

# Performance of the CalTOX fate and exposure model in a case study for a dioxin-contaminated site

Annika Åberg · Matthew MacLeod · Karin Wiberg

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**Abstract** Soil with high levels of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) is found at contaminated sites all over the world. Transfer of PCDD/Fs from contaminated soil to the food chain could lead to elevated human exposure. As a complement to available monitoring data, multimedia fate and exposure modeling can be applied to support risk assessment of sites with PCDD/F contaminated soil. In this study, we evaluated the performance of the CalTOX fate and exposure model for 2,3,7,8-substituted PCDD/Fs against measured concentrations in air, soil, grass, carrots, potatoes, milk, meat, and eggs from a contaminated site in northern Sweden. The calculated total toxic equivalent (TEQ) concentrations agree with measurements within a factor of 10 for all exposure media but one. Results for individual congeners demonstrated that the model did not always perform well at describing key processes that mobilize PCDD/Fs out of soils, such as transfer into root crops and ingestion of soil by chickens. Uncertainty in only a small subset of input parameters affects the model output. Improved information and models describing transfer of soil particles onto leafy vegetation by rain splash and biotransfer

factors for PCDD/Fs to milk, meat, and eggs are particular research needs to reduce uncertainties in model-based assessments.

**Keywords** CalTOX · Contaminated soil · Fate and exposure modeling · PCDD/F · Dioxins · Risk assessment · Uncertainty analysis · Monte Carlo analysis

## Introduction

The past production and use of chlorinated chemicals is recognized as a historical source of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs or ‘dioxins’) in soil all over the world. The seventeen 2,3,7,8-substituted congeners of PCDD/Fs are known to be highly toxic, and their concentrations can be expressed either as individual compounds or as weighted toxic equivalents (TEQs). Typical background levels of PCDD/Fs in soil are in the nanogram per kilogram (ppb) range, but sites contaminated by industrial activity can have levels that are several orders of magnitude higher (Åberg et al. 2010).

Atmospheric deposition is generally the main source of PCDD/F in food chains, but other sources can be important at local and regional scales, especially near contaminated sites (Braga et al. 2002; Costera et al. 2006; Pirard et al. 2005). Food chain transfer is a major concern in human health risk assessments of PCDD/Fs because they are strongly bioaccumulative (European Commission 1999). However, high costs for sampling and analysis and the large number of contaminated sites are obstacles that deter detailed site-specific exposure assessments. In such cases, multimedia fate and exposure modeling can be applied to support site-specific assessments (McKone and MacLeod 2003; Wiberg et al.

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A. Åberg  
ÅF Infrastructure, Linnégatan 9, SE-582 25 Linköping, Sweden

M. MacLeod  
Department of Applied Environmental Science, Stockholm  
University, Stockholm SE-114 18, Sweden

K. Wiberg (✉)  
Department of Aquatic Sciences and Assessment, Swedish  
University of Agricultural Sciences (SLU), Uppsala SE-750 07,  
Sweden  
e-mail: karin.wiberg@slu.se

2007). In particular, CalTOX is a multimedia total exposure model for hazardous waste sites that was developed for the California Environmental Protection Agency to improve risk assessment information used in decision-making (McKone 1993). The model describes 23 different human exposure pathways that are coupled to the modeled fate of chemicals in a seven-compartment multimedia region. CalTOX has been applied for risk assessment of hazardous compounds that include organophosphorus pesticides (McKone et al. 2007), chlorinated hydrocarbons (Chen and Ma 2006), carcinogenic organic compounds (Chang et al. 2004), and PCDD/Fs (Wiberg et al. 2007).

The sources of uncertainty in risk assessments based on model results are numerous and are related to factors that include the problem formulation, the model framework, uncertainties in input parameters, and the interpretation of the results (McKone and MacLeod 2003). Whenever possible, application of multimedia fate and exposure models to assess exposure to contaminants should be complimented by measurement data that allow for evaluation of model performance and, if necessary, optimization of the model. Wiberg et al. (2007) applied CalTOX to PCDD/Fs in a typical Swedish environmental scenario and compared model outputs to measured national data. It was concluded that physico-chemical property data, landscape parameters, and the default model algorithms can all introduce significant uncertainties in the assessment, and adjustments to the default parameterization and model equations were recommended. For example, the default model equations define a linear relationship between biotransfer factors (BTFs) and the octanol-water partition coefficient ( $K_{OW}$ ), and if applied to super-hydrophobic substances such as PCDD/Fs, the model overestimates the levels in biota. In the absence of an improved model equation, inserting empirical BTFs into the calculation was recommended as an alternative.

