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Validation of the VOLASOIL model using air measurements from Dutch contaminated sites
Concentrations of four chlorinated compounds

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Het rapport in het kort

Validatie van het VOLASOIL model met luchtmetingen van verontreinigde locaties in Nederland
Concentraties van vier gechloreerde verbindingen

Uit deze studie bleek het VOLASOIL model goed bruikbaar om bij bodemverontreiniging met tetrachlooretheen en trichlooretheen de binnenluchtconcentratie in te schatten. Voor verontreiniging met de afbraakproducten cis-dichlooretheen en vinylchloride is het model waarschijnlijk ook bruikbaar, maar dit kon minder goed worden vastgesteld omdat veel concentraties beneden de detectielimiet lagen. VOLASOIL is een model dat op basis van metingen in verontreinigd grondwater (door vluchtige stoffen), de gerelateerde binnenluchtconcentratie in gebouwen inschat. In dit onderzoek is gekeken naar de toepasbaarheid van VOLASOIL voor de risicobeoordeling voor vier gechloreerde verbindingen. Er is een aantal aanpassingsvoorstellen gedaan om de voorspelling van het model te verbeteren. Zo is gebleken dat VOLASOIL voor deze vier stoffen vaak te hoge luchtconcentraties voorspelt, vooral op sterk verontreinigde locaties. Aangezien het model echter vooral wordt gebruikt om de risico's voor de mens in te schatten en om te zien of meer metingen noodzakelijk zijn, is een beperkte overschatting door het model juist gewenst en zijn aanpassingen niet noodzakelijk. Mocht van het model worden verwacht dat het binnenluchtconcentraties zo nauwkeurig mogelijk inschat, dan zijn de voorgestelde aanpassingen wel gewenst.

Trefwoorden: VOLASOIL; validatie; binnenlucht; bodemlucht; grondwater; bodemverontreiniging

Abstract

Validation of the VOLASOIL model using air measurements from Dutch contaminated sites
Concentrations of four chlorinated compounds

The study reported here has shown the VOLASOIL model to be very useful for estimating the indoor air concentrations of the pollutants, tetrachloroethene and trichloroethene. The model is probably also useful for the degradation products, cis-dichloroethene and vinylchloride, but this was more difficult to determine with any certainty since many of the concentrations are lower than the detection limit. VOLASOIL is a model that estimates the contamination of indoor air in buildings in relation to measurements based on water contaminated by volatile substances.This investigation was more concerned with the applicability of VOLASOIL for four chlorinated compounds in the Netherlands, and resulted in several recommendations for model adjustment. For example, VOLASOIL was found, in the case of the four compounds, to often predict concentrations that were too high, especially in the seriously polluted areas. Considering, however, that the model is used to estimate risks to humans and to ascertain if more measurements are necessary, limited overestimation by the model is all right, making adjustments unnecessary. The proposed adjustments will be desirable if the model needs to be able to predict concentrations as accurately as possible.

Key words: VOLASOIL; validation; indoor air; soil air; groundwater; soil contamination

Preface

The site specific human risk assessment on contaminated soil is carried out in order to determine the urgency for remediation. In order to improve the methods for this risk assessment, the Directorate General for the Environment commissioned the National Institute for Public Health and the Environment (RIVM) to carry out a project on the improvement of the site specific human risk assessment. Amongst others, special attention was given to validation of the risk assessment of volatile compounds.

This report gives the results of a validation study on the modelling of (indoor) air concentrations based on groundwater measurements. First, we would like to thank all the people who have selected suitable cases, which made it possible to perform this study. These cases were obtained from Tauw, Grontmij, Royal Haskoning, DHV, Consultancy of 'Gemeentewerken Rotterdam' , Tebodin, Witteveen & Bos and the municipality of Hilversum.

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Finally, we would like to thank the members of an expert group on volatile compounds who were asked to comment on the study and to give recommendation for the improvement of the risk assessment: Andi Mayer (Mayer Milieuadvies), Jaap Tuinstra (Royal Haskoning), Job Schreuder (DHV), Jeroen Provoost (VITO, B), Jeroen ter Meer (TNO), Michiel Waitz (Tauw), Joost Bakker, (RIVM). We also owe gratitude to two reviewers for their critical comments on the draft report: Job Spijker (RIVM) and Frank Swartjes (RIVM).

Contents

Samenvatting

Dit rapport bevat een vergelijking tussen wat het VOLASOIL model voorspelt aan binnenluchtconcentraties van vluchtige stoffen en wat er in een aantal praktijkgevallen is gemeten. Met deze vergelijking kan worden bekeken in hoeverre het model overeenkomt met de metingen en welke factoren de verschillen zouden kunnen verklaren. Verder zijn er aanbevelingen gedaan om het model te verbeteren. De belangrijkste conclusie van het onderzoek is dat het model de luchtconcentratie van tetrachlooretheen en trichlooretheen in het algemeen redelijk goed voorspelt. Het model voorspelt echter minder goed bij hoge en zeer lage grondwaterconcentraties, dus in sterk verontreinigde gebieden en in gebieden waar de concentratie dicht bij de detectielimiet ligt. Op sterk verontreinigde locaties schat het model de luchtconcentratie te hoog in ten opzichte van de metingen, terwijl het op licht verontreinigde locaties de concentratie te laag inschat. Dit hoeft geen probleem te zijn als uitgegaan wordt van een ‘worst-case’ scenario, omdat de werkelijke concentraties in sterk verontreinigde locaties nooit hoger zullen zijn dan op basis van het model wordt voorspeld. Als echter een zo realistisch mogelijke luchtconcentratie moet worden berekend, dan zou een aanpassing van het model gewenst zijn. Er worden in dit rapport een aantal factoren behandeld die van belang zijn bij het gebruik van dit model. Zo kan afbraak in de bodem een belangrijke rol spelen, is de heterogeniteit in de bodem en het grondwater van belang en is het type gebouw en het seizoen van invloed op de uitkomst. Met al deze factoren moet rekening worden gehouden om een goede risicobeoordeling te kunnen doen. Op basis van de conclusies en bespreking van de resultaten met deskundigen zijn aanbevelingen gedaan voor aanpassing en gebruik van het model.

1. Introduction

1.1 Background

This study is carried out to support the improvement of the site specific human risk assessment of groundwater contamination. The risk assessment should help to determine the need for remediation as a result of groundwater pollution.

For the risk assessment of volatile compounds in soil and groundwater, human exposure models are used to estimate the concentrations in indoor air. In the current remediation urgency method (in Dutch: 'Saneringsurgentie systematiek': SUS (Koolenbrander, 1995)), the CSOIL model is used. Also, the VOLASOIL model (Waitz *et al*., 1996) is developed and in use since 1996. The VOLASOIL model was specifically developed to carry out site specific risk assessment of volatile compounds in groundwater. The current (revised) CSOIL model (Otte *et al*., 2001) is similar to the VOLASOIL-model. The VOLASOIL model will be briefly described in chapter 2.

The intended new Dutch soil policy includes a (further) shift to fitness for use (VROM, 2003). This means that the site specific risk assessment will gain importance. In Lijzen *et al*. (2003) objectives were defined for further improvement of the site specific risk assessment. One part of the human risk assessment is the exposure to soil and groundwater contamination with volatile compounds. Lijzen *et al*. (2003) describes the limitations concerning the methodology within the evaluation of the SUS, with a focus on the site specific risk assessment for humans and for contaminant migration. Based on interviews with experts and earlier evaluations of the method, the main limitations were indicated as:

a) Uncertainty about the methodology of human risk assessment for inhalation of indoor air.
b) A Lack of human risk assessment of volatile compounds in buildings with a slab-on-grade floor (a concrete floor directly on the soil, with no crawl space or cellar).
c) Comparison of results from model calculations versus measurements.
d) A lack of pragmatic guidelines for additional measurements (bioavailability, indoor air).

1.2 Goal and Method

In order to improve the quality of the assessment it is necessary to get more insight in the uncertainties of the risk assessment of volatile compounds. A study to identify the differences between modelled and measured air concentrations in buildings was carried out. Although the practical experience was that in general the model seems to overestimate the air concentrations, no systematic validation or verification of the model was available. The goal of this study is to get an indication of the amount of uncertainty of the model predictions in relation to measurements. To achieve this, the model is verified with actual measured field data, which is described in this report. Besides knowledge about differences and similarities of predicted and measured concentrations, factors were identified that may cause these differences. The results of this study have lead to recommendations on the improvement of the model, the use of the model and/or the use of measurements.

The following topics will be dealt with:
1) What is the effect of uncertainty/variability in model-input parameters on the variability of predicted air concentrations, and how does this relate to the measured variability of air concentrations?
2) How do measurements of air concentrations relate to calculated concentrations for several cases in the Netherlands?
3) How do the measured and calculated ratios of concentrations in different air compartments relate to each other (e.g. the ratio of indoor air and crawl space air concentration)?
4) What can explain the observed differences between measured and calculated concentrations and ratios?

Two approaches are used. To obtain a first impression of systematic differences between measured and calculated concentrations, a general approach was used. Variability in predicted indoor-air concentrations is quantified by varying the most relevant model-input parameters based on literature and field data. The overall model-output distributions of air concentrations were compared to the measured air distributions of the selected cases.

In the second approach, a more site specific analysis was done in order to quantify and explain whether measurements at certain sites differ more from predictions than at other sites.

In chapter 2 a short description of the VOLASOIL model is given.
Chapter 3 describes how the calculations and the interpretation of the measurements was carried out for the two approaches.
Chapter 4 gives the generic and the site-specific results.
The results are discussed in chapter 5 and the possible sources of the observed differences are described.

2. The VOLASOIL model

The VOLASOIL model was developed in 1996 and is described in detail by Waitz *et al*. (1996). Based on the CSOIL model, the volatilisation in VOLASOIL from groundwater to indoor air was adapted to perform more site specific risk assessments.

The VOLASOIL model is developed to estimate the actual human risk for volatile compounds. Calculation with this model is often combined with measurements in the indoor and crawl-space air, when the calculations indicate that the Tolerable Concentration in Air (TCA) is exceeded.
The following steps can be distinguished in the model:

- Calculation of the concentration in soil air (for different contamination scenario's);
- Calculation of the flux to the crawl space;
- Calculation of the crawl space air concentration;
- Calculation of the flux from the crawl space to the indoor air;
- Calculation of the indoor air concentration.

In the following paragraph these steps are explained.

2.1 Main concept and distribution over the soil phases

2.1.1 Assumptions and fluxes

The VOLASOIL model is based on stationary transport and has, to some extend, the same assumptions and limitations as the CSOIL module:

- no biological degradation is included;
- the contaminant source in a soil is considered inexhaustible;
- the soil is assumed to be homogeneous;
- equilibrium sorption at the depth of the contamination, but above this, no (non-equilibrium) sorption is assumed;
- no lateral transport or leaching is considered.

A distinction has been made between the groundwater, the full capillary zone and the open capillary zone, separated by the groundwater table and the capillary transition boundary, CTB, respectively (Figure 2.1). Two important transport processes are modelled in the open capillary zone:

- diffusion in soil air.
- pressure driven vapour flow.

Diffusion and dispersion in pore water, and the convective transport by water flow are the most important transport mechanisms below the CTB.

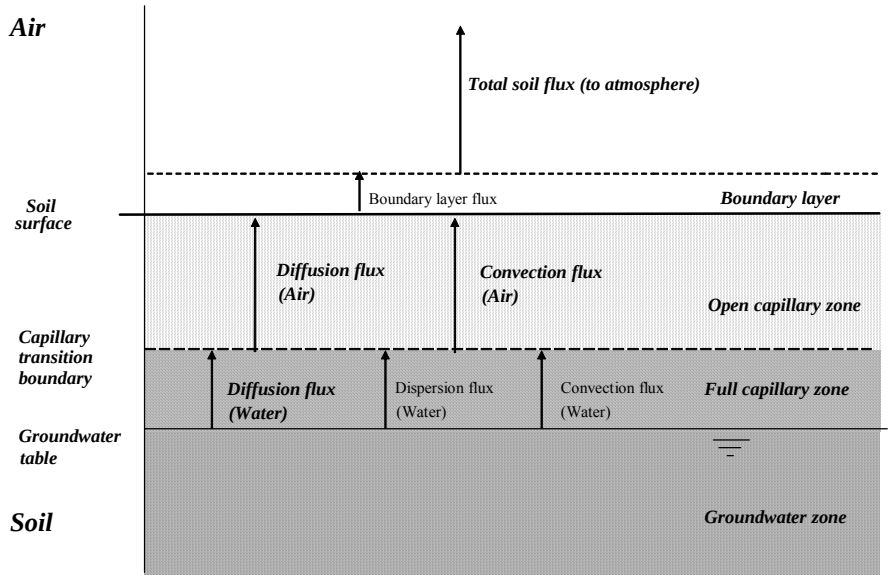


Figure 2.1 Zones and fluxes in the soil within VOLASOIL. The fluxes in bold are incorporated in VOLASOIL.

Eight options can be distinguished in VOLASOIL. Option A (groundwater contamination, well-mixed container) is the basic scenario and is closest to the assumptions within the CSOIL module. Within VOLASOIL the depth of the groundwater table can be changed, just like other site specific parameters. For the calculations of fluxes to the soil surface it is important to know the height of the CTB above the groundwater table. For the 18 soils of the Staring series (Wösten *et al*., 1994) the CTB lies between 12 and 84 cm. The arithmetic mean for all soils is 50 cm, just like for sandy soil. More details can be found in Waitz *et al*. (1996).

Soil air concentration
The concentration in the soil air at the capillary transition boundary is calculated by:

$$C_{sa} = K_{lw} \cdot C_{sw} \qquad (1)$$

C_{sa} :	soil-air concentration	[g/m^3]
K_{lw} :	air-water distribution coefficient or dimensionless Henry constant [(mol/m^3 air)/(mol/m^3 water)]	[-]
C_{sw} :	soil-moisture concentration	[g/m^3]

The soil air concentration at other depths can be calculated also. It is assumed that the measured groundwater concentration and the soil moisture concentration are equal. The dimensionless Henry constant (K_{lw}=H/R·T) is normalised for the average soil temperature of 10ºC.

2.1.2 Flux from soil to crawl space

Two fluxes are calculated in the open capillary zone:

- diffusion in soil air (diffusive transport).
- pressure-driven vapour flow (convective transport).

The *diffusion flux* is described as:

$$Jd_{ss} = D_{sa} \frac{C_{sa}}{L_s} \quad (2)$$

Jd_{ss} :	diffusion flux from soil to soil surface	[g/m^2 h]
D_{sa} :	diffusion coefficient in the soil air	[m^2/h]
C_{sa} :	concentration in soil air at dp (depth of contaminant)	[mol/dm^3 or g/m^3]
L_s :	magnitude of soil column (= dp-dc; average depth of contaminant - depth of crawl space below soil surface)	[m]

The average depth of the contaminant (dp) is assumed to be equal with the CTB. The diffusion coefficient in soil air (D_{sa}) is derived from the diffusion coefficient in free air (D_a, based on the molecular weight), the volume fraction of soil air (V_a) and volume fraction of pore water (V_w). These are identical to the calculated parameters in CSOIL.

Second, the *pressure-driven air flow* in VOLASOIL is described as:

$$Fsc = K_s \frac{\Delta p_{cs}}{L_s} \quad (3)$$

Fsc :	air flux from soil to crawl space	[m^3/m^2.h]
K_s :	air conductivity of soil	[m^2/Pa.h]
ΔP_{cs} :	air pressure difference between crawl space and soil	[Pa]
L_s :	magnitude of soil column (= dp-dc; average depth of contaminant - depth of crawl space below soil surface)	[m]

The factor K_s, the air conductivity, depends on the air permeability (κ) and the dynamic viscosity of air (η):

$$K_s = \frac{\kappa}{\eta} \quad (4)$$

The air permeability of different soils is found in several references with a range of 10^{-10} - 10^{-16} m^2, from coarse sand to clay (Waitz *et al.*, 1996).

The *total contaminant flux* to the crawl space is a combination of the convective flux and the diffusive flux, which are closely related. Therefore one equation is derived from the equations for diffusion and convection. With a negligibly low concentration (zero) at the surface (C_0) as an upper boundary condition, the flux from soil to crawl space (J1) is described by:

$$J1 = \frac{-Fsc \cdot C_{sa}}{\exp\left(\frac{-Fsc}{D_{sa}} L_s\right) - 1} \quad (5)$$

J1 :	total contaminant flux from soil to crawl space	[g/m^2.h]
Fsc :	air flux from soil to crawl space	[m^3/m^2.h]
C_{sa} :	concentration in soil air at dp	[mol/dm^3 or g/m^3]
L_s :	magnitude of soil column (= dp-dc; average depth of contaminant - depth of crawl space below land surface)	[m]
D_{sa} :	diffusion coefficient in soil air	[m^2/h]

2.1.3 Crawl space air concentration

The concentration in the crawl space can be calculated from the total contaminant flux from soil to crawl space, the air-exchange rate and the volume of the crawl space, (assuming that the surface area of the crawl space is equal to that of the floor):

$$C_{ca} = J1\frac{A_f}{V_c \cdot vv_c} \tag{6}$$

C_{ca} :	concentration in crawl-space air	[g/m^3]
J1 :	total contaminant flux from soil to crawl space	[g/m^2.h]
A_f :	surface area of floor	[m^2]
V_c :	volume of crawl space	[m^3]
vv_c :	air-exchange rate of crawl space	[h^{-1}]

The air-exchange rate (vv_c) used in VOLASOIL was measured by Fast *et al*. (1987) with a geometric mean of 1.05 h^{-1}.

2.1.4 Flux from crawl space to indoor air

Within VOLASOIL, an air flux is derived for the flux from the crawl space through the gaps, cracks and holes in the floor. This air flux (Fci) can be estimated by:

$$Fci = \frac{{f_{of}}^2}{n\pi \cdot 8\eta}\frac{\Delta p_{ic}}{L_f} \tag{7}$$

Fci :	air flux from crawl space through floor to indoor space	[m^3/m^2.h]
f_{of} :	fraction openings in the floor	[m^2/m^2]
η :	dynamic viscosity of air	[Pa.h]
n:	number of openings per floor area	[m^{-2}]
Δp_{ic} :	air pressure difference between indoor space and crawl space	[Pa]
L_f :	floor thickness	[m]

The contaminant flux to the indoor air can be estimated as follows:

$$Jc_{ci} = Fci \cdot C_{ca} \tag{8}$$

Jc_{ci} :	convective flux from crawl space to indoor air space	[g/m^2.h]
Fci :	air flux from crawl space to indoor space	[m^3/m^2.h]
C_{ca}:	concentration in crawl-space air	[g/m^3]

2.1.5 Indoor air concentration

The indoor air concentration can be calculated from the total contaminant flux from soil to crawl space, the air-exchange rate and the volume of the crawl space, (assuming that the surface area of the crawl space is equal to that of the floor):

$$C_{ia} = Jc_{ci}\frac{A_f}{V_i \cdot vv_i} \tag{9}$$

C_{ia} :	indoor air concentration	[g/m^3]
Jc_{ci} :	total contaminant flux crawl space to indoor space	[g/m^2.h]
A_f :	surface area of floor	[m^2]
V_i :	volume of indoor space	[m^3]
vv_i :	air-exchange rate of indoor space	[h^{-1}]

The calculation of human exposure is not a part of VOLASOIL; the calculated air concentration is compared with the TCA (Tolerable Concentration in Air) (Waitz *et al*., 1996).

3. Methods

3.1 Cases described

In total 18 cases were selected for the verification (Table 3.1). Four substances were used for this analysis: tetrachloroethene (PER), trichloroethene (TRI), cis-1,2-dichloroethene (CIS) and vinylchloride (VC). BTEX was not selected, since it was measured in a few cases only. The sites are located in several parts of the Netherlands. Not all substances and compartments (indoor, crawl space- and soil-air) were measured at all sites. Also, the number of samples per case differed and the date of sampling was not the same between and within cases. For instance, in case 21, groundwater was sampled in 1998, whereas soil air was sampled in 1996 and indoor air was sampled in 2000. The main soil type was sand, but some sites were located on clay or peat. The groundwater table varied between 0.8 meter in case 10, and 11 meter in case 12. Some houses had a cellar, whereas others had a crawl space. The type of floor varied between wood and concrete.

The main concern for the data of each case was not only the differences in methodology between cases and the lack of information, but mainly the linking of groundwater measurements with air measurements. In order to be able to compare the measured and calculated air concentrations, corresponding groundwater concentrations were needed as input for VOLASOIL. Therefore, the groundwater wells closest to the locations of the air measurements were selected and used for the verification. At first we selected the wells within 5 meter distance. If there were no wells within this distance, a distance of 10 meter was used. If there were still no wells within 10 meter distance, wells within 25 meter distance were selected. This occurred only once. The data from the most shallow groundwater measurements were used for the analyses.

Table 3.1 Description of the selected cases, where No. = the number of measurements.

