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Modeled and monitored variation in space and time of PCB-153 concentrations in air, sediment, soil and aquatic biota on a European scale

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ABSTRACT

We evaluated various modeling options for estimating concentrations of PCB-153 in the environment and in biota across Europe, using a nested multimedia fate model coupled with a bioaccumulation model. The most detailed model set up estimates concentrations in air, soil, fresh water sediment and fresh water biota with spatially explicit environmental characteristics and spatially explicit emissions to air and water in the period 1930–2005. Model performance was evaluated with the root mean square error ($RMSE_{log}$), based on the difference between estimated and measured concentrations. The $RMSE_{log}$ was 5.4 for air, 5.6–6.3 for sediment and biota, and 5.5 for soil in the most detailed model scenario. Generally, model estimations tended to underestimate observed values for all compartments, except air. The decline in observed concentrations was also slightly underestimated by the model for the period where measurements were available (1989–2002). Applying a generic model setup with averaged emissions and averaged environmental characteristics, the $RMSE_{log}$ increased to 21 for air and 49 for sediment. For soil the $RMSE_{log}$ decreased to 3.5. We found that including spatial variation in emissions was most relevant for all compartments, except soil, while including spatial variation in environmental characteristics was less influential. For improving predictions of concentrations in sediment and aquatic biota, including emissions to water was found to be relevant as well.

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1. Introduction

Persistent organic pollutants released into the environment can be transported to different regions and be accumulated in environmental compartments, including organisms. Internal concentrations in biota can be estimated from concentrations in abiotic compartments with food chain models, such as developed by Gobas et al. (1999), Thomann and Komlos (1999), Hendriks et al. (2001), and Czub and McLachlan (2004). These models use a one-compartment first order kinetic approach and predict accumulation levels in biota on the basis of mechanistic modeling of uptake and elimination kinetics. If concentrations in abiotic compartments have not been measured, they can be estimated from emissions with multimedia fate models as described by Mackay et al. (1992), McKone (1993), Wania and Mackay (1999), US-EPA (2002) and Den Hollander and Van de Meent (2004). These models use a mass-balance approach to describe transport between various environmental compartments and estimate concentrations in these compartments based on emissions, degradation and physico-chemical properties and environmental characteristics.

Internal concentrations in organisms can be linked to emissions by coupling fate and bioaccumulation models. These coupled models can improve ecological risk assessment because internal concentrations are expected to be a better indication for risk than environmental concentrations (MacLeod et al., 2001). Various authors showed that such coupled models can indeed be useful tools for screening level risk assessment (MacLeod et al., 2001; Arnot and Gobas, 2006; Arnot et al., 2006; Arnot and Mackay, 2008; Arnot et al., 2008). For evaluative purposes, these models applied standard environments and unit emissions. Mattila and Verta (2008) applied a spatially explicit coupled model with a realistic emissions scenario to the Baltic Sea. They explored the influence of adding new processes or compartments, such as sorption to Black Carbon, on estimated internal concentrations. Czub and McLachlan (2004) used realistic time trends in emissions to estimate concentrations in the environment, including fish, as input in their human intake model. No reports are known to us about how including spatial and temporal variation in emissions and spatial variation in environmental conditions affects predictions of internal concentration in a realistic emission scenario for Europe.

The aim of this paper was to investigate how including spatially explicit environmental characteristics, emissions to water, and spatial and temporal differentiation of emissions influence estimations of concentrations in air, soil, fresh water sediment and fresh water biota. PCB-153 was chosen as a model substance because of its multimedia

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and bioaccumulative behavior, and because spatially and temporally resolved emission estimates and monitoring data were available for this substance. To assess model performance, the modeled concentrations were compared to measurements. A nested box model based on SimpleBox (Den Hollander and Van de Meent, 2004) was used to estimate environmental concentrations. The local scale in SimpleBox was re-parameterized to represent specific regions in Europe on a 100×100 km grid, following Hollander et al. (2007). A generic food chain based on the model OMEGA (Hendriks et al., 2001) was coupled to the nested box model to estimate internal concentrations in freshwater biota. To compare the influence of including temporal and spatial variability in emissions and spatial variability in environmental characteristics and emissions to water, concentrations were calculated in 6 scenarios reflecting different levels of variation.

2. Materials and methods

2.1. Model concept

Concentrations in the environmental and biotic compartments were estimated from emissions using a nested multimedia modeling approach based on SimpleBox (Den Hollander and Van de Meent, 2004) in combination with the bioaccumulation model OMEGA (Hendriks et al., 2001). Calculations were performed for grid cells of 100×100 km (the 'target cell'). This scale was chosen because spatially explicit emission data were available with a corresponding resolution. For each cell, environmental parameters such as organic carbon content and temperature were set at a value taken from a dataset with realistic environmental property combinations as done earlier for fate modeling purposes (Pistocchi and Pennington, 2006; Hollander et al., 2008).

