-1},x_{i+1},\ldots,x_k \middle| x_i^*\right) \prod_{\substack{j=1 \\ j\neq i}}^{k} dx_j \right\}^2 p(x_i)dx_i - E^2[Y] \tag{5}$$

In addition, S_{Ti} is defined as follows (Saltelli and Annoni, 2010):

$$S_{Ti} = \frac{E[V[Y|X_{-i}]]}{V[Y]} \tag{6}$$

where X_{-i} represents all factors but X_i, and $E[V[Y|X_{-i}]]$ is the expectation of conditional variance of X_{-i} (Eq. (7)), which involves an inner one-dimensional integral for calculating $V[Y|X_{-i}]$ and an outer multi-dimensional integral for calculating the expectation.

$$E[V[Y|X_{-i}]] = E\left[Y^2\right] - \int \cdots \int \left\{ \int f\left(x_1^*,\ldots,x_{i-1}^*,x_i,x_{i+1}^*,\ldots,x_k^*\right) p\left(x_i \middle| x_1^*,\ldots,x_{i-1}^*,x_{i+1}^*,\ldots,x_k^*\right)dx_i \right\}^2 p(x_1,\ldots,x_{i-1},x_{i+1},\ldots,x_k)\prod_{\substack{j=1 \\ j\neq i}}^{k} dx_j \tag{7}$$

Although the above complex integrals can be approximated via Monte Carlo methods with multi-dimensional samples generated by the Markov Chain Monte Carlo (MCMC) method, this brute-force approach is computationally expensive and slow to converge. Therefore, the more efficient methods including the Sobol' (Saltelli, 2002) and the importance measurement (IM) method (McKay, 1995) are employed instead. In this study, the Sobol' method calculates S_i and S_{Ti} in noncorrelated-factor setting to address the main and interaction effects, while the IM method calculates S_i in both noncorrelated-factor and correlated-factor settings to address the correlation effects. With the Sobol' method, $\sum S_i$ and ($S_{Ti} - S_i$) suggest the interaction effects among the factors in each submodel. Using the IM method, ($S_{i,C} - S_{i,NC}$) indicates the correlation effect for each factor, where $S_{i,C}$ and $S_{i,NC}$ are S_i in noncorrelated-factor and correlated-factor settings, respectively. The numerical experiment where the S_i in noncorrelated-factor setting are calculated by both the Sobol' and IM methods allows for not only comparing the two methods in noncorrelated-factor setting but also removing the artificial effect brought by method difference on $(S_{i,C} - S_{i,NC})$ if $S_{i,NC}$ is calculated by the IM method while $S_{i,C}$ is calculated by the Sobol' method. Finally, it should be noted that the Sobol' method is inapplicable in correlated-factor setting while the IM method can only calculate S_i, so the interaction effects in correlated-factor setting are not analyzed in this study. Although the SDP method (Ratto et al., 2007) can efficiently calculate S_i plus interaction terms up to third order, the estimates of S_{Ti} may be biased and this method is difficult to implement (Gatelli et al., 2009; Yang, 2011).

2.3.1. Sobol' sensitivity analysis

In noncorrelated-factor setting the Sobol' method can calculate S_i, S_{Ti}, and other high-order sensitivity indices, *e.g.*, second-order interaction effect S_{ij}, based on the decomposition of total unconditional variance ($V[Y]$) (Saltelli, 2002):

$$V[Y] = \sum_i V_i + \sum_i \sum_{j>i} V_{ij} + \cdots + V_{12\ldots k} \tag{8}$$

where $V_i = V[E[Y|X_i]]$,

$$V_{ij} = V\left[E\left[Y|X_i, X_j\right]\right] - V_i - V_j \tag{9}$$

$$V_{12\ldots k} = V[E[Y|X_1, X_2, \ldots, X_k]] \tag{10}$$

At this point, Eq. (1) is applied to calculate S_i. Moreover, the sum of $S_i(\sum_i S_i)$ can tell whether the model is additive. If no interaction effect exists, $V[Y] = \sum_i V_i$, and consequently $\sum_i S_i = 1$. In other words, $\sum_i S_i < 1$ indicates the model is nonadditive. It is easily derived that $\sum_i S_i$ cannot be larger than 1 in noncorrelated-factor setting. However, due to numerical errors, the estimations of $\sum_i S_i$ may be a slightly deviated from 1 even when the model is additive. In this study, when $\sum_i S_i \in [0.95, 1.05]$, the model is considered additive. To further identify which factors have interaction effects, S_{Ti} is an efficient indicator, which can be delineated as follows:

$$S_{Ti} = S_i + \sum_j S_{ij} + \ldots + S_{12\ldots k} \tag{11}$$

$$S_{ij} = \frac{V_{ij}}{V} \tag{12}$$

$$S_{12\ldots k} = \frac{V_{12\ldots k}}{V} \tag{13}$$

where S_{ij} is the second order sensitivity index showing the unique interaction effect between X_i and X_j.

The Sobol' method (Sobol', 1993) implements a substituted-column sampling plan to calculate sensitivity indices efficiently. $(2k+1)^*N$ model runs are required to calculate S_i and S_{Ti}, where k is the number of indices to estimate, and N is the base sample size. Saltelli (2002) refined the computation procedure and reduced the number of model runs to $(k+2)^*N$ in calculating S_i and S_{Ti}. Moreover, the bootstrap technique (Efron and Tibshirani, 1994) can be used to estimate confidence intervals for sensitivity indices.

2.3.2. Importance measurement (IM)

In correlated-factor setting the importance measurement (IM) method with the replicated Latin Hypercube Sampling (r-LHS) plan (McKay, 1995) calculates S_i, which requires N^*R model runs, where N is the base sample size and R is the number of replications. One advantage of r-LHS is that the number of model runs is independent of the number of factors. S_i is also calculated by Eq. (1), while the unconditional total variance is calculated as follows.

$$V[Y] = \frac{1}{N \cdot R} \sum_n \sum_r (y_{nr} - E[Y])^2 \tag{14}$$

where y_{nr} is the model output when using sample n of replicate r, and $E[Y]$ is the unconditional mean (Eq. (15)). It should be noted that for LHS, the N-divided sum of squares is preferred to the $(N-1)$-divided one because the former generates unbiased estimates for simple random sampling (McKay, 1995).

$$E[Y] = \frac{1}{N \cdot R} \sum_n \sum_r y_{nr} \tag{15}$$

The variance of conditional expectation (V_i) is calculated as follows:

$$\begin{aligned} V_i = & \frac{1}{N} \sum_n (E[Y|X_i = X_{in}] - E[Y])^2 \\ & - \frac{1}{N \cdot R^2} \sum_n \sum_r (y_{nr} - E[Y|X_i = X_{in}])^2 \end{aligned} \tag{16}$$

where $E[Y|X_i = X_{in}]$ is the conditional mean when using X_i value in sample n (Eq. (17)).

$$E[Y|X_i = X_{in}] = \frac{1}{R} \sum_r y_{(i)nr} \tag{17}$$

where $y_{(i)nr}$ is the model output in replicate r when using X_i value in sample n.

