



# Spatial variability versus parameter uncertainty in freshwater fate and exposure factors of chemicals



Carl O.P. Nijhof, Mark A.J. Huijbregts, Laura Golsteijn, Rosalie van Zelm\*

Department of Environmental Science, Institute for Water and Wetland Research, Radboud University Nijmegen, P.O. Box 9010, 6500, GL, Nijmegen, The Netherlands

## HIGHLIGHTS

- We compared parameter uncertainty and spatial variability in freshwater fate and exposure factors.
- Depending on partitioning behaviour, either variability or uncertainty dominates.
- Variability and uncertainty factors were up to 2 and 3 orders of magnitude, respectively.
- Both spatial variability and parameter uncertainty should be accounted for in freshwater fate factors.

## ARTICLE INFO

### Article history:

Received 12 March 2015  
 Received in revised form  
 11 January 2016  
 Accepted 19 January 2016  
 Available online 6 February 2016

Handling Editor: I. Cousins

### Keywords:

Statistical uncertainty  
 European regions  
 Landscape parameters  
 Multimedia fate modelling  
 Environmental partitioning

## ABSTRACT

We compared the influence of spatial variability in environmental characteristics and the uncertainty in measured substance properties of seven chemicals on freshwater fate factors (FFs), representing the residence time in the freshwater environment, and on exposure factors (XFs), representing the dissolved fraction of a chemical. The influence of spatial variability was quantified using the SimpleBox model in which Europe was divided in  $100 \times 100$  km regions, nested in a regional ( $300 \times 300$  km) and supra-regional ( $500 \times 500$  km) scale. Uncertainty in substance properties was quantified by means of probabilistic modelling. Spatial variability and parameter uncertainty were expressed by the ratio  $k$  of the 95%ile and 5%ile of the FF and XF. Our analysis shows that spatial variability ranges in FFs of persistent chemicals that partition predominantly into one environmental compartment was up to 2 orders of magnitude larger compared to uncertainty. For the other (less persistent) chemicals, uncertainty in the FF was up to 1 order of magnitude larger than spatial variability. Variability and uncertainty in freshwater XFs of the seven chemicals was negligible ( $k < 1.5$ ). We found that, depending on the chemical and emission scenario, accounting for region-specific environmental characteristics in multimedia fate modelling, as well as accounting for parameter uncertainty, can have a significant influence on freshwater fate factor predictions. Therefore, we conclude that it is important that fate factors should not only account for parameter uncertainty, but for spatial variability as well, as this further increases the reliability of ecotoxicological impacts in LCA.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Life Cycle Assessment (LCA) focuses on the assessment of impacts of products and services on human health and environment. The impact of a product or service for the impact categories of interest, e.g. ecotoxicity, is determined in the Impact Assessment (LCIA) phase, and quantified with Characterisation factors (CF) of

individual chemicals. Characterisation factors for ecotoxicity express the magnitude of the impact of a unit mass released and depend, besides on the toxicity, on the environmental fate and exposure of a chemical. Fate and exposure is quantified with fate factors (FF [days]), which represents the compartment-specific residence time of the chemical in the environment, and exposure factors (XF [-]), which is depended on the dissolved fraction of the chemical (Huijbregts et al., 2000a; Pennington et al., 2004; Rosenbaum et al., 2008). The assessment of a chemical's fate and exposure can be done with multimedia fate models (Den Hollander et al., 2004; Pennington et al., 2005; Rosenbaum et al., 2008; Van

\* Corresponding author.

E-mail address: [r.vanzelm@science.ru.nl](mailto:r.vanzelm@science.ru.nl) (R. van Zelm).

Zelm et al., 2009). These models require information on landscape parameters, such as the fraction of organic carbon in soil, as well as physicochemical properties, such as the degradation rate of a chemical in water.

Fate and exposure predictions are subject to spatial variability, i.e. randomness of nature (Walker et al., 2003). Whereas uncertainty can be reduced with additional measurements, variability is inherent in the environment and cannot be reduced by additional research. Hollander et al. (2009) showed that variation in substances' environmental fate mainly depends on chemical properties (partition coefficients and degradation rates) and less on spatial variability.

Hertwich et al. (1999) investigated the influence of parameter uncertainty and spatial variability on potential human dose calculations for multiple chemicals, but this was never done for the environmental fate and exposure of chemicals in an LCA context. Several environmental fate analyses focused on either parameter uncertainty (e.g. Huijbregts et al., 2000b; Luo and Yang, 2007; MacLeod et al., 2002; Van Zelm et al., 2010) or spatial variability (e.g. Ciuffo and Sala, 2013; Hauck et al., 2010; Hauschild et al., 2006; Hollander et al., 2012; Manneh et al., 2010; Oldenkamp et al., 2014; Sleeswijk, 2011; Wania, 1996). The goal of this study was to compare the influence of spatial variability and parameter uncertainty on freshwater fate and exposure predictions. The freshwater fate and exposure of 2,4-dichlorophenol (2,4-DCP), aniline, dichlorodiphenyltrichloroethane (DDT), glyphosate, heptachlor, propiconazole and trichloroethylene were modelled with the nested multimedia fate model Simplebox (Den Hollander et al., 2004; Hollander et al., 2007). These chemicals were selected according to their physical–chemical equilibrium partitioning in air, water, and soil, so that every partitioning region as described by Gouin et al. (2000) was represented. The influence of spatial variability in environmental characteristics was addressed with a scenario analysis of Europe divided into regional grids. The influence of uncertainty in physicochemical properties was quantified by means of probabilistic modelling.