In the current study, we further evaluate CalTOX as a tool for quantitatively describing food chain transfer of 2,3,7,8-substituted PCDD/Fs. Our previous evaluation (Wiberg et al. 2007) used a generic background soil scenario and non-site-specific field samples to evaluate the model. Here, a case study for a well-defined contaminated site in northern Sweden is described, including two exposure scenarios for low-level (LL) and high-level (HL) concentrations in soil at the site. Model results for the two scenarios are compared to each other and to site-specific field measurements. Both measured levels and congener patterns are used to evaluate the model. The results and accompanying uncertainty analysis provide insight into the utility of CalTOX for human exposure assessments of contaminated sites. Specifically, we use the model to determine the key processes that control food chain transfer at the contaminate site, and we identify research priorities to improve the performance of the model.

## Materials and methods

### Study site

Our study site is a decommissioned sawmill and wood preservation facility in northern Sweden. A short description of the site is provided in the Supporting Information, and a full description of the site can be found in a previous paper from our research consortium (Åberg et al. 2010). Soils at the site were contaminated when chlorophenol (CP) preservatives were used for treatment of processed timber beginning in the mid-1940s. The contamination is highly spatially heterogeneous, with levels ranging over several orders of magnitude (1 to 110,000 ng TEQ kg<sup>-1</sup> dry weight (d.w.)). PCDD/Fs at the site are characterized by a high abundance of highly chlorinated dibenzofuran congeners, particularly 1,2,3,4,6,7,8-HpCDF and OCDF (Åberg et al. 2010). Highly chlorinated PCDD/Fs have relatively low bioavailability but are still transferred from soil to food chains (e.g., Matscheko et al. 2002). Our earlier study identified present and future risks for contamination of the human food chain at this site including a vegetable garden maintained by a local resident with highly contaminated soil (~600 ng WHO-TEQ kg<sup>-1</sup> d.w. soil) and a farm adjacent to the former industrial site with pastures used for dairy cows and free-range chickens (2–25 ng WHO-TEQ kg<sup>-1</sup> d.w. soil) (Åberg et al. 2010).

### Modeling scenarios

We modified an existing CalTOX version 4.0 beta parameterization of a typical Swedish landscape (Wiberg et al. 2007) to represent our study site using climate data from a meteorological station near the contaminated site. Annual averages of temperature (282 K), wind speed (9.9 km h<sup>-1</sup>), and precipitation (1.9 mm day<sup>-1</sup>) were used as model inputs (data from the Swedish Meteorological Institute). The size of the landscape is 100,000 m<sup>2</sup>, which approximates the area of the former industrial site that is now a pasture and a farmyard.

We defined two modeling scenarios to describe different levels of soil contamination at the study site: (i) a low-level (LL) scenario with 3 ng WHO-TEQ kg<sup>-1</sup> wet weight (w.w.) corresponding to the soil levels at the farm, and (ii) a high-level (HL) scenario with 530 ng WHO-TEQ kg<sup>-1</sup> w.w. corresponding to the levels in the garden. There is thus a factor of 180 higher TEQ-levels in the HL scenario and up to a factor of 9,100 higher concentration for individual congeners (see details of the two scenarios in Table 1). To represent long-range transport of PCDD/Fs into the model domain, both scenarios included continuous emissions to air calibrated so that the modeled concentration of each PCDD/F congener in air corresponds to measurements at a rural site on the Swedish west coast (Table 1, data from the Swedish Environmental Research Institute et al. 2006).

**Table 1** Input PCDD/F concentrations in the root-zone soil compartment (ng kg<sup>-1</sup> w.w.) and continuous air emissions (mole day<sup>-1</sup>) in the low-level (LL) scenario and the high-level (HL) scenario

Congener	Concentration in soil		Emission rate to air LL and HL
	LL	HL	
2,3,7,8-TeCDD	0.070 <sup>a</sup>	0.46 <sup>b</sup>	6.4 × 10 <sup>-10</sup>
1,2,3,7,8-PeCDD	0.083 <sup>a</sup>	17	1.8 × 10 <sup>-9</sup>
1,2,3,4,7,8-HxCDD	0.018 <sup>a</sup>	23	2.5 × 10 <sup>-9</sup>
1,2,3,6,7,8-HxCDD	0.36	1,640	3.7 × 10 <sup>-9</sup>
1,2,3,7,8,9-HxCDD	0.25 <sup>a</sup>	146	3.2 × 10 <sup>-9</sup>
1,2,3,4,6,7,8-HpCDD	2.5	3,290	4.3 × 10 <sup>-8</sup>
OCDD	12	2,740	1.0 × 10 <sup>-7</sup>
2,3,7,8-TeCDF	1.3	21	5.3 × 10 <sup>-9</sup>
1,2,3,7,8-PeCDF	0.35 <sup>a</sup>	13	4.1 × 10 <sup>-9</sup>
2,3,4,7,8-PeCDF	0.38 <sup>a</sup>	16	4.3 × 10 <sup>-9</sup>
1,2,3,4,7,8-HxCDF	1.2	219	4.7 × 10 <sup>-9</sup>
1,2,3,6,7,8-HxCDF	0.17	110	3.5 × 10 <sup>-9</sup>
2,3,4,6,7,8-HxCDF	0.36 <sup>a</sup>	201	3.7 × 10 <sup>-9</sup>
1,2,3,7,8,9-HxCDF	0.70 <sup>a</sup>	183	8.0 × 10 <sup>-10</sup>
1,2,3,4,6,7,8-HpCDF	2.3	21,000	1.1 × 10 <sup>-8</sup>
1,2,3,4,7,8,9-HpCDF	0.19	42	1.6 × 10 <sup>-9</sup>
OCDF	4.2	33,800	6.2 × 10 <sup>-9</sup>
Sum TEQ	3.0	530	–