Hollander et al. (2007) showed that results of a nested box model, where values for the environmental conditions and emissions were re-parameterized consecutively for these target cells to represent different regions in Europe one by one, resemble results of a spatially explicit model for average concentrations and spatial patterns of PCB-153 in air and soil. They used a nested modeling approach with three spatial scales where the smallest scale represented a grid cell of 25×25 km. Air concentrations in grid cells with low emission were overestimated in their study, because inflow from high emissions cells in the continental average had a large influence on the small cells with low emissions (Hollander et al., 2007). Preliminary calculations showed that air concentrations in grid cells with low emission of 100×100 km also tended to be overestimated when using three spatial scales. Therefore, in our study, the nested model contained a local, regional, supra-regional, continental scale and hemispheric scale, with air, water, soil and sediment compartments.

Each of the target cells of 100×100 km was surrounded by a regional scale of 300×300 km. Additionally, the regional scale was surrounded by a supra-regional scale of 500×500 km. Europe was parameterized as the sum of all local grid cells, covering an area of about 8,000,000 km^2. The model concept is visualized in Fig. S1 in the Supporting Information. In this study, spatial variation in estimated concentrations was a result of variation in environmental characteristics and emissions, whereas temporal variation in estimated concentrations was a result of variation in emissions only.

A generic food chain consisting of fresh water mollusks and fish was added to the water compartment of the local scale. Dissolved fresh water concentrations modeled by the coupled fate model were used as input into the food chain calculations:

$$C_i = \frac{k_{w,in} \cdot C_w + k_{f,in} \cdot C_{i-1}}{\sum k_{out}} \quad (1)$$

Intake is represented as the product of external concentrations (concentration in water C_w and concentration in food C_{i-1}) with influx rate constants ($k_{w,in}$ for intake from water and $k_{f,in}$ for intake from food). Whereas fish take in substance from food and water, invertebrates only take in substances from water in the model. Internal concentrations (C_i) result from the difference between intake and elimination (k_{out}), including excretion, egestion and growth dilution.

Rate constants for influx and efflux were predicted based on species-weight following allometric relationships. Additionally, these constants were considered inversely proportional to water and lipid layer resistances and flow delays that substances encounter (Hendriks et al., 2001). Details of the food chain calculations are described in the Supporting Information.

2.2. Data

Emission data and environmental and chemical parameter values were required for our study. Environmental property combinations of the target cells were derived from a dataset on a 100×100 km grid. Details about individual parameters were discussed in Pistocchi et al. (2006). More details on the spatially explicit environmental characteristics included in the analysis are shown in Table S3 of the Supporting Information. Environmental characteristics of the regional and supra-regional scales were averages of the environmental characteristics of the grid cells of 100×100 km within them. Environmental conditions for the continental scale were averages of all local scales for reasons of simplicity.

Physico-chemical properties of PCB-153 are summarized in Table S4 of the Supporting Information. Emission estimates to air and water were derived for the years 1930–2005. Breivik et al. (2007) estimated yearly averaged global emissions of PCB-153 to air on a 1°×1° grid, generally comparable to a 100×100 km grid. They used a mass-balance approach to estimate emissions from production and consumption, including emissions during use, accidental releases and disposal of technical mixtures. Details of the methodology are given in Breivik et al. (2002a, b). To include uncertainty in emission estimates, Breivik et al. (2002a,b, 2007) developed a minimum, a default and a maximum scenario. Meijer et al. (2003) concluded that actual emissions are probably near or above the upper boundary given by Breivik et al. (2002b). Maximum and minimum ranges are similar to the values in Breivik et al. (2007) for the period considered. Therefore estimations were performed for the maximum emission scenario, in line with earlier PCB fate modeling studies (Wania and Daly, 2002; Shatalov et al., 2006). Besides the emissions to air estimated by Breivik et al. (2007), direct emissions of PCBs to water may also be relevant for concentrations in water, sediment and aquatic biota (Nisbet and Sarofim, 1972; Annema et al., 1995; Gandrass and Salomons, 2001). Leakage during use is considered a main PCB source to the aquatic environment (Nisbet and Sarofim, 1972). Based on Annema et al. (1995), a ratio of 1:2 was derived for emissions to air and to water due to leakage. This ratio was used to derive water emissions from air emissions due to leakage, as specified by Breivik et al. (2002a, 2007). This approach implies that we assumed emissions to water to follow temporal and spatial patterns of leakage emissions to air.

European air and water emissions were attributed to the target cells with GIS software using a 'spatial join' operation to the cells of 100×100 km grid. The spatial distribution of emissions averaged over the years is shown in Fig. S2 in the Supporting Information. From these cell-specific emissions, the emissions to the surrounding scales were derived. No emissions on the Northern Hemisphere outside Europe were taken into account, because preliminary modeling results (not shown) had indicated that their influence on concentrations in target cells was small.