## 2. Materials and methods

### 2.1. Fate and exposure factor

Freshwater fate factors (FFs) were predicted with the nested multimedia model SimpleBox (version 3.31) (Den Hollander et al., 2004; Hollander et al., 2007). SimpleBox is an environmental multimedia model, which can be used to simulate a chemical's emission to one of the homogenous environmental compartments. Through a set of linear equations, the model subsequently determines the chemical's environmental fate throughout all the compartments, based on its physicochemical properties and the environmental parameters. The model thereby accounts for inter-compartmental chemical transfer and degradation. SimpleBox forms the basis of the European Union System for the Evaluation of Substances (EUSES) as a regional distribution model (Vermeire et al., 1997) as well as the USEtox consensus model (Rosenbaum et al., 2008), and was shown to predict in line with comparable multimedia fate models (see e.g. Hollander et al., 2007; Kounina et al., 2014; Rosenbaum et al., 2008). SimpleBox 3.31 includes default values for the enthalpy of phase change. Since chemical partitioning properties are temperature dependent, the enthalpy of vaporization was changed from the default value to a temperature and vapour pressure dependent regression following MacLeod et al. (2007).

Here, the FF was calculated by the sum of the chemical steady state mass in the freshwater compartment on the local, regional

and supra-regional scale per unit of emission:

$$FF_{x,w,i} = \frac{(\Delta C_{i \rightarrow i} \times V_l) + (\Delta C_{i \rightarrow r} \times V_r) + (\Delta C_{i \rightarrow sr} \times V_{sr})}{\Delta M_w} \quad (1)$$

Where  $V_l$ ,  $V_r$  and  $V_{sr}$  are the volumes of the receiving compartment on the local (grid  $i$ ), regional and supra-regional scale respectively;  $\Delta C_{i \rightarrow i}$ ,  $\Delta C_{i \rightarrow r}$  and  $\Delta C_{i \rightarrow sr}$  are the steady-state total concentration changes in the receiving compartment on each scale, as a result of the change in emission  $M$  to compartment  $w$  in local grid  $i$ ;  $FF_{x,w,i}$  is the grid-specific fate factor [day] for substance  $x$  emitted to compartment  $w$ .

The exposure factor (XF) represents the average dissolved fraction in the freshwater compartment on the local, regional, and supra-regional scale.

$$XF_{x,i} = \frac{(\Delta C_{d,i \rightarrow i} \times V_l) + (\Delta C_{d,i \rightarrow r} \times V_r) + (\Delta C_{d,i \rightarrow sr} \times V_{sr})}{(\Delta C_{i \rightarrow i} \times V_l) + (\Delta C_{i \rightarrow r} \times V_r) + (\Delta C_{i \rightarrow sr} \times V_{sr})} \quad (2)$$

Where  $\Delta C_{d,i \rightarrow i}$ ,  $\Delta C_{d,i \rightarrow r}$  and  $\Delta C_{d,i \rightarrow sr}$  are the steady-state concentration changes of the dissolved fractions of the substance in freshwater on each scale.

### 2.2. Spatial variability

To quantify spatial variability in fate and exposure factors, the SimpleBox model was modified following Hauck et al. (2010) and Hollander et al. (2012). Europe was divided into  $100 \times 100$  km grids (local scale), each with its own environmental characteristics. This model was then nested into a regional scale ( $300 \times 300$  km), a supra-regional scale ( $500 \times 500$  km) and the continental scale. We used this spatially adapted SimpleBox model to simulate the freshwater fate and exposure of an emission to air, freshwater, and agricultural soil on a local scale. The resulting range of the FFs and XFs per emission compartment over all grids was presented as the ratio between its 95%ile and 5%ile, here named variability factor  $k_{var}$

$$k_{var,x} = \frac{95\%ile \text{ of the grid - specific FFs or XFs}}{5\%ile \text{ of the grid - specific FFs or XFs}} \quad (3)$$

### 2.3. Parameter uncertainty

To account for the uncertainty in the FFs and XFs, Monte Carlo simulations were performed applying Latin Hypercube sampling by using the spreadsheet-based application Crystal Ball (Oracle®, Release 11.1.2.0.00) in MS Excel 2010 with 10,000 iterations per run. Results were presented as the ratios of the 95%ile and 5%ile of the uncertainty ranges, the latter referred to as the uncertainty factor  $k_{unc,i,x}$ .

$$k_{unc,i,x} = \frac{95\%ile \text{ of the FF or XF uncertainty per grid}}{5\%ile \text{ of the FF or XF uncertainty per grid}} \quad (4)$$

### 2.4. Sensitivity analysis

A sensitivity analysis was conducted to determine which chemical-specific input parameters contribute the most to the uncertainty in FFs and XFs and which environmental parameters contribute the most to the variability in FFs and XFs respectively. The sensitivity analysis was performed by using the Spearman's

rank correlation method (Zar, 2005). The Spearman's rank correlation method was used as it is robust and treats sensitivity over the complete range of values. The Spearman rank correlation coefficients for uncertainty were calculated during the Monte Carlo analysis with a tool in Crystal Ball (Oracle®, Release 11.1.2.0.00), while the Spearman rank correlation coefficients for variability were manually determined in a separate test in MS Excel 2010. Subsequently, these Spearman rank correlation coefficients between all uncertain and variable parameters and the FFs and XFs were individually squared and normalized to 100%. The result of this can be interpreted as a proxy of the contribution of an uncertain or variable parameter to the overall uncertainty or variability in FFs, relative to the contribution of the other parameters.

