APPLICATION OF A HUMAN EXPOSURE MODEL IN A PCDD/F CONTAMINATED SITE CASE STUDY – EVALUATION OF MODEL PERFORMANCE AND ASSOCIATED UNCERTAINTIES

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Introduction

Although atmospheric deposition is generally the main source for PCDD/F contamination of food chains, other sources can be important at local and regional scales. The former production and use of chlorinated pesticides, such as chlorophenols (CP), is recognized as an important historical source of PCDD/F that has resulted in numerous hot spot sites. Because of strong bioaccumulation properties, soil to food chain transfer of PCDD/Fs is of major concern in human health risk. High costs for sampling and analysis and the large number of contaminated sites are, however, obstacles that prevent detailed site-specific exposure assessments. In such cases, multimedia fate and exposure modeling can usefully be applied to support the risk assessment[1,2].

The multimedia fate and exposure model CalTOX has earlier been applied for risk assessment of several hazardous compounds, such as organophosphorus pesticides[3], chlorinated hydrocarbons[4] and PCDD/Fs[2]. CalTOX models 23 different human exposure pathways, which are coupled to the fate of chemicals in seven connected environmental compartments. In a study that compared different modeling tools, Wiberg et al.[2] recommended that experimental biotransfer data should be used if CalTOX is applied to superhydrophobic substances such as PCDD/Fs. This is necessary because the default model algorithms estimate the food chain transfer using a linear relationship with the octanol-water partition coefficient (K_{OW}), which can overestimate uptake of substances with log K_{OW} >6 that have low bioavailability.

The current study reports on an application of CalTOX for 2,3,7,8-substituted PCDD/Fs in two contaminated site scenarios. The scenarios are based on a former saw mill site in northern Sweden that is heavily contaminated with PCDD/Fs[5]. Here, comparisons between model results and field data are used to evaluate model outputs and algorithms. Improvements in the agreement between model results and field data were achieved by adjusting the initial model parameterization, guided by a sensitivity analysis. The results are used to discuss the utility and credibility of CalTOX for human exposure assessments of contaminated sites, and highlight also the issue of contaminated soils as secondary source of PCDD/F to the local environment.

Materials and methods

The study site is a decommissioned saw mill and wood preservation facility in northern Sweden. The site was contaminated when chlorophenol (CP) preservatives were used for treatment of processed timber from the mid 1940s until closure. The past activities at the site have resulted in an extensive PCDD/F contamination of the soils in the area. The contamination is highly spatially heterogeneous, with levels ranging over several orders of magnitude (1 to 110 000 ng TEQ kg^{-1} d.w.)[5]. A previously created generic Swedish landscape in CalTOX[2] was modified to represent our study site using climate data from a nearby meteorological data station. Annual averages of temperature (282 K), wind speed (9.9 km h^{-1}) and precipitation (1.9 mm day^{-1}) were used.

Two modeling scenarios were defined, based on the PCDD/F contamination situation: *i)* a farm with moderate level soil contamination (2-25 ng WHO-TEQ kg^{-1} d.w.) and *ii)* a garden with high level soil contamination (~600 ng WHO-TEQ kg^{-1} d.w.). These two scenarios are referred to as the ML (moderate level) and HL (high level) scenarios. To represent long range transport of PCDD/Fs into the model domain, the model was calibrated with continuous air emissions so that the predicted air concentrations correspond to measured air concentrations at a rural site at the Swedish west coast[6].

Recommended values for the physical-chemical properties of ten of the seventeen 2,3,7,8-substituted congeners were taken from Åberg et al.[7]. For the remaining compounds, properties were estimated from quantitative structure-property relationships of these values[7]. All properties were temperature adjusted to the annual mean temperature of 282 K using enthalpies of phase change recommended by Åberg et al.[7]. Environmental half lives of the compounds were adopted from Sinkkonen and Paasivirta[8], and congener specific empirical cow´s milk and meat biotransfer factors (BTFs) were estimated by linear regression using data compiled by Rosenbaum et al.[9].

Site specific field data for evaluation of model outputs were available for 9 of 14 model outputs[5]. The field data included PCDD/F concentrations in samples collected near or at the farm (ambient air, grass, cow´s milk and egg from free-range chicken) and near or at the highly contaminated garden (ambient air, carrots, potatoes and grass). The performance of the model was assessed by calculating "deviation factors" for the model outputs, and these factors represent the ratio of the highest and lowest values for each pair of data (i.e. one predicted concentration and one field reference concentration for each congener). Sensitivity analysis of the model input parameters was carried out using the uncertainty and risk analysis software Crystal Ball.

Results and discussion

The predicted concentrations from the ML and HL scenarios agreed fairly well with the field measurements, generally showing deviation factors 2-4, with higher values only for 3 out of 9 comparison cases (Table 1).

Table 1. Predicted exposure media concentrations in the moderate level (ML) and high level (HL) scenarios and corresponding field data (WHO-TEQ)[5], together with calculated deviation factors.