General info						Houses			Air measurements						Groundwater measurements			Soil measurements	
									soil air		crawlspace air		indoor air						
Case nr	VC	Cis	Tri	Per	Location	number of houses measured	basement type	floor material	No.	date	No.	date	No.	date	No.	date	depth (m)	organic matter content	soil type
01		x	x	x	Zwanenburg	18	crawlspace	wood	-	-	12	Jun 2000	9	Jun 2000	24	1998-2000	1.5	?	sandy soil; moderately coarse with peat and clay underneath
02	x	x	x	x	Terneuzen	2	crawlspace	wood	2	Sep 2002	2	Sep 2002	2	Sep 2002	1	Jun 2002	2.58	0.2-2 %	clay until 2-3 m deep
03	x	x	x	x	Uithuizen	1	?	wood	-	-	4	Feb/Aug 1995	4	Feb/Aug 1995	5	1996	1.6-2.7	0.50%	sandy soil, very fine, locally sandy clay
04				x	Zwolle	2	crawlspace	wood	-	-	2	Feb 1996	2	Feb 1996	1	1992	1.8	?	sandy soil
06	x	x	x	x	Deventer	-	-	-	20	Feb 2003	-	-	-	-	8	2003	3.15-5.78	?	sandy soil: fine to moderately coarse
09				x	Den Haag	1	cellar	concrete	-	-	1	Aug 2003	1	Aug 2003	2	Jan 2002	2	2%	sandy soil, fine to moderately coarse until 10 m deep
10	x	x	x	x	Leiden	2	cellar	concrete	-	-	2	Jun 2003	2	Jun 2003	4	Dec 2002	0.8	3%	silt to fine sand 0-1 m, clay 1-2 m
12		x	x	x	Hilversum	15	cellar	wood	37	Aug 1997 and Oct 2002	40	1998-2004	31	1998-2004	18	1997, 1998, 2002	11	0.20%	sandy soil
14	x	x	x	x	Rotterdam	3	crawlspace	?	1	Jul 1996		Nov 1996		Nov 1996	2	Apr 1996	1	0.44% - 1 %	upper 3 meter sandy soil (also with lumps of clay/peat); clay/peat (from 3 m until 17 m deep).
15	x	x	x	x	Rotterdam	1; 5 sites	crawlspace	concrete	1	Sep 1998		Sep 1998		Sep 1998	7	1998-1999	1.8	1.5% in sandy soil; 13% in clay; 70% in peat	sandy soil until 2 m deep; clay/peat underneath
16	x	x	x	x	Rotterdam	1	crawlspace	?	-	-	1	July 2002	-	-	1	?	1-1.5	1.1 % in sandy soil, 30-80% in clay and peat	upper 3 meter sandy soil (also with clay/peat); clay/peat (from 3 m until 17 m deep).
17		x	x	x	Rotterdam	1	crawlspace	concrete	-	-	1	Aug 2002	1	Aug 2002	1	Oct 2001	1.8	1-3 % in upper layer. 6 % underneath	sandy soil until 2 m deep; clayey soil underneath
18	x	x	x	x	Rotterdam	-	-	-	2	Mar 2002	-	-	-	-	3	7-1-2000 and 19-2-2002	1.3	3%	upper 2 meter sandy soil (also with lumps of clay/peat); clay/peat (from 3 m until 17 m deep).
19		x	x	x	Oldenzaal	1; 2 sites	crawlspace	concrete	-	-	2	Apr 2002	2	Apr 2002	1	Dec 2001	1	2%	sandy soil until 2 m, silt and clay underneath
20	x	x	x	x	Rotterdam	2	-	concrete on sand	-	-	-	-	2	Mar 2001	11	Dec 1999	1.2	1.50%	moderately coarse silty sand until 3 m deep; peat underneath
21			x	x	Venray	1	cellar (2 m deep)	concrete 50 cm thick	1	Nov 1996	1	May 2000	1	May 2000	1	Mar 1998	4.5	1.70%	silt - fine sand
22		x	x	x	Hilversum	4	cellar	probably concrete	4	Oct 1994	16	Dec 1993	14	Dec 1993	13	1998 and 2002	4.3	< 1 %	moderately fine sand until 3 m deep; moderately to very coarse sand with gravel underneath
23				x	Hilversum	7	crawlspace	wood; concrete at one house	7	Sep 2001	6	Aug-Oct 2002	3	Aug-Oct 2002	10	Jan 2001	3.6	?	moderately fine sand until 3 m deep; moderately to very coarse sand

Table 3.1 Description of the selected cases (continued).

General info						Miscellaneous				
Case nr	VC	Cis	Tri	Per	Location	distance house to groundwater measurements	pollution also in unsaturated zone?	measurement method indoor air	other	remarks
01		x	x	x	Zwanenburg	5-10 meter	yes, also in groundwater	diffusion badges	Area with upward seepage. When it rains, drainage may occur	Horizontal flow of groundwater is approximately 2 m per year in a South to Southwest direction
02	x	x	x	x	Terneuzen	10-15 meter	?	active carbon		
03	x	x	x	x	Uithuizen	5-10 meter	yes, also in groundwater	active carbon	Degradation from tetrachloroethene towards vinylchloride took place	widely spread pollution
04				x	Zwolle	5-10 meter	?	active carbon	Degradation from tetrachloroethene towards vinylchloride took place	Concentration Per in groundwater in 1996 has dropped to approximately a third of the concentration in 1992
06	x	x	x	x	Deventer	?	?	mobile GC		
09				x	Den Haag	5 meter	no, from groundwater	active carbon	Dune area with infiltration. Aerobic conditions, few degradation products found. In deeper layers, more degradation takes place, but not beyond Cis.	
10	x	x	x	x	Leiden	5-10 meter	?	active carbon	Potentially, a high degree of degradation	
12		x	x	x	Hilversum	1-10 meter	yes, also in groundwater	active carbon, mobile GC, badges	Soil air permeability is high, no degradation observed	
14	x	x	x	x	Rotterdam	5-10 meter	yes, also in groundwater	active carbon	Degradation from tetrachloroethene towards vinylchloride has taken place	Soil air was measured at 0.7 meter deep
15	x	x	x	x	Rotterdam	5 meter	yes, also in groundwater	mobile GC	Probably anaerobic circumstances, which makes degradation likely. Pollution has entered the soil as Per and Tri. Cis and VC are degradation products.	Pollution source underneath the house
16	x	x	x	x	Rotterdam	5-10 meter	?	?	Very little information available	Very little information available
17		x	x	x	Rotterdam	5 meter	?	active carbon	Very little information available	Crawl space is very small
18	x	x	x	x	Rotterdam	5-10 meter	yes, also in groundwater	tenax for soil air	Probably anaerobic circumstances	Soil polluted between 3 and 5 m
19		x	x	x	Oldenzaal	2.5 - 5 meter	yes, also in groundwater	active carbon	Degradation from tetrachloroethene towards vinylchloride took place	Polluted area underneath private and business property
20	x	x	x	x	Rotterdam	5 meter	no, from groundwater	active carbon	Biological degradation is taking place due to high groundwater level (anaerobic) and high microbiological activity.	Pollution source at 20 m distance; pollution probably adsorbed on the peat.
21			x	x	Venray	< 15 meter	no, from groundwater	active carbon	Situated at +26 m NAP (Dutch Ordnance Level); Few degradation products found.	No holes in the floor
22		x	x	x	Hilversum	10 meter	no, from groundwater	?	No degradation products found; aerobic conditions in the environment.	Business area
23				x	Hilversum	10 meter	no, from groundwater	active carbon	No degradation products found; aerobic conditions in the environment.	Low concentration in groundwater

3.2 Generic approach

3.2.1 Sensitivity and uncertainty analyses

Both sensitivity and uncertainty analyses were performed in order to get insight in the model behaviour and in the importance of input parameters. A sensitivity analysis shows the effect of changes of input variables on model predictions, whereas uncertainty analysis shows the importance of the input uncertainties in term of their relative contributions to uncertainty in the outputs (Morgan and Henrion, 1990).

For the sensitivity analysis, all parameters that are described in Tables 3.2 and 3.3 are varied one at a time by ± 2 % around the mean (tetrachloroethene was the substance). A uniform distribution is used for all parameters. A Monte Carlo sampling method is used with 200 runs, using the Crystal Ball add-in of Excel. The output air concentrations are correlated to each parameter and a Normalized Regression Coefficient (NRC) is calculated:

$$NRC = \frac{\Delta y}{\bar{y}} / \frac{\Delta x_i}{\bar{x}_i}$$

Where $\bar{y}$ is the mean output air concentration and $\bar{x}_i$ is the mean input parameter i that is varied with Δx_i, resulting in Δy. The advantage of the NRC is that it is independent of the scale or dimension of the input parameters (Janssen *et al*., 1992). It shows the relative change of the model output due to a relative change of a model input.

The uncertainty analysis was performed with a Monte Carlo sampling method, using input uncertainties and distributions that are described in Tables 3.2 and 3.3 for all substances. The 'sensitivity analysis' option in Crystal Ball was used. It shows the relative contribution of each input variable to the output variance. The output uncertainty depends on the sensitivity of the input parameter (see sensitivity analysis) and on the amount of variability of the input parameter.

Table 3.2 Compound specific uncertainty and the type of distribution that was used for the Monte Carlo analysis with all cases together. L=Log-Normal, VP= Vapour pressure (Otte et al., 2001), SOL = Solubility (Otte et al. 2001), Csw = Groundwater concentration (derived from case-data), dg = Depth of groundwater table (derived from case-data).

		tetrachloroethene	trichloroethene	cis-dichloroethene	vinylchloride
VP	Distribution	L	L	L	L
	Mean	2500 Pa	9900 Pa	27000 Pa	352196 Pa
	95th percentile	2666 Pa	10029 Pa	33000 Pa	381339 Pa
SOL	Distribution	L	L	L	L
	Mean	0.9 mol/m^3	8.4 mol/m^3	36.1 mol/m^3	30.5 mol/m^3
	95th percentile	2.9 mol/m^3	11.2 mol/m^3	79.4 mol/m^3	44.2 mol/m^3
Csw	Distribution	L	L	L	L
	Mean	0.7 g/m^3	$3.9 \cdot 10^{-3}$ g/m^3	0.02 g/m^3	$1.7 \cdot 10^{-3}$ g/m^3
	95th percentile	33.7 g/m^3	0.3 g/m^3	6.25 g/m^3	$2.8 \cdot 10^{-2}$ g/m^3
dg	Distribution	L	L	L	L
	Mean	5.1 m	3.2 m	2.6 m	2.5 m
	95th percentile	11.0 m	11.0 m	11.0 m	5.7 m

Table 3.3 Soil and house specific uncertainty used in VOLASOIL, taken from literature. The type of distribution that was used is given as T for a Triangular distribution and as L for a Lognormal distribution. Ranges are given as minimum and maximum. For more details, see Appendix 1.

Parameter	Type	Mean	Range	Remarks
Soil specific				
kappa (air permeability of soil)	T	$3.16 \cdot 10^{-12}$ m^2	1.10^{-12} - 1.10^{-11}	
Va (volume fraction air in soil)	L	0.2	0.1 – 0.3	correlated with Vs
Vs (volume fraction solids in soil)	L	0.6	0.4 – 0.8	correlated with Va
House specific				
vri (ventilation rate indoor space)	T	75 m^3 h^{-1}	25 – 150	
vrcb (basic ventilation rate crawl space)	T	24 m^3 h^{-1}	8 – 48	
Δ Pcs (air pressure difference crawlsp. – soil)	T	2 Pa	0 – 6	
Δ Pic (air pressure difference indoor – crawlsp.)	T	2 Pa	0 – 6	
Aof (total area of floor openings)	T	0.0005 m^2	0.00005 – 0.005	
Lf (floor thickness)	T	0.1 m	0.05 – 0.2	
Af (floor surface area)	T	50 m^2	30 - 100	

3.2.2 Monte Carlo Analyses

A Crystal Ball simulation was done in the VOLASOIL model (version 1.9), where uncertainty/variability in the available input-parameters was introduced for tetrachloroethene (per), trichloroethene (tri), cis-dichloroethene (cis) and vinylchloride (Tables 3.2 and 3.3). Figure 3.1 gives an idea of how the VOLASOIL spreadsheet version 1.9 is set up. The grey cells are the parameter values that were made variable. The Monte Carlo sampling method was used with 1000 runs. A cumulative distribution of the calculated soil air, crawl space air and indoor air concentration was generated. These distributions were compared with the cumulative distributions of the measured air concentrations. This approach may give a first indication of the systematic differences between measured and calculated air concentrations for all substances. For a detailed description of the variability in each input-parameter value, see Appendix 2.

A log-normal distribution was used when data were abundant, or when this distribution was previously used for the same parameter in the literature. Otherwise, a triangle distribution was used. For the input-parameter distributions, only the groundwater concentration (Csw in Table 3.2) and the depth of the groundwater table (dg) were not taken from literature, but were derived from the case data. Model output distributions were the concentration in soil air at 0.5 meter below soil surface (sa), crawl space air (csa) and indoor air (ia). These parameters are used for the comparison of the model predictions with measured field data.

VOLATILIZATION OF SOIL CONTAMINANTS (VOLASOIL, version 1.9)

Formulas in: M.F.W. Waitz, J.I. Freijer, P. Kreule, F.A. Swartjes (1996): The VOLASOIL risk assessment model based on CSOIL for soils contaminated with volatile compounds. RIVM report no. 715810014. Bilthoven, the Netherlands

INPUT

	Description	Notation	Input	Calculation	Dimension
Compound	Name		**per**	per	
	Molecular mass	M	**165.82**	165.82	[g.mol^{-1}]
	Vapor pressure	Vp	**2500**	2500	[Pa]
	Solubility	S	**0.90**	0.90	[mol.m^{-3}]
	Tolerable Concentration in Air	TCA	**0.0006**	0.0006	[g.m^{-3}]
	Concentration in groundwater	Csw	**24.80**	24.80	[g.m^{-3}]
Soil	Volume fraction air	Va	**0.2**	0.2	[-]
	Volume fraction water	Vw	**0.2**	0.2	[-]
	Volume fraction solids	Vs	**0.6**	0.6	[-]
	Air permeability of soil	kappa	**3.16E-12**	3.16E-12	[m^2]
	Depth of groundwater table	dg	**3.15**	3.15	[m]
	Height of capillary transition boundary above groundwater table	z		0.5	[m]
	Temperature	T		283	[K]
House	Volume of indoor space	Vi	**150**	150	[m^3]
	Volume of crawl space	Vc	**25**	25	[m^3]
	Depth of crawl space beneath soil surface	dc	**0.5**	0.5	[m]
	Basic ventilation rate of crawl space (horizontal ventilation)	vrcb	**24**	24	[m^3.h^{-1}]
	Ventilation rate of indoor space	vri		75	[m^3.h^{-1}]
	Surface area of floor	Af	**50**	50	[m^2]
	Floor thickness	Lf		0.1	[m]
	Total area of openings in floor	Aof		0.0005	[m^2]
	Total number of openings in floor	N		10	[-]
	Air pressure difference between indoor space and crawl space	delta pic		2	[Pa]
	Air pressure difference between crawl space and soil	delta pcs		2	[Pa]
Constants	Gas constant	R		8.31	[Pa.m^3.mol^{-1}.K^{-1}]
	Viscosity of air	eta		6.00E-09	[Pa.h]

Figure 3.1 Illustration of input parameter values in VOLASOIL for Tetrachloroethene (spreadsheet version). Bold values were entered specifically for Per and grey cells were varied with the Crystal Ball add-in of Excel.

3.3 Case by case approach

3.3.1 Concentrations

In a second approach the cases were analysed individually, using VOLASOIL with site specific data. In this way the predicted and measured concentrations are analysed in more detail. The calculated air concentrations were compared with the measured air concentrations in soil, crawl space and indoor air. The most relevant input parameter values were adjusted for each case separately, in order to obtain a site specific result (Table 3.4). Mean groundwater concentration (Csw) and the mean depth of the groundwater table were derived from the case-data, including the standard deviation around the mean.

Table 3.4 Input parameter values in VOLASOIL for each case (Groundwater concentration including 95th percentile between brackets).

case number	Csw (95th percentile) tetrachloroethene [g/m^3]	depth groundwater below soil surface [m]	air permeability [m^2]	floor openings [m^2]
1	$5.0\cdot10^{-5}$ ($1.44\cdot10^{-3}$)	1.5	$3.16\cdot10^{-12}$	0.005
2	$3.1\cdot10^{-2}$	2.6	$3.16\cdot10^{-14}$	0.005
3	$6.7\cdot10^{-1}$ ($6.8\cdot10^{-1}$)	2.0	$3.16\cdot10^{-13}$	0.005
4	2.1	1.8	$3.16\cdot10^{-12}$	0.005
6	$1.5\cdot10^{-1}$ ($2.5\cdot10^{1}$)	5.1 (5.8)	$3.16\cdot10^{-12}$	0.0005
9	$4.2\cdot10^{-2}$	2.0	$3.16\cdot10^{-12}$	0.005
10	$5.0\cdot10^{-5}$	0.8	$3.16\cdot10^{-13}$	0.005
12	6.4 ($2.3\cdot10^{1}$)	11.0	$3.16\cdot10^{-12}$	0.005
14	6.4	1.0	$3.16\cdot10^{-12}$	0.0005
15	$6.0\cdot10^{-4}$ ($2.5\cdot10^{-1}$)	1.8	$3.16\cdot10^{-12}$	0.0005
16	$1.0\cdot10^{-4}$	1.25	$3.16\cdot10^{-12}$	0.0005
17	$5.0\cdot10^{-5}$	1.8	$3.16\cdot10^{-13}$	0.0005
18	$1.8\cdot10^{-2}$ ($3.3\cdot10^{-2}$)	1.3	$3.16\cdot10^{-12}$	0.0005
19	$7.9\cdot10^{1}$	1.0	$3.16\cdot10^{-12}$	0.0005
20	$1.0\cdot10^{-4}$ ($1.9\cdot10^{-3}$)	1.2	$3.16\cdot10^{-13}$	0.0005
21	1.2	4.5	$3.16\cdot10^{-12}$	0.005
22	$2.2\cdot10^{-1}$ ($5.7\cdot10^{-1}$)	4.3	$3.16\cdot10^{-12}$	0.005
23	$3.0\cdot10^{-2}$ ($9.4\cdot10^{-2}$)	3.6	$3.16\cdot10^{-12}$	0.005

Mean air permeability was estimated from the case-data also, by using the description of the soil type and data from Waitz *et al*. (1996; Table 3.5). Total area of floor openings was estimated by qualifying a wooden floor or a cellar as bad floor quality and a concrete floor as normal floor quality. According to Waitz *et al*. (1996), a bad floor quality contains a total of 0.005 m^2 of openings, whereas a normal floor contains 0.0005 m^2 of openings. The depth of the groundwater table, the air permeability and the total area of floor openings were not varied, because information on variability within the location of a case was not available for these parameters. Only for case 6 information on the spatial variability of the groundwater level was available. For the other input parameter distributions (compound and house specific data) the same distributions were used as in the generic approach (Tables 3.2 and 3.3). Cases 16 and 17 were not analysed further in Chapter 4.3 due to insufficient background information which makes interpretation difficult.

Table 3.5 Permeability of soils at field capacity moisture content (Waitz et al., 1996)

Soil	Permeability kappa (m^2)
Coarse sand	10^{-10}
Medium sand	$10^{-10.5}$
Fine sand	$10^{-11.5}$
Silty sand	$10^{-12.5}$
Silt	$10^{-13.5}$
Clay	10^{-16}

3.3.2 Ratios

Ratios were calculated in order to compare the cases independently from the specific level of concentrations in the groundwater and the air compartments. They give information on the most critical part of the transport from groundwater to indoor air (Figure 3.2). Comparisons between predicted and observed ratios may reveal differences in transport which can lead to suggestions for model improvement. The following ratios were calculated:

R_1 = Csam/Csag = Concentration in soil air at 0.5 m below soil surface / Concentration in soil air near groundwater level
R_2 = Ccsam/Csam = Concentration in crawl space air / Concentration in soil air
R_3 = Ciam/Ccsam = Concentration in indoor air / Concentration in crawl space air
R_4 = Ccsam/Csag = Concentration in crawl space air / Concentration in soil air near groundwater level
R_5 = Ciam/Csam = Concentration in indoor air / Concentration in soil air
R_6 = Ciam/Csag = Concentration in indoor air / Concentration in soil air near groundwater level

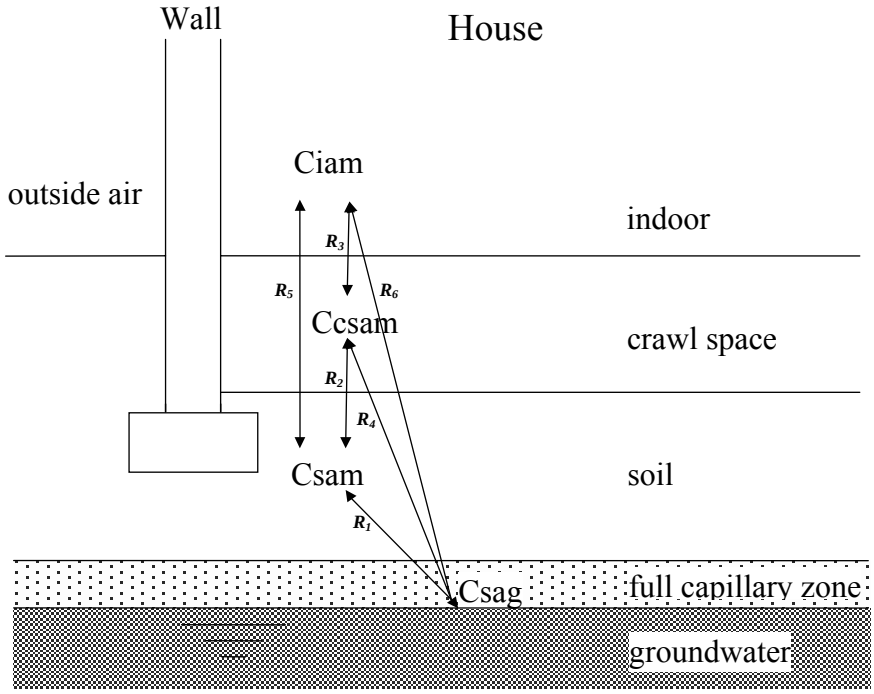


Figure 3.2 Scheme, showing the ratio approach. Concentrations of substances measured in indoor-air (Ciam), measured in crawl space-air (Ccsam), measured in soil-air at 0.5 m below soil surface (Csam) and (calculated) soil air at groundwater level (Csag) are used to calculate ratios (R_{1-6}).