### 2.5. Data collection

Chemicals were selected according to their physical–chemical equilibrium partitioning in air, water, and soil, based on their octanol–water partitioning coefficient ( $K_{ow}$ ) and air–water partitioning coefficient ( $K_{aw}$ ), so that every partitioning region as described by Guin et al. (2000) was represented (see SI). Experimental data on chemical properties of 2,4-DCP, aniline, DDT, glyphosate, heptachlor, propiconazole and trichloroethylene were retrieved from literature (Bhatarai and Gramatica, 2011; Cassani et al., 2013; Gramatica et al., 2007; Mackay et al., 2006) and the Pesticides Properties Database (PPDB) (University of Hertfordshire, 2009). Degradation rates of propiconazole in air were not available, hence a generic QSAR model for organic compounds was used to predict the rate constants of hydroxyl radicals in air and its assigned uncertainty distribution for the multimedia fate modelling (Roy et al., 2011). Following Slob (1994) and Rikken et al. (2003), each experimentally determined chemical property was assigned a lognormal uncertainty distribution. Log-normally distributed variables have been reported in many scientific fields (Gaddum, 1945; Slob, 1994). Some advantages of the lognormal distribution are that it avoids negative numbers, captures a large value range, and the uncertainty in many processes and parameters follows a skewed distribution (Slob, 1994). The physicochemical properties and uncertainty ranges are shown in Table S1 of the Supporting Information.

## 3. Results

### 3.1. Spatial variability and parameter uncertainty

Fig. 1 shows the variability factors over the grids and the minimum and maximum uncertainty factors of the chemicals' freshwater FFs and XFs for each emission scenario. More detailed results can also be found in the supporting information (Figures S2 and S3, and Table S3). The spatial variability in FFs of all chemicals, except DDT, were generally in the same order of magnitude. For these chemicals, emission to air and soil resulted in a variability factor between 9.5 and  $9.5 \cdot 10^1$ , whereas emission to water led to lower variability factors between 3.1 and 6.2. DDT had a variability factor which was 1 order of magnitude larger than average, regardless of the emission compartment.

For emission to air, trichloroethylene showed the largest uncertainty factor (from  $4.6 \cdot 10^1$  to  $5.8 \cdot 10^3$ ). Aniline and propiconazole had the most uncertain FFs after emission to water, with uncertainty factors from  $3.9 \cdot 10^1$  to  $2.1 \cdot 10^2$  and from  $1.4 \cdot 10^1$  to  $1.5 \cdot 10^2$ , respectively. Furthermore, uncertainty in FF for emission to soil proved largest for aniline ( $2.7 \cdot 10^2$  to  $1.7 \cdot 10^3$ ), followed by 2,4-DCP ( $8.7 \cdot 10^1$  to  $8.2 \cdot 10^2$ ) and propiconazole ( $3.6 \cdot 10^1$  to  $5.3 \cdot 10^2$ ). DDT displayed the largest differences between minimum and maximum uncertainty factors (more than 1 order of magnitude).

This was also the case for trichloroethylene after emission to air and soil, and glyphosate after emission to air.

As shown in Fig. 1, the spatial variability of 2,4-DCP, aniline and propiconazole was always smaller than the parameter uncertainty (up to 1 order of magnitude smaller compared to the minimum uncertainty). Interestingly, the variability of DDT and heptachlor was up to 4 times larger than the uncertainty for most grids (>75% of grids). This was the case for glyphosate after emission to air and freshwater as well. The spatial variability of DDT and heptachlor after emission to air, and of trichloroethylene after emission to water, were even up to 3 times larger than the maximum uncertainty reported for these chemicals.

The variability and uncertainty in freshwater XFs of 2,4-DCP, aniline, glyphosate, heptachlor, propiconazole, and trichloroethylene were relatively small ( $k < 1.5$ ). The only exception is DDT which had a maximum uncertainty factor of 6.3.

### 3.2. Sensitivity analysis

Table 1 shows the results of the sensitivity analysis of the uncertainty in freshwater FFs, presented as the average contribution to uncertainty of all grids. For DDT and glyphosate, the  $K_{oc}$  was the most important contributor to uncertainty in FFs (>70.0%). For 2,4-DCP, aniline and propiconazole, the water degradation showed the highest contribution (>45.0%). For trichloroethylene, parameters that contributed most was the degradation rate in the respective emission compartment (>90.0%). The water solubility of heptachlor displayed the highest contribution after emission to air (70.6%). All other chemical properties contributed <10% to the uncertainty in FF predictions for each chemical. Sensitivity results of XFs can be found in the supporting information (Table S4). Uncertainty in the XFs was fully driven by uncertainty in the  $K_{oc}$ .