2.4. Sampling

The sample generation is based on the factor distribution parameters (Table A.1) and correlation coefficients (Table A.2). In noncorrelated-factor setting the Sobol' quasi-random sequence (Sobol', 1967, 1976) is used to generate a set of samples for the Sobol' method, while r-LHS is used to generate a set of samples for the IM method. The original samples generated by r-LHS are noncorrelated. In correlated-factor setting r-LHS is again used to generate another set of samples, which are then adjusted to a set of correlated samples with the required correlation structure (Table A.2) by using the Iman and Conover's (1982) method.

As mentioned earlier, the Sobol' method requires $(k+2)^*N$ model runs, and the IM method demands N^*R model runs. The submodels of the air, soil, groundwater, and surface water risk assessments have three, eight, 14, and 16 factors, respectively. For the Sobol' method, the base sample size is set to 2000 for each submodel, resulting in 10,000, 20,000, 32,000, and 36,000 model runs for these submodels (in the same order as above), respectively. For the IM method, 20 replications are sampled in r-LHS, and the number of model runs for each submodel is set to the same value as the Sobol' method. Therefore, the IM method employs 500, 1000, 1600, and 1800 base samples for these submodels (in the same order as above), respectively. To inspect the convergence of the estimations, the base sample sizes gradually increase in 100 uniform steps.

2.5. Programming aspects

PURE is coded in Java, while all the sensitivity analysis approaches are programmed in R, a free and versatile software environment for scientific computation (R Development Core

Table 1
Sensitivity analysis results for air risk evaluation.[a]

	Sobol'						Importance measurement[b]			
	S_i	95% CI	Rank	S_{Ti}	95% CI	Rank	$S_{i,C}$	Rank	$S_{i,NC}$	Rank
RATE	0.538	(0.473, 0.599)	1	0.537	(0.492, 0.578)	1	0.463	1	0.528	1
EP	0.363	(0.310, 0.406)	2	0.358	(0.323, 0.399)	2	0.254	2	0.347	2
AMAF	0.125	(0.100, 0.146)	3	0.121	(0.098, 0.142)	3	0.150	3	0.126	3
Sum	1.025			1.016			0.866		1.001	

[a] The variable definitions are listed in Table A.1.
[b] $S_{i,C}$: S_i in correlated-factor setting; $S_{i,NC}$: S_i in noncorrelated-factor setting.

Team, 2013). The third-party R packages referenced in this study are listed as follows: (1) *sensitivity* (Pujol, 2012) to perform the Sobol' sensitivity analysis; (2) *randotoolbox* (Dutang and Savicky, 2012) to generate the Sobol' quasi-random sequences; (3) *lhs* (Carnell, 2012) to carry out Latin hypercube sampling; (4) *mc2d* (Pouillot and Delignette-Muller, 2010) to add correlations to noncorrelated samples; (5) a truncated sampling script by Nadrajah and Kotz (2006); and (6) *doSnow* (Revolution Analytics, 2012a) and *foreach* (Revolution Analytics, 2012b) for parallel computation. In addition, the IM method with r-LHS is programmed in R.

3. Results and discussion

The estimations of S_i and S_{Ti} for each submodel of PURE are listed in Tables 1–4, while the evolutions of these estimations are shown in Figs. 1–3. For S_i in noncorrelated-factor setting, the point estimations are generally similar between the Sobol' and IM methods, and the IM's point estimations all fall in the Sobol's 95% confidence intervals (CI). The interaction and correlation effects are derived from the estimations of S_i and S_{Ti}. It should be noted that the ranks for the insensitive ($S_i < 0.05$) or slightly-sensitive (S_i slightly larger than 0.05) factors are less accurate and should be used with caution in that their values are relatively unsteady due to numerical errors. Nevertheless, for any pair of these factors, if both the Sobol' and IM methods give the same relative ranks or if their S_i CI do not overlap, then the relative ranks are considered reliable.

3.1. Sensitivity analysis of the air risk assessment

In noncorrelated-factor setting the air risk score (R_A), indicating the potential VOC emission amount, is sensitive to the pesticide application rate (*RATE*), the emission potential (*EP*), and the application method adjustment factor (*AMAF*) (Table 1). All the point estimations of S_i by the IM method fall in the 95% confidence intervals (CI) estimated by the Sobol' method, and the point estimations of S_i by the Sobol' and IM methods are very similar. Using the IM method, the S_i for *RATE*, *EP*, and *AMAF* are 0.528, 0.347, and 0.126, respectively. With the Sobol' method, the S_i for these factors (in the same order) are 0.538 (CI: [0.473, 0.599]), 0.363 (CI: [0.310, 0.406]), and 0.125 (CI: [0.100, 0.146]), respectively. In our literature search, this study is the first global sensitivity analysis on the *EP*-based air risk assessment method. The sensitivity ranks of the three factors are the same as the ranks of their sampling variations. *RATE* that is of lognormal distribution and ranges across nine orders of magnitude (from 1.12E-7 to 8.73E2; Table A.1) gets the highest S_i. *RATE* provides the basic mass for VOC emission. A low *RATE* results in a low VOC emission, and a high *RATE* is necessary for a high VOC emission. In addition, *EP*, as an exponentially distributed variable ranging from 0 to 100%, is in the middle of the sensitivity ranking. *EP* measures the portion of the pesticide mass that potentially emits to the air (all is assumed to be VOC) under a standard condition, which highly affects the VOC emission quantity. Finally, *AMAF* that has 17 discrete levels ranging from 9% to 100% (Table A.1) obtains the lowest S_i. Derived from long-term field experimental data, *AMAF* was used to adjust *EP* based on the pesticide application method, and its effect on the VOC emission quantity is lower than *RATE* and *EP*.