<sup>a</sup> Congener concentration below limit of detection (LOD) in 1–3 samples out of 5

<sup>b</sup> Concentration below LOD

Physical-chemical property data

Physical-chemical property data for PCDD/Fs used in this study are the recommended final adjusted values (FAVs) from the review by Åberg et al. (2008) for ten of the seventeen 2,3,7,8-substituted congeners for which FAVs are available. Properties of the remaining compounds were estimated from quantitative structure-property relationships of the FAVs reported by Åberg et al. (2008). All properties were temperature-adjusted to the annual mean temperature of 282 K in the model landscape using internal energies of phase change recommended in the same paper (Åberg et al. 2008). A list of physical-chemical input data used in this study is compiled in Table S1 in the Supporting Information. Degradation half-lives of the compounds in air, water, and soil were adopted from Sinkkonen and Paasivirta (2000).

Biotransfer factors

The use of empirical cow’s milk and meat biotransfer factors (BTFs) from Birak et al. (2001) markedly improved the performance of CalTOX in a previous study of food chain transfer of PCDD/Fs (Wiberg et al. 2007). However, experimental BTFs were not available for all of the 2,3,7,8-substituted

congeners for milk and meat, respectively. Missing data were therefore estimated by regression of the available experimental BTFs against log *K*<sub>OW</sub>. The empirical value of 0.1 for 1,2,3,6,7,8-HxCDD reported by Birak et al. was excluded as it was unexpectedly high in relation to other values (0.00016–0.063). When that apparent outlier was excluded in the regression analysis, the *R*<sup>2</sup> for BTFs to meat increased from 0.042 to 0.63. The BTF values used in this study are given in Table S2 in the Supporting Information. For eggs, no experimental BTFs were available, so the modeling relied upon the default equations in CalTOX.

Model outputs

CalTOX calculates contaminant concentrations in exposure media that include air, groundwater, soil, plants, and animal food products. Since the concentrations in exposure media are extrapolated over the time of exposure (defined by the model parameter *exposure duration*, *ED*, measured in years), they depend on the exposure scenario selected in the model. In this case, an adult scenario with an *ED* of 70 years was used. The model generates two different exposure concentrations for plant products: (i) ‘exposed produce,’ which represents plant parts that grow above the ground and are contaminated by gas exchange, particle deposition from the atmosphere, and soil particles adsorbed on the leaf surface and (ii) ‘unexposed produce,’ representing plant parts that grow underground (e.g., root crops) and protected produce (e.g., citrus). In addition, CalTOX calculates the concentration of chemicals in ‘total leaf’ (i.e., cuticle plus leaf interior) that are contaminated by gas exchange and particles deposited from the atmosphere, but not by adsorbed soil particles. The ‘total leaf’ is solely used within the model to calculate the food chain transfer of the pollutants.

Model evaluation and parameter sensitivity analysis

The performance of the model was assessed using the ratio of the calculated and measured values (*C/M*-ratios). A ratio >1 thus indicates overestimation by the model, while a ratio <1 indicate underestimation by the model. Measured PCDD/F concentrations available from the contaminated site (Åberg et al. 2010) allowed for nine out of the 14 modeled exposure media concentrations to be evaluated (Table 2; *C/M* ratios) when measurements in grass were assumed to represent modeled concentrations in ‘exposed produce.’ The measurements include samples collected at the LL scenario farm (ambient air, grass, cow’s milk, and free-range chicken egg) and at or adjacent to the HL scenario garden (ambient air, grass, carrots, and potatoes). TEQ values were calculated using the revised WHO-TEFs (Van den Berg et al. 2006).