4. Results

4.1 Sensitivity and uncertainty analysis

4.1.1 Sensitivity analysis

A sensitivity analysis was performed to show the sensitivity of the model parameters in relation to the calculated indoor air, crawl space air and soil air concentration, independent of the actual uncertainty or variability. The sensitivity analysis of the VOLASOIL model showed that depth of the groundwater table (dg) was the most sensitive parameter for all compartments (Table 4.1). An increase of 1% in the depth of the groundwater table, resulted in a decrease of more than 3% in the air concentration (a negative NRC value means a negative regression coefficient). For the indoor air compartment, the total area of floor openings (Aof) is also a sensitive parameter. Other parameters show a NRC that is less than or equal to one, which means that a change of 1% in the parameter value results in a change of 1% or less in the air concentration.

4.1.2 Uncertainty analysis

The uncertainty analysis shows the contribution of input uncertainty to uncertainty (variability) in the output air concentrations. The larger the uncertainty in a (sensitive) input parameter, the larger the uncertainty in the output and therefore the larger the contribution of this input parameter to the total output uncertainty. In this case, not only the sensitivity of the parameters is important, but also the amount of input-uncertainty. Most of the variation in predicted air concentration could be attributed to the variation in the groundwater concentration, and to a lesser extent to the depth of the groundwater table (Table 4.2). Other input parameters did not contribute much to the output-variation, although the solubility was relatively important for the air concentration of tetrachloroethene. The data show that uncertainty in the groundwater concentration is high due to high spatial variation, both horizontally and vertically.

Table 4.1 Ranked results of VOLASOIL sensitivity analysis for Tetrachloroethene in indoor air, crawl space air and soil air, using the Normalized Regression Coefficient (NRC)

Input-parameter	**Code**	**Units**	**NRC indoor**
Depth of groundwater table	dg	m	-3.0141
Total area of openings in floor	Aof	m^2	1.6731
Depth of crawl space beneath soil surface	dc	m	1.0004
Concentration in groundwater	Csw	g/m^3	1.0000
Surface area of floor	Af	m^2	1.0000
Vapor pressure	Vp	Pa	1.0000
Height of capillary transition boundary above groundwater table	z	m	0.9999
Solubility	S	mol/m^3	-0.9986
Ventilation rate of indoor space	vri	m^3/h	-0.9570
Basic ventilation rate of crawl space (horizontal ventilation)	vrcb	m^3/h	-0.8758
Total number of openings in floor	N	-	-0.8377
Air pressure difference between indoor space and crawl space	Δ pic	Pa	0.8362
Floor thickness	Lf	m	-0.8356
Air pressure difference between crawl space and soil	Δ pcs	Pa	0.5639
Air permeability of soil	kappa	m^2	0.5633
Molecular mass	M	g/mol	-0.2182
Volume of crawl space	Vc	m^3	0.0000
Volume of indoor space	Vi	m^3	0.0000

Parameter	**Code**		**NRC crawlsp.**
Depth of groundwater table	dg	m	-3.0141
Depth of crawl space beneath soil surface	dc	m	1.0004
Concentration in groundwater	Csw	g/m^3	1.0000
Surface area of floor	Af	m^2	1.0000
Vapor pressure	Vp	Pa	1.0000
Height of capillary transition boundary above groundwater table	z	m	0.9999
Solubility	S	mol/m^3	-0.9982
Basic ventilation rate of crawl space (horizontal ventilation)	vrcb	m^3/h	-0.8758
Air pressure difference between crawl space and soil	Δ pcs	Pa	0.5639
Air permeability of soil	kappa	m^2	0.5633
Total area of openings in floor	Aof	m^2	-0.2425
Molecular mass	M	g/mol	-0.2182
Total number of openings in floor	N	-	0.1215
Floor thickness	Lf	m	0.1213
Air pressure difference between indoor space and crawl space	Δ pic	Pa	-0.1213
Ventilation rate of indoor space	vri	m^3/h	0.0000
Volume of crawl space	Vc	m^3	0.0000
Volume of indoor space	Vi	m^3	0.0000

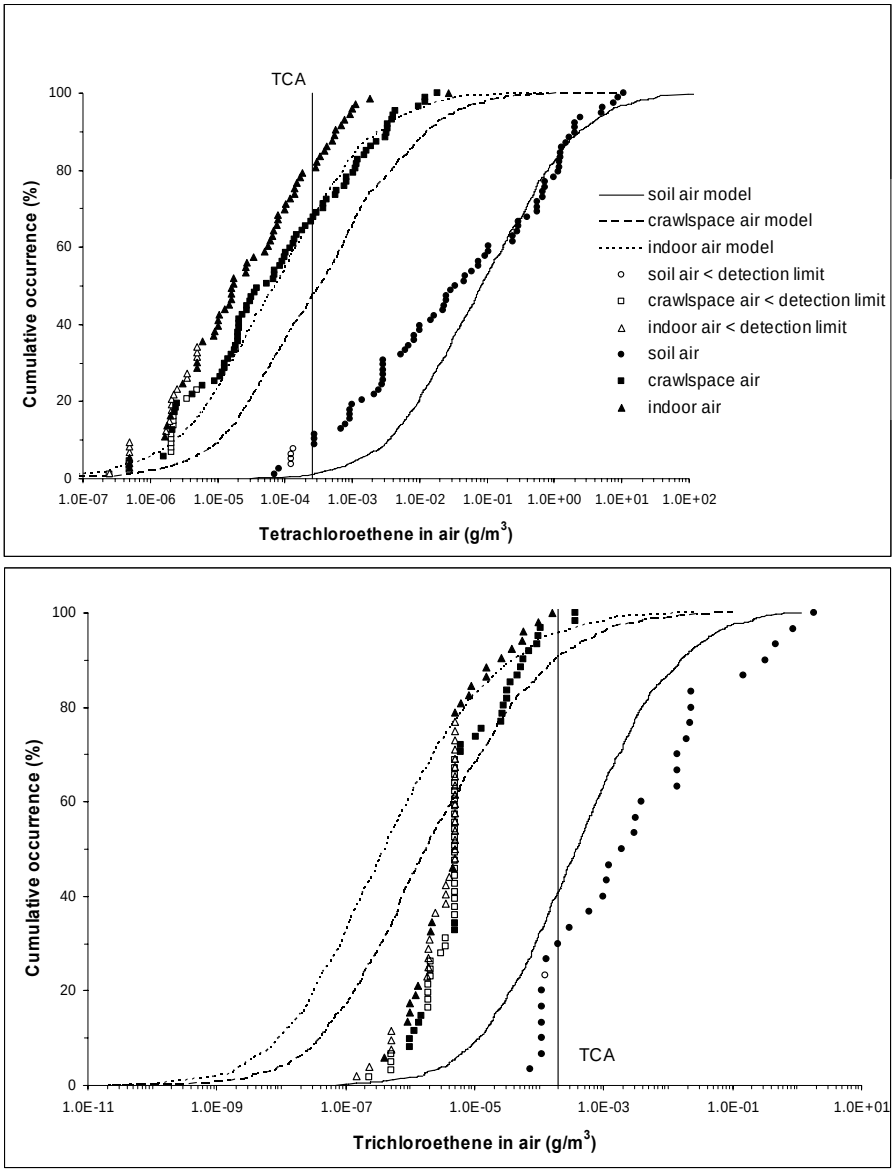
Parameter	**Code**		**NRC soil**
Depth of groundwater table	dg	m	-1.5029
Vapor pressure	Vp	Pa	1.0000
Concentration in groundwater	Csw	g/m^3	0.9999
Solubility	S	mol/m^3	-0.9982
Height of capillary transition boundary above groundwater table	z	m	0.5001
Air permeability of soil	kappa	m^2	0.0000
Air pressure difference between crawl space and soil	Δ pcs	Pa	0.0000
Air pressure difference between indoor space and crawl space	Δ pic	Pa	0.0000
Basic ventilation rate of crawl space (horizontal ventilation)	vrcb	m^3/h	0.0000
Depth of crawl space beneath soil surface	dc	m	0.0000
Floor thickness	Lf	m	0.0000
Molecular mass	M	g/mol	0.0000
Surface area of floor	Af	m^2	0.0000
Total area of openings in floor	Aof	m^2	0.0000
Total number of openings in floor	N	-	0.0000
Ventilation rate of indoor space	vri	m^3/h	0.0000
Volume of crawl space	Vc	m^3	0.0000
Volume of indoor space	Vi	m^3	0.0000

Table 4.2 Crystal Ball uncertainty analysis. Percentage of variation in the output-parameter that was caused by the variation in each input-parameter.

	Input-parameter	Soil (g/m^3)	Crawl space (g/m^3)	Indoor (g/m^3)
Vinylchloride	Groundwater concentration (g/m^3)	84.3%	61.0%	63.9%
	Depth of groundwater table (m)	12.9%	22.0%	22.9%
	Basic ventilation rate crawl space (m^3/h)	0.2%	2.0%	2.1%
	Area of floor openings (m^2)	0.0%	8.6%	2.0%
	S (solubility) (mol/m^3)	2.0%	1.1%	1.9%
	Floor surface area (m^2)	0.0%	1.0%	1.6%
	Kappa (air permeability of soil) (m^2)	0.0%	1.5%	1.1%
	Va (Volume fraction air in soil)	0.0%	0.4%	0.9%
	Air pressure diff crawl-soil (Pa)	0.1%	1.0%	0.9%
	Ventilation rate indoor space (m^3/h)	0.0%	0.0%	0.9%
	Vs (volume fraction solids in soil)	0.0%	0.4%	0.9%
	Floor thickness (m)	0.1%	0.1%	0.5%
	Air pressure diff indoor-crawl (Pa)	0.0%	0.8%	0.3%
	Vp (Vapour pressure) (Pa)	0.1%	0.0%	0.1%
Cis-1,2-dichloroethene	Groundwater concentration (g/m^3)	90.7%	67.9%	70.5%
	Depth of groundwater table (m)	6.6%	25.4%	25.4%
	S (solubility) (mol/m^3)	1.6%	1.3%	1.3%
	Floor surface area (m^2)	0.4%	0.8%	1.0%
	Area of floor openings (m^2)	0.0%	2.5%	0.6%
	Air pressure diff crawl-soil (Pa)	0.1%	0.1%	0.3%
	Ventilation rate indoor space (m^3/h)	0.1%	0.0%	0.3%
	Floor thickness (m)	0.1%	0.8%	0.2%
	Kappa (air permeability of soil) (m^2)	0.0%	0.3%	0.2%
	Basic ventilation rate crawl space (m^3/h)	0.0%	0.1%	0.2%
	Vp (Vapour pressure) (Pa)	0.1%	0.1%	0.1%
	Air pressure diff indoor-crawl (Pa)	0.0%	0.6%	0.0%
	Va (Volume fraction air in soil)	0.1%	0.0%	0.0%
	Vs (volume fraction solids in soil)	0.1%	0.0%	0.0%
Trichloroethene	Groundwater concentration (g/m^3)	90.3%	68.6%	71.8%
	Depth of groundwater table (m)	8.4%	19.8%	22.5%
	Ventilation rate indoor space (m^3/h)	0.2%	0.1%	1.1%
	Air pressure diff crawl-soil (Pa)	0.1%	0.6%	0.8%
	Kappa (air permeability of soil) (m^2)	0.0%	0.7%	0.8%
	Floor surface area (m^2)	0.0%	0.5%	0.8%
	Va (Volume fraction air in soil)	0.1%	0.2%	0.6%
	Vs (volume fraction solids in soil)	0.1%	0.2%	0.6%
	Air pressure diff indoor-crawl (Pa)	0.0%	0.7%	0.4%
	Basic ventilation rate crawl space (m^3/h)	0.0%	0.2%	0.2%
	Area of floor openings (m^2)	0.3%	7.7%	0.2%
	S (solubility) (mol/m^3)	0.3%	0.1%	0.1%
	Vp (Vapour pressure) (Pa)	0.0%	0.0%	0.0%
	Floor thickness (m)	0.2%	0.5%	0.0%
Tetrachloroethene	Groundwater concentration (g/m^3)	85.8%	75.8%	82.6%
	S (solubility) (mol/m^3)	8.5%	7.8%	9.0%
	Depth of groundwater table (m)	3.4%	3.3%	3.9%
	Air pressure diff crawl-soil (Pa)	0.0%	1.7%	2.2%
	Kappa (air permeability of soil) (m^2)	0.0%	1.2%	1.2%
	Area of floor openings (m^2)	0.1%	8.4%	0.7%
	Air pressure diff indoor-crawl (Pa)	0.1%	0.5%	0.2%
	Vp (Vapour pressure) (Pa)	0.0%	0.0%	0.0%
	Ventilation rate indoor space (m^3/h)	1.0%	0.8%	0.0%
	Floor thickness (m)	0.0%	0.5%	0.0%
	Basic ventilation rate crawl space (m^3/h)	0.2%	0.0%	0.0%
	Va (Volume fraction air in soil)	0.0%	0.0%	0.0%
	Vs (volume fraction solids in soil)	0.0%	0.0%	0.0%
	Floor surface area (m^2)	0.9%	0.0%	0.0%

4.2 Generic approach

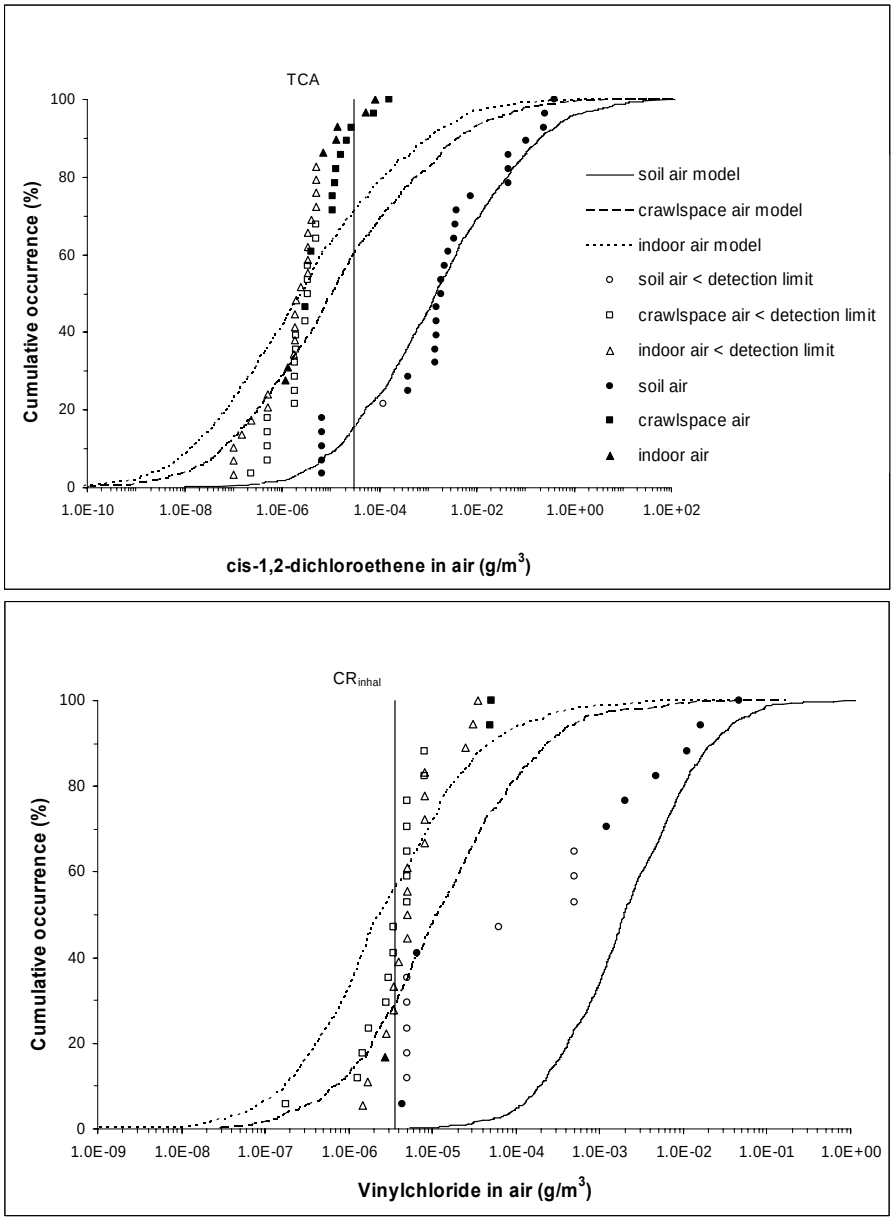
All measured air concentrations together were compared to predictions (Figures 4.1a and 4.1b). The mean measured air concentration was approximately one order of magnitude lower than the predicted distribution for tetrachloroethene, with equal variation around the mean (Figure 4.1a). For trichloroethene, differences for indoor air and crawl space air were smaller and measured concentrations were lower than predicted, when detection-limits were not taken into account (open symbols). Soil air concentrations were higher than predicted for trichloroethene. Patterns were easier to interpret for tetrachloroethene than for the other substances, where many concentrations were below the detection limit.



TCA = Tolerable Concentration in Air

Figure 4.1a Cumulative distributions of indoor-air concentrations, derived from measurements (symbols) and predictions by the VOLASOIL model (lines), for Per and Tri. Detection limits are indicated with open symbols.

The results for cis 1,2-dichloroethene (cis) and vinylchloride are difficult to interpret due to the large amount of measurements that fall below the detection limit (Figure 4.1b). Measured soil air concentrations are in general well predicted, while indoor and crawl space air concentrations are overestimated by the model. Indoor air and crawl space air differences were larger for these substances than for per and tri. So, the aboveground model prediction for the air concentration of cis and vinylchloride is less accurate than for per and tri.



CR_{inhal} = $1:10^{-4}$ lifetime excess cancer risk inhalation
TCA = Tolerable Concentration in Air

Figure 4.1b Cumulative distributions of indoor-air concentrations, derived from measurements in the selected cases (symbols) and predictions by the VOLASOIL model (lines), for cis 1,2-dichloroethene and vinylchloride. Detection limits are indicated with open symbols.

Considering median values with confidence intervals for predicted and measured indoor air concentrations, the overlap between observed and predicted concentrations was large for all substances (Figure 4.2). When predictions fall below the detection limit (dashed line in the figure), observed concentrations are generally higher than predicted. If not, the median observed values are systematically lower than predicted, except for the soil compartment. Overall, this indicates that the VOLASOIL model overestimates air concentrations for indoor air and crawl space air. This pattern becomes less clear when concentrations are low.