Compared with the Sobol' method, the IM method has a shorter burn-in period but provides less stable estimations after a decent number of model runs (Fig. 1a). The IM method starts oscillating around the equilibrium statuses at fewer than 2000 model runs, while the Sobol' method approaches the equilibrium statues after around 4000 model runs. When estimating S_i only, the sampling strategy used by the Sobol' method (*i.e.*, substituted column sampling strategy) is less efficient than the sampling strategy employed by the IM method (*i.e.*, permuted column sampling strategy), because the former only utilizes $2N$ of the total of $(k+1)^*N$ model runs (Morris et al., 2008). Moreover, in this study the Sobol' method requires N extra runs for simultaneously estimating S_{Ti}. On the other hand, the evolution curves of the Sobol' method are smoother than the ones of the IM method, indicating the estimations by the Sobol' method are more accurate at large sample size thanks to the

Table 2
Sensitivity analysis results for soil risk evaluation.[a]

	Sobol'						Importance Measurement[b]			
	S_i	95% CI	Rank	S_{Ti}	95% CI	Rank	$S_{i,C}$	Rank	$S_{i,NC}$	Rank
BD	0.004	(0.000, 0.008)	6	0.000[c]	(−0.007, 0.001)	7	0.004	6	0.001	8
T_M	0.004	(−0.004, 0.012)	6	0.000[c]	(−0.010, 0.007)	7	0.002	7	0.006	6
DT_{SO}	0.012	(−0.014, 0.039)	5	0.027	(−0.004, 0.054)	5	0.008	5	0.019	5
LC_W	0.057	(0.014, 0.101)	3	0.068	(0.021, 0.115)	3	0.158	3	0.042	4
$NOEC_W$	0.183	(0.116, 0.254)	2	0.178	(0.103, 0.247)	2	0.234	2	0.146	2
$RATE_{AI}$	0.714	(0.550, 0.857)	1	0.696	(0.559, 0.836)	1	0.671	1	0.696	1
CT	0.002	(−0.014, 0.018)	8	0.007	(−0.009, 0.024)	6	0.002	7	0.005	7
AM	0.057	(0.017, 0.100)	3	0.056	(0.011, 0.096)	4	0.050	4	0.055	3
Sum	1.034			1.027			1.129		0.969	

[a] The variable definitions are listed in Table A.1.
[b] $S_{i,C}$: S_i in correlated-factor setting; $S_{i,NC}$: S_i in noncorrelated-factor setting.
[c] The value is slightly smaller than 0 (due to numerical errors), so it is reset to 0.

Table 3
Sensitivity analysis results for groundwater risk evaluation.[a]

	Sobol'						Importance Measurement[b]			
	S_i	95% CI	Rank	S_{Ti}	95% CI	Rank	$S_{i,C}$	Rank	$S_{i,NC}$	Rank
K_{OC}	0.429	(0.352, 0.501)	1	0.585	(0.513, 0.646)	1	0.441	1	0.400	1
K_H	0.023	(0.001, 0.047)	5	0.040	(0.020, 0.059)	5	0.112	3	0.016	5
DT_{SA}	0.296	(0.230, 0.360)	2	0.476	(0.416, 0.537)	2	0.280	2	0.263	2
DT_{SO}	0.000	(−0.001, 0.001)	14	0.000	(−0.001, 0.000)	12	0.019	6	0.000[c]	13
ADI	0.004	(−0.001, 0.008)	9	0.002	(0.000, 0.004)	11	0.051	4	0.003	10
BD	0.008	(−0.002, 0.016)	7	0.010	(0.001, 0.018)	8	0.006	9	0.000	13
OM	0.032	(0.005, 0.059)	4	0.080	(0.052, 0.108)	4	0.012	7	0.029	4
CC	0.006	(−0.006, 0.018)	8	0.012	(0.000, 0.022)	7	0.001	13	0.006	7
L	0.060	(0.027, 0.095)	3	0.130	(0.097, 0.161)	3	0.044	5	0.050	3
Q	0.015	(−0.001, 0.031)	6	0.024	(0.007, 0.041)	6	0.012	7	0.013	6
T	0.002	(−0.005, 0.009)	10	0.005	(−0.003, 0.012)	9	0.001	13	0.004	9
$RATE_{AI}$	0.001	(−0.005, 0.007)	11	0.004	(0.001, 0.007)	10	0.005	10	0.006	7
CT	0.001	(0.000, 0.001)	11	0.000	(−0.001, 0.000)	12	0.002	11	0.001	12
AM	0.001	(0.000, 0.003)	11	0.000	(−0.001, 0.001)	12	0.002	11	0.003	10
Sum	0.878			1.368			0.989		0.792	

[a] The variable definitions are listed in Table A.1.
[b] $S_{i,C}$: S_i in correlated-factor setting; $S_{i,NC}$: S_i in noncorrelated-factor setting.
[c] The value is slightly smaller than 0 (due to numerical errors), so it is reset to 0.

Sobol' quasi-random sequence (Sobol', 1967, 1976), which is a low-discrepancy sequence and accelerates convergence in estimating integrals.

The sensitivity analysis results in noncorrelated-factor setting show that no interaction effect exists in the air risk evaluation, according to $\sum S_i$ and $(S_{Ti} - S_i)$ by the Sobol' method (Table 1). $\sum S_i$ $(=1.025)$ is very close to 1, suggesting the entire process is additive. Furthermore, the S_{Ti} estimations for *RATE*, *EP*, and *AMAF* are 0.537 (CI: [0.492, 0.578]), 0.357 (CI: [0.323, 0.399]), and 0.121 (CI: [0.098, 0.142]); the S_{Ti} estimations converge to steady status after about 3000 model runs (Fig. 2a). S_{Ti} is very close to S_i for each of these factors. For example, the S_i for *RATE* is 0.538 (CI: [0.492, 0.578]), and hence the $(S_{Ti} - S_i)$ is −0.001. The negligible differences (due to numerical errors) support the finding that none factor has interaction effect in the air risk evaluation.

In correlated-factor setting the S_i estimations by the IM method for *RATE*, *EP*, and *AMAF* are 0.463, 0.254, and 0.150, respectively (Table 1). The S_i estimations become relatively stable after 4000 model runs (Fig. 3a). A negative correlation between *RATE* and *EP* $(\rho = -0.175)$, reflecting the fact that a pesticide with higher *EP* tends to be applied less, is introduced in the sensitivity analysis sample generation. Although the sensitivity ranks remain the same as the ones in noncorrelated-factor setting, the S_i for *RATE* and *EP* decrease considerably while the S_i for *AMAF* increases slightly. The negative correlation between *RATE* and *EP* induces counteractive effect against each other, which can be considered as negative interaction effect emerging in the sampling process. Additionally, the negative correlation between *RATE* and *EP* has a side effect on the S_i for *AMAF*, *i.e.*, the denominator decreases to a larger extent than the nominator does (Eq. (1)) and hence leads to a higher S_i. Finally, $\sum S_i$ $(=0.866)$ becomes much lower than 1, which is due to interaction effects resulting from the correlation between *RATE* and *EP*. As stated in the introduction, interaction and correlation effects are properties of the model and the input factors, respectively (Saltelli and Tarantola, 2002). As the sensitivity analysis results in noncorrelated-factor setting have already shown there is no interaction effect in the air risk assessment, the additive property of the model should remain in correlated-factor setting. Therefore, the parameter correlations play a role in decreasing $\sum S_i$.