2.3. Empirical model evaluation

To compare modeled with measured concentrations, data on PCB-153 levels in the environment and in biota were gathered (Chevreuil

et al., 1995; Halsall et al., 1995; Hendriks, 1995; Oehme et al., 1995; Korhonen et al., 1997; Vartiainen et al., 1997; Hendriks et al., 1998; Lee et al., 1998; EU-COMMPSdatabase, 1999; Fromme et al., 1999; Haugen et al., 1999; Reinhold et al., 1999; Vigano et al., 2000; Dauberschmidt and Hoffmann, 2001; Binelli and Provini, 2003; Meijer et al., 2003; Belpaire and Goemans, 2004; Bervoets et al., 2005; Schmid et al., 2005; Antoniadou et al., 2007). The spatial distribution of sampling locations is shown in Fig. 1. Measured concentrations were selected if information on congener, location and year was available. Measurements were found for the period 1989–2004 (see Table S5 in the Supporting Information). If several measurements in the same compartment were available for the same target cell in the same year, the geometric mean of these data was used.

Model performance was quantitatively evaluated by expressing the difference between modeled and observed concentrations in terms of the root mean square error of the log-transformed concentrations (Eq. (2)).

$$\mathrm{RMSE}_{\log} = 10\sqrt{\frac{1}{n}\cdot\sum(\log C_{\mathrm{obs},i,j} - \log C_{\mathrm{est},i,j})^2} \quad (2)$$

where $\mathrm{RMSE}_{\log}$ is the exponentiation with base 10 of the Root Mean Square Error of the log-transformed values, $C_{\mathrm{obs},i,j}$ is the measured concentration in target cell i and year j, $C_{\mathrm{est},i,j}$ is the estimated concentration in target cell i and year j and n is the number of comparisons. The $\mathrm{RMSE}_{\log}$ is a measure of accuracy of model predictions and summarizes both random error and systematic bias. Additionally, as it is a dimensionless figure, the $\mathrm{RMSE}_{\log}$ is comparable between compartments. The $\mathrm{RMSE}_{\log}$ has been quantified for estimated concentrations in air, soil, fresh water sediment and biota.

In addition to calculating the $\mathrm{RMSE}_{\log}$ for all sets of modeled and measured concentrations, modeled time trends were compared to observed time trends for those grid cells for which observations in at least five different years were available and for these 5 to 13 years. Time trends were quantified by fitting regressions of the form $\ln(C_t/C_0) = a \cdot t$, where t is in years after the first year of observation. Due to availability of measurement data, only years in the period 1990–2002 were included. Results were expressed as the slopes and the levels of significance (p) of the slopes. Slopes were compared to the similarly calculated time trends in the estimated concentrations. Additionally, regression lines of observed concentrations were visualized together with observed concentrations and estimated concentrations in the grid cell with the highest and the grid cell with the lowest estimated concentrations of those grid cells for which measurements over at least 5 years were available.

2.4. Scenario analysis

Effects of model improvements on predicted concentrations were evaluated by comparing a series of model setups. A model setup that