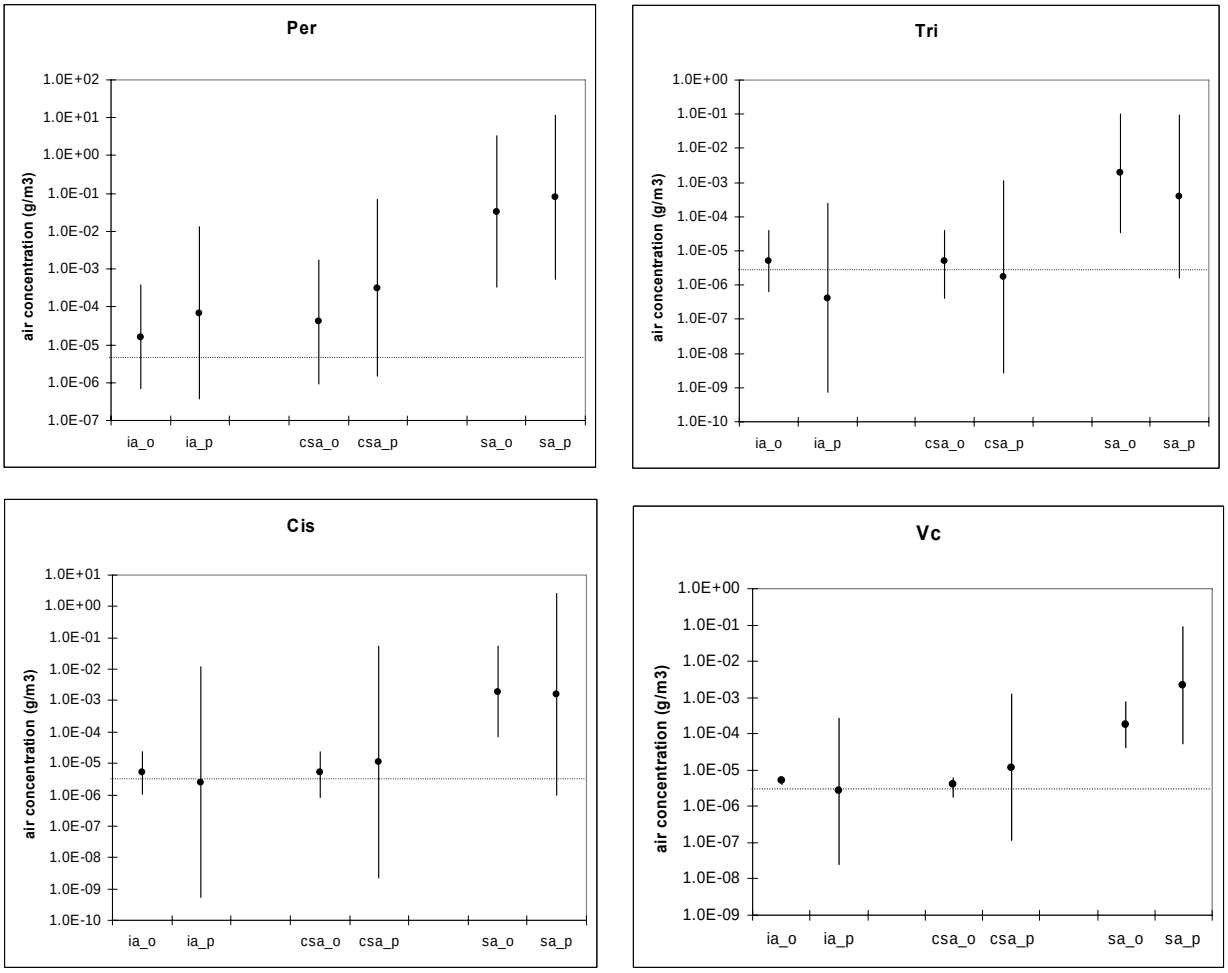


Figure 4.2 Median values and confidence limits of air concentrations for all cases (dispersion factor k was used; 95 % of the values is within a factor k from the median, see Slob 1994). Dashed line indicates mean detection limit. ia_o =observed indoor air concentration from measurements; ia_p = predicted indoor air concentration; csa_o = observed crawl space air concentration; csa_p = predicted crawl space air concentration; sa_o = observed soil air concentration; sa_p = predicted soil air concentration.

Groundwater concentration effects

The tetrachloroethene concentration in air is positively related to the groundwater concentration of tetrachloroethene for all compartments (Figure 4.3, thick black line). These relationships are significant at the 95% confidence level.

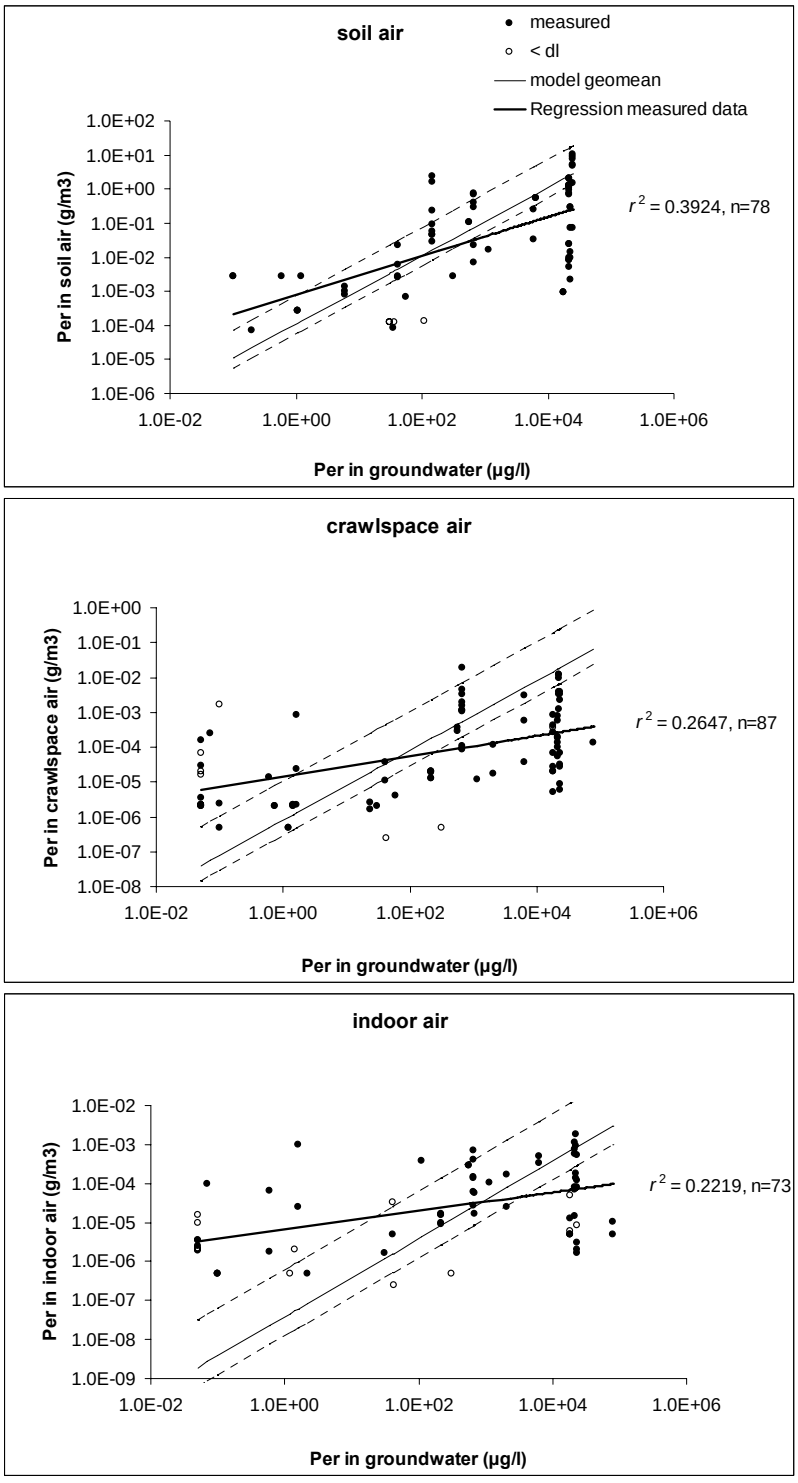


Figure 4.3 Air concentrations of tetrachloroethene in relation to groundwater concentration for measured field data (symbols) and the VOLASOIL model (thin line). Detection limits were incorporated in the linear regression analysis (thick line). Model variation (min and max- dotted lines) was caused by variation in the depth of the groundwater table.

The model predicted a steeper slope for all compartments than the actual field data showed, especially for the aboveground compartments. This indicates that the model might underestimate air concentrations of tetrachloroethene at low groundwater concentration, and overestimates air concentrations at high groundwater concentration. This may be due to an artefact in the model. It may also be that other sources influence the indoor air concentration at low groundwater concentrations. At high groundwater concentrations there may be an unknown barrier to prevent high indoor air concentrations. These trends also become apparent in section 4.3, where cases were investigated in more detail. The regression coefficients of the other substances (trichloroethene, cis-1,2-dichloroethene and vinylchloride) were not significantly different from zero. The correlation coefficient of the soil air compartment for these substances was higher (a steeper slope) than for the other compartments, similar to tetrachloroethene.

Indoor air – crawl space air

When analysing differences between indoor air and crawl space air concentrations for all substances, it was striking that differences were larger when crawl space air concentrations were higher (Figure 4.4). At low concentrations, crawl space values were equal to indoor values. At high crawl space air concentrations, the indoor air concentration approached the predicted value. This, again, shows that the model underestimates at low concentrations (see also Figure 4.3). The model assumes a concentration gradient from crawl space air towards indoor air. These results suggests that this gradient is only present at higher concentrations. Trends were similar for all house categories (cellar, crawl space with concrete floor and crawl space with wooden floor).

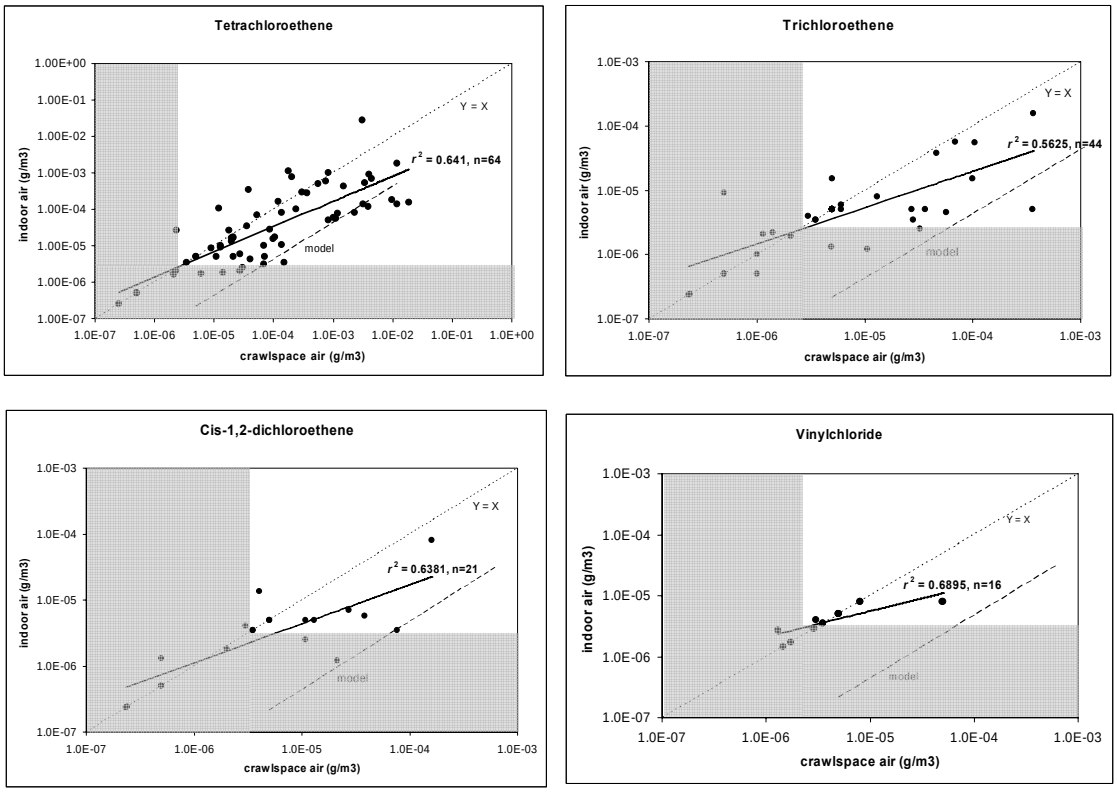


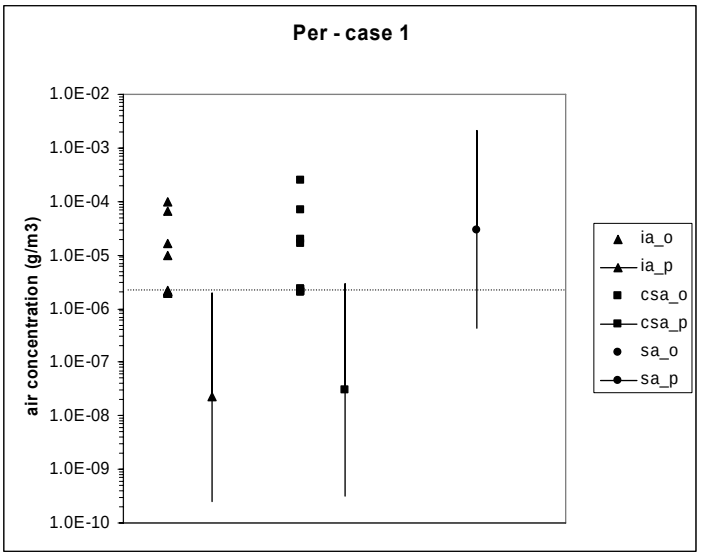
Figure 4.4 Concentration in crawl space and indoor air for measured data (symbols) and model predictions (dashed line). The dotted line shows when crawl space air concentration equals indoor air concentration. The solid line is the result of linear regression analysis. The gray areas represent the area with detection limits.

4.3 Case by case approach

Here we present in more detail the results of case-by-case comparisons between observed and predicted concentrations. The results focus on tetrachloroethene only, since most of the data are available for this substance and the amount of detection limits is low. Information in Table 3.1 was used to draw preliminary conclusions on the possible cause for the observed differences. The predicted uncertainty in the following graphs of section 4.3 is the 95 % confidence limits around the mean. The dotted line in the graphs is the mean detection limit. Also, ia_o = observed indoor air concentration from measurements; ia_p = predicted indoor air concentration; csa_o = observed crawl space air concentration; csa_p = predicted crawl space air concentration; sa_o = observed soil air concentration; sa_p = predicted soil air concentration.

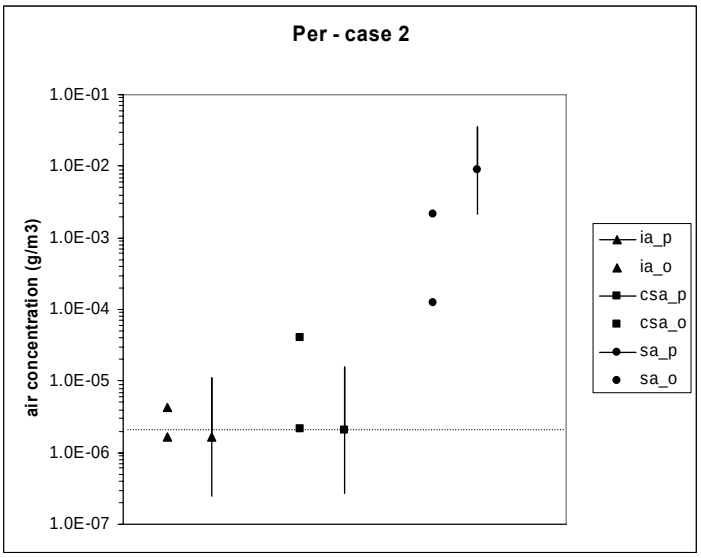
Case 01

Type of contamination: The groundwater is contaminated with chlorinated compounds over an area of roughly 100 by 100 meter, with a heterogenic horizontal and vertical distribution. Some sources of contamination are identified and it is likely that more companies contributed to the contamination. Both tetrachloroethene and trichloroethene were present as contaminant.
Soil type: The groundwater level is about 1.5 meter below soil surface. The top soil consists of moderately coarse sand or humus clayey sand.
Type of building: Most of the houses have crawl spaces.
Measurements: both in indoor air and/or crawl space air. Soil air was not analysed. Passive as well as active measurements were carried out.
Results: The comparison of the predicted and measured concentrations of tetrachloroethene show that both in indoor air and crawl space air the measured concentrations are higher than the calculated concentrations. A large heterogeneity of the groundwater concentrations is observed. Concentrations in the deeper groundwater were much higher than in the top meter of the groundwater. A reason for the observed differences could be that the groundwater concentrations near the houses (< 10 meter) were relatively low, compared to other area's on the site, or that other unknown sources were present. Further analysis is necessary to explain the results.



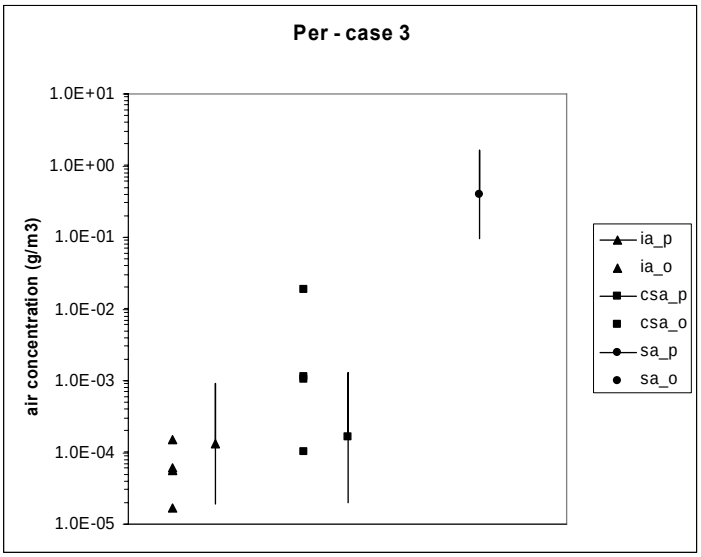
Case 02

Type of contamination: The groundwater is contaminated with chlorinated compounds with in principle one hotspot due to leakage of the sewage pipe of a dry cleaner business. The contaminated soil was already excavated, and the groundwater was under remediation. Tetrachloroethene was probably used.
Soil type: The groundwater level is about 2.5 meter below soil surface. The top soil consists of a clayey soil.
Type of building: the air concentrations in 2 houses with crawl spaces have been measured.
Measurements: indoor air, crawl space air and soil air was measured. Only active measurements were carried out. All measurements were taken in the same period of time.
Results: The comparison of the predicted and measured concentrations of tetrachloroethene (per) shows that in soil air the predicted concentrations are higher than the measured concentrations (1 order of magnitude). In the indoor air and crawl space air the measured concentrations are in the same order of magnitude as the calculated range of concentrations. So although the soil air concentration is lower than expected, the indoor air concentrations are within the predicted range. This may indicate that the air permeability of the soil is higher than expected.



Case 03

Type of contamination: The groundwater is contaminated with chlorinated compounds with in principle one hotspot caused by a former dry cleaner business. Only tetrachloroethene was used.
Soil type: The groundwater level is between 1.6 and 2.7 meter below the soil surface. The top soil consists of very fine sand, moderately silty and locally sandy clay.
Type of building: The air concentrations in 1 house with a crawl space were measured.
Measurements: Indoor air and crawl space air were measured two times at different locations. Only active measurements were carried out.
Results: The comparison of the predicted and measured concentrations of tetrachloroethene show that in the indoor air the measured concentrations are in the same order of magnitude but slightly lower as the predicted concentration range. The crawl space air concentrations tend to be the same and higher. So the measurements show a difference between the indoor air and the crawl space, whereas the predicted concentrations are only slightly different.



Case 04

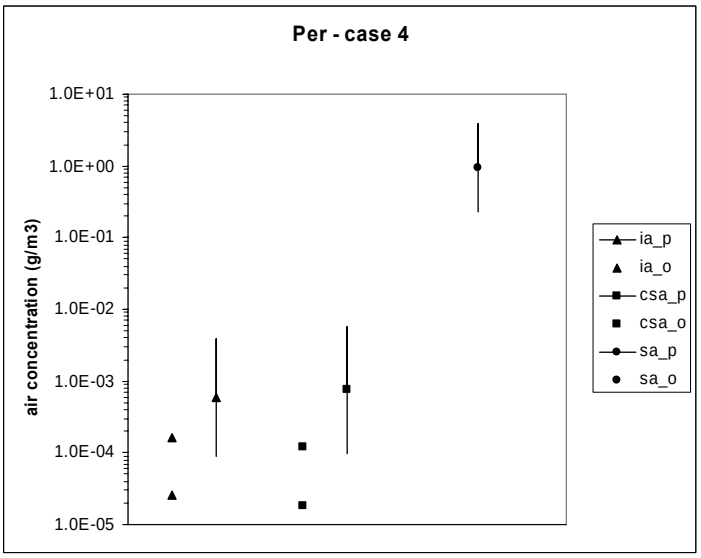
Type of contamination: The groundwater is contaminated with chlorinated compounds with in principle one hotspot due to a former dry cleaner business. Only tetrachloroethene was used.

Soil type: The groundwater level is about 1.8 meter below soil surface. The top soil consists of sand.

Type of building: the air concentrations in 2 houses have been measured (one with a cellar, one with a crawl space).

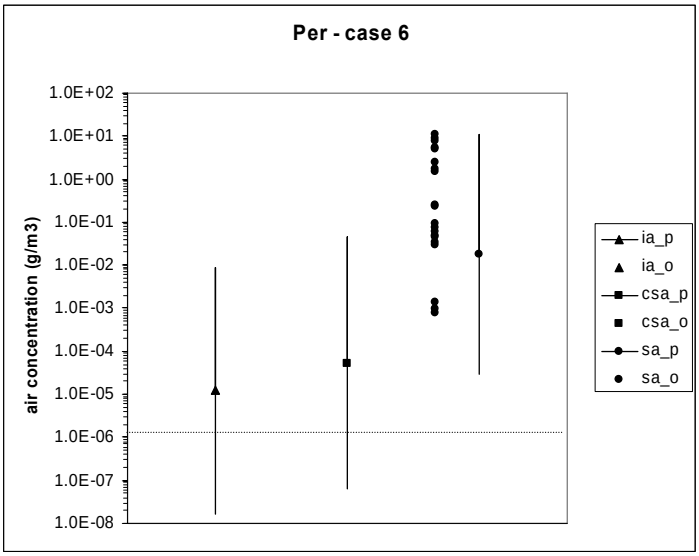
Measurements: indoor air and cellar/crawl space air was measured. Only active measurements were carried out.