Table 4
Sensitivity analysis results for surface water risk evaluation.[a]

	Sobol'						Importance Measurement[b]			
	S_i	95% CI	Rank	S_{Ti}	95% CI	Rank	$S_{i,C}$	Rank	$S_{i,NC}$	Rank
K_{OC}	0.004	(−0.002, 0.009)	5	0.005	(0.003, 0.007)	7	0.002	13	0.006	6
DT_{SO}	0.004	(−0.001, 0.007)	5	0.001	(−0.001, 0.003)	9	0.005	7	0.004	9
DT_W	0.001	(−0.001, 0.004)	9	0.000	(0.000, 0.001)	10	0.005	7	0.003	12
LEC_A	0.004	(−0.002, 0.009)	5	0.005	(0.004, 0.007)	7	0.009	6	0.007	5
$NOEC_A$	0.004	(−0.003, 0.012)	5	0.010	(0.007, 0.012)	5	0.013	4	0.011	4
BD	0.000	(0.000, 0.000)	12	0.000	(0.000, 0.000)	10	0.001	15	0.004	9
OM	0.000	(−0.001, 0.002)	12	0.000	(0.000, 0.001)	10	0.002	13	0.005	7
SC	0.000	(0.000, 0.000)	12	0.000	(0.000, 0.000)	10	0.003	11	0.003	12
SL	0.000[c]	(−0.013, 0.008)	12	0.015	(0.000, 0.027)	4	0.005	7	0.002	16
D	0.014	(0.002, 0.023)	3	0.067	(0.034, 0.096)	3	0.026	3	0.021	3
R_M	0.536	(0.417, 0.639)	1	0.810	(0.741, 0.882)	1	0.607	1	0.605	1
T_M	0.000	(−0.001, 0.002)	12	0.000	(0.000, 0.001)	10	0.004	10	0.003	12
$RATE_{AI}$	0.008	(0.002, 0.015)	4	0.007	(0.005, 0.009)	6	0.012	5	0.005	7
HG	0.095	(0.037, 0.153)	2	0.300	(0.243, 0.357)	2	0.090	2	0.090	2
CT	0.001	(0.000, 0.002)	9	0.000	(0.000, 0.000)	10	0.000	16	0.003	12
AM	0.001	(0.000, 0.003)	9	0.000	(0.000, 0.001)	10	0.003	11	0.004	9
Sum	0.671			1.220			0.786		0.775	

[a] The variable definitions are listed in Table A.1.
[b] $S_{i,C}$: S_i in correlated-factor setting; $S_{i,NC}$: S_i in noncorrelated-factor setting.
[c] The value is slightly smaller than 0 (due to numerical errors), so it is reset to 0.

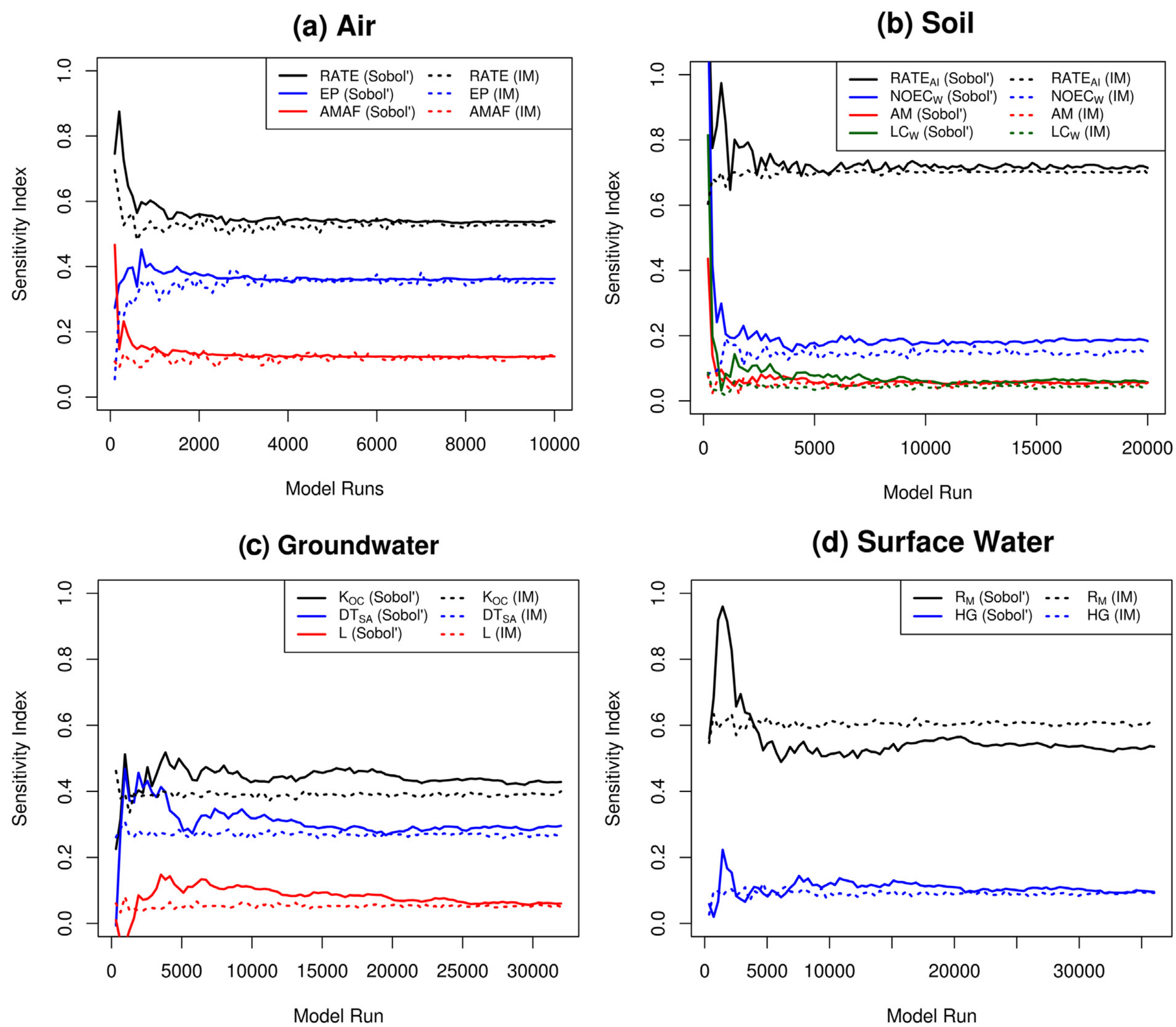

Fig. 1. Evolution of first-order sensitivity indices (S_i) by the Sobol' and importance measurement (IM) methods in noncorrelated-factor setting for (a) air, (b) soil, (c) groundwater, and (d) surface water.