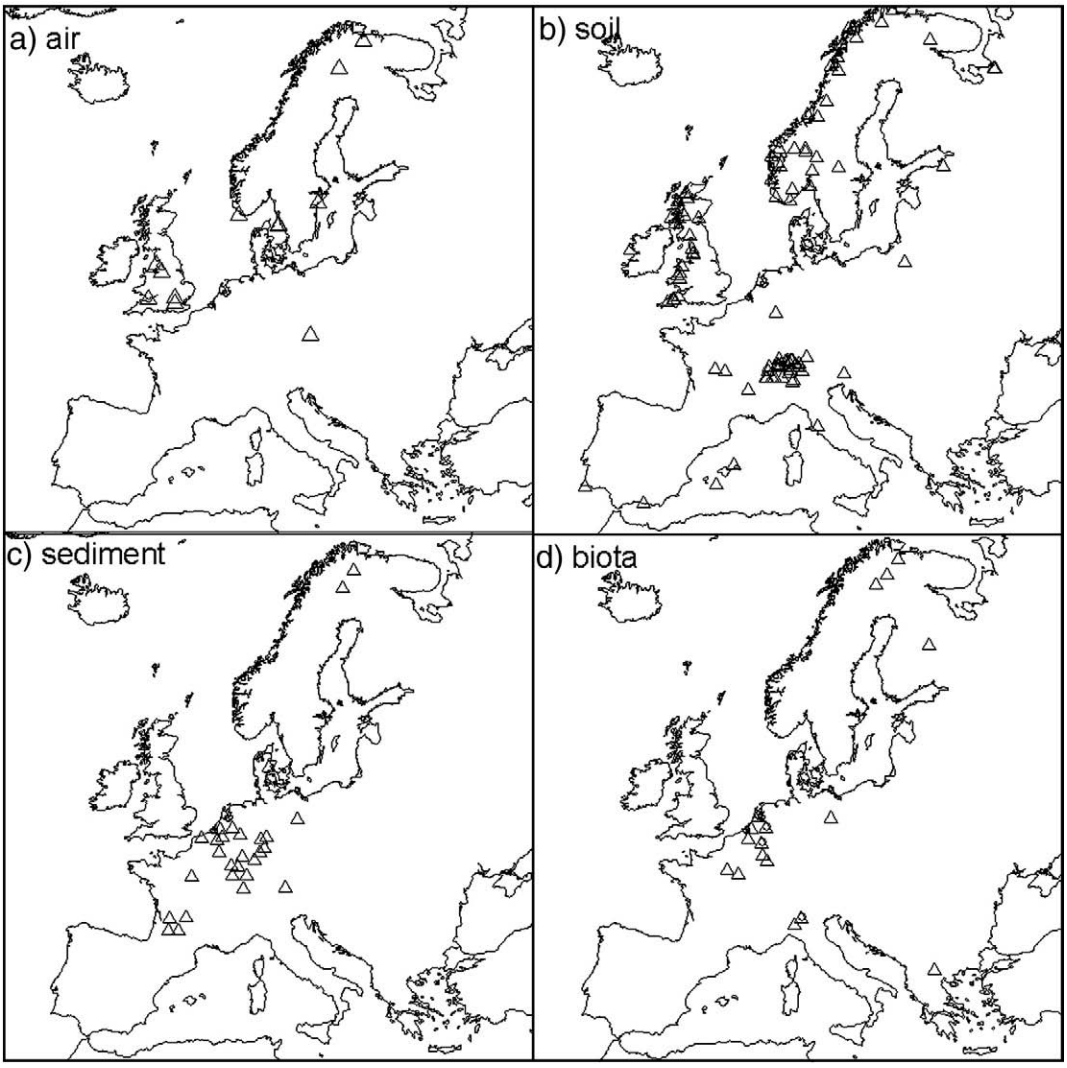

Fig. 1. Locations of measured concentrations of PCB-153 in air (a), soil (b), sediment (c), and biota (d). Triangles in panel d indicate fish, circles indicate invertebrates.

included long-term spatially explicit emissions to air and water and spatially explicit environmental characteristics as described above was compared to a basic model setup without variability in emissions, without variability in environmental characteristics and without emissions to water and to intermediate model setups in which the improvements were left out one at the time. Comparison of these setups shows whether the increased level of variation in the first setup improved estimated concentrations in air, soil, fresh water