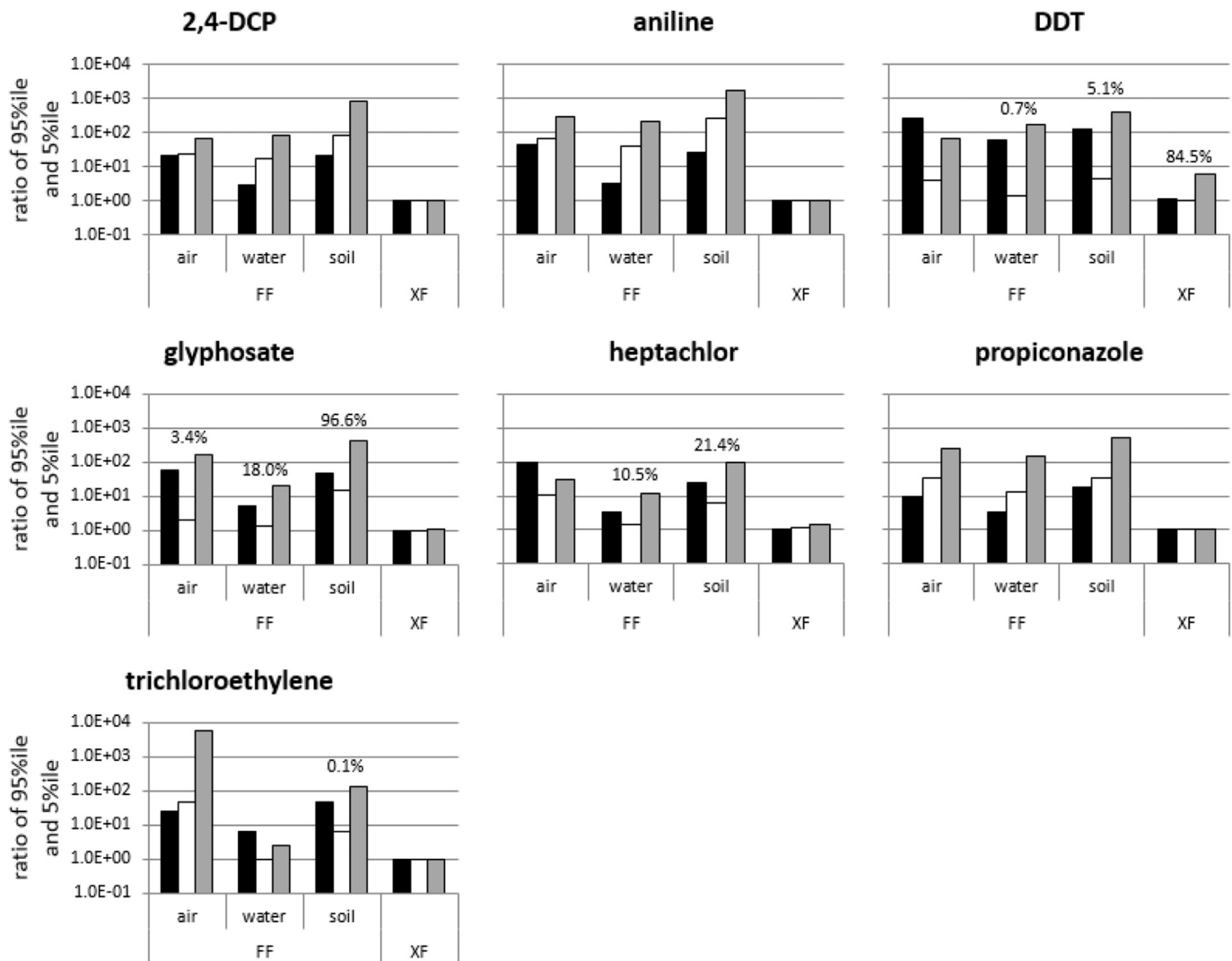
Contributions of environmental parameters to variability in FFs are shown in Supporting Information Table S5–S11. Contributions to variability were always lower than 20.0%. For emissions to air, the fractions of water contributed the most for all chemicals (3.7–8.8%). For emissions to water, the temperature was the most important contributor to variability in FFs for all chemicals (3.3–12.1%), except DDT. In the case of DDT, the fractions of water contributed the most to the variability, regardless of emission compartment (4.2–8.8%). Soil run-off and the fractions of soil showed the highest contribution after emissions to soil (3.8–12.2%), except for trichloroethylene. For trichloroethylene this was the annual rain rate (3.2–15.7%).

## 4. Discussion

In the present study, we compared the influence of spatial variability and parameter uncertainty on the FF and XF predictions for 2,4-DCP, aniline, DDT, glyphosate, heptachlor, propiconazole and trichloroethylene in Europe. Here, we discuss our results and describe the practical implications of our findings.

### 4.1. Spatial variability

Up to now, the environmental fate of a substance in LCA is modelled by using generic multimedia models (e.g. Rosenbaum et al., 2008). Such models determine environmental concentrations with “average” local or regional landscape parameters for a large area, e.g. Europe. The results are a generic FF and XF that does not account for spatial differences of landscape characteristics between regions within that area. In the present study, freshwater fate and exposure factors were modelled with a spatially adapted SimpleBox model, simulating the spatial variability of environmental characteristics within Europe.



**Fig. 1.** Variability factors  $k_{var}$  (black bars) and min and max uncertainty factors  $k_{unc,i}$  (white and grey bars, resp.) in freshwater fate factors (FF [days]) and exposure factors (XF [-]) of 2,4-DCP, aniline, DDT, glyphosate, heptachlor, propiconazole and trichloroethylene emitted to air, water and soil. In cases where  $\min k_{unc,i} < k_{var} < \max k_{unc,j}$ , percentages indicate the fraction of grids for which the uncertainty range  $k_{unc,i}$  was larger than the variability range  $k_{var}$ .