Monte Carlo uncertainty analysis was carried out for six of the congeners in the LL scenario (2,3,7,8-TeCDD; 1,2,3,4,7,8-HxCDD, OCDD; 2,3,7,8-TeCDF; 2,3,4,7,8-PeCDF and

**Table 2** Calculated concentration in exposure media (WHO-TEQ) in the low-level (LL) scenario and high-level (HL) scenario together with corresponding site-specific field concentrations (Åberg et al. 2010). Weight-based units are wet weight-based

	Air (fg m <sup>-3</sup> )	Exposed prod. (ng kg <sup>-1</sup> )	Unexposed prod. (ng kg <sup>-1</sup> )	Milk (ng kg <sup>-1</sup> )	Meat (ng kg <sup>-1</sup> )	Egg (ng kg <sup>-1</sup> )
Calculated, LL	5.8	0.14	0.00047	0.10	0.057	0.041
Field concentration	13 <sup>a</sup>	0.082 <sup>b</sup>	–	0.016 <sup>c</sup>	–	0.35 <sup>h</sup>
C/M-ratio <sup>i</sup>	0.45	1.7	n.a.	6.3	n.a.	0.12
Calculated, HL	8.9	1.5	0.061	0.96	0.98	2.4
Field concentration	25 <sup>d</sup>	0.083 <sup>e</sup>	0.097 <sup>f</sup> /0.25 <sup>g</sup>	–	–	–
C/M-ratio <sup>i</sup>	0.36	18	0.63/0.24	n.a.	n.a.	n.a.

n.a. not applicable since corresponding field measurements were not available, *Exposed prod.* exposed produce, represents aboveground plant parts contaminated by particle deposition from the atmosphere, soil particles adsorbed on the leaf surface and gaseous uptake from air, *Unexposed prod.* unexposed produce, represents belowground plant parts, in this study carrots and potatoes

<sup>a</sup> Sampled at farm

<sup>b</sup> Grass from the pasture (79 % water)

<sup>c</sup> A content of 5 % fat

<sup>d</sup> Sampled at the hot spot close to the contaminated garden

<sup>e</sup> Grass from the contaminated garden (52 % water)

<sup>f</sup> Potatoes

<sup>g</sup> Carrots

<sup>h</sup> Calculated assuming 10 % fat in whole egg

<sup>i</sup> Ratio between calculated and measured value; ratios >1 indicate overestimation by the model while ratios <1 indicate underestimation

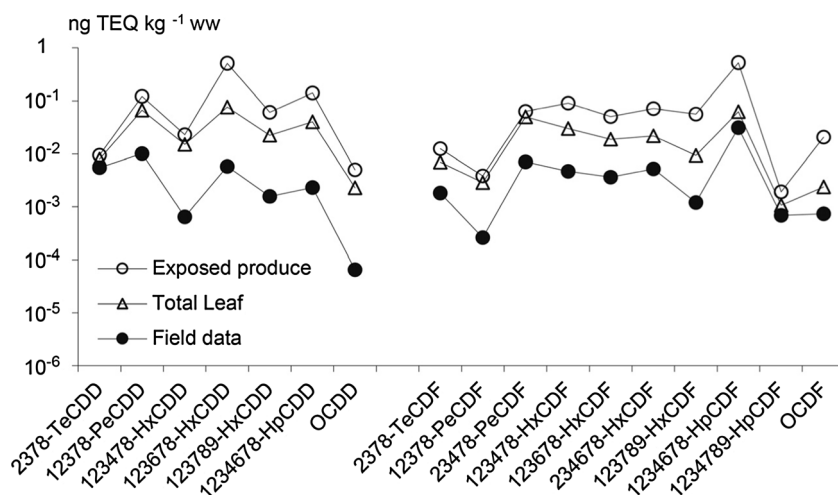
OCDF) using the uncertainty and risk analysis software Oracle Crystal Ball. The sensitivity analysis considered output concentrations in six exposure media: milk, meat, eggs, exposed and unexposed produce and outdoor air.

## Results

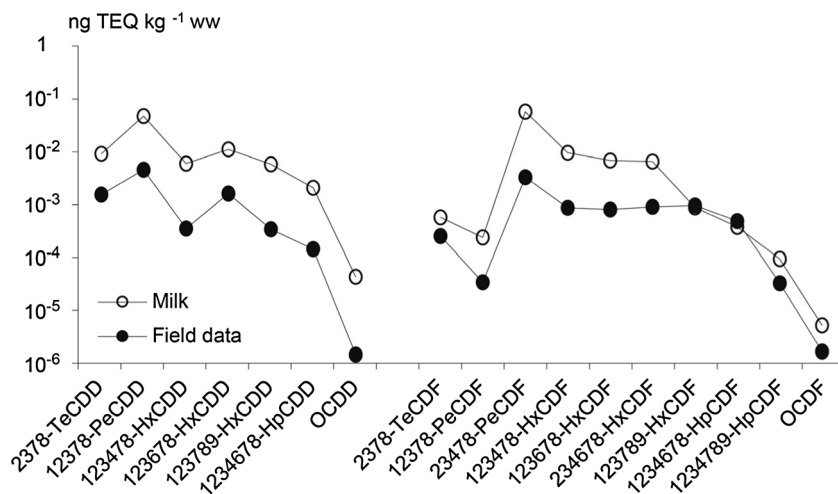
The C/M-ratios from the LL (farm) and HL (garden) scenarios were in the range 0.1–10 in all cases except for exposed produce in the HL scenario (C/M=18) (Table 2). The C/M ratios for each exposure medium are discussed in