Results: The comparison of the predicted and measured concentrations of tetrachloroethene show that in the indoor air and the crawl space/cellar air the measured concentrations are roughly an order of magnitude lower as the predicted concentration range. So the prediction overestimates the measurements. The time between the groundwater measurement (1 location in 1992) and the air measurements (in 1996) could contribute to this difference. In the report was indicated that the groundwater concentration had dropped to a third between 1992 and 1996 which means that the observed and predicted air concentrations becomes much more similar.



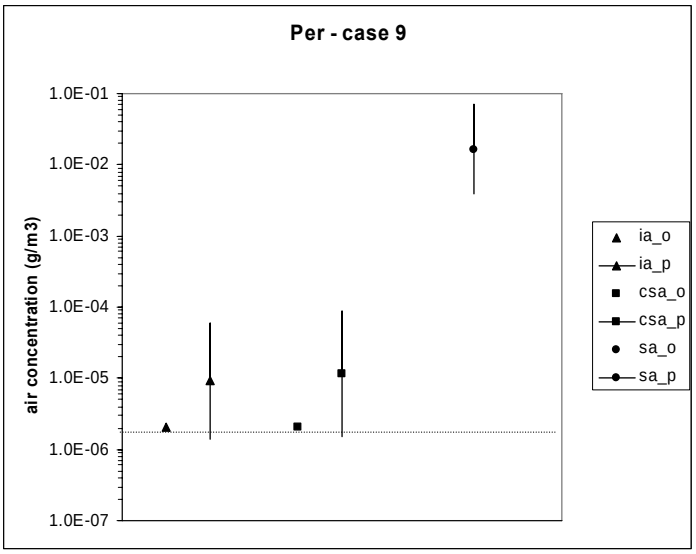
Case 06

Type of contamination: The groundwater is contaminated with chlorinated compounds with probably one hotspot. The source of contamination is not known.
Soil type: The groundwater level is about 3 to 5.5 meter below soil surface. The top soil consists of fine to moderately coarse sand.
Type of building: Buildings are present but no measurements inside houses were carried out.
Measurements: Only (a large amount of) soil air measurements were carried out. The measurements were done with a mobile GC.
Results: The comparison of the predicted and measured concentrations of tetrachloroethene shows that the soil air predictions and measurements were similar. Also the range of values is similar.



Case 09

Type of contamination: The groundwater is contaminated with chlorinated compounds with in principle one hotspot from a dry cleaners business.
Soil type: The groundwater level is about 2 meter below soil surface. The soil (< 10 meter) consists of fine to moderately coarse sand.
Type of building: House with a cellar.
Measurements: Measurements of indoor air and cellar air were carried out in two periods. The active measurements were done with active carbon as an adsorbent.
Results: For tetrachloroethene both the indoor air as the cellar air concentrations were below the detection limit, whereas predictions were 1 order of magnitude higher.



Case 10

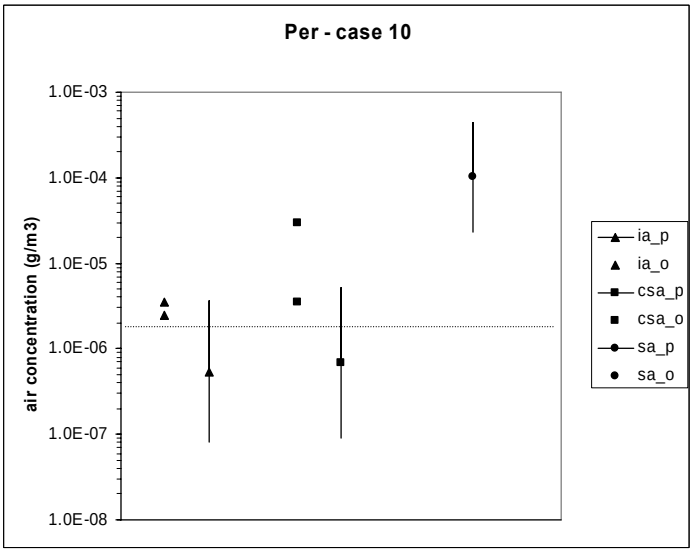
Type of contamination: The groundwater is contaminated with trichloroethene, tetrachloroethene and mineral oil, originating from a business on surface treatment of metals and the trade of these compounds. The size of the contamination is roughly 15x50 meters. 1,2-dichloroethene and vinylchloride are present in high concentrations, due to natural attenuation.

Soil type: The groundwater level is about 0.8 meter below soil surface. The top soil (0-1 meter) consists of silty fine sand, 1-2 meter is clay, followed by silty fine sand. At a certain location the top 2 meter can be rich in rubble.

Type of building: Houses with a cellar.

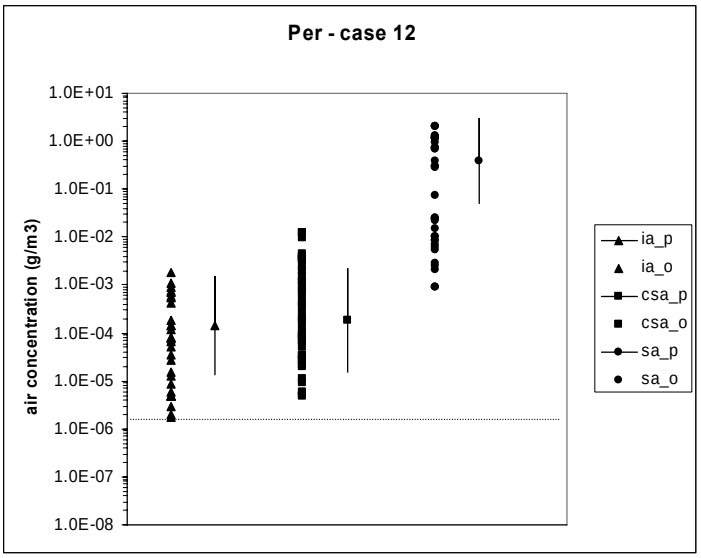
Measurements: Measurements of indoor air and cellar air were carried out in 2 houses. The active measurements were done using the activated carbon as sorbent.

Results: Only in the cellar of one house the concentrations are higher than the detection limit (but not for vinylchloride) For tetrachloroethene the indoor air concentrations were below the detection limit in both houses (< 7 µg/m^3). Based on the low concentrations in the groundwater (< 0.5 µg/l), it was not predicted that the concentrations were high above the detection limit for tetrachloroethene.



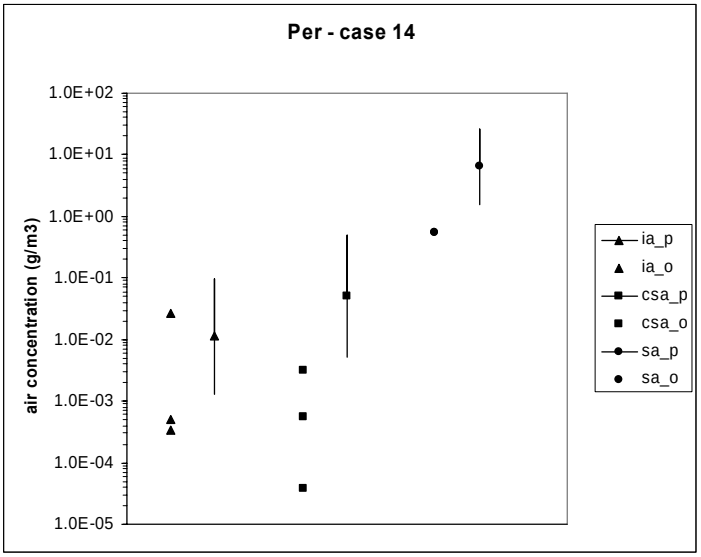
Case 12

Type of contamination: The groundwater is contaminated with chlorinated compounds in a larger area, probably originating from two locations with a former dry cleaner business. Probably only tetrachloroethene was used.
Soil type: The groundwater level is about 11 meter below the soil surface. The top soil consists of sand.
Type of building: Air concentrations have been measured in 15 houses in different periods (in indoor air and in cellar air).
Measurements: indoor air, cellar air and soil air was measured. Only active measurements were carried out.
Results: The comparison of the predicted and measured concentrations of tetrachloroethene shows that in the indoor air and the cellar air the measured concentrations are roughly in the same order of magnitude as the predicted concentration range. In the cellars the concentrations are up to an order of magnitude higher than in the indoor air. The measured soil air concentrations are in the same order of magnitude as the predicted concentrations up to 2 orders of magnitude lower. This means that in general the model shows an overestimation, but not at every spot. The reason could be that in certain areas the contamination is still mainly present in the unsaturated zone, leading to concentrations in the soil air that are the same as in the model.



case 14

Type of contamination: The groundwater is contaminated with chlorinated compounds. The contaminated area is approximately 2500 m^2. There is one hotspot at a site where a dry cleaner business was situated. Tetrachloroethene was used. There is also contamination in the unsaturated zone.
Soil type: A 3 meter thick sandy topsoil, with peat and clay underneath until 17 meter below soil surface. The groundwater level is approximately 1 meter below soil surface.
Type of building: Air concentrations in 3 houses was measured. The houses have a crawl space.
Measurements: Both indoor and crawl space. Measurements in air and groundwater were done in the same year (1996). Only active measurements were carried out. Two measurements were done in the groundwater.
Results: Measured concentrations were lower than the predictions. Only one indoor air concentration value is relatively high. No explaination was found to explain the differences.

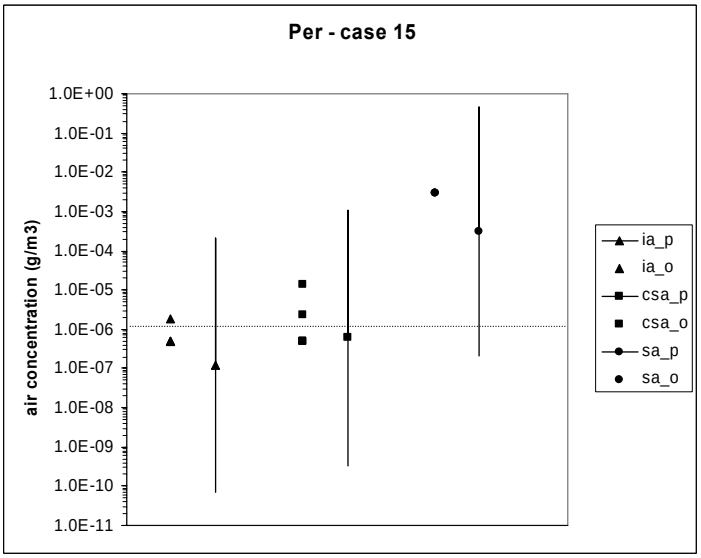


Case 15

Type of contamination: The groundwater is contaminated with chlorinated compounds, due to leakage of the sewage pipe of a dry cleaners business. The contaminated area is approximately 240 m^2. There is one hotspot at the site where the dry cleaner business was situated. Both tetrachloroethene and trichloroethene were used. There is also contamination in the unsaturated zone.

Soil type: A 2 meter thick sandy topsoil, with peat and clay underneath. The groundwater level is approximately 1.8 meter below soil surface.

Type of building: Air concentration in 1 house, at 5 sites, was measured. The house had a crawl space.

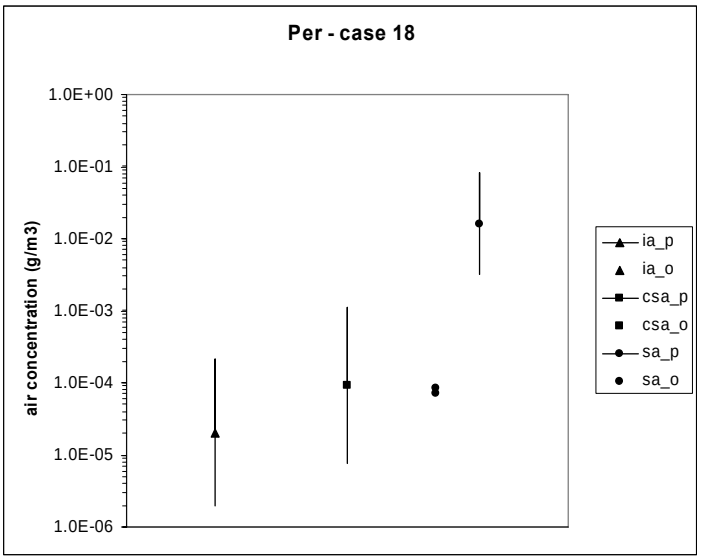


Measurements: Both indoor and crawl space. Active measurements in air and groundwater were done the same year (1998). Seven measurements were done in the groundwater.

Results: Measured and predicted concentrations were within one order of magnitude from the mean. Concentrations were close to the detection limit. Due to anaerobic conditions at the site, conversion into trichloroethene, cis-dichloroethene and vinylchloride probably took place.

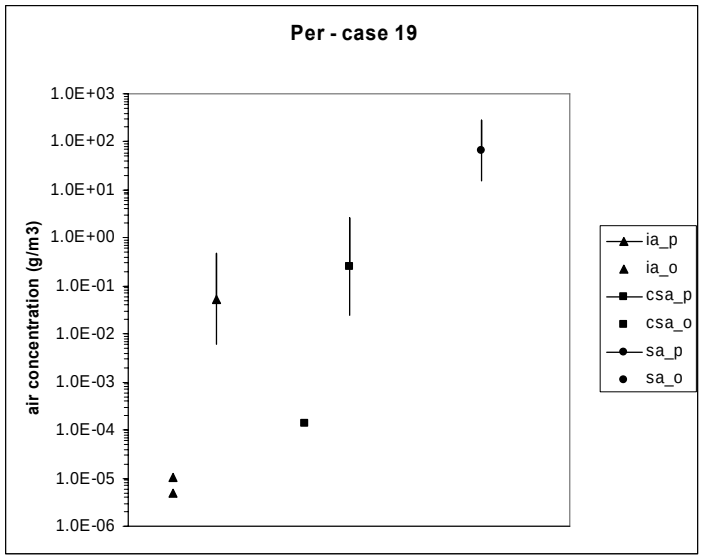
Case 18

Type of contamination: The groundwater is contaminated with chlorinated compounds. There is one hotspot at the site where a dry cleaner business was situated. Both tetrachloroethene and trichloroethene were used. There is also contamination in the unsaturated zone.
Soil type: A 2 meter thick sandy topsoil, with peat and clay underneath until 19 meter below soil surface. The groundwater level is approximately 1.3 meter below soil surface.
Type of building: Only soil air measurements were done. The house had no crawl space or cellar.
Measurements: Only active soil air measurements were done. Groundwater concentration was measured in 2000 and 2002, and soil air was measured in 2002. Three measurements were done in the groundwater and two in soil air.
Results: Measured soil air concentration was much lower than predicted (two orders of magnitude). Due to anaerobic conditions at the site, conversion into vinylchloride probably took place, which may have caused a decrease in the groundwater concentration. Since soil air measurements were done in 2002, this may explain the differences found between observed and predicted soil air concentration.



Case 19

Type of contamination: The groundwater is contaminated with chlorinated compounds. There is one hotspot underneath the house where a dry cleaner business was situated. Both tetrachloroethene and trichloroethene were used. There is also contamination in the unsaturated zone.
Soil type: A 2 meter thick sandy topsoil, with loamy sand / clay underneath. The groundwater level is approximately 1.3 meter below soil surface.
Type of building: The house had a crawl space and a concrete floor.
Measurements: No soil air measurements. Active measurements were done in December 2001 and April 2002 in 1 house. One measurement was done in the groundwater and two in crawl space air and indoor air.
Results: Measured air concentrations were much lower than predicted (three orders of magnitude). Conversion into vinylchloride has taken place at the site. One other option is that the concrete floor blocked most of the contaminants.



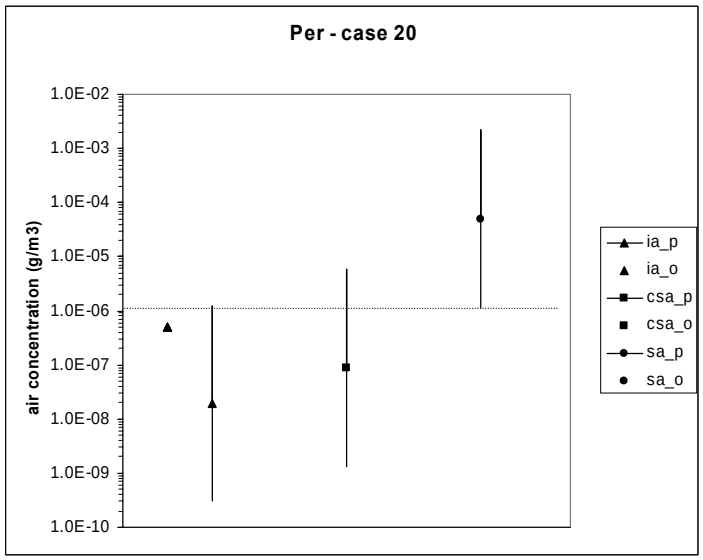
Case 20

Type of contamination: The groundwater is contaminated with chlorinated compounds. There is one hotspot 20 meter from the house, where a dry cleaner business was situated. Both tetrachloroethene and trichloroethene were used. There is no contamination in the unsaturated zone. Conversion into vinylchloride has taken place in the past and still takes place, due to high groundwater level and high microbial activity. Contaminants are possibly adsorbed to the peat.

Soil type: A 2 meter thick sandy topsoil, with peat / clay underneath. The groundwater level is approximately 1.2 meter below soil surface.

Type of building: The house had no crawl space or cellar and the floor consisted of concrete directly on the sand.

Measurements: Soil air measurements were done, but no detectable concentrations were found. Groundwater measurements were done in December 1999 and indoor air measurements were done in March 2001. Only active measurements were carried out. Eleven measurements were done in the groundwater and two in indoor air.

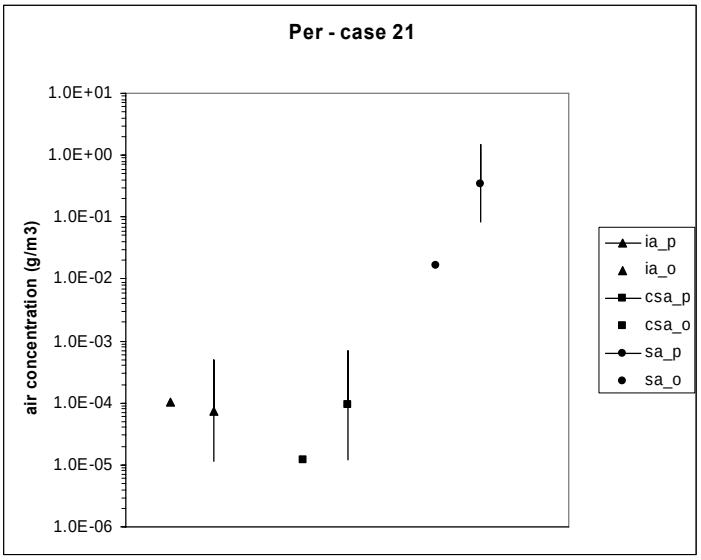


Results: Measured indoor air concentrations and predictions were similar. Observed concentration was close to the detection limit. The soil air concentration was found below the detection limit (data not in the figure), which is different from the prediction.

Case 21

Type of contamination: The groundwater is contaminated with chlorinated compounds. There is one hotspot where a dry cleaner business was situated. Both tetrachloroethene and trichloroethene were used. There was no contamination in the unsaturated zone. Conversion from tetrachloroethene into vinylchloride has probably not taken place in the past due to aerobic conditions.

Soil type: Sandy soil. The groundwater level is approximately 4.5 meter below soil surface.



Type of building: The house has a cellar instead of a crawl space and the floor is made of concrete.

Measurements: One soil air measurement was done in November 1996. One groundwater measurement was done in March 1998 and indoor air measurements were done in May 2000 in one house. Only active measurements were carried out.

Results: Measured indoor air concentrations and predictions were similar. Observed crawl space air and soil air concentrations were lower than predictions. Due to the small amount of measurements, it is difficult to draw conclusions. Predicted indoor air and crawl space air concentrations were similar due to the cellar.