Spatial variability ranges of FFs were the lowest in the case of emissions directly to water. In this case, the environmental concentrations are less influenced by intermedia transfer. Emissions to air and soil led to FFs that can vary more than two orders of magnitude between grids. Helmes et al. (2012) derived spatially explicit fate factors of phosphorus emissions on a global scale, and found a similar spatial variability of more than two orders of magnitude between grids. Here, DDT, glyphosate and trichloroethylene showed the largest variation in FFs for the different emission scenarios. DDT (high  $K_{oc}$ ), glyphosate (low  $K_{oc}$ ) and trichloroethylene (high  $K_{aw}$ ) exhibit properties with relatively high affinity to the soil, water and air compartment, respectively. Hence, they are most affected by the differences in air height, and fractions of water and soil between each emitting grid, resulting in relatively larger variability ranges (Pennington et al., 2005). For emissions to water and soil, the spatial variability clearly increased with lower water degradation rates, indicating that this chemical property has a relative large influence on the spatial variability of FFs.

Furthermore, the XFs in water hardly varied as a result of spatial variability between emitting grids. In freshwater, the dissolved concentration of the chemicals that were selected for this study is

nearly equal to the total concentration in the compartment, meaning that the dissolved fraction is almost invariable and close to 1.0. Chemicals with higher  $K_{oc}$ , i.e.  $> 10^7$  (and thus with XFs lower than 1.0) were not selected for this study. This implies that the importance of spatial variability on the XF of the current chemicals is not representative for chemicals with high  $K_{oc}$ . For these high- $K_{oc}$  chemicals, the spatial variability in suspended particle concentration will result in a larger variability of the XF compared to low- $K_{oc}$  chemicals.

#### 4.2. Parameter uncertainty

The parameter uncertainty in freshwater FFs and XFs was investigated via probabilistic modelling by means of Monte Carlo simulations. For all seven chemicals, the  $K_{oc}$  and the degradation rates contributed most to the uncertainty. This can be explained by the fact that these properties are the most important determinants of chemical transfer and removal (Meyer et al., 2005; Rosenbaum et al., 2008).

Similar to variability, uncertainty was smallest in the case of freshwater emissions. Huijbregts et al. (2000b) demonstrated that a

**Table 1**

The relative contribution to uncertainty (%) in FFs of the chemical properties of 2,4-DCP, aniline, DDT, glyphosate, heptachlor, propiconazole and trichloroethylene emitted to air, freshwater and soil, as average over all grids. The largest contributors (>10%) in each scenario are presented in bold. Contributions of the  $K_{ow}$  and  $K_{deg, sed}$  were negligible (<4%), and therefore not shown.

Partitioning region	Chemical	Emission compartment	Vapour pressure	Water solubility	Soil organic carbon–water partitioning coefficient	Air degradation	Water degradation	Soil degradation
			Pvap25	Sol25	$K_{oc}$	$k_{deg, air}$	$k_{deg, water}$	$k_{deg, soil}$
Air, water & soil	2,4-DCP	Air	<0.05	<0.05	1.4	1.3	<b>96.2</b>	0.9
		Water	<0.05	0.1	<0.05	<0.05	<b>99.9</b>	<0.05
		Soil	<0.05	0.1	<b>28.6</b>	0.1	<b>45.8</b>	<b>25.5</b>
Air & water	Aniline	Air	<0.05	0.1	0.6	<b>11.4</b>	<b>87.4</b>	0.5
		Water	<0.05	<0.05	<0.05	<0.05	<b>99.9</b>	<0.05
		Soil	<0.05	0.1	<b>27.4</b>	<0.05	<b>52.9</b>	<b>19.6</b>
Soil	DDT	Air	4.7	0.5	<b>92.2</b>	0.3	<0.05	2.3
		Water	1.5	1.0	<b>97.5</b>	<0.05	<0.05	<0.05
		Soil	0.1	<0.05	<b>96.7</b>	0.1	<0.05	3.1
Water	Glyphosate	Air	3.2	<0.05	<b>73.2</b>	<b>12.5</b>	2.5	8.5
		Water	<0.05	<0.05	<b>87.1</b>	<0.05	<b>12.6</b>	<0.05
		Soil	<0.05	<0.05	<b>71.8</b>	<0.05	0.3	<b>27.8</b>
Air & soil	Heptachlor	Air	3.2	<b>70.6</b>	4.1	<b>17.7</b>	4.2	0.2
		Water	<0.05	1.0	<b>26.2</b>	<0.05	<b>68.4</b>	<0.05
		Soil	0.3	7.7	<b>55.3</b>	0.3	3.7	<b>32.6</b>
Water & soil	Propiconazole	Air	<0.05	0.1	3.4	0.1 <sup>a</sup>	<b>78.3</b>	<b>18.1</b>
		Water	<0.05	<0.05	0.1	<0.05	<b>99.8</b>	<0.05
		Soil	<0.05	<0.05	5.6	<0.05	<b>68.7</b>	<b>25.6</b>
Air	Trichloroethylene	Air	0.8	0.9	<0.05	<b>97.7</b>	0.4	<0.05
		Water	0.1	0.3	2.7	0.1	<b>96.7</b>	<0.05
		Soil	0.7	1.4	<0.05	<0.05	1.3	<b>91.1</b>

<sup>a</sup> For propiconazole, the degradation in air was determined with a triazole-specific QSAR model for the prediction of the hydroxyl reaction in air (see Table S2).

larger contribution of transport mechanisms in the multimedia fate modelling generally leads to larger uncertainty estimates, as a result of uncertainty in parameters involved in describing these mechanisms. Water degradation rates of aniline and propiconazole were more uncertain compared to the other five chemicals included and therefore showed the most uncertain FFs for emissions to water.