	Air	**Above-ground plants**		**Below-ground**	**Milk**	**Meat**	**Egg**
		Exp. produce	Total leaf	Unexp. produce			
	fg m^{-3}	ng kg^{-1}	ng kg^{-1}	ng kg^{-1}	ng kg^{-1}	ng kg^{-1}	ng kg^{-1}
Predicted, ML	5.8	0.14	0.13	0.00047	0.10	0.057	0.041
Field concentration	13[a]	0.082[b]	0.082[b]	-	0.016[c]	-	0.35[h]
Deviation factor[i]	**2(-)**	**2(+)**	**2(+)**	**n.a.**	**6(+)**	**n.a.**	**9(-)**
Predicted, HL	8.9	1.5	0.20	0.061	0.96	0.98	2.4
Field concentration	25[d]	0.082[e]	0.082[e]	0.097[f]/0.25[g]	-	-	-
Deviation factor[i]	**3(-)**	**18(+)**	**2(+)**	**2(-)/4(-)**	**n.a.**	**n.a.**	**n.a.**

[a]sampled at farm; [b]grass from the contaminated garden (52% water); [c] 5% fat; [d]sampled at the hot spot close to the contaminated garden; [e]grass from the contaminated pasture (79% water); [f]potatoes; [g]carrots; [h]assuming 10% fat in whole egg; [i]calculated as the ratio of the highest and lowest value for each pair of data, (+)- and (-)-signs indicate whether it was over- or underestimations; n.a.= not applicable since corresponding field measurements were not available; Exp. produce = exposed produce in the model, represents contamination of above-ground plant parts via particle adherence; Total leaf = total leaf in the model, represents contamination of above-ground plant parts via gaseous uptake from air; Unexp.produce= unexposed produce in the model, represents below-ground plant parts

Despite the introduction of a highly contaminated soil in the HL scenario, total leaf concentrations (gaseous contamination of above-ground plant parts) were only slightly elevated as compared to the ML scenario (Table 1), indicating that leafy vegetables grown at a CP contaminated site will not be a significant source of exposure for humans living in the area as long as soil particles are rinsed away. However, in high level contamination scenarios, soil splash and other particle contamination will become important, as illustrated by large difference between modeled total leaf and exposed produce concentrations in the HL scenario. The contribution from soil and dust particles on leaf surfaces is difficult to estimate as it depends on several site-specific variables. The contribution from particle pollution is therefore a source of high uncertainty in model assessments.

The modeled outputs for below-ground (unexposed) plant parts were 2 and 4 times lower than concentrations in potatoes and carrots grown at the study site (Table 1). It is possible that the treatment of the field samples is the reason for the higher field values. The root crops were washed but unpeeled prior to analysis, which means that pollutants accumulated in the peel were included in the field concentration. Additionally, it is possible that some of soil particles were not washed away, resulting in apparently high concentrations.

The 6-fold overestimation of PCDD/F in milk may be related to uncertainties in real soil concentrations and estimated BTFs, as well as to overestimation of dioxin concentrations in above-ground plant parts (Table 1). Despite this, the model simulated the risk scenario at the study site reasonably well and suggested that the TEQ concentrations in cow´s milk would have been at least 10 times higher if the milk was produced at contamination levels corresponding to the HL scenario.

The modeled WHO-TEQ concentration in eggs of the ML scenario was 9 times lower than the field data (Table 1). One major uncertainty is the soil ingestion rate for free range chickens, which is highly variable. In contrast to other exposure media, the modeled and measured congener patterns for egg showed pronounced disagreements. This confirms a low credibility of the model output in this application. An underestimated soil ingestion rate can only partly explain the difference, since the disagreement was larger for PCDFs than for PCDDs. A parameter that probably introduced even higher uncertainty is the default biotransfer algorithm of CalTOX. This was used since experimental BTF data was lacking.

Considering that soil is assumed to be a major source for PCDD/Fs in free range eggs, empirical egg/soil concentration ratios can be used as a simple model to assess the risk for human exposure. Such ratios (expressed as pg TEQ g fat^{-1} in egg / pg TEQ g^{-1} d.w. in soil) were calculated using data from a number of studies (*n*=41)[5,10-12] .The ratios range from 0.4 to 26, with a median value of 1.9 The large ratio span illustrates that PCDD/Fs may be transferred from soil to egg in a highly variable manner. The highest ratio was considered as a non-representative outlier, and after exclusion, the mean ratio was found to be 2.4.

The introduction of the highly contaminated soil in the HL scenario increased the modeled ambient air concentrations by 50% compared to the ML scenario, due to volatilization and resuspension from the ground. Field data also indicated higher concentrations in air close to the hot spot compared to the farm. Despite many uncertainties in air measurements, these results indicate that the local ambient air may be affected by the contaminated soil at the study site. Similarities between modeled congener patterns of total leaf and grass from the study site supported the hypothesis that volatilization of PCDD/F from soil at the contaminated study site is likely.

The sensitivity analysis showed that only a sub-set of all model parameters were found to be important for the outputs in this exercise. Several of them can be optimized for PCDD/Fs, while others are truly site specific or linked with high uncertainty. 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, depends mostly on how well the biotransfer factors can be defined. This call for a better understanding on how these processes should be described.

Our study shows that if there is a limited understanding of the fate of PCDD/Fs in a real-world application, model calculations may generate results that are erroneous and the risk for misinterpretation by the model users is high. On the other hand, if the model performance has been tested with field data from contaminated sites, model calculations can successfully support other risk assessment and thereby improve the quality of the decision process.

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