3.2. Sensitivity analysis of the soil risk assessment

Table 2 shows that in noncorrelated-factor setting the soil risk score (R_S) is sensitive to the following factors: the application rate of pesticide active ingredient ($RATE_{AI}$), the chronic no-observable-effect concentration to earthworms ($NOEC_W$), the application month (*AM*), and the acute 50%-lethal concentration to earthworms (LC_W). Although all the point estimations of S_i by the IM method fall in the CI of S_i by the Sobol' method, the point estimations of S_i by the two methods are slightly different. The S_i estimations by the IM method for $RATE_{AI}$, $NOEC_W$, *AM*, and LC_W are 0.696, 0.146, 0.055, and 0.042, respectively. While, the S_i estimations by the Sobol' method for these factors (in the same order) are 0.714 (CI: [0.550, 0.857]), 0.183 (CI: [0.116, 0.254]), 0.057 (CI: [0.017, 0.100]), and 0.057 (CI: [0.014, 0.101]), respectively. It is noted that the Sobol' result shows LC_W is a slightly sensitive factor while the IM result suggests not, although its S_i is only a little lower than 0.05 (the predefined sensitivity threshold). These sensitive factors are considered important empirically. The soil risk evaluation doesn't have pesticide off-site transportation, which is consistent with the finding that $RATE_{AI}$ is the most sensitive factor. In addition, *AM* affects the soil risk via the crop interception rate (f_{int}), which could largely change the portion of pesticides reaching soil. For instance, f_{int} for orchards is 78% in the growing season and 44% in dormant season (settings in PURE), resulting in 34% difference in the amount of pesticide exposure. Besides exposure amount, pesticide toxicity to the organisms in soil (indicated by earthworms) is a sensitive factor in soil risk evaluation. Risk emerges only when both exposure and toxicity take effect. It's unexpected that DT_{SO} is an insensitive factor, which has a high impact on long-term pesticide concentration in topsoil. There are very few sensitivity analysis studies on modeling pesticide concentration in soil. In a local sensitivity analysis study covering pesticide concentration in soil (Ma et al., 2004), DT_{SO} is sensitive in predicting pesticide concentration in topsoil. The result that DT_{SO} is insensitive in PURE is probably because the preset exposure period (21 days) is insufficiently long to reflect the degradation effect on long-term concentration. Further investigation is required to resolve this issue.

In estimating the S_i for the sensitive factors in the soil risk evaluation, the Sobol' method has a longer burn-in period than the IM method does (Fig. 1b). The Sobol' method takes about 10000 model runs to reach the equilibrium status while the IM method takes about 2500 model runs. The difference between the burn-in periods is mainly due to the different sampling strategies

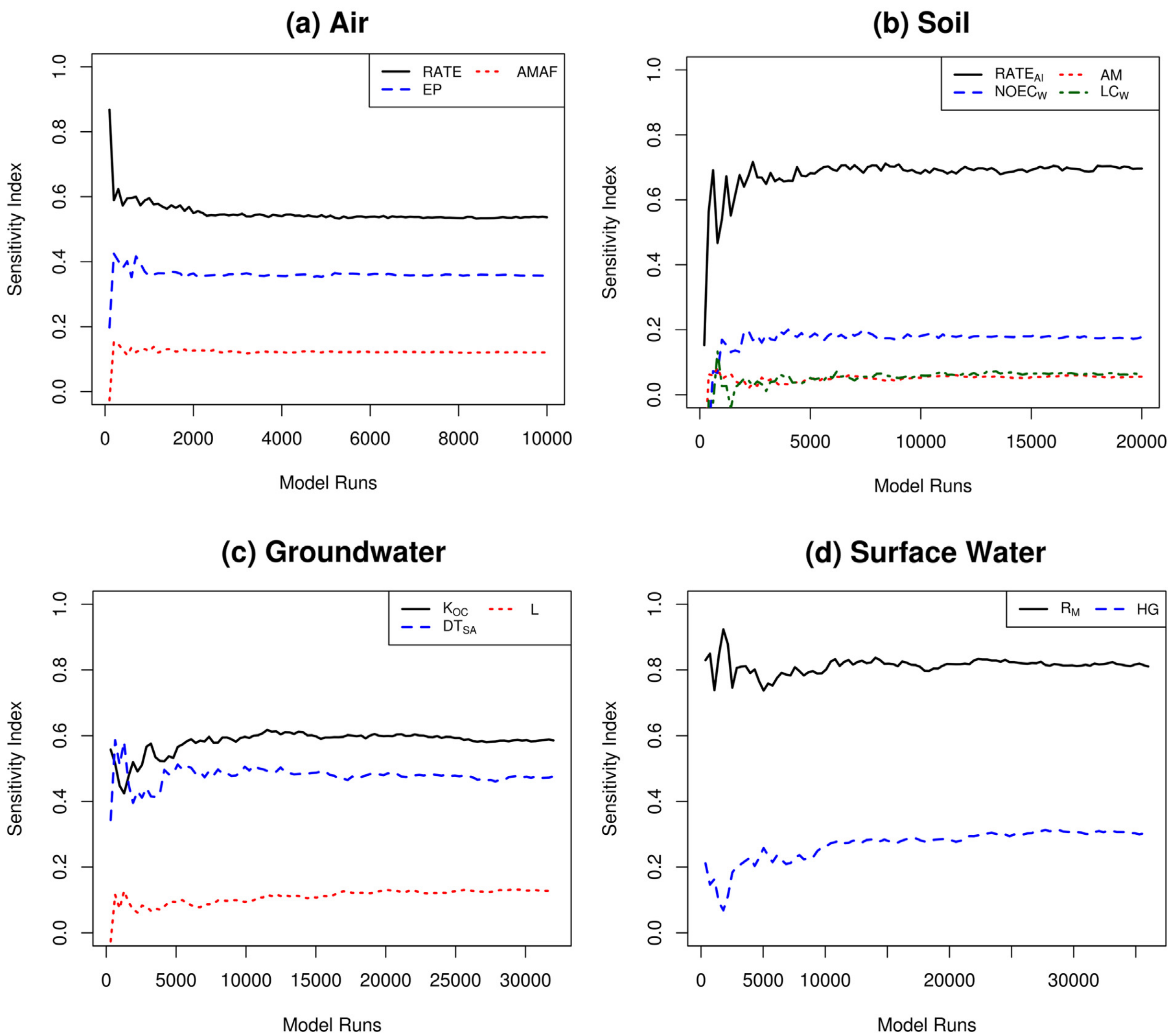

Fig. 2. Evolution of the total effect sensitivity indices (S_{Ti}) by the Sobol' method in noncorrelated-factor setting for (a) air, (b) soil, (c) groundwater, and (d) surface water.