For emissions to air, aniline and propiconazole were also among the chemicals with most uncertain FFs, mainly as a result of the large uncertainty in their water degradation rates. However, grid-specific FFs of trichloroethylene were even more uncertain due to the large uncertainty in air degradation rate. The largest uncertainty ranges after emissions to soil were found for aniline, propiconazole, and 2,4-DCP, due to large uncertainties in their  $K_{oc}$ , and water and soil degradation predictions.

The uncertainty ranges of freshwater XFs of 2,4-DCP, aniline, glyphosate, propiconazole, and trichloroethylene were negligible (close to 1.0), meaning that the dissolved fractions of these chemicals are not influenced by the uncertainty in their physico-chemical properties. Although negligible, these uncertainties were fully driven by the  $K_{oc}$ , as it is the determining factor in a chemical's partitioning between water and soil. DDT showed some difference in the uncertainty factor between grids, as a result of its relatively high  $K_{oc}$ .

#### 4.3. Variability versus uncertainty

The magnitude of spatial variability and parameter uncertainty depends on the chemical, emission compartment and emitting grid. In the present study, variability was always up to 1 order of magnitude lower than uncertainty for chemicals that partition between water and one or more other environmental compartment(s), rather than partition predominantly into one compartment. For the selection of chemicals studied here, these are 2,4-DCP, aniline and propiconazole. Freshwater FFs of chemicals that tend to dominantly persist in one compartment are more spatially variable than uncertain for the majority of emitting grids. Our

results showed this for DDT, glyphosate (excl. soil emissions) and trichloroethylene (excl. air emissions), which had up to 2 orders of magnitude larger variability ranges in comparison to uncertainty ranges. FFs of heptachlor were also more variable than uncertain for most grids, because its uncertainty ranges were (among) the smallest compared to the other chemicals, regardless of emission compartment.

According to the recommendations of the International Reference Life Cycle Data System (ILCD), spatial variability is presumably of less influence than parameter uncertainty in the calculation of characterization factors for ecotoxicity compared to other impact categories like water use, acidification and particulate matter formation (EC-JRC, 2011). But it is also mentioned that limited research was done in this area. We found that for aquatic fate and exposure modelling, accounting for spatial variability in landscape parameters, as well as accounting for parameter uncertainty, can have a significant influence on model predictions, particularly for environmentally persistent chemicals. Hence, the accuracy of ecotoxicological impact assessments in LCA can improve when the impacts are determined in a spatially explicit way, e.g. by using region-specific characterization factors, instead of the more commonly applied generic approach. When addressing impacts of new chemicals in LCA, efforts should be made to estimate  $K_{oc}$  and degradation rates as well as possible, since these parameters cause most uncertainty in FF estimations. Alternatively, a sensitivity analysis can be performed by estimating FFs for high and low  $K_{oc}$  and degradation rates to show the robustness of FFs. Accounting for spatial variability or parameter uncertainty is of less importance for freshwater XFs of organic chemicals, since (differences between) variability and uncertainty in XFs of most chemicals were close to 1.0.

#### 4.4. Limitations

Besides parameter uncertainty and spatial variability, other sources of uncertainty and variability have not been assessed in the present study. Several authors, e.g. Geisler et al. (2005) and Sala

et al. (2011), pointed out that temporal variability (e.g. seasonal variation in chemical use, temperature or wind speed) and model uncertainty (e.g. the assumption of homogeneity of compartments within fate models), can also introduce uncertainty in fate and exposure model outcomes. Furthermore, we did not account for the ionized fractions of organic acids and bases. According to data from Van Zelm et al. (2013), accounting for the ionization of e.g. aniline and 2,4-dichlorophenol can change freshwater fate factors from 0.1 for emissions to freshwater up to 2 order of magnitude for emissions to soil. Also, Van Zelm et al. (2010) showed for 15 pesticides and perchloroethylene, that excluding transformation products can lead to an underestimation of the overall persistency and parameter uncertainty of these chemicals. For propiconazole, for example, multiple metabolites have been identified (University of Hertfordshire, 2009). We also did not account for environmental variability in the nature of the microbial community, which may lead to an underestimation of the degradation rate constants of the chemicals.

## 5. Conclusion

Up to now, the relative importance of spatial variability versus parameter uncertainty in fate and exposure factors has not been systematically investigated. We found that accounting for region-specific environmental characteristics in multimedia fate modeling can have a significant influence on freshwater fate factor predictions. This particularly holds for chemicals that partition predominantly into one environmental compartment. Spatial specification of emissions of chemicals is thus important to further increase the reliability of ecotoxicological impacts in LCA. Therefore, we recommend that the influence of spatial variation in environmental parameters and uncertainty in chemical properties should be jointly accounted for in the deviation of fate and exposure factors.