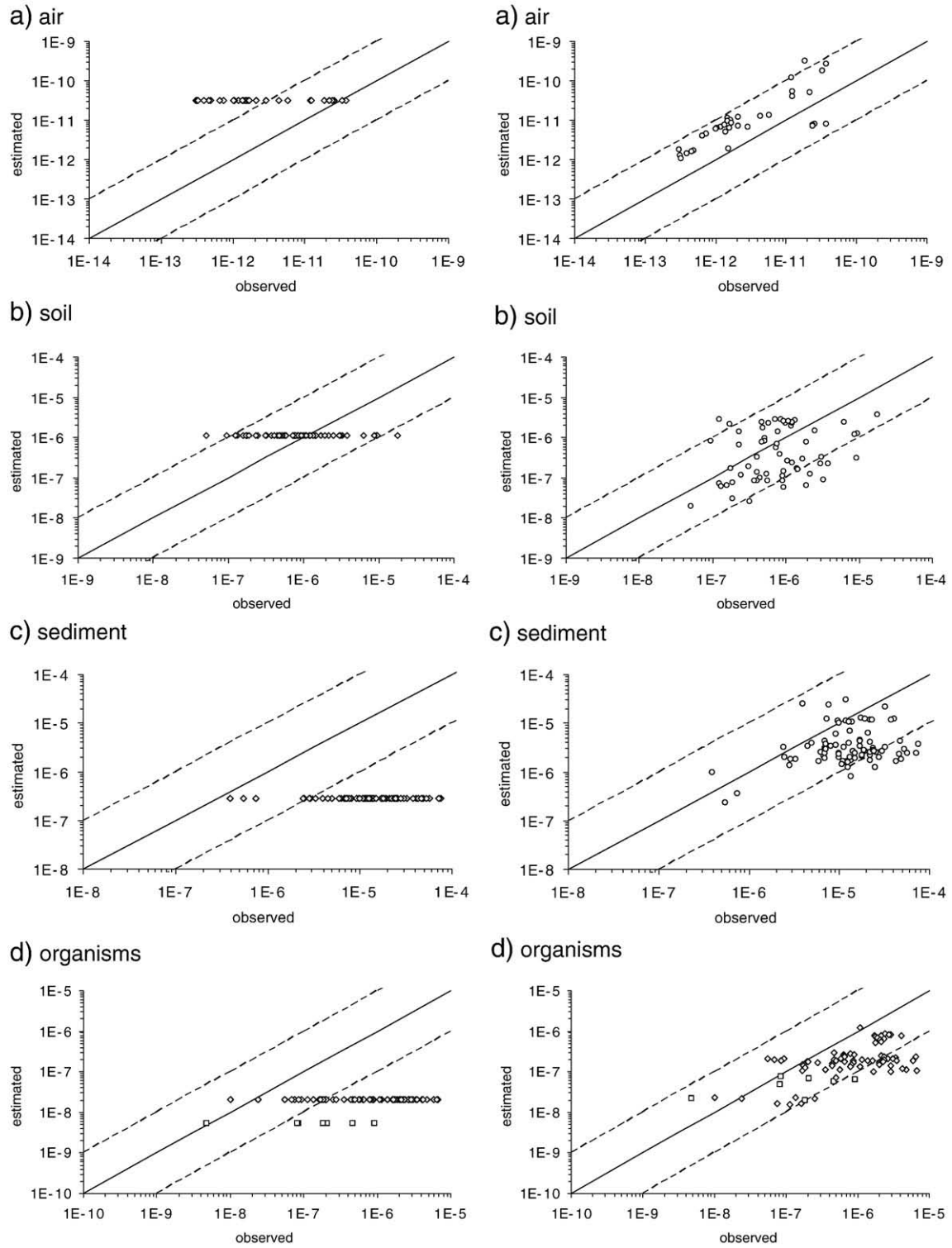

Fig. 2. Estimated concentrations versus observed concentrations for air [g/m^3], soil [kg/kg dry weight], fresh water sediment [kg/kg dry weight] and fresh water organisms [kg/kg lipid weight] (squares indicate invertebrates, diamonds represent fresh), solid line: 1:1; dashed line above the solid line: overestimation by a factor of 10; dashed line below the 1:1 line: underestimation by a factor of 10. Panels a), c), e), and g) refer to the minimum scenario, panels b), d), f), and h) refer to the maximum scenario.

sediment and fresh water biota. The following scenarios were formulated:

1. the 'explicit emissions and environment scenario' with spatially and temporally explicit emissions to air and water and spatially explicit environmental characteristics;
2. the 'uniform emissions and environment scenario' with emissions to air averaged over space and equally distributed in space and averaged over time assuming steady-state conditions, average environmental characteristics uniformly distributed in space, with no emissions to water;
3. the 'steady-state scenario' with spatially explicit environmental characteristics and spatially explicit but temporally averaged emissions to air and water, assuming steady-state conditions;
4. the 'uniform environment' scenario, with spatially and temporally explicit emissions to air and water, but average environmental characteristics uniformly distributed in space;
5. the 'emissions to air only' scenario, with spatially and temporally explicit emissions to air, and spatially explicit environmental characteristics, but no emissions to water.
6. the 'uniform emission' scenario, with spatially explicit environmental characteristics and temporally explicit but spatially averaged emissions to air and water uniformly distributed in space;

Spatial averages were calculated from characteristics of all grid cells and long-term temporally averaged emissions were calculated over the period 1930–2005. Calculations with long-term temporally averaged emissions (in scenarios 1 and 4) were performed assuming steady-state, whereas all other calculations were performed dynamically, with constant emissions per year and with mean concentrations per year as output. For each scenario the $RMSE_{log}$ was calculated as described above.

3. Results

Fig. 2 shows estimated versus observed concentrations in air, soil, fresh water sediment and fresh water biota for the uniform emissions and environment and explicit emissions and environment scenarios. In the uniform emissions and environment scenario, estimated values are equal over cells and years and show little relation to observed values. In the soil compartment, estimated concentrations were mostly within a factor of 10 of estimated concentrations, whereas concentrations in air tend to be overestimated and concentrations in sediment and biota were systematically underestimated by two orders of magnitude. In the explicit emissions and environment scenario, estimated concentrations approached observed concentrations better, with exception of the soil compartment. For all compartments, except air, observed concentrations tended to be underestimated. Estimated versus observed concentrations for the other scenarios are shown in Figs. S3–S6 of the Supporting Information.

Fig. 3 shows the development over time of estimated concentrations, together with the corresponding observed values, and regression lines for the observed values. Table 1 shows the slopes and the levels of significance of the slopes. Fig. S4 and Table 1 indicate that in the period 1990–2003 concentrations in air and sediment declined. The same is true in two grid cells for fish. Table 1 shows a stronger decline in observed concentrations than in modeled concentrations for air, for three grid cells in sediment, and for one grid cell in fish (a factor of 2–8 steeper slopes for observations). For fish, observed concentrations showed an increase in three grid cells, whereas estimated concentrations decreased.

Table 2 shows the root mean square error of the log-transformed concentrations ($RMSE_{log}$) for air, soil, sediment and biota for the 'uniform emissions and environment ', the 'explicit emissions and