Case 22

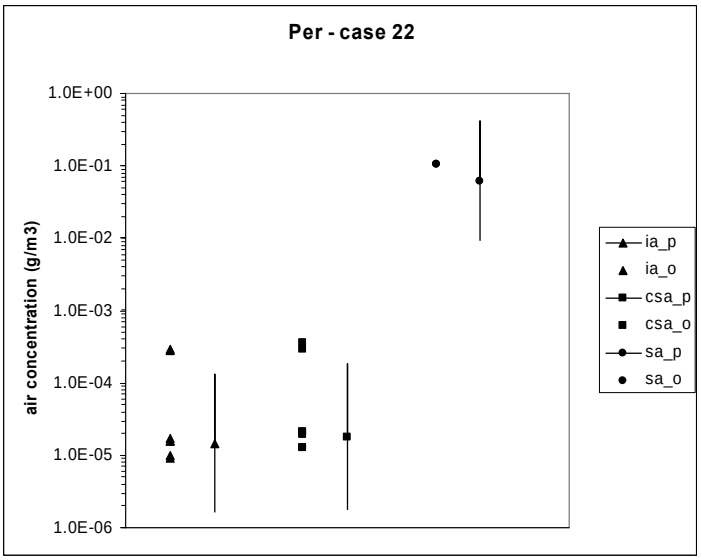
Type of contamination: The groundwater is contaminated with chlorinated compounds. There is one hotspot where a dry cleaner business was situated. Both tetrachloroethene and trichloroethene were used. There was no contamination in the unsaturated zone. Conversion into vinylchloride probably did not take place in the past due to aerobic conditions.

Soil type: Sandy soil. The groundwater level is approximately 4.3 meter below soil surface.

Type of building: Four houses, without a crawl space but with a cellar were sampled in December 1993. The floor probably consisted of concrete.

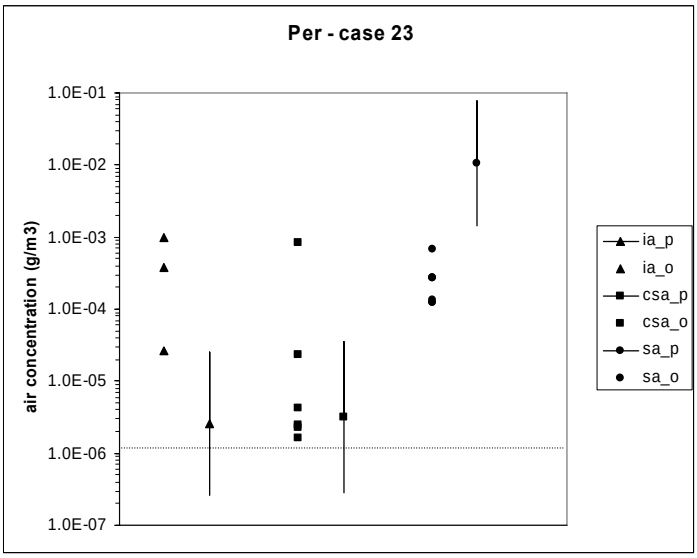
Measurements: Four soil air measurements were done in October 1994. Thirteen groundwater measurements were done in 1998 and 2002. Indoor air measurements were done in December 1993. In total 14-16 air measurements were done.

Results: Measured indoor air, crawl space air and soil air concentrations were similar in comparison with predictions. Some measured indoor and crawl space air concentrations were higher than predicted. These values are from the house, where the former dry cleaner business was located.



Case 23

Type of contamination: The groundwater is contaminated with chlorinated compounds. There is one hotspot where a dry cleaner business was situated. Tetrachloroethene was used. There was no contamination in the unsaturated zone. There was probably no conversion into Vinylchloride due to aerobic conditions.
Soil type: Sandy soil. The groundwater level is approximately 3.6 meter below soil surface.
Type of building: Seven houses, with a crawl space were sampled in August 2002. The floor probably consisted of concrete in the house near the hotspot, but surrounding houses probably had wooden floors.
Measurements: Seven soil air measurements were done in September 2001. Ten groundwater measurements were done in January 2001. Indoor air measurements were done in August 2002.
Results: Measured indoor air and crawl space air concentrations were clearly higher than predicted, whereas the soil air concentration was lower. This discrepancy could have been caused by the floor type, which was concrete at house near the hotspot, but wood in the surrounding houses. In the model, a concrete floor was used as input, which may have led to an underestimation of the indoor air concentrations. No explanation can be found for the lower soil air concentrations.

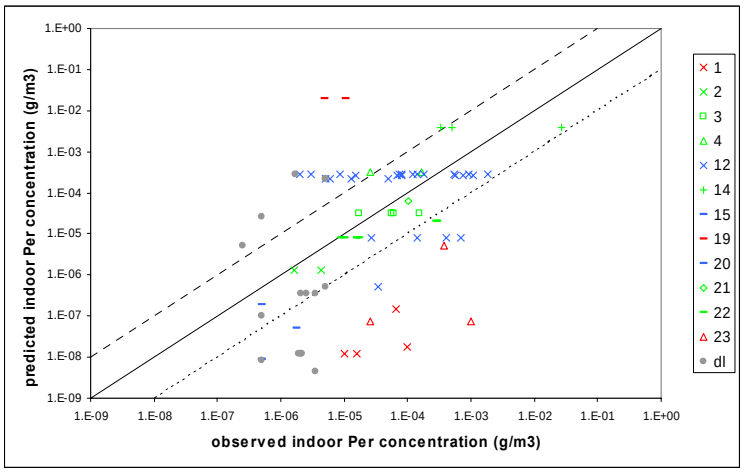


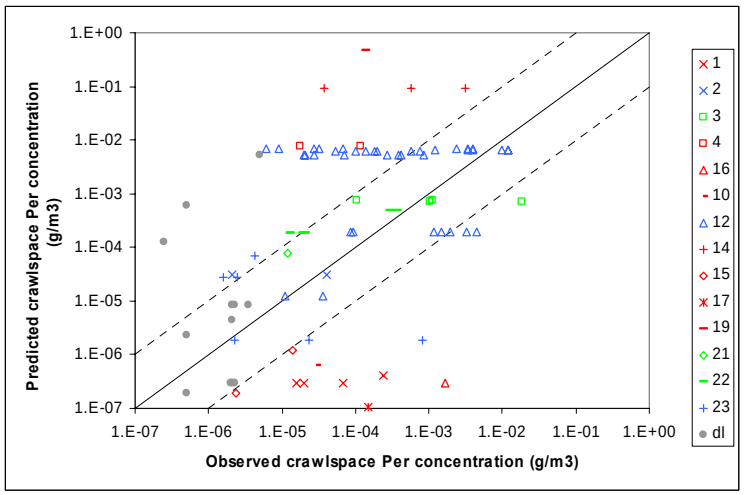
4.4 Case by case approach: conclusions

Predicted and measured air concentrations of tetrachloroethene for all cases and all three compartments are plotted in Figure 4.5 (see also Appendix 2 for exact values). Here, the solid line indicates where observed values are equal to predicted values and dotted lines indicate one order of magnitude difference. The predicted values were calculated, using the groundwater concentration and depth of the groundwater table of each separate case. Also the differences in air permeability and floor quality between cases were taken into account. For the other parameters the default value was taken. Colors in the figure indicate the amount of similarity between observed and predicted values. Green indicates high similarity, where predictions are approximately within 1 order of magnitude, and red indicates low similarity, where all predicted values are more than 1 order of magnitude from observations. Not all compartments were measured in all cases, which explains why some cases are missing in the figures. On average, tetrachloroethene concentrations in cases 2, 3, 10, 14 and 22 seemed to be predicted well by the model, whereas cases 1, 6, 16, 17 and 19 were predicted less (Figure 4.5). Others were in between. In some cases measurements were higher than predictions, whereas in others measurements were lower. Especially in the crawl space and soil air compartment, concentrations were overestimated with more than 1 order of magnitude difference (Table 4.3). Indoor air was predicted best, with more than 50 % of the measurements within one order of magnitude from prediction and an equal amount of under- and overestimation. Similar results were previously reported by OVAM (2004). As was stated earlier, the cases which deviate most from predicted had either a low concentration in groundwater (model underestimates measurements), or a high concentration in groundwater (model overestimates measurements).

Table 4.3 Differences between measured and predicted air concentrations of PER, indicated as percentage of total amount of measurements.

	Indoor air	Crawl space air	Soil air
< 1 order of magnitude difference	53	41	44
Underestimated > 1 order of magnitude difference	28	19	8
Overestimated > 1 order of magnitude difference	19	40	48





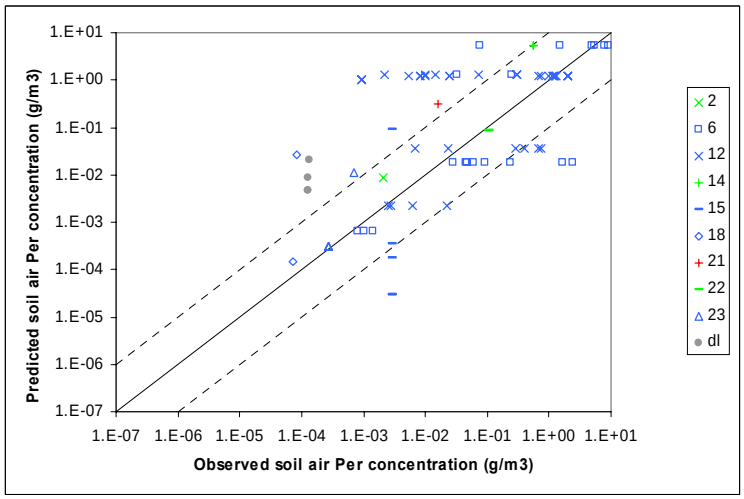


Figure 4.5 Observed versus predicted air concentrations of tetrachloroethene in the indoor, crawl space and soil compartment. Cases are differentiated with a number and a symbol. Detection limits for air concentrations are indicated in gray (dl). Colors indicate the amount of similarity (green) or dissimilarity (red), with blue in between. Dotted lines indicate one order of magnitude difference.

4.5 Case by case: ratios

When two compartments have the same air concentration, the ratio between them will be 1. It is expected, however, that the concentration in the compartment closer to the source is higher than in the compartment further from the source. This means that the ratio will be lower than 1 in most cases. The lower the ratio, the greater the difference in air concentration between the compartments.

Differences between measured and predicted ratios for Csam/Csag were small (**R_1** in Figure 4.6; see caption for an explanation of the abbreviations). Case 14, 15 and 21 showed the largest differences. Most measured and predicted ratios for Ccsam/Csam (**R_2** in Figure 4.6) were not similar and mostly higher than predicted. This may well have been due to different groundwater levels than expected. At high groundwater levels, the ratio is expected to be higher (a lower difference between crawl space air and soil air concentration). so for cases 2, 12, 21, 22 and 23 the average groundwater level might have been higher than expected, whereas for cases 14 and 15 the average level might have been lower.

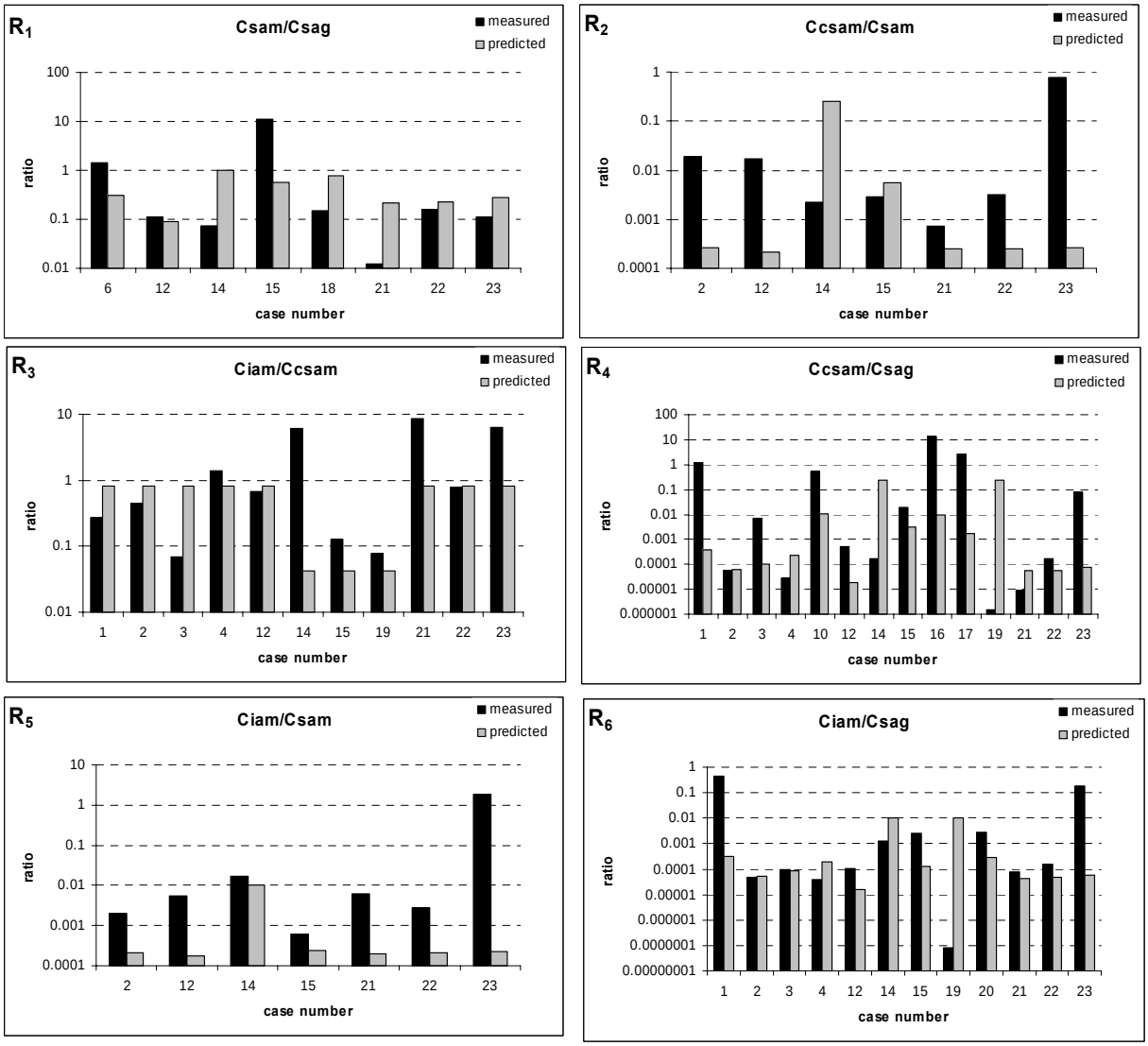


Figure 4.6 Observed (black bars) and predicted (grey bars) ratios for all cases, where csam=concentration soil air measured at 0.5 meter below surface, csag=concentration soil air at groundwater level, ccsam=concentration crawl space air and ciam=concentration indoor air. Detection limits were not included.

The predicted ratio Ciam/Ccsam (**R_3**) is either close to 1 (in case of a cellar or wooden floor) or close to 0.05 (in case of a concrete floor). Measurements for this ratio are more or less similar to predictions, except for cases 3 and 14. Looking at the ratio of case 3, it seems as if the house has a concrete floor, where a wooden floor was assumed. Similarly, in case 14, it seems as if the houses had either a wooden floor or a cellar, where a concrete floor with crawl space was assumed. Since the floor quality was unknown from the available information, the houses probably had a floor similar to a wooden floor or cellar, which may explain the observed differences.

Ratios for Ciam/Csam (**R_5**) were in all cases higher than expected, especially in case 23. This means that the difference in concentration between the compartments is smaller than expected. It seems that the difference in concentration between crawl space and soil is particularly responsible for the observed differences between indoor air and soil air (see also ratio R_2).

Looking at the last two ratios (Ccsam/Csag – **R_4**, Ciam/Csag – **R_6**), it appears that especially cases 1, 16, 17 and 23 show much higher ratios than expected, whereas the ratio of cases 14 and 19 are much lower than expected. For these cases, there may be unknown factors that may explain these differences such as different groundwater levels, other sources of contamination or barriers that prevent the flow into the houses. For case 1 it was confirmed that other sources of contamination may have been important (pers. comm. M. Waitz). All differences between observed and predicted ratios are summarized in Table 4.4. Differences range from 0 to more than 5 orders of magnitude.

Table 4.4 Differences between measured and predicted ratios (log) for all cases. Numbers in bold indicate differences larger than 1 order of magnitude. Numbers are positive when measured ratios are higher than predicted. Concentrations below the detection limit were not included in the analyses (which explains the missing values for case 9).

	R_1	**R_2**	**R_3**	**R_4**	**R_5**	**R_6**
case	Csam/Csag	Ccsam/Csam	Ciam/Ccsam	Ccsam/Csag	Ciam/Csam	Ciam/Csag
1			-0.47	**3.49**		**3.14**
2		**1.86**	-0.27	-0.03	0.97	-0.05
3			**-1.07**	**1.80**		0.02
4			0.24	-0.94		-0.70
6	0.66					
10				**1.68**		
12	0.10	**1.89**	-0.09	**1.42**	**1.50**	0.81
14	**-1.13**	**-2.05**	**2.16**	**-3.18**	0.20	-0.93
15	**1.29**	-0.29	0.48	0.81	0.43	**1.29**
16				**3.14**		
17				**3.17**		
18	-0.71					
19			0.26	**-5.23**		**-5.11**
20						0.99
21	**-1.26**	0.47	**1.02**	-0.79	**1.49**	0.23
22	-0.16	**1.09**	-0.01	0.48	**1.12**	0.53
23	-0.40	**3.47**	0.88	**3.01**	**3.94**	**3.48**

5. Discussion and conclusion

5.1 Discussion

The VOLASOIL model was most sensitive to variation in the groundwater depth. Estimating this depth is difficult due to the spatial and temporal variation of the groundwater table. This may largely explain the differences between observed and predicted air concentrations. The groundwater concentration contributed most to the output variation because this parameter value varied several orders of magnitude between the selected cases, probably due to the large spatial heterogeneity. Variability in predicted and measured air concentration was similar for tetrachloroethene and trichloroethene. Lower variability was observed for measured concentration of cis-dichloroethene and vinylchloride, probably due to the large amount of values below the detection limit.

Overall, VOLASOIL overestimated the air concentrations, especially for tetrachloroethene and at sites with a high groundwater concentration. There was a clear positive relationship between groundwater concentration and air concentration. At sites with low groundwater concentrations (near the detection limit), the model generally underestimated air concentrations.

Many reasons can be mentioned for the observed differences between predicted and measured concentrations. Among these, for example, are the errors that are generated by the measurements. Based on the present results it is to some extend possible to indicate which factors are more relevant than others.

Binding to organic matter
In the VOLASOIL model the soil air concentration is calculated from groundwater concentrations. Currently, the organic matter content is not used in this calculation. In a field situation, part of the contamination will bind to organic carbon, but it will not influence the calculated soil air concentration when there is equilibrium. When total concentration in soil (bound and not bound to organic matter) is used for the calculation, organic matter content needs to be part of the model. However, based on the available cases in this study, there is no indication that binding to organic matter plays an important role, due to the low organic matter content.

Soil porosity
In the VOLASOIL and the CSOIL model, the volume fraction of air in the soil is default set to 0.2. This air-porosity value can be regarded as a kind of upper limit. First, the air-filled pore space will decline towards deeper layers due to compaction and due to an increase in water-filled pore space. Secondly, the volume fraction of air will change in time, depending on the amount of rainfall and the height of the groundwater table. A lower actual air-filled pore space in deeper layers could be a reason for overestimation of air concentration. The soil porosity also depends on the soil type. In a sandy soil the air filled pore space will be higher than in a clay and peat soil. Since the sites in our study differed in soil type, and thus soil porosity, this soil characteristic was made a site-specific parameter. In most cases the top soil consisted of an artificial sandy layer, or a layer rich in sand and, therefore, differences between cases in the type of topsoil are small compared to deeper layers. This makes it difficult to assess the importance of porosity for explaining the observed differences.

Contamination in the unsaturated zone / depletion of the source
The unsaturated zone may also be contaminated in addition to groundwater. In some cases there are high concentrations (or pure product) in the unsaturated zone and in other cases groundwater is the only source. A changing groundwater table may also lead to higher concentrations in the unsaturated zone. When there is no source of contamination in the unsaturated zone, we expect that volatile compounds can only reach the unsaturated zone by diffusion through a thin water-phase. This could be a limiting process, leading to a lower flux from groundwater to soil air and from soil air to indoor air. When there is a source of contamination in the unsaturated zone, there is no limitation in the flux. The fact that the measured soil air concentrations are often lower than the calculated concentration might be due to this limitation-effect. On the other hand there could be a problem with the quality of the soil air measurements, leading to a lower measured concentration than actually is present.

Degradation in the unsaturated zone or in a building (aerobic, anaerobic)
It was suspected that contamination is degraded during the transport through the unsaturated zone. Vinylchloride and to a lesser extend (cis/trans) 1,2-dichloroethene can be degraded under aerobic conditions, due to the characteristics of the compounds. (Sinke *et al*., 1999). These compounds act as an electron donor (and oxygen as an electron acceptor). Under anaerobic conditions chlorinated hydrocarbons act as an electron acceptor and e.g. SO_4^{2-} or H_2 as electron donor. These processes are only important in the unsaturated zone when some specific conditions are met (Sinke *et al*., 2001).