## Acknowledgements

We thank Rik Oldenkamp for his help with combining Monte Carlo simulations and our spatially adapted model and for his useful comments on our model setup. This research was partly funded by the European Commission under the Industry-Academia Partnerships and Pathways; IAPP 2011: TOX-TRAIN – The implementation of a toxicity assessment tool for practical evaluation of life-cycle impacts of technologies, grant agreement number 285286.

## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2016.01.079>.

## References

- Bhatarai, B., Gramatica, P., 2011. Modelling physico-chemical properties of (benzo) triazoles, and screening for environmental partitioning. *Water Res.* 45, 1463–1471.
- Cassani, S., Kovarich, S., Papa, E., Roy, P.P., Van der Wal, L., Gramatica, P., 2013. Daphnia and fish toxicity of (benzo)triazoles: validated QSAR models, and interspecies quantitative activity-activity modelling. *J. Hazard. Mater.* 258, 50–60.
- Ciuffo, B., Sala, S., 2013. Climate-based archetypes for the environmental fate assessment of chemicals. *J. Environ. Manag.* 129, 435–443.
- Den Hollander, H., van Eijkeren, J., van de Meent, D., 2004. Multimedia Mass Balance Model for Evaluating the Fate of Chemicals in the Environment. Report 601200003. National Institute for Public Health and the Environment (RIVM), Bilthoven, The Netherlands.
- EC-JRC., 2011. ILCD Handbook. Recommendations for Life Cycle Assessment in European Context - Based on Existing Environmental Impact Assessment Models and Factors. EC-JRC, Ispra, Italy.
- Gaddum, J., 1945. Lognormal distributions. *Nature* 156, 463–466.
- Geisler, G., Hellweg, S., Hungerbühler, K., 2005. Uncertainty analysis in life cycle assessment (LCA): case study on plant-protection products and implications for decision making. *Int. J. Life Cycle Assess.* 10, 184–192.
- Gouin, T., Mackay, D., Webster, E., Wania, F., 2000. Screening chemicals for persistence in the environment. *Environ. Sci. Technol.* 34, 881–884.
- Gramatica, P., Giani, E., Papa, E., 2007. Statistical external validation and consensus modeling: a QSPR case study for K-oc prediction. *J. Mol. Graph. Model.* 25, 755–766.
- Hauck, M., Huijbregts, M.A.J., Hollander, A., Hendriks, A.J., van de Meent, D., 2010. Modeled and monitored variation in space and time of PCB-153 concentrations in air, sediment, soil and aquatic biota on a European scale. *Sci. Total Environ.* 408, 3831–3839.
- Hauschild, M.Z., Potting, J., Hertel, O., Schopp, W., Bastrup-Birk, A., 2006. Spatial differentiation in the characterisation of photochemical ozone formation - the EDIP2003 methodology. *Int. J. Life Cycle Assess.* 11, 72–80.
- Helmes, R.J., Huijbregts, M.A., Henderson, A.D., Jolliet, O., 2012. Spatially explicit fate factors of phosphorous emissions to freshwater at the global scale. *Int. J. Life Cycle Assess.* 17, 646–654.
- Hertwich, E.G., McKone, T.E., Pease, W.S., 1999. Parameter uncertainty and variability in evaluative fate and exposure models. *Risk Anal.* 19, 1193–1204.
- Hollander, A., Hauck, M., Cousins, I.T., Huijbregts, M.A.J., Pistocchi, A., Ragas, A.M.J., van de Meent, D., 2012. Assessing the relative importance of spatial variability in emissions versus landscape properties in fate models for environmental exposure assessment of chemicals. *Environ. Model. Assess.* 17, 577–587.
- Hollander, A., Pistocchi, A., Huijbregts, M.A.J., Ragas, A.M.J., De Meent, D.V., 2009. Substance or space? the relative importance of substance properties and environmental characteristics in modeling the fate of chemicals in Europe. *Environ. Toxicol. Chem.* 28, 44–51.
- Hollander, A., Sauter, F., den Hollander, H., Huijbregts, M., Ragas, A., van de Meent, D., 2007. Spatial variance in multimedia mass balance models: comparison of LOTOS-EUROS and SimpleBox for PCB-153. *Chemosphere* 68, 1318–1326.
- Huijbregts, M.A.J., Thissen, U., Guinee, J.B., Jager, T., Kalf, D., van de Meent, D., Ragas, A.M.J., Sleeswijk, A.W., Reijnders, L., 2000a. Priority assessment of toxic substances in life cycle assessment. Part I: calculation of toxicity potentials for 181 substances with the nested multi-media fate, exposure and effects model USES-LCA. *Chemosphere* 41, 541–573.
- Huijbregts, M.A.J., Thissen, U., Jager, T., van de Meent, D., Ragas, A.M.J., 2000b. Priority assessment of toxic substances in life cycle assessment. Part II: assessing parameter uncertainty and human variability in the calculation of toxicity potentials. *Chemosphere* 41, 575–588.
- Kounina, A., Margni, M., Shaked, S., Bulle, C., Jolliet, O., 2014. Spatial analysis of toxic emissions in LCA: a sub-continental nested USEtox model with freshwater archetypes. *Environ. Int.* 69, 67–89.
- Luo, Y.Z., Yang, X.S., 2007. A multimedia environmental model of chemical distribution: fate, transport, and uncertainty analysis. *Chemosphere* 66, 1396–1407.
- Mackay, D., Shiu, W.-Y., Ma, K.-C., Lee, S.C., 2006. Handbook of Physical-chemical Properties and Environmental Fate for Organic Chemicals: Fungicides. CRC Press Inc., Boca Raton.
- MacLeod, M., Fraser, A.J., Mackay, D., 2002. Evaluating and expressing the propagation of uncertainty in chemical fate and bioaccumulation models. *Environ. Toxicol. Chem.* 21, 700–709.
- MacLeod, M., Scheringer, M., Hungerbühler, K., 2007. Estimating enthalpy of vaporization from vapor pressure using Trouton's rule. *Environ. Sci. Technol.* 41, 2827–2832.
- Manneh, R., Margni, M., Deschenes, L., 2010. Spatial variability of intake fractions for canadian emission scenarios: a comparison between three resolution scales. *Environ. Sci. Technol.* 44, 4217–4224.
- Meyer, T., Wania, F., Breivik, K., 2005. Illustrating sensitivity and uncertainty in environmental fate models using partitioning maps. *Environ. Sci. Technol.* 39, 3186–3196.
- Oldenkamp, R., Huijbregts, M.A., Hollander, A., Ragas, A.M., 2014. Environmental impact assessment of pharmaceutical prescriptions: does location matter? *Chemosphere* 115, 88–94.
- Pennington, D.W., Margni, M., Ammann, C., Jolliet, O., 2005. Multimedia fate and human intake modeling: spatial versus nonspatial insights for chemical emissions in Western Europe. *Environ. Sci. Technol.* 39, 1119–1128.
- Pennington, D.W., Payet, J., Hauschild, M., 2004. Aquatic ecotoxicological indicators in life-cycle assessment. *Environ. Toxicol. Chem.* 23, 1796–1807.
- Rikken, M., Van Wijnen, H., Linders, J., Jager, D., 2003. Uncertainty Analysis of USES 3.0. Improving Risk Management Through Probabilistic Risk Assessment of Agricultural Pesticides. Report 601450011. National Institute for Public Health and the Environment (RIVM), Bilthoven, The Netherlands.
- Rosenbaum, R.K., Bachmann, T.M., Gold, L.S., Huijbregts, M.A.J., Jolliet, O., Juraske, R., Koehler, A., Larsen, H.F., MacLeod, M., Margni, M., McKone, T.E., Payet, J., Schuhmacher, M., van de Meent, D., Hauschild, M.Z., 2008. USEtox—the UNEP-SETAC toxicity model: recommended characterisation factors for human toxicity and freshwater ecotoxicity in life cycle impact assessment. *Int. J. Life Cycle Assess.* 13, 532–546.
- Roy, P.P., Kovarich, S., Gramatica, P., 2011. QSAR model reproducibility and applicability: a case study of rate constants of hydroxyl radical reaction models applied to polybrominated diphenyl Ethers and (Benzo-)Triazoles. *J. Comput. Chem.* 32, 2386–2396.