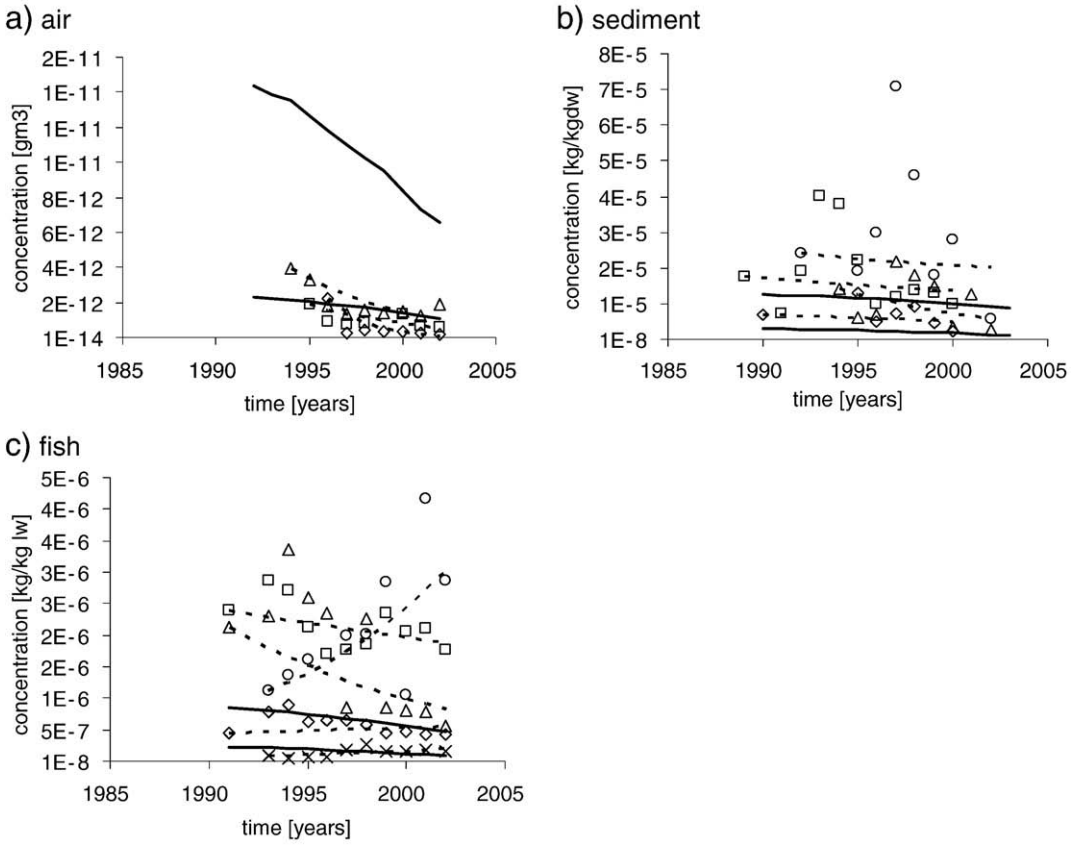

Fig. 3. Modeled (solid curves) and observed concentrations in a) air, b) fresh water sediment and c) fresh water organisms and concentrations estimated with regression from Table 1 for observed concentrations (dashed line). For estimated concentrations, the target cells with the highest and lowest estimated concentrations from the target cells for which measurements were available are shown. Different symbols indicate observations in different grid cells within one compartment.

Table 1
Regression slopes a (in yr^{-1}) with corresponding *p*-values from regressions of the form $\ln(C_t/C_0) = a \cdot t$ (where *t* is in years after first year of observation) for the observed and modeled time trends. Concentration was in $g\,m^{-3}$ for air, kg kg dry $weight^{-1}$ for sediment and kg kg lipid $weight^{-1}$ for fish.

Grid cell	Compartment	Observed		Modeled	Years for which measurements were available
		a	*p* of *a*	*a**	
A	Air	−0.48	0.001	−0.06	1996–2002
B	Air	−0.17	0.003	−0.06	1995–2001
C	Air	−0.17	<0.001	−0.07	1994–2002
D	Sediment	−0.03	0.276	−0.03	1990, 1995–2000
E	Sediment	−0.02	0.358	−0.02	1989, 1991–2000
F	Sediment	−0.11	0.053	−0.06	1994–2002
G	Sediment	−0.02	0.689	−0.05	1992, 1995–2000, 2002
D	Fish	0.02	0.231	−0.06	1991, 1993–2002
E	Fish	−0.02	0.007	−0.05	1991, 1993–2002
H	Fish	−0.08	0.002	−0.07	1991, 1993–2002
I	Fish	0.09	0.003	−0.07	1993–2001
G	Fish	0.11	0.001	−0.06	1993–1995, 1997–2002

* All *p*-values for modeled slopes are smaller than 0.001, indicating that they deviate significantly from 0.

environment ', the 'steady-state', the 'uniform environment', the 'emissions to air only', and the 'uniform emission' scenarios. $RMSE_{log}$ for the uniform emissions and environment scenario ranged from 3.5 for soil to 49 for sediment. $RMSE_{log}$ for the explicit emissions and environment scenario ranged from 5.4 for air to 6.3 for biota. $RMSE_{log}$ for assuming steady-state and using temporally averaged emissions led to a slight decrease in the $RMSE_{log}$ for soil, the $RMSE_{log}$s for air, sediment and aquatic biota slightly increased compared to the explicit emissions and environment scenario. $RMSE_{log}$s were slightly higher for the scenario with average environmental characteristics (within a factor of 2) compared to explicit emissions and environment scenario. Fig. S4 in the Supporting Information shows that this increase in $RMSE_{log}$ compared to the explicit emissions and environment scenario was due to an increased number of grid cells where concentrations in biota were underestimated. Taking into account emissions to air only, and no emissions to fresh water, resulted in a factor of 3–4 higher $RMSE_{log}$ compared to the explicit emissions and environment scenario for sediment and aquatic biota. The scenario in which uniform distribution of emissions was assumed showed relatively high $RMSE_{log}$s, i.e. up to a factor of 9 higher than in the explicit emissions and environment scenario. In both, the 'emissions to air only' and the 'uniform emission' scenarios the increase in $RMSE_{log}$ in sediment and biota was due to an increased underestimation compared to the explicit emissions and environment scenario (Figs. S5 and S6 in the Supporting Information). The $RMSE_{log}$ in soil, in contrast to other compartments, showed the lowest $RMSE_{log}$s in the uniform emissions scenario and the highest $RMSE_{log}$ in the explicit emissions and environment scenario.