more detail in the sections below. The PCDD/F congeners considered in this study span a range of physical-chemical properties. Thus, additional insights into the performance of the CalTOX model can be gained by comparing calculated and measured congener patterns, and these patterns are shown in Figs. 1, 2, 3, and 4. The uncertainty analyses showed that although both the HL and LL scenarios require values for 121 input parameters, only a few of them are critical when CalTOX is applied for PCDD/Fs. Parameters that contributed >5 % to the variability of calculated concentrations of a range of PCDD/F congeners in exposure media (eggs, milk, meat, exposed and unexposed

**Fig. 1** Calculated concentrations of PCDD/Fs (ng WHO-TEQ kg<sup>-1</sup> w.w.) in ‘exposed produce’ (contaminated through gaseous uptake from air, particles deposited from air and soil particles transferred by rain splash) and ‘total leaf’ (contaminated through gaseous uptake from air and particles deposited from air only) in the high-level (HL) scenario together with average concentrations in grass samples from the highly contaminated garden (field data from Åberg et al. (2010))



**Fig. 2** Calculated concentrations of PCDD/Fs in milk (ng WHO-TEQ kg<sup>-1</sup> w.w.) in the low-level (LL) scenario and average concentrations in milk samples from the low-contaminated farm close to the study site (field data from Åberg et al. (2010))



produce, total leaf, and outdoor air) are compiled in Table 3.

**Discussion**

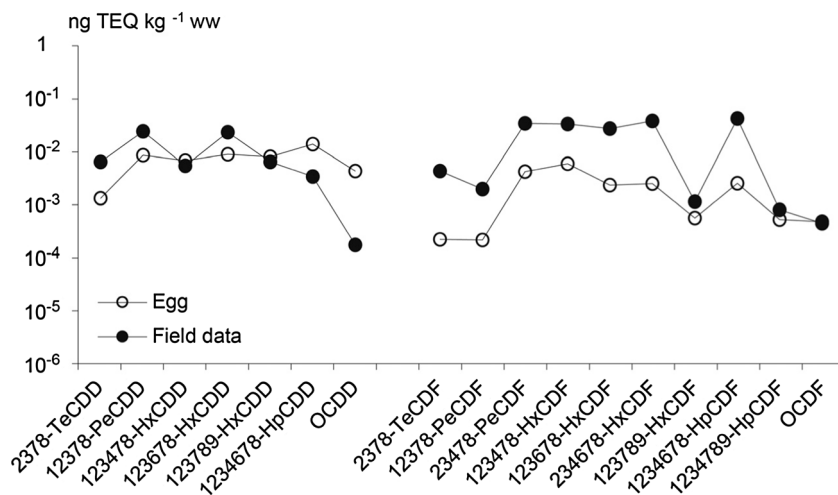
Evaluation of model performance for exposure media

*Air* The calculated PCDD/F concentration in ambient air was 5.8 fg WHO-TEQ m<sup>-3</sup> (Table 2). Somewhat higher concentrations (13 fg WHO-TEQ m<sup>-3</sup>; C/M ratio=0.45) were measured in air sampled at the LL-scenario farm (Åberg et al. 2010). The small underestimation by the model is not unexpected since emissions to air were adjusted in order to achieve a good agreement with measurements from a background site. Relative to the LL scenario, the calculated concentration in air in the HL scenario was higher (8.9 fg TEQ m<sup>-3</sup>), as were measurements from close to the highly contaminated garden (25 fg TEQ m<sup>-3</sup>). The C/M-ratio in the HL scenario (0.36) is slightly lower than the LL scenario, indicating slightly stronger underestimation of measured concentrations by the model.