employed by the two methods, which were discussed in depth in Section 3.1. In addition, the evolution line of the S_i for $NOEC_W$ drawn by the Sobol' method is consistently above the one drawn by the IM method (Fig. 1b). The estimations by the IM method may be biased in that the sampling strategy of random column permutation results in imperfect mixing of the input factors, *i.e.*, no two input values paired together in one array also were paired in another array (Castaings et al., 2012; Morris et al., 2008).

In noncorrelated-factor setting, it is found that the soil risk evaluation is an additive process as $\sum S_i$ (=1.034) by the Sobol' method is very close to 1 (Table 2). Moreover, the S_{Ti} estimations for $RATE_{AI}$, $NOEC_W$, AM, and LC_W are 0.696 (CI: [0.559, 0.836]), 0.178 (CI: [0.103, 0.247]), 0.056 (CI: [0.011, 0.096]), and 0.068 (CI: [0.021, 0.115]) (Table 2). The S_{Ti} estimations converge at about 10000 model runs (Fig. 2b). The S_{Ti} estimation is very close to the S_i estimation for each sensitive factor, which indicates none of the factors has interaction effect.

In correlated-factor setting the S_i estimations by the IM method for $RATE_{AI}$, $NOEC_W$, LC_W, and AM are 0.671, 0.234, 0.158, and 0.050, respectively (Table 2). The S_i estimations converge at about 1000 model runs (Fig. 3b). Compared with the S_i estimations for LC_W (0.042) and $NOEC_W$ (0.146) in noncorrelated-factor setting, the S_i estimations for the two factors largely increase and even $\sum S_i$ (=1.129) becomes much higher than 1, which are induced by the high positive correlation between LC_W and $NOEC_W$ (ρ = 0.65; Table A.2a). As LC_W and $NOEC_W$ are both positively related to the soil risk, the positive correlation between LC_W and $NOEC_W$ carries over the effect of one of them to the other. When an insensitive factor is correlated with another insensitive factor, their correlation effects reflected in the change of S_i are very limited. For instance, while the insensitive factors, the bulk density (BD) and T_M, are positively correlated ($\rho = 0.19$; Table A.2b), their S_i estimations are consistently low in both noncorrelated-factor and correlated-factor settings.

3.3. *Sensitivity analysis of the groundwater risk assessment*

The groundwater risk score (R_G) is sensitive to the organic carbon sorption constant (K_{OC}), the anaerobic half-life in soil (DT_{SA}), and the groundwater depth (L) (Table 3). In noncorrelated-factor setting the S_i estimations for these factors are consistent between the Sobol' and IM methods. With the IM method, the S_i for K_{OC}, DT_{SA}, and L are 0.400, 0.263, and 0.050, respectively. Using the Sobol' method, the S_i for these factors (in the same order) are 0.429 (CI: [0.352, 0.501]), 0.296 (CI: [0.230, 0.360]), and 0.060 (CI: [0.027, 0.095]), respectively. Fig. 1c shows that the S_i estimations by the IM method converge much faster (around 1000 model runs) than by