Table 2
Root mean square errors of log-transformed concentrations in the 'explicit emissions and environment', the 'uniform emissions and environment', the 'steady-state', the 'uniform environment', the 'emissions to air only' and the 'uniform emissions' scenario for air, soil, fresh water sediment and fresh water biota.

Scenario	Air	Soil	Sediment	Biota
Unit of estimated concentrations	g/m^3	kg/kg dw	kg/kg dw	kg/kg lw
Explicit emissions and environment	5.4	5.5	5.6	6.3
Uniform emissions and environment	21	3.5	49	48
Steady-state	6.1	4.8	6.8	7
Uniform environment	7.4	5.3	7.4	11
Emissions to air only	5.3	5.5	21	18
Uniform emissions	14	3.3	49	35

dw = dry weight; lw = lipid weight.

4. Discussion

4.1. Explicit emissions and environment scenario

Monitoring data used in this study were not evenly distributed in time or space. For instance, most measurements in fresh water sediment were concentrated in the higher industrialized regions of Europe. As a consequence, they may not represent average conditions that are used in the model scenarios for the whole modeling area. Moreover, comparison with monitoring data at other locations or times, could lead to different conclusions.

A relatively large deviation between estimated and observed concentrations in soil has been shown in an earlier European evaluation study of fate models for different persistent organic pollutants and emissions to air only (Armitage et al., 2007). Concentrations measured in air were generally lower than estimated, whereas concentrations in soil, sediment and biota were often higher than predicted (Fig. 2a vs. b–d). These results correspond with the findings of Armitage et al. (2007) who showed that concentrations were also mainly underestimated by the fate models in soil and sediment but not in air. Armitage et al. (2007) discuss possible reasons for this underestimation, such as quality and representativeness of monitoring data, time-averaging environmental properties and neglecting sorption to black carbon, however, a single reason for this underestimation could not be found.

Several authors (Halsall et al., 1995; Haugen et al., 1999) reported that seasonal variation in PCB air concentrations can stretch up to a factor of 2 to 20. Since our calculations were performed using yearly averages of emission rates and environmental characteristics, producing average concentrations as well, this seasonal variation was not reflected in the modeled concentrations. As most observations in Figs. 2a and 3a represent geometric means of measurements spread over the year, seasonal differences could explain few differences between observations at different locations.

A decreasing but ongoing decline in estimated air concentrations in the 1990s (Fig. 3a) has also been found in another study on PCB-153 (Hollander et al., 2007). Modeled decline underestimated observed decline in air in our study. Observed decline, however, was slow, which is in agreement with Haugen et al. (1999) and others (Panshin and Hites, 1994) who concluded for different areas that no significant decline in PCB air concentrations in the early 1990s could be observed.

A decline of PCB concentrations in sediment and fish has been reported by several authors up to the early 1990s (Beurskens et al., 1993; Hendriks and Pieters, 1993; Sanders et al., 1994, 1998; Comber and Gardner, 1999; Tanabe et al., 2003), and later (Maes et al., 2008). These trends are also reflected in our results that showed a slight decline in observed and modeled concentrations in sediment and fish for most but not for all locations. However, decline in modeled concentrations was slower than in observed concentrations for most cells in sediment. This might be due to an underestimation of decrease in emissions to water in our study. However, observed trends for fish are somewhat contradictory and significance of observed trends in sediment is low, making it difficult to draw conclusions on model performance.

4.2. Uniform emissions and environment scenario

In the uniform emissions and environment scenario, estimated concentrations were equal, independent of time and space and show a relatively large deviation from measurements. For the soil compartment, however, the uniform emissions and environment scenario performed best of all scenarios. Armitage et al. (2007) found that a generic version of SimpleBox yielded about the same results for estimated concentrations in soil as three spatially explicit fate models. These similarities indicate that the current models, both box models and spatially explicit ones, are not able to capture the realistic spatial

variation in soil concentrations within Europe. For all other compartments, concentrations estimated in the explicit emissions and environment scenario, showed more variation and better reflect observed values. It can be hypothesized that in the uniform emissions and environment scenario, concentrations in air were overestimated in grid cells with low observed concentrations because of a lack of spatial differentiation in emissions. As concentrations in air are closely related to emissions to air, a uniform emission rate will lead to an overestimation of emissions and air concentrations in grid cells were actual emissions are low. Neglecting emissions to water explains the large underestimation of concentrations in sediment and biota compared to the explicit emissions and environment scenario (to be discussed later). Increase in model error due to leaving out different sources of variation, namely variation in time by year specific emissions and performing dynamic calculations, variation in space by spatially explicit environmental characteristics, variation in emission by including emissions to fresh water, and variation in space by spatially explicit emissions will be discussed below. It should be kept in mind, however, that model estimations could deviate from measurements for different reasons and variability in measurements can also be caused by differences in sampling and analytical techniques between different studies.