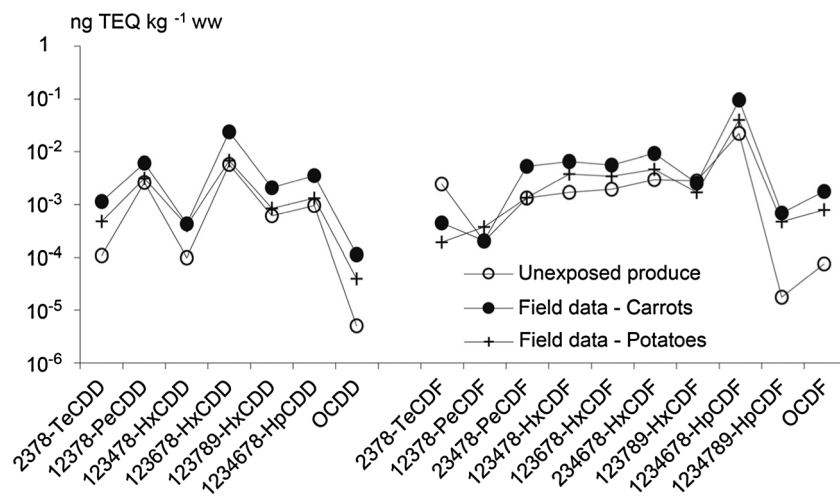
*Leafy plants* Local concentrations of PCDD/Fs in grass from the study site are used for comparison to the ‘exposed produce’ concentrations in Table 2. Grass samples were not rinsed before analysis and had dust and soil particles adhered to their surfaces (Åberg et al. 2010). Agreement between measurements of the grass samples and ‘exposed produce’ concentrations calculated in the LL scenario was good (C/M-ratio=1.7).

The calculated total WHO-TEQ concentration in ‘exposed produce’ in the HL scenario was higher by a factor of 11 than that in the LL scenario (Table 2); however, measured concentrations in grass at sites that correspond to the two scenarios are virtually identical. Differences in transfer of PCDD/F from soil to ‘exposed produce’ by soil splash largely accounts for the higher calculated WHO-TEQ concentrations in the HL scenario. The levels and calculated congener pattern in the model’s ‘total leaf’ compartment are much more similar to the levels and congener pattern measured in grass samples than the calculated concentrations in ‘exposed produce’ (Fig. 1). The calculated congener pattern in ‘exposed produce’ is especially divergent from measurements for the OCDF

**Fig. 3** Calculated concentrations of PCDD/Fs in egg (ng WHO-TEQ kg<sup>-1</sup> w.w.) in the low-level (LL) scenario and average concentrations in free-range chicken eggs from the farm close to the study site (field data from Åberg et al. (2010))



**Fig. 4** Calculated concentrations of PCDD/Fs in ‘unexposed produce’ (ng WHO-TEQ kg<sup>-1</sup> w.w.) in the high-level (HL) scenario and concentrations in carrots and potatoes from the highly contaminated garden at the study site (field data from Åberg et al. (2010))



congener, which is a low-volatility congener that is highly abundant in the soil and thus also in soil splash.

There is no pathway for direct transport of soil to the ‘total leaf’ compartment in CalTOX; therefore, the results shown in Fig. 1 confirm that soil-plant transfer with soil particles drives the discrepancy between calculated concentrations in ‘exposed produce’ and measured concentrations in grass. The presence of soil and dust particles on leaf surfaces varies over time and is challenging to parameterize (Smith and Jones 2000), but it seems likely that either (i) our model scenarios overestimate the importance of soil-leaf transfer of soil particles or (ii) grass is a poor surrogate for ‘exposed produce’ with respect to deposition of soil particles. We used CalTOX default values for the *Rainsplash* input parameter that describes transfer from soil to leaf surfaces; the sensitivity of model results to the *Rainsplash* parameter is quantified and discussed in more detail below.

**Milk** The calculated WHO-TEQ level in milk in the LL scenario (0.10 ng TEQ kg<sup>-1</sup>) was a factor of 6 higher than that the field data (0.016 ng TEQ kg<sup>-1</sup>, Table 2). In CalTOX, cattle take up contaminants via ‘exposed produce,’ soil, air, and water. Thus, biased values in those model outputs can affect the predicted food chain transfer. The WHO-TEQ concentration in exposed produce in the LL scenario was higher than the field data by a factor of 1.7 and contributes to the overestimations for milk.

The BTFs used in the model calculation are another source of uncertainty and potential bias for the soil-feed-cattle contamination route. We estimated BTF values from experimental data that were available for PCDD/Fs (Birak et al. 2001). It has been argued that measured BTFs are not appropriate for long-term exposure scenarios since the experimental durations are too short in relation to the time needed for hydrophobic compounds to reach steady state (Rosenbaum et al. 2009). Another method to estimate the BTFs would be to apply one of the more general estimation methods for organic chemicals

that have been recently proposed (Rosenbaum et al. 2009; Hendriks et al. 2007). However, the agreement between congener patterns calculated in the LL scenario and the field data is good (Fig. 2), and the calculated concentrations are higher than the measured values, which is not consistent with the BTFs representing experimental conditions in which steady state was not reached.

**Meat** Measurements of PCDD/F concentrations in meat from the study site were not available (Table 2). Calculated total WHO-TEQs for meat were similar to those for milk. On a congener level, there was, however, nearly an order of magnitude difference in calculated concentrations of 1,2,3,4,6,7,8-HpCDF in meat and milk ( $4.8 \times 10^{-3}$  and  $4.1 \times 10^{-4}$  ng TEQ kg<sup>-1</sup>, respectively). This discrepancy was related to a high experimental BTF in meat (0.0158) in relation to the BTF for milk (0.00126) from Birak et al. (2001).