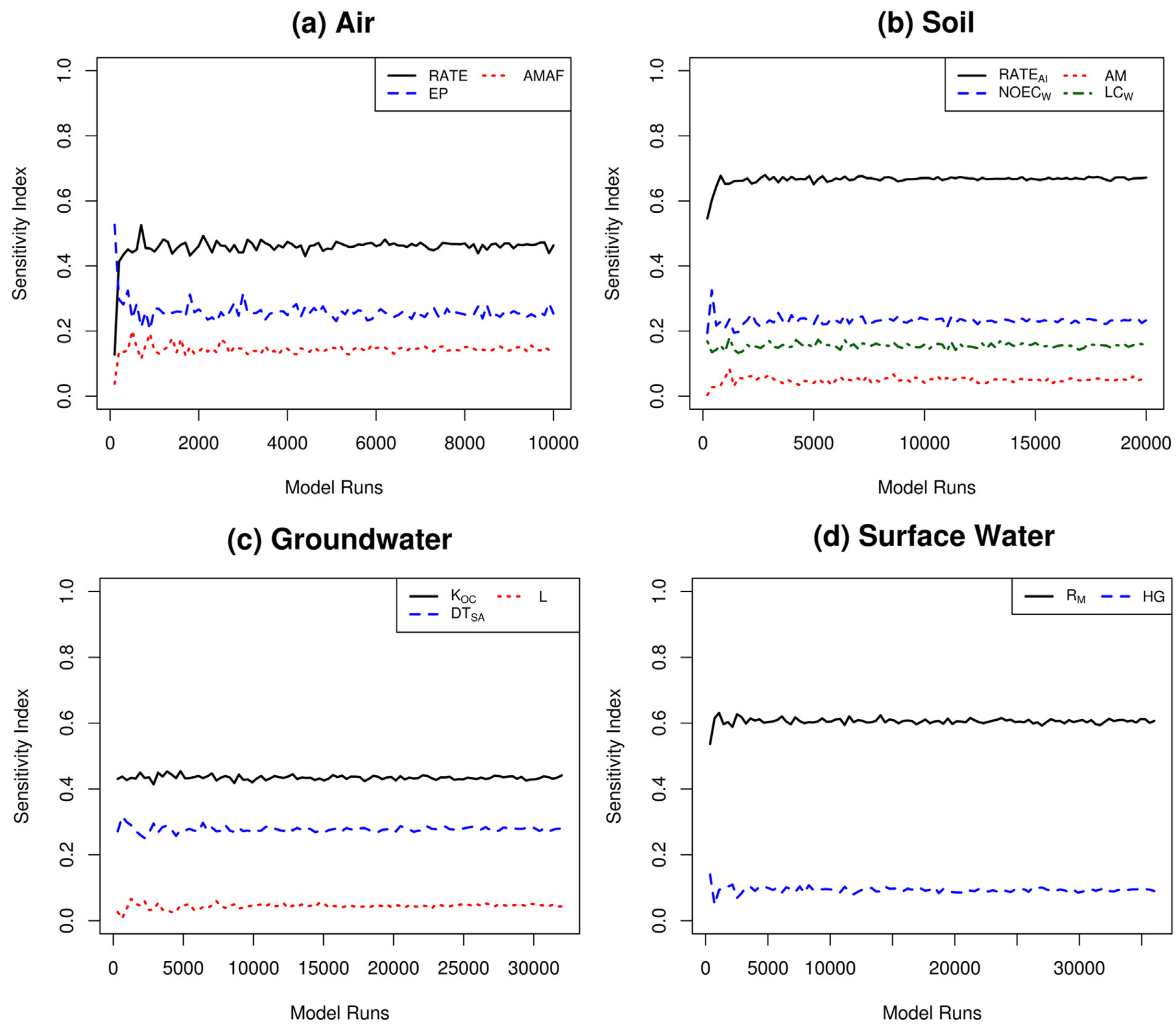

Fig. 3. Evolution of the first-order sensitivity indices (S_i) by the importance measurement (IM) in correlated-factor setting for (a) air, (b) soil, (c) groundwater, and (d) surface water.

the Sobol' method (greater than 25,000 model runs), and the Sobol' lines are generally above the IM lines.

The sensitivity rankings conform to the findings of groundwater monitoring and some other sensitivity analysis studies. Pesticide movement in soil towards groundwater is generally slow, which may take 3–33 years (Spurlock et al., 2000) and involves three main processes, including adsorption, convection, and degradation. The adsorption process retards pesticide movement as a pesticide compound sorbs to soil particles, and the adsorption strength is indicated by K_{OC} in PURE. The degradation process reflects the persistence of pesticides in soil, which is indicated by DT_{SA} in PURE. In a national groundwater survey, pesticides were commonly detected in shallow groundwater regions, and the detection frequencies were highly correlated with pesticide K_{OC} and half-life (Kolpin et al., 2000). In addition, the groundwater 6800 list, a pesticide regulation list by California Department of Pesticide Regulation (CEPA, 2012), also considers K_{OC} and DT_{SA} as important indicator factors to determine whether a pesticide is of high risk to groundwater. Moreover, in a few sensitivity analysis studies on pesticide leaching models (*e.g.*, Cheviron and Coquet, 2009; Dubus et al., 2003; Soutter and Musy, 1999; Wolt et al., 2002), the pesticide leaching to groundwater was found to be consistently sensitive to the adsorption and degradation processes, even though those sensitivity analysis studies tested different models and used different sensitivity analysis techniques. For example, Dubus et al. (2003) compared the sensitivity of four models (*i.e.*, PELMO, PRZM, PESTLA, and MACRO) by using a local sensitivity analysis approach, while Cheviron and Coquet (2009) analyzed the HYDRUS-1D model by using a one-group-at-a-time sensitivity analysis method. However, none of those sensitivity analysis studies implemented global sensitivity analysis or analyzed interaction effects, and only Soutter and Musy (1999) took factor correlation into account in their study.

In noncorrelated-factor setting it is found that the groundwater risk evaluation is a nonadditive process. $\sum S_i$ (=0.878) by the Sobol' method is much lower than 1 (Table 3), demonstrating the entire process is nonadditive. Specific interactions are detected by examining ($S_{Ti} - S_i$) for each factor. The S_{Ti} estimations for K_{OC}, DT_{SA}, and L are 0.585 (CI: [0.513, 0.646]), 0.476 (CI: [0.416, 0.537]), and 0.130 (CI: [0.097, 0.161]), respectively. Fig. 2c shows that the S_{Ti} estimations converge at around 20000 model runs. The ($S_{Ti} - S_i$) for K_{OC}, DT_{SA}, and L are 0.156 (=0.585 − 0.429), 0.18 (=0.476 − 0.296), 0.07 (=0.130 − 0.060), respectively, indicating that K_{OC} and DT_{SA} have high interaction effects with each other.

In correlated-factor setting the S_i estimations by the IM method for K_{OC}, DT_{SA}, and L (the sensitive factors in noncorrelated-factor setting) are 0.441, 0.280, and 0.044, respectively (Table 3), which converge at fewer than 10,000 model runs (Fig. 3c). The S_i estimations for K_{OC} and DT_{SA} increase a little when compared with the ones in noncorrelated-factor setting, while the S_i estimation for L decreases a bit. Additionally, the Henry's law constant (K_H) and the acceptable daily intake (*ADI*), which are insensitive factors in noncorrelated-factor setting ($S_i = 0.016$ and 0.003, respectively), become sensitive in correlated-factor setting ($S_i = 0.112$ and 0.051, respectively) (Table 3). These changes are caused by their correlations with the sensitive factors, *i.e.*, K_{OC} and DT_{SA}. The correlation structure here is more complex than the ones in the air and soil risk evaluations. First, K_{OC} tends to have a negative effect on the groundwater risk, *i.e.*, increasing K_{OC} tends to decrease the groundwater risk by enhancing the adsorption strength. Bridged by the positive correlation with K_{OC} ($\rho = 0.21$) (Table A.2a), K_H gains a negative effect on the groundwater risk; a negative effect generates another negative effect via a positive correlation. Second, DT_{SA} tends to have a positive effect on the groundwater risk, *i.e.*, increasing DT_{SA} tends to increase the groundwater risk via slowing the degradation process. Through the negative correlation with DT_{SA} ($\rho = -0.29$) (Table A.2a), K_H gains another negative effect on the groundwater risk; a positive effect results in a negative effect via a negative correlation. Therefore, the negative effect of K_H on the groundwater risk is enlarged through restricting the sampling distributions of both K_{OC} and DT_{SA}. Similarly, the increase of the S_i for *ADI* is mainly because *ADI* has opposite correlations with K_{OC} ($\rho = -0.11$) and DT_{SA} ($\rho = 0.27$) (Table A.2a).

3.4. Sensitivity analysis of the surface water risk assessment

In noncorrelated-factor setting our finding is that the surface water risk score (R_W) is sensitive to the monthly maximum daily water input (R_M) and the hydrology group (*HG*) (Table 4). The S_i point estimations for the two factors by the Sobol' and IM methods are slightly different, though all the point estimations by the latter fall in the CI estimations by the former. With the IM method, the S_i estimations for R_M and *HG* are 0.605 and 0.090, respectively. Using the Sobol' method, the S_i estimations for R_M and *HG* are 0.536 (CI: [0.417, 0.639]) and 0.095 (CI: [0.037, 0.153]), respectively. The S_i estimations by the Sobol' method converge at about 20,000 model runs while the S_i estimations by the IM method converge at about 5000 model runs; for R_M the Sobol' line lay below the IM line after 5000 model runs (Fig. 1d).