The observed concentrations of vinylchloride and cis-1,2-dichloroethene are often much lower than the predicted concentrations, whereas the observed concentrations of tetrachloroethene are much closer to the predicted concentrations. This is a strong indication that degradation in the unsaturated zone may be a relevant process. On the other hand the physicochemical parameters (Vp, S) could cause the difference, since vinylchloride may be less volatile than expected. The method for measuring vinylchloride may be a problem too. This could all lead to an underestimation of the actual concentration present.

Handling heterogeneity; distance between the building and the locations where measurements in groundwater and soil were done
It is often unknown where the highest contaminant concentrations in the groundwater or the soil are. These concentrations can show a high spatial heterogeneity, which makes it difficult to locate hot spots. Some cases in this report support the occurrence of a high horizontal and vertical variability (from lower than the detection limit to more than $10 \cdot 10^3$ µg/kg within a few meters). When a groundwater measurement is further than about 5-10 meter from a building it seems therefore uncertain whether the same concentration is also present under the building. Often a reasonable worst case concentration is chosen for model calculations, where we have used the relevant average concentration and the distribution of the location. The question is on which choice the assessment should be based. When measurements do not meet the predicted concentration, heterogeneity in the groundwater concentrations could be a reason.

Characteristics of buildings (type of building, permeability of the floor)
According to the VOLASOIL model, the type of building has a large influence on the predicted concentrations. For buildings with a crawl space and a wooden floor, a larger transport from the crawl space to the indoor air is expected than in buildings with an intact concrete floor directly on the soil surface (‘slab on grade’). The observed concentration differences between compartments might help to revise the parameters in the model. Looking

at the ratios of measured indoor air concentrations compared to crawl space air concentrations for tetrachloroethene (see also Appendix 3), there is a tendency that when there is a cellar, more often ratios near or above 1 are found than when there is a crawl space (Figure 5.1). Also, differences in the floor quality seem to have an effect, although these trends were not significant ($P = 0.671$). Ratios were slightly higher in houses with a wooden floor compared to houses with a concrete floor. This means that differences between indoor air and crawl space air concentrations were larger in houses with a concrete floor than in houses with a cellar.

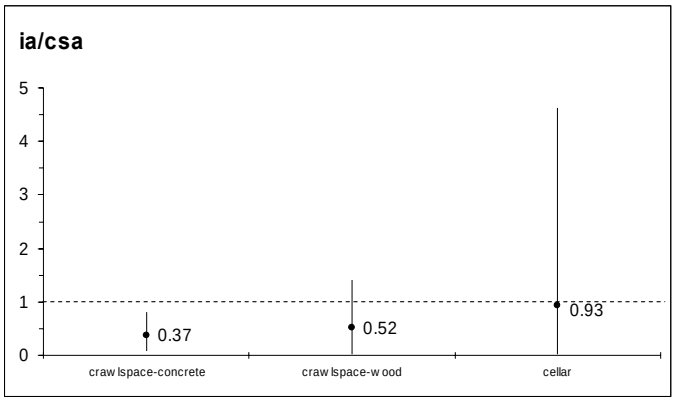


Figure 5.1 Average ratios of PER concentration (indoor air/crawl space air, with 5 and 95 percentile) in houses with a crawl space and concrete floor, houses with a crawl space and wooden floor and houses with a cellar.

Influence of time of measurement

Due to temperature differences in summer and winter, the convective transport through the soil and through the house can change. The chimney effect in the winter is a classic example (warm air in houses ascends and cold air from the crawl space/soil enters the building). This may result in different air concentrations in summer and winter (Fast *et al*., 1987). Therefore, besides the model concept, especially the parameters describing this process should be chosen as realistic as possible. In our dataset, we found a seasonal effect on the crawl space air and indoor air concentration (Figure 5.2). When measurements were done in summer, then air concentrations were lower.

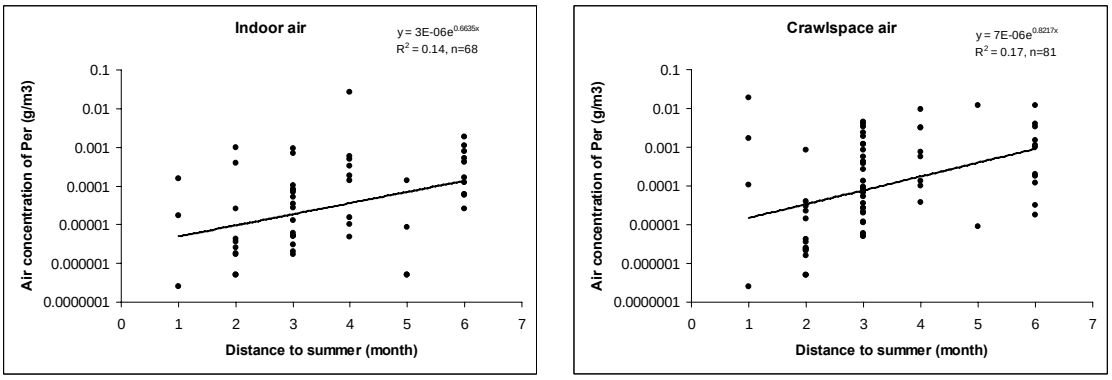


Figure 5.2 Air concentration in relation to month of measurement. Summer months were July and August (number 1 on the x-axis). Winter months were January and February (number 6 on the x-axis). Number 2 = March/September, 3 = April/October, 4 = May/November, 5 = June/December.

When ratios were related to the period of measurement (discarding detection limits), then no trend was observed (Figure 5.3).

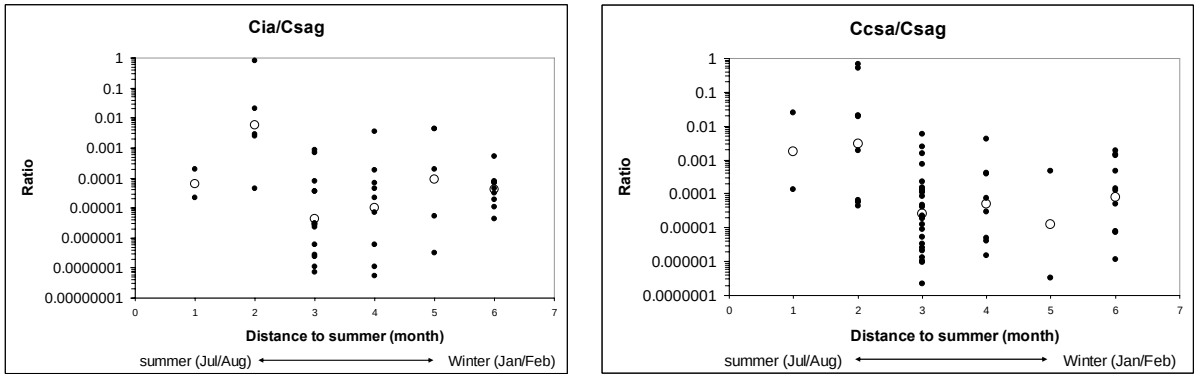


Figure 5.3 Air concentration ratios in relation to month of measurement. Geometric mean values are indicated with large open circles. Trends were not significan t at P<0.05 (Tukey post-hoc test on log transformed data).

Period between the measurements in groundwater and air

A difficulty is the fact that not all measurements at each site are done at the same time. When there are several years between the measurements, the concentrations in the groundwater can change due to transport and degradation. In general it is not possible to derive a maximum number of years after which groundwater concentrations are outdated, but a period of more than 3 years between measurements is not recommended for modelling and new measurements should be done. For instance in case 4, groundwater concentrations decreased to a third in 4 years, which could explain much of the difference between observed and predicted air concentrations (Chapter 4.3). The period between groundwater and air measurements in our dataset, however, does not show any relationship with the difference between observed and predicted air concentrations (R^2 = 0.0004; Figure 5.4).

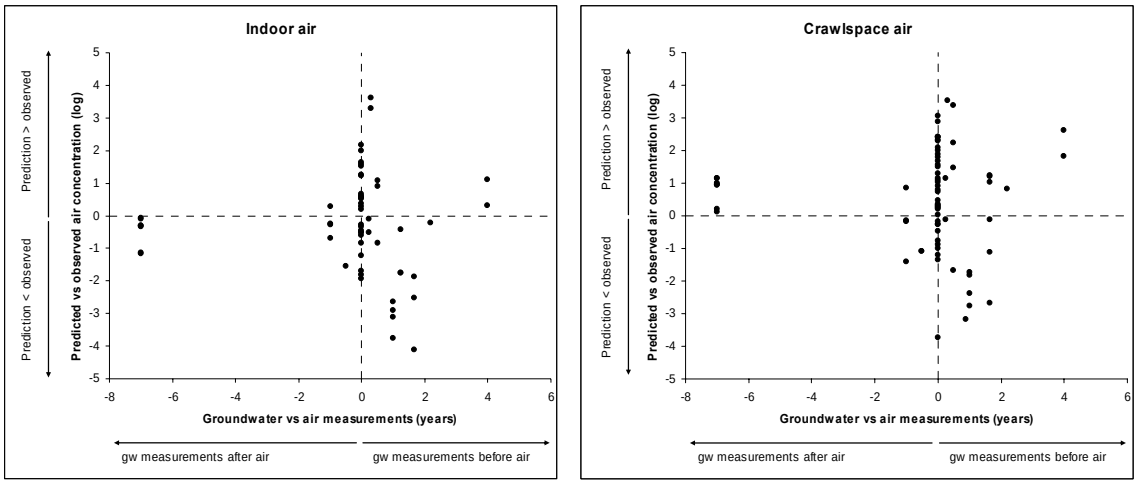


Figure 5.4 Effects of the length of time between air and groundwater measurements on the difference between observed and predicted air concentration for indoor air and crawl space air. When groundwater measurements were done before the air concentration measurements, then values are positive. Also, when predicted air concentration is higher than observed air concentration, then values are positive.

5.2 Conclusions

- The model performs reasonably well for tetrachloroethene and trichloroethene compared to the compounds cis 1,2-dichloroethene and vinylchloride. The predictions for the last two compounds deviate more from the measurements than for the other compounds. A possible reason for these differences is the breakdown of both compounds in the vadose zone of the soil and in the air.
- At high groundwater concentration, air concentrations are frequently overestimated, whereas low groundwater concentrations often lead to underestimation of air concentrations.
- The predicted concentration of tetrachloroethene in crawl space air is in most cases higher than the observed concentration (Table 4.3, Figure 4.3 and 4.5).
- The predicted concentration of tetrachloroethene in indoor air is equally higher as lower than the observed concentration from measurements (Table 4.3, Figure 4.5). This mainly depends on the groundwater concentration (Figure 4.3).
- The measured tetrachloroethene concentration in soil air is in general one order of magnitude lower than the predicted soil air concentration. For some cases this is even 2 orders of magnitude, although there are also some cases where the measured concentrations are higher (see also Appendix 2, Table 4.3, Figure 4.3 and 4.5).
- The predicted difference between the crawl space air and the indoor air concentration of all substances is usually higher than the measured differences between both compartments. This means that there is more mixing of air (higher exchange rate) between the crawl space and indoor air than assumed in the default situation of the model. This might be attributed to the fact that some houses had cellars instead of crawl spaces.
- Large differences in goodness of prediction are observed between cases. It is concluded that the heterogeneity of the groundwater contamination determines to a large extend the predicted variability in the air concentrations. Also the heterogeneity of the soil will contribute to these differences.
- There is a clear seasonal effect on the air concentration.
- In case of a building with a ‘slab on grade’ floor, soil-air measurements can be a good alternative for the crawl space measurements in order to prove that the contaminant originated from the soil.
- Soil air measurements can be used as an alternative for groundwater measurements, because predicted and observed soil air concentrations were similar. Predicted soil air concentrations are based on groundwater concentrations.

5.3 Recommendations based on this study

- When the model must predict realistic concentrations (not worst case), then adjustment of the model is necessary for the relationship between *crawl space air* and *indoor air.* In case of a cellar, the concentration in the cellar should be equal to indoor air. In case of a crawl space, the default contribution of crawl space air to indoor air should be lowered to a value between 0.1 and 0.3.

- Similarly, adjustment of the model is necessary for the relationship between *groundwater concentration* and air concentration. The model systematically overestimates at high groundwater concentrations and underestimates at low concentrations. When worst case scenarios are acceptable, then no adjustments are needed.
- Only groundwater concentrations within 10 meter of a building should be used for the risk assessment within the same buildings (e.g. within 10 meter upstream and downstream of a building). In this way the effect of heterogeneity of the contamination can be reduced. In the planning of groundwater sampling this should also be a factor to account for.
- A guideline must be created on how to deal with variation of groundwater concentrations on a spatial and temporal scale. Old measurements give a less accurate estimation of the risk.
- It is not recommended to carry out measurements exclusively during summer. In summer, temperature differences between outdoor and indoor air are small (no chimney effect) and ventilation rates are higher. This leads to underestimations of the average indoor air concentrations. Average air concentrations (over a year) can best be measured in April/May and October/November.

5.4 Recommendations based on discussions with experts

- Besides default values, more information about the distribution of input-parameters must be present in the VOLASOIL model in order to make it easier to select the best parameter value and give insight in uncertainties. This may be especially useful for the sensitive parameters such as the quality of the floor and soil characteristics.
- The default height of the capillary transition boundary above the groundwater table (z) should be at least 10 cm, instead of 0.5 cm. This prevents the occurrence of unrealistic fluxes from soil to the crawl space.
- The default volume fraction of air in the soil must be soil type dependent. Although not observed, it is expected that diffusion in clayey soils is lower than sandy soils.
- A mass balance calculation must be added to the model to be able to check how long the derived flux can occur based on the estimated total amount of contamination.
- Besides the depth of the groundwater table, the depth of the unsaturated zone should be indicated. The difference between both could overrule the default value for the CTB.
- A guideline should define when modelling is preferred over measurements and vice versa. Modelling can be used as a screening method before carrying out measurements.
- More choice in the parameter value for floor quality should be offered in the VOLASOIL model (parameter: total area of openings in the floor), because the current three options give large differences in the output.
- The degradation of compounds in the vadose zone must be studied in more detail. Notably for vinylchloride and cis-1,2-dichloroethene this could be a relevant process

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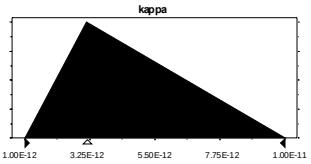
Appendix 1 Input parameter distributions and ranges

Assumption: kappa (air permeability of soil; m^2)

Triangular distribution with parameters:

Minimum	1.00E-12
Likeliest	3.16E-12
Maximum	1.00E-11



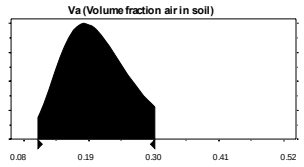
Selected range is from $1 \cdot 10^{-12}$ to $1 \cdot 10^{-11}$

From: Rikken *et al.* (2001)

Assumption: Va (Volume fraction air in soil)

Lognormal distribution with parameters:

Geometric Mean	0.2
90% - tile	0.3



Selected range is from 0.1 to 0.3

Correlated with:

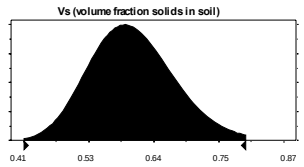
Vs (volume fraction solids in soil)	-1.00

From: Vissenberg and Swartjes (1996)

Assumption: Vs (volume fraction solids in soil)

Lognormal distribution with parameters:

Geometric Mean	0.6
90% - tile	0.7



Selected range is from 0.4 to 0.8

Correlated with:

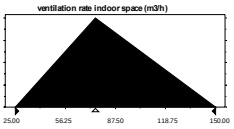
Va (Volume fraction air in soil)	-1.00

From: Vissenberg and Swartjes (1996)

Assumption: ventilation rate indoor space (m^3/h)

Triangular distribution with parameters:

Minimum	25
Likeliest	75
Maximum	150

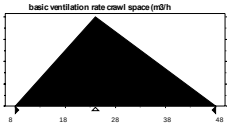


Selected range is from 25 to 150
From: Rikken *et al.* (2001)

Assumption: basic ventilation rate crawl space (horizontal ventilation; m^3/h)

Triangular distribution with parameters:

Minimum	8
Likeliest	24
Maximum	48

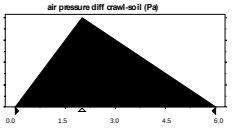


Selected range is from 8 to 48
From: Otte *et al.* (2001)

Assumption: air pressure difference crawlspace-soil (Pa)

Triangular distribution with parameters:

Minimum	0
Likeliest	2
Maximum	6

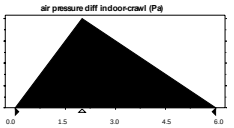


Selected range is from 0 to 6
From: Rikken *et al.* (2001)

Assumption: air pressure difference indoor-crawlspace (Pa)

Triangular distribution with parameters:

Minimum	0
Likeliest	2
Maximum	6

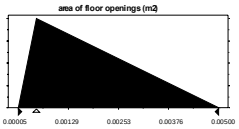


Selected range is from 0 to 6
From: Rikken *et al.* (2001)

Assumption: area of floor openings (m^2)

Triangular distribution with parameters:

Minimum	0.00005
Likeliest	0.0005
Maximum	0.005



Selected range is from 0.00005 to 0.005
From: table in VOLASOIL model

Assumption: Floor thickness (m)

Triangular distribution with parameters:

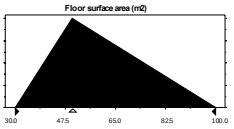
Minimum	0.05
Likeliest	0.10
Maximum	0.20

Selected range is from 0.05 to 0.20
From: expert judgement

Assumption: Floor surface area (m^2)

Triangular distribution with parameters:

Minimum	30
Likeliest	50
Maximum	100



Selected range is from 30 to 100
From: expert judgement

Appendix 2 Observed and predicted air concentrations (in g/m^3) in indoor, crawl space and soil of tetrachloroethene

	Indoor			Crawl space			Soil		
case no.	dl	Observed	Predicted	dl	Observed	Predicted	dl	Observed	Predicted
1	<	2.0E-06	1.2E-08	<	2.1E-06	2.9E-07			
1	<	2.1E-06	1.2E-08	<	2.1E-06	2.9E-07			
1	<	2.1E-06	3.6E-07	<	2.1E-06	2.9E-07			
1	<	2.1E-06	1.2E-08	<	2.1E-06	4.3E-06			
1	<	2.2E-06	1.2E-08	<	2.1E-06	8.5E-06			
1		1.0E-05	1.2E-08	<	2.3E-06	2.9E-07			
1		1.6E-05	1.2E-08	<	2.3E-06	2.9E-07			
1		6.6E-05	1.5E-07	<	2.3E-06	8.5E-06			
1		9.9E-05	1.8E-08		1.6E-05	2.9E-07			
1					2.0E-05	2.9E-07			
1					6.9E-05	2.9E-07			
1					2.4E-04	4.2E-07			
2		1.7E-06	1.3E-06		2.1E-06	3.0E-05	<	1.3E-04	8.8E-03
2		4.3E-06	1.3E-06		4.1E-05	3.0E-05		2.1E-03	8.8E-03
3		1.7E-05	3.1E-05		1.0E-04	7.4E-04			
3		5.6E-05	3.1E-05		1.0E-03	7.2E-04			
3		6.0E-05	3.1E-05		1.1E-03	7.4E-04			
3		1.5E-04	3.1E-05		1.9E-02	7.2E-04			
4		2.6E-05	3.3E-04		1.8E-05	7.7E-03			
4		1.7E-04	3.3E-04		1.2E-04	7.7E-03			
6								8.0E-04	6.6E-04
6								1.0E-03	6.6E-04
6								1.4E-03	6.6E-04
6								2.9E-02	1.9E-02
6								3.3E-02	1.3E+00
6								4.5E-02	1.9E-02
6								4.7E-02	1.9E-02
6								5.9E-02	1.9E-02
6								7.5E-02	5.5E+00
6								9.3E-02	1.9E-02
6								2.4E-01	1.9E-02
6								2.5E-01	1.3E+00
6								1.5E+00	5.5E+00
6								1.7E+00	1.9E-02
6								2.4E+00	1.9E-02
6								5.0E+00	5.5E+00
6								5.3E+00	5.5E+00
6								7.7E+00	5.5E+00
6								9.0E+00	5.5E+00
6								1.1E+01	5.5E+00
9	<	2.5E-07	7.7E-06	<	2.5E-07	9.5E-06			
10	<	2.5E-06	5.2E-07	<	3.5E-06	6.3E-07			
10	<	3.5E-06	5.2E-07		3.0E-05	6.3E-07			
12	<	1.7E-06	2.9E-04	<	5.0E-06	5.3E-03		9.2E-04	1.0E+00
12		2.0E-06	2.9E-04		6.0E-06	6.7E-03		9.2E-04	1.0E+00
12		3.0E-06	2.9E-04		9.0E-06	6.7E-03		9.2E-04	1.0E+00
12	<	5.0E-06	5.1E-07		1.1E-05	1.2E-05		2.1E-03	1.3E+00
12		5.0E-06	2.2E-04		2.0E-05	5.3E-03		2.5E-03	2.3E-03
12	<	5.0E-06	2.2E-04		2.1E-05	5.3E-03		2.8E-03	2.3E-03
12	<	5.0E-06	2.2E-04		2.7E-05	5.3E-03		5.3E-03	1.2E+00