**Eggs** The calculated WHO-TEQ concentration in eggs in the LL scenario was nine times lower than the measurements (i.e., C/M-ratio=0.12, Table 2). Soil is generally considered to be a major source of PCDD/Fs in eggs (Waegeneers et al. 2009; Schuler et al. 1997), and the commercial chicken feed used at the farm did not constitute an additional source (Åberg et al. 2010). We adjusted the CalTOX default soil ingestion rate for chickens (0.013 g day<sup>-1</sup>) to 2 g day<sup>-1</sup>, since chickens have been reported to ingest ~2–10 g of soil per day (European Commission 2001). If the higher soil ingestion rate of 10 g had been chosen, the C/M-ratio would have been five times higher, i.e., 0.6.

The calculated and measured congener patterns for eggs do not match as well as those for other exposure media (Fig. 3). Even if one presumes that the soil ingestion rate was underestimated, it cannot explain the larger discrepancy between the calculated and measured levels of PCDFs compared to PCDDs. The calculated congener pattern, with a relatively high abundance of OCDD and OCDF relative to other

**Table 3** Parameter sensitivity (%) of different model outputs in relation to changes of the parameterization of congeners (2,3,7,8-TeCDF; 2,3,7,8-TeCDD; 2,3,4,7,8-PeCDF; 123478-HxCDD, OCDF, and OCDD). Parameters that contributed to >5 % of the response in one of several of the model outputs are listed. The highest sensitivity scores are in italic font

Parameter	Eggs	Milk	Meat	Exposed produce	Unexposed produce	Total leaf	Outdoor air
<b>Biotransfer factors</b>							
<i>Be—egg</i>	<i>45–86</i>	0	0	0	0	0	0
<i>Bk—milk</i>	0	<i>40–86</i>	0	0	0	0	0
<i>Bt—meat</i>	0	0	<i>50–87</i>	0	0	0	0
<b>Chemical properties</b>							
<i>K<sub>OW</sub></i>	1–4	<0.4	<0.3	0.1–3	<i>10–19</i>	1–3	<0.1
<i>K<sub>OC</sub></i>	0	0	0	0	<i>13–24</i>	0	0
<i>H</i>	0	<1	<1	<i>0.1–16</i>	0	0.1–6	0
<i>Thalf<sub>s</sub></i>	1–4	0.4–5	0.2–5	2–23	<i>1–16</i>	0	0
<b>Landscape parameters</b>							
<i>Area</i>	0.2–5	0.1–6	0.2–5	<i>19–36</i>	0	<i>20–37</i>	<i>52–92</i>
<i>Rho<sub>leaf</sub></i>	1–7	2–8	1–8	<i>8–32</i>	0	<i>8–32</i>	0
<i>Thalf<sub>le</sub></i>	2–6	3–8	2–7	<i>16–36</i>	0	<i>16–35</i>	0
<i>Foc<sub>s</sub></i>	0	0	0	0	<i>24–50</i>	0	0
<i>Rhob<sub>a</sub></i>	<1	<1	<1	1–5	0	0	0
<b>Exposure factors</b>							
<i>ED</i>	<1	1–4	1–4	<i>0.3–19</i>	<i>2–13</i>	0	0
<i>Rainsplash</i>	0.4–1	7–9	2–7	<i>40–90</i>	0	0	0
<i>Ish</i>	4–7	0	0	0	0	0	0

*Be, Bk, Bt*=biotransfer factors for eggs, milk, meat

*K<sub>OW</sub>*=octanol-water partition coefficient

*K<sub>OC</sub>*=organic carbon partition coefficient

*H*=Henry’s law constant

*Thalf<sub>s</sub>*=reaction half-life in root zone soil

*Area*=contaminated site area

*Rho<sub>leaf</sub>*=leaf wet density\

*Thalf<sub>le</sub>*=erosion half-life of the leaf surface

*Foc<sub>s</sub>*=organic carbon fraction in upper soil zone

*Rhob<sub>a</sub>*=atmospheric dust load

*ED*=exposure duration for humans

*Ish*=ingestion of soil by hens

*Rainsplash*=soil to leaf surface transfer rate

congeners, depends on a model equation that does not reflect the reduced bioavailability of super-hydrophobic compounds (log *K<sub>OW</sub>* >6; (Birak et al. 2001; Travis and Arms 1988)). We therefore believe that a significant uncertainty is related to the default equations describing biotransfer of PCDD/Fs to eggs in CalTOX.