4.3. Temporally explicit emissions

Using emissions averaged over the period 1930–2005 and assuming steady-state led to a $RMSE_{log}$ only slightly higher to the one for the explicit emissions and environment scenario, although emissions varied in time and it could be expected that neglecting this variation would lead to much higher $RMSE_{log}$s compared to the explicit emissions and environment scenario. However, model performance was assessed with monitoring data from a period when the largest variation in emissions already had occurred; therefore this variation was no longer reflected in monitoring data, leading to comparably small differences between estimated and observed concentrations. Calculations by Sweetman et al. (2002) showed that the air–soil fugacity ratio for a PCB dropped from above 4 when emission were high to 1 (the steady-state ratio) and below about 10 years after maximum emissions, indicating that after emission reduction, error introduced by assuming steady-state conditions decreases. For soil, where concentrations were generally underestimated in the explicit emissions and environment scenario, $RMSE_{log}$ were smaller when uniform emissions were assumed compared to the explicit emissions and environment scenario, because time-averaged emissions were higher than emissions in the years of soil monitoring data, leading to less underestimation in the steady-state scenario.

4.4. Spatially explicit environmental characteristics

In the scenario with uniform environmental conditions, $RSME_{log}$ was slightly larger than in the explicit emissions and environment scenario particularly for the biota compartment. This was due to an averaging out of inflow and outflow rates of water to the target cell (and thereby equal water retention times in all grid cells). Concentrations in biota were calculated from dissolved concentrations in water equally for all locations. Spatial patterns of internal concentrations in biota therefore followed the spatial patterns of concentrations in water. In the scenario with uniform environmental conditions concentrations in biota tended to be underestimated more often than in the explicit emissions and environment scenario. In most of the grid cells with measurements in biota, cell-specific outflow rates were lower than the average outflow rate, leading to higher estimated concentrations compared to concentrations that are estimated using average outflow rates. Armitage et al. (2007), and Hauck et al. (2008) concluded that neglecting spatial variability in characteristics of water bodies is a main source of model error. Retention time in water had been shown to be the most important factor affecting concentration estimates for water bodies (Pennington et al., 2005; Hollander et al., 2008) which are directly linked to concentrations in biota.

4.5. Emission compartment

The increased $RMSE_{log}$ for biota and sediment in the scenario with emissions to air only compared to the explicit emissions and environment scenario indicates that not taking into account direct emissions to water leads to an underestimation of concentrations in sediment and biota.

In our approach, emissions to water were estimated from emissions to air. This approach might not always be correct. For instance it neglects early or ongoing sources of PCB emissions to water, such as from antifouling of ships (De Voogt and Brinkman, 1985) or from painted surfaces (Jartun et al., 2008, 2009). $RMSE_{log}$ was much smaller when spatially explicit emissions were taken into account (explicit emissions and environment scenario) than for uniformly distributed emissions to water or no emissions to water at all. Together, the results of these scenarios suggest that deriving spatial-explicit emissions to water from air emissions due to leakage is a reasonable first approach for PCB-153.

4.6. Spatially explicit emissions

In the air, sediment and biota compartments, $RMSE_{log}$ approached values of the uniform emissions and environment scenario, when emissions were evenly distributed in space. This demonstrates that ignoring spatial variation in emission intensities is the largest source of model error in this study. The difference to the explicit emissions and environment scenario was larger for sediment and biota, because air mixes more easily between locations, leading to a reduction of the differences in concentrations between locations. The importance of spatial differentiation of emissions has been highlighted by others (Prevedouros et al., 2004; Breivik et al., 2006; Hauck et al., 2008). Larger $RMSE_{log}$ in the 'uniform emission' scenario compared to the 'uniform environment' scenario implies that for PCB-153 in Europe, spatial variation in emissions has a larger influence on the spatial variation in concentrations than the spatial variations in environmental characteristics.

For the soil compartment, $RMSE_{log}$s decreased in the scenario with uniform emissions compared to the explicit emissions and environment scenario. Average emissions are generally higher than grid-specific emissions in the grid cells for which measurements were available, leading to higher estimates of soil concentrations that were better in line with field concentrations in several grid cells.

5. Conclusions

We conclude that modeling environmental concentrations of PCB-153 can greatly benefit from accounting for spatial and temporal variation in emissions and environmental characteristics. While regulatory decisions are often based largely upon steady-state non-spatial model calculations, our systematic comparison of modeling options demonstrates a number of significant possible model improvements. Including spatially and temporally resolved emissions, emissions to water, spatially explicit environmental characteristics and calculating concentrations dynamically, led to the best agreement with observed concentrations in the air, fresh water sediment and fresh water biota. For the soil compartment, neither including temporal or spatial variability in emissions nor including spatial variability in environmental conditions improved estimations of concentrations compared to a more generic model set up.

Including spatially resolved emissions led to the largest improvement in model performance for estimating concentration in air,

sediment and biota. Spatial variation in emissions had a larger influence on the spatial variation in concentrations than the spatial variations in environmental characteristics. Including emissions to water also played an important role to improve the concentration predictions in sediment and aquatic biota.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.scitotenv.2009.11.037.

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