The result that R_M and *HG* are sensitive factors is consistent with the knowledge and sensitivity analysis studies on pesticide transport to surface water, which mainly includes surface runoff, spray drift, and lateral flow. The first two pathways are taken into account by the PURE indicator. Spray drift plays an important role when farmlands are close to surface water, while surface runoff is the dominant pathway in general. It is considered that pesticide loss via surface runoff is primarily determined by hydrological factors rather than pesticide properties (van der Werf and Zimmer, 1998). R_M and *HG*, as the two major hydrological factors in PURE, deserve high sensitivity weightings. In California, USA, pesticide runoff mostly occurs in the irrigation season or storm days during the dormant season (Luo and Zhang, 2010), when a large amount of water input (including precipitation and irrigation) is essential in transporting pesticide to surface water. Ma et al. (2004) carried out a local sensitivity analysis on the RZWQM model and found the pesticide runoff load in surface water runoff was most sensitive to rainfall. Therefore, increasing irrigation efficiency and decreasing surface water runoff (such as by using a field-edge pond) are important mitigation method to reduce pesticide surface water risk. The second most important factor, *HG*, determines the curve number (CN), for estimating the amount of surface water runoff, with the land use type. Several sensitivity analysis studies on the pesticide simulation models, employing the CN method to estimate surface water runoff, agree on the high influence of CN on pesticide surface runoff (Holvoet et al., 2005; Luo and Zhang, 2009; Wolt et al., 2002). Nevertheless, neither interaction effects nor factor correlations were considered in those sensitivity analysis studies.

In noncorrelated-factor setting it is found that there exists interaction effect in the surface water risk evaluation as $\sum S_i$ (=0.671) is lower than 1 (Table 4). Furthermore, the S_{Ti} estimations for R_M and *HG* are 0.810 (CI: [0.741, 0.882]) and 0.300 (CI: [0.243, 0.357]), respectively, which lead to large ($S_{Ti} - S_i$) for the two factors, *i.e.*, 0.274 (=0.810 − 0.536) and 0.205 (=0.300 − 0.095), respectively. Therefore, R_M and *HG* are interacted in the surface water risk evaluation. The S_{Ti} estimations converge at about 15,000 model runs (Fig. 2d).

In correlated-factor setting the correlation structure among the factors imposes little effect on S_i in that the sensitive factors (R_M and $RATE_{AI}$) are not or little correlated with the other factors. The S_i for R_M and $RATE_{AI}$ are 0.607 and 0.090, respectively, which are very similar to the S_i estimations in noncorrelated-factor setting (IM: 0.605 and 0.090). The S_i estimations converge at fewer than 5000 model runs (Fig. 3d). A part of the factors are correlated, such as the pair of DT_{SO} and DT_W ($\rho = 0.36$), and the pair of LEC_A and $NOEC_A$ ($\rho = 0.95$), but they have little influence on S_i as they are insensitive factors.

3.5. Implication for pesticide regulation

The sensitivity analysis results suggest that the sensitive factors (*i.e.*, properties) of a pesticide should be measured under a set of typical conditions in pesticide regulation, in particular for pesticide registration and evaluation. The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) in the United States and the regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) in the European Union both require pesticide manufacturers to submit essential pesticide properties for registration or reregistration. Considering pesticide properties may vary widely under different conditions, *e.g.*, the sorption constant (K_{OC}) affected by soil properties (Weber et al., 2004), the sensitive factors regarding pesticide risk should be measured under all typical conditions in a region, such as the pesticide-fate-oriented scenarios identified for Europe (Blenkinsop et al., 2008; Centofanti et al., 2008). Consequently, the uncertainty of input factors would be narrowed, and hence the overall uncertainty existing in pesticide risk evaluation would be reduced, resulting in more confident decisions in pesticide regulation.

4. Conclusions

This sensitivity analysis identifies the sensitive factors in PURE, with associated interaction or correlation effects. Firstly, the air risk evaluation is an additive process. R_A is sensitive to *RATE*, *EP*, and *AMAF*. The negative correlation between *RATE* and *EP* induces counteractive effects against each other. Secondly, the soil risk evaluation is also an additive process. R_S is sensitive to $RATE_{AI}$, $NOEC_W$, LC_W, and *AM*. The positive correlation between $NOEC_W$ and LC_W largely increases the importance of LC_W. Thirdly, the groundwater risk evaluation is a nonadditive process. R_G is sensitive to K_{OC}, DT_{SA}, K_H, and *ADI*, while K_{OC} and DT_{SA} have high interaction effects on R_G. The correlations among the four factors make K_H and *ADI* (both are insensitive in noncorrelated-factor setting) sensitive. Finally, the surface water risk evaluation is a nonadditive process as well. R_W is sensitive to R_M and *HG*, while the two factors have high interaction effects on R_W. As most of these sensitive factors are also considered sensitive or important in other sensitivity analysis or monitoring studies, the above findings enhance the understanding of PURE and improve the confidence in the risk scores.

In noncorrelated-factor setting the S_i estimations by the Sobol' and the IM methods are very similar but with different convergence performances. The IM method generally has shorter burn-in periods while the Sobol' method tends to give more precise estimations after burn-in periods, where the sampling strategies play an important role. The IM method uses the permutated-column sampling with pseudo-random numbers, while the Sobol' method implements the substituted-column sampling with quasi-random sequences (Morris et al., 2008).

That the Sobol' and the IM methods give very similar S_i estimations provides the common ground for combining the two methods to address both interaction and correlation effects, *i.e.*, calculating S_i and S_{Ti} by the Sobol' method in noncorrelated-factor setting and calculating S_i by the IM method in both noncorrelated-factor and correlated-factor settings. In this study, the S_i estimations in correlated-factor setting are relatively different from the ones in noncorrelated-factor setting, which again demonstrates that it is cautious to assume all factors are independent in sensitivity analysis. In summary, the combined approach, utilizing the strengths of the Sobol' and IM methods but unable to investigate interaction effects in correlated-factor setting, provides an easy-to-implement alternative to metamodelling techniques (*e.g.*, Ratto et al., 2007) for investigating both the interaction and correlation effects.

Acknowledgement

The authors would like to thank Dr. Mike Grieneisen and Dr. Yuzhou Luo for reviewing this manuscript and also highly appreciated the constructive comments of the anonymous reviewers.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envsoft.2013.08.005.

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