Considering that soil is potentially a major source of PCDD/Fs in free-range eggs, ingestion of locally produced eggs is highly relevant for exposure assessments at contaminated sites. Empirical egg/soil concentration ratios might be considered as a simple method to assess the risk for human exposure. We calculated such ratios (expressed as pg TEQ g<sup>-1</sup> fat in egg/pg TEQ g<sup>-1</sup> d.w. in soil) using data from a number of studies (Pirard et al. 2005; Schuler et al. 1997; van

Overmeire et al. 2009; Åberg et al. 2010) and found ratios ranging from 0.4 to 11, with a single outlier measurement of 26 (Table 4). Since the ratios cover a large interval, estimation of the soil-to-egg transfer route by extrapolation from other PCDD/F contaminated sites will be associated with a high degree of uncertainty.

**Root crops** The calculated total WHO-TEQ concentrations in ‘unexposed produce’ were two and four times lower in the HL scenario than concentrations measured in potatoes and carrots grown at the study site (Table 2). The input soil concentrations in the scenario were identical to the PCDD/F concentration of a composite soil sample from the cultivation area of the garden. There are several possible reasons for the imperfect

**Table 4** Calculated egg/soil concentration ratios (pg TEQ g<sup>-1</sup> fat in egg/pg TEQ g<sup>-1</sup> d.w. in soil) based on empirical data from Pirard et al. (2005), Schuler et al. (1997), Van Overmeire et al. (2009), and Åberg et al. (2010). The reduced data set excludes the maximum value (25.7)

	Complete data set (n=41)	Reduced data set (n=40)
Mean	3.0	2.4
Median	1.9	1.9
Standard deviation	4.2	2.1
Min	0.4	0.4
Max	25.7	11.0

agreement between calculations and measurements. For example, the field samples were analyzed unpeeled, and strongly adsorbed soil particles were likely not washed away during the sample preparation (Åberg et al. 2010). If so, the field samples are not completely comparable to the modeling scenario that takes only diffusive uptake from the soil into account.

#### Uncertainty analysis

Although both the HL and LL scenarios require values for 121 input parameters, we found that only a few of them are critical when CalTOX is applied for PCDD/Fs. Parameters that contributed >5 % to variability of calculated concentrations of a range of PCDD/F congeners in exposure media (eggs, milk, meat, exposed and unexposed produce, total leaf, and outdoor air) are compiled in Table 3. For eggs, milk, meat, and outdoor air, only one parameter for each output was of importance: the BTFs for the food chains (*Be*, *Bk*, and *Bt* for egg, milk, and meat, respectively) and the ground surface area (*Area*) for ambient air. The high importance of the *Bk* parameter (BTF for milk) illustrates the importance of using a reliable approach to estimate these values. Considering the high sensitivity of the *Be* parameter (BTF for egg), it is important to again stress that experimental data for this parameter is lacking, and high uncertainties will remain in future modeling applications until the parameterization can be improved.

For ‘exposed produce,’ the calculated concentration depends on a variety of parameters related to the landscape (ground surface area, erosion half-life of leaf surface, and leaf wet density), properties of the compounds (Henry’s law constant and half-lives in soil), and exposure factors (exposure duration and the soil-to-leaf surface transfer rate). However, in the context of food chain transfer from soil to leaf, the *Rainsplash* parameter is highly important. Unfortunately, the *Rainsplash* rate is difficult to define accurately since it depends on soil characteristics, plant morphology, climate, and other site-specific properties. As a consequence, the impact of the ‘exposed produce’ ingestion route on human exposure is

difficult to assess with a high accuracy. For ‘unexposed produce,’ the output is very sensitive to the octanol-water partition coefficient ( $K_{OW}$ ), which is used to estimate the organic carbon/water partition coefficient ( $K_{OC}$ ). Published physical-chemical properties of PCDD/Fs are highly variable, but recent attempts have been made to facilitate the selection of reliable data (Åberg et al. 2008). Since site-specific data on the organic carbon fraction on soil, represented by the *Foc<sub>s</sub>* parameter in the model, will improve the reliability of the unexposed produce output, it is recommended to perform site-specific measurements of this factor if risk scenarios include ingestion of root crops.

#### Conclusions

In our contaminated site case study, the CalTOX model calculated total WHO-TEQ concentrations of PCDD/Fs in exposure media that were in agreement with site-specific measurement data within a factor of 10 in all cases except for ‘exposed produce’ in the HL scenario. The large discrepancy for ‘exposed produce’ in the HL scenario is likely attributable to overestimation of transfer of PCDD/Fs adsorbed to soil particles to leaf surfaces. Only a small subset of all model parameters were found to be important for determining the calculated concentrations in exposure media. Several of these important parameters can be optimized for PCDD/Fs with further research; however, some are highly variable and site-specific, such as the *Rainsplash* parameter that describes transfer of soil to the surface of ‘exposed produce.’ The success of predicting food chain transfer, which is probably one of the most important model applications in risk assessments of PCDD/F-contaminated sites, also depends strongly on how well biotransfer factors (BTFs) for meat, milk, and eggs can be defined.

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