- Sala, S., Marinov, D., Pennington, D., 2011. Spatial differentiation of chemical removal rates from air in life cycle impact assessment. *Int. J. Life Cycle Assess.* 16, 748–760.
- Sleeswijk, A.W., 2011. Regional LCA in a global perspective. A basis for spatially differentiated environmental life cycle assessment. *Int. J. Life Cycle Assess.* 16, 106–112.
- Slob, W., 1994. Uncertainty analysis in multiplicative models. *Risk Anal.* 14, 571–576.
- University of Hertfordshire, Agriculture and Environment Research Unit (AERU), 2009. Pesticide Properties Database (PPDB) 2.0. <http://sitem.herts.ac.uk/aeru/projects/ppdb/index.htm>.
- Van Zelm, R., Huijbregts, M.A.J., Van de Meent, D., 2009. USES-LCA 2.0—a global nested multi-media fate, exposure, and effects model. *Int. J. Life Cycle Assess.* 14, 282–284.
- Van Zelm, R., Huijbregts, M.A.J., van de Meent, D., 2010. Transformation products in the life cycle impact assessment of chemicals. *Environ. Sci. Technol.* 44, 1004–1009.
- Van Zelm, R., Stam, G., Huijbregts, M.A.J., Van de Meent, D., 2013. Making fate and exposure models for freshwater ecotoxicity in life cycle assessment suitable for organic acids and bases. *Chemosphere* 90, 312–317.
- Vermeire, T., Jager, D., Bussian, B., Devillers, J., Den Haan, K., Hansen, B., Lundberg, I., Niessen, H., Robertson, S., Tyle, H., 1997. European union system for the evaluation of substances (EUSES). Principles and structure. *Chemosphere* 34, 1823–1836.
- Walker, J.D., Jaworska, J., Comber, M.H.I., Schultz, T.W., Dearden, J.C., 2003. Guidelines for developing and using quantitative structure-activity relationships. *Environ. Toxicol. Chem.* 22, 1653–1665.
- Wania, F., 1996. Spatial variability in compartmental fate modelling - linking fugacity models and GIS. *Environ. Sci. Pollut. Res.* 3, 39–46.
- Zar, J.H., 2005. Spearman Rank Correlation. *Encyclopedia of Biostatistics*.