	Indoor			Crawl space			Soil	
case no.	dl	Observed	Predicted	dl	Observed	Predicted	dl	Observed	Predicted
12		6.0E-06	2.2E-04		2.7E-05	6.7E-03		6.2E-03	2.3E-03
12		8.7E-06	2.9E-04		3.2E-05	6.7E-03		6.9E-03	3.7E-02
12		1.3E-05	2.2E-04		3.6E-05	1.2E-05		8.3E-03	1.2E+00
12		1.5E-05	2.7E-04		5.3E-05	6.3E-03		8.3E-03	1.2E+00
12		2.7E-05	8.2E-06		6.8E-05	6.7E-03		1.0E-02	1.2E+00
12		3.4E-05	5.1E-07		7.0E-05	5.3E-03		1.0E-02	1.3E+00
12		5.0E-05	2.2E-04		8.6E-05	1.9E-04		1.5E-02	1.3E+00
12		6.8E-05	2.7E-04		9.2E-05	1.9E-04		2.2E-02	2.3E-03
12		7.5E-05	2.7E-04		1.0E-04	6.3E-03		2.3E-02	3.7E-02
12		7.9E-05	2.7E-04		1.4E-04	6.3E-03		2.5E-02	1.2E+00
12		8.0E-05	2.9E-04		1.8E-04	6.3E-03		2.5E-02	1.2E+00
12		1.2E-04	2.9E-04		2.0E-04	6.3E-03		7.4E-02	1.3E+00
12		1.4E-04	8.2E-06		2.7E-04	5.3E-03		2.8E-01	3.7E-02
12		1.4E-04	2.7E-04		3.8E-04	5.3E-03		3.0E-01	1.3E+00
12		1.8E-04	2.7E-04		4.2E-04	5.3E-03		3.0E-01	1.3E+00
12		4.2E-04	8.2E-06		5.8E-04	6.3E-03		3.9E-01	3.7E-02
12		5.3E-04	2.9E-04		7.6E-04	6.3E-03		6.8E-01	3.7E-02
12		5.7E-04	2.7E-04		8.4E-04	5.3E-03		6.8E-01	1.2E+00
12		6.9E-04	8.2E-06		1.2E-03	1.9E-04		7.4E-01	3.7E-02
12		7.6E-04	2.7E-04		1.2E-03	6.5E-03		7.4E-01	1.2E+00
12		9.1E-04	2.7E-04		1.5E-03	1.9E-04		9.7E-01	1.2E+00
12		1.1E-03	2.7E-04		1.9E-03	1.9E-04		1.1E+00	1.2E+00
12		1.8E-03	2.7E-04		2.3E-03	6.7E-03		1.2E+00	1.2E+00
12					3.2E-03	1.9E-04		1.2E+00	1.2E+00
12					3.4E-03	6.5E-03		1.2E+00	1.2E+00
12					3.4E-03	6.7E-03		1.2E+00	1.2E+00
12					3.9E-03	6.7E-03		1.3E+00	1.2E+00
12					4.0E-03	6.5E-03		2.0E+00	1.2E+00
12					4.4E-03	1.9E-04		2.0E+00	1.2E+00
12					9.7E-03	6.5E-03		2.0E+00	1.2E+00
12					1.2E-02	6.5E-03			
12					1.2E-02	6.5E-03			
14		3.4E-04	4.0E-03		3.8E-05	9.4E-02		5.6E-01	5.4E+00
14		5.0E-04	4.0E-03		5.6E-04	9.4E-02		5.6E-01	5.4E+00
14		2.7E-02	4.0E-03		3.1E-03	9.4E-02		5.6E-01	5.4E+00
15	<	5.0E-07	8.3E-09	<	5.0E-07	2.0E-07		2.9E-03	2.9E-05
15	<	5.0E-07	9.9E-08	<	5.0E-07	2.3E-06		2.9E-03	2.9E-05
15	<	5.0E-07	2.6E-05	<	5.0E-07	6.1E-04		2.9E-03	1.8E-04
15		1.8E-06	5.0E-08		2.4E-06	2.0E-07		2.9E-03	3.5E-04
15					1.4E-05	1.2E-06		2.9E-03	9.1E-02
16					1.6E-03	2.9E-07			
17	<	3.5E-06	4.4E-09		1.5E-04	1.0E-07			
18								7.1E-05	1.5E-04
18								8.3E-05	2.6E-02
19		4.9E-06	2.0E-02		1.4E-04	4.6E-01			
19		1.0E-05	2.0E-02						
20		5.0E-07	8.7E-09						
20		5.0E-07	8.7E-09						
20		5.0E-07	1.9E-07						
21		1.0E-04	6.3E-05		1.2E-05	7.7E-05		1.6E-02	3.1E-01
22		9.0E-06	7.8E-06		1.3E-05	1.8E-04		1.1E-01	8.4E-02
22		1.0E-05	7.8E-06		1.3E-05	1.8E-04		1.1E-01	8.4E-02
22		1.6E-05	7.8E-06		1.9E-05	1.8E-04			
22		1.6E-05	7.8E-06		2.0E-05	1.8E-04			
22		1.7E-05	7.8E-06		2.1E-05	1.8E-04			
22		2.8E-04	2.0E-05		2.1E-05	1.8E-04			
22		2.9E-04	2.0E-05		3.0E-04	4.8E-04			
22					3.7E-04	4.8E-04			
23		2.6E-05	7.6E-08		1.6E-06	2.7E-05	<	1.3E-04	4.5E-03
23		3.8E-04	5.3E-06		2.3E-06	1.8E-06	<	1.3E-04	4.5E-03

	Indoor			Crawl space			Soil	
case no.	dl	Observed	Predicted	dl	Observed	Predicted	dl	Observed	Predicted
23		1.0E-03	7.6E-08		2.5E-06	2.7E-05	<	1.4E-04	2.1E-02
23					4.2E-06	6.8E-05		2.7E-04	3.0E-04
23					2.3E-05	1.8E-06		2.7E-04	3.0E-04
23					8.3E-04	1.8E-06		2.7E-04	3.0E-04
23								6.9E-04	1.1E-02

Appendix 3 Calculated and measured ratios for each case and substance

substance	case #	Csam/Csag calculated	Csam/Csag measured	5 percentile	95 percentile	n
cis	all	$1.9x10^{-1}$	$1.8x10^{-3}$	$3.7x10^{-6}$	$4.9x10^{-2}$	27
cis	6	$1.4x10^{-1}$	$8.7x10^{-1}$	$8.9x10^{-2}$	$2.1x10^{1}$	17
cis	14	$7.1x10^{-1}$	$3.6x10^{-2}$	$3.6x10^{-2}$	$3.6x10^{-2}$	3
cis	15	$2.5x10^{-1}$	$4.8x10^{-4}$	$2.2x10^{-4}$	$3.4x10^{-2}$	5
cis	18	$6.3x10^{-1}$	$3.3x10^{-1}$			2
per	all	$1.2x10^{-1}$	$6.7x10^{-3}$	$4.4x10^{-5}$	1.3	74
per	6	$1.4x10^{-1}$	$2.1x10^{-1}$	$4.7x10^{-2}$	$1.0x10^{1}$	20
per	12	$4.8x10^{-2}$	$9.8x10^{-3}$	$4.4x10^{-5}$	$5.8x10^{-1}$	37
per	14	$7.1x10^{-1}$	$7.5x10^{-2}$	$7.5x10^{-2}$	$7.5x10^{-2}$	3
per	15	$2.5x10^{-1}$	2.1	$4.1x10^{-1}$	$2.4x10^{1}$	5
per	18	$6.3x10^{-1}$	$2.5x10^{-2}$			2
per	21	$1.1x10^{-1}$	$1.2x10^{-2}$			1
per	22	$1.2x10^{-1}$	$1.6x10^{-1}$			2
per	23	$1.6x10^{-1}$	$7.3x10^{-2}$	$3.0x10^{-2}$	$1.4x10^{-1}$	4
tri	all	$1.8x10^{-1}$	$7.6x10^{-3}$	$2.2x10^{-5}$	5.1	29
tri	6	$1.4x10^{-1}$	$7.5x10^{-1}$	$5.3x10^{-2}$	$1.6x10^{1}$	16
tri	14	$7.1x10^{-1}$	$8.5x10^{-3}$	$8.5x10^{-3}$	$8.5x10^{-3}$	3
tri	15	$2.5x10^{-1}$	$1.6x10^{-1}$	$2.9x10^{-2}$	2.2	5
tri	18	$6.2x10^{-1}$	$1.6x10^{-1}$			2
tri	21	$1.1x10^{-1}$	$5.7x10^{-2}$			1
tri	22	$1.3x10^{-1}$	7.1			2
vinylchloride	all	$2.4x10^{-1}$	$6.6x10^{-4}$	$7.4x10^{-5}$	$4.7x10^{-3}$	8
vinylchloride	6	$1.3x10^{-1}$	1.4	$3.6x10^{-1}$	5.0	6
vinylchloride	18	$6.2x10^{-1}$	$6.9x10^{-5}$			2

substance	case #	Ccsam/Csam calculated	Ccsam/Csam measured	5 percentile	95 percentile	n
cis	all	$8.7x10^{-3}$	1.6			2
cis	14	$2.0x10^{-2}$	$1.7x10^{-3}$			1
cis	15	$7.6x10^{-3}$	3.2			1
per	all	$8.5x10^{-3}$	$6.6x10^{-3}$	$1.5x10^{-4}$	$8.2x10^{-2}$	23
per	2	$6.6x10^{-3}$	$1.9x10^{-2}$			1
per	12	$5.2x10^{-3}$	$8.6x10^{-3}$	$2.1x10^{-3}$	$4.0x10^{-2}$	10
per	14	$1.7x10^{-2}$	$7.2x10^{-4}$	$1.6x10^{-4}$	$5.1x10^{-3}$	3
per	15	$6.7x10^{-3}$	$2.0x10^{-3}$			2
per	21	$5.6x10^{-3}$	$7.4x10^{-4}$			1
per	22	$5.7x10^{-3}$	$3.1x10^{-3}$			2
per	23	$6.0x10^{-3}$	$6.1x10^{-2}$	$6.5x10^{-3}$	2.6	4
tri	all	$7.8x10^{-3}$	$5.5x10^{-3}$	$2.6x10^{-4}$	$8.1x10^{-2}$	7
tri	14	$1.8x10^{-2}$	$7.4x10^{-3}$			1
tri	15	$7.0x10^{-3}$	$3.9x10^{-2}$	$1.7x10^{-2}$	$9.1x10^{-2}$	3
tri	21	$5.9x10^{-3}$	$4.7x10^{-3}$			1
tri	22	$6.0x10^{-3}$	$2.6x10^{-4}$			2

substance	case #	Ciam/Ccsam calculated	Ciam/Ccsam measured	5 percentile	95 percentile	n
cis	all	$4.2x10^{-2}$	$3.3x10^{-1}$	$7.6x10^{-2}$	2.8	5
cis	1	$4.2x10^{-2}$	$2.8x10^{-1}$			2
cis	9	$4.2x10^{-2}$	3.4			1
cis	15	$4.2x10^{-2}$	$5.7x10^{-2}$			1
cis	19	$4.2x10^{-2}$	$2.6x10^{-1}$			1
per	all	$4.2x10^{-2}$	$3.3x10^{-1}$	$2.5x10^{-2}$	8.6	51
per	1	$4.2x10^{-2}$	$2.4x10^{-1}$			2
per	2	$4.2x10^{-2}$	$2.9x10^{-1}$			2
per	3	$4.2x10^{-2}$	$4.4x10^{-2}$	$1.4x10^{-2}$	$1.5x10^{-1}$	4
per	4	$4.2x10^{-2}$	1.4			2
per	12	$4.2x10^{-2}$	$2.0x10^{-1}$	$2.2x10^{-2}$	3.2	26
per	14	$4.2x10^{-2}$	4.1	1.7	8.8	3
per	15	$4.2x10^{-2}$	$1.3x10^{-1}$			1
per	19	$4.2x10^{-2}$	$7.6x10^{-2}$			1
per	21	$4.2x10^{-2}$	8.6			1
per	22	$4.2x10^{-2}$	$7.9x10^{-1}$	$7.1x10^{-1}$	$9.3x10^{-1}$	7
per	23	$4.2x10^{-2}$	3.7			2
tri	all	$4.2x10^{-2}$	$5.1x10^{-1}$	$1.0x10^{-1}$	1.7	14
tri	1	$4.2x10^{-2}$	$2.6x10^{-1}$			2
tri	9	$4.2x10^{-2}$	1.8			1
tri	12	$4.2x10^{-2}$	$8.3x10^{-1}$			1
tri	14	$4.2x10^{-2}$	$5.3x10^{-1}$			1
tri	15	$4.2x10^{-2}$	$1.7x10^{-1}$			2
tri	19	$4.2x10^{-2}$	$7.9x10^{-2}$			1
tri	21	$4.2x10^{-2}$	1.6			1
tri	22	$4.2x10^{-2}$	$8.4x10^{-1}$	$6.6x10^{-1}$	1.0	5

substance	case #	Ccsam/Csag calculated	Ccsam/Csag measured	5 percentile	95 percentile	n
cis	all	$1.7x10^{-3}$	$3.1x10^{-3}$	$8.3x10^{-5}$	2.2	11
cis	1	$5.7x10^{-3}$	$3.5x10^{-2}$	$2.9x10^{-3}$	3.7	3
cis	3	$1.9x10^{-3}$	$1.6x10^{-4}$			2
cis	9	$2.9x10^{-3}$	$6.3x10^{-2}$			1
cis	10	$2.9x10^{-1}$	$3.4x10^{-1}$			1
cis	14	$1.4x10^{-2}$	$5.9x10^{-5}$			1
cis	15	$1.9x10^{-3}$	$3.5x10^{-3}$			1
cis	16	$2.9x10^{-3}$	$4.3x10^{-4}$			1
cis	19	$5.7x10^{-3}$	$1.3x10^{-4}$			1
per	all	$4.9x10^{-3}$	$2.0x10^{-4}$	$1.0x10^{-6}$	$7.8x10^{-1}$	73
per	1	$5.0x10^{-3}$	$7.5x10^{-1}$	$2.8x10^{-1}$	2.7	4
per	2	$1.6x10^{-3}$	$5.8x10^{-5}$			1
per	3	$1.7x10^{-3}$	$1.6x10^{-3}$	$3.1x10^{-4}$	$2.1x10^{-2}$	4
per	4	$3.1x10^{-3}$	$1.9x10^{-5}$			2
per	10	$2.5x10^{-1}$	$5.1x10^{-1}$			1
per	12	$2.5x10^{-4}$	$3.4x10^{-5}$	$8.5x10^{-7}$	$2.7x10^{-3}$	38
per	14	$1.2x10^{-2}$	$5.4x10^{-5}$	$1.2x10^{-5}$	$3.8x10^{-4}$	3
per	15	$1.7x10^{-3}$	$2.0x10^{-2}$			2
per	16	$2.5x10^{-3}$	$1.4x10^{1}$			1
per	17	$3.1x10^{-3}$	2.6			1
per	19	$5.0x10^{-3}$	$1.5x10^{-6}$			1
per	21	$6.2x10^{-4}$	$8.9x10^{-6}$			1
per	22	$7.1x10^{-4}$	$1.1x10^{-4}$	$5.0x10^{-5}$	$5.1x10^{-4}$	8
per	23	$9.6x10^{-4}$	$1.1x10^{-3}$	$5.7x10^{-5}$	$3.3x10^{-1}$	6
tri	all	$1.4x10^{-3}$	$1.4x10^{-2}$	$1.1x10^{-4}$	3.3	26
tri	1	$5.3x10^{-3}$	1.1	$1.8x10^{-1}$	9.0	5
tri	3	$1.8x10^{-3}$	$2.1x10^{-3}$			2
tri	9	$2.6x10^{-3}$	$2.3x10^{-3}$			1
tri	10	$2.6x10^{-1}$	1.3			1
tri	12	$2.6x10^{-4}$	$1.5x10^{-3}$			2
tri	14	$1.3x10^{-2}$	$6.3x10^{-5}$			1
tri	15	$1.8x10^{-3}$	$2.4x10^{-2}$	$8.8x10^{-3}$	$6.6x10^{-2}$	3
tri	16	$2.6x10^{-3}$	1.0			1
tri	17	$3.3x10^{-3}$	1.1			1
tri	19	$5.3x10^{-3}$	$2.8x10^{-5}$			1
tri	21	$6.6x10^{-4}$	$2.7x10^{-4}$			1
tri	22	$7.5x10^{-4}$	$2.7x10^{-3}$	$3.2x10^{-4}$	$2.7x10^{-2}$	7
vinylchloride	3	$2.2x10^{-3}$	$1.7x10^{-4}$			2

substance	case #	Ciam/Csag calculated	Ciam/Csag measured	5 percentile	95 percentile	n
cis	all	$2.4x10^{-4}$	$9.8x10^{-3}$	$8.2x10^{-5}$	2.9	7
cis	1	$2.4x10^{-4}$	$2.4x10^{-1}$	$2.1x10^{-1}$	3.1	3
cis	9	$1.2x10^{-4}$	$2.1x10^{-1}$			1
cis	15	$8.1x10^{-5}$	$3.0x10^{-4}$			2
cis	19	$2.4x10^{-4}$	$3.2x10^{-5}$			1
per	all	$2.1x10^{-4}$	$6.2x10^{-5}$	$1.1x10^{-7}$	$1.9x10^{-1}$	57
per	1	$2.1x10^{-4}$	$2.7x10^{-1}$	$1.1x10^{-1}$	1.1	4
per	2	$6.7x10^{-5}$	$4.6x10^{-5}$			1
per	3	$7.0x10^{-5}$	$6.9x10^{-5}$	$2.9x10^{-5}$	$1.8x10^{-4}$	4
per	4	$1.3x10^{-4}$	$2.7x10^{-5}$			2
per	12	$1.1x10^{-5}$	$6.9x10^{-6}$	$1.4x10^{-7}$	$6.6x10^{-4}$	26
per	14	$5.3x10^{-4}$	$2.2x10^{-4}$	$4.7x10^{-5}$	$3.3x10^{-3}$	3
per	15	$7.0x10^{-5}$	$2.6x10^{-3}$			1
per	19	$2.1x10^{-4}$	$7.7x10^{-8}$			2
per	20	$1.3x10^{-4}$	$1.5x10^{-3}$	$6.0x10^{-4}$	$4.3x10^{-3}$	3
per	21	$2.6x10^{-5}$	$7.6x10^{-5}$			1
per	22	$3.0x10^{-5}$	$9.4x10^{-5}$	$3.6x10^{-5}$	$4.3x10^{-4}$	7
per	23	$4.1x10^{-5}$	$2.8x10^{-2}$	$4.0x10^{-3}$	$4.8x10^{-1}$	3
tri	all	$3.3x10^{-4}$	$3.4x10^{-3}$	$1.1x10^{-5}$	$6.0x10^{-1}$	21
tri	1	$2.2x10^{-4}$	$6.3x10^{-1}$	$1.8x10^{-1}$	3.9	4
tri	9	$1.1x10^{-4}$	$4.2x10^{-3}$			1
tri	12	$1.1x10^{-5}$	$1.0x10^{-3}$			2
tri	14	$5.6x10^{-4}$	$3.4x10^{-5}$			1
tri	15	$7.4x10^{-5}$	$3.7x10^{-3}$			2
tri	19	$2.2x10^{-4}$	$2.2x10^{-6}$			1
tri	20	$1.4x10^{-4}$	$1.6x10^{-3}$	$1.8x10^{-3}$	$2.0x10^{-2}$	3
tri	21	$2.8x10^{-5}$	$4.2x10^{-4}$			1
tri	22	$3.2x10^{-5}$	$2.2x10^{-3}$	$6.3x10^{-4}$	$1.4x10^{-2}$	6
vinylchloride	10	$1.4x10^{-2}$	$1.4x10^{-3}$			1

substance	case #	Ciam/Csam calculated	Ciam/Csam measured	5 percentile	95 percentile	n
cis	all	$4.9x10^{-4}$	$1.9x10^{-1}$			2
cis	15	$3.2x10^{-4}$	$1.9x10^{-1}$			2
per	all	$3.6x10^{-4}$	$5.1x10^{-3}$	$5.6x10^{-4}$	$4.6x10^{-1}$	19
per	2	$2.8x10^{-4}$	$2.0x10^{-3}$			1
per	12	$2.2x10^{-4}$	$3.3x10^{-3}$	$5.0x10^{-4}$	$1.4x10^{-2}$	9
per	14	$7.4x10^{-4}$	$3.0x10^{-3}$	$6.3x10^{-4}$	$4.4x10^{-2}$	3
per	15	$2.8x10^{-4}$	$6.3x10^{-4}$			1
per	21	$2.4x10^{-4}$	$6.3x10^{-3}$			1
per	22	$2.4x10^{-4}$	$2.7x10^{-3}$			2
per	23	$2.5x10^{-4}$	$6.0x10^{-1}$			2
tri	all	$4.6x10^{-4}$	$2.5x10^{-3}$	$2.3x10^{-4}$	$1.2x10^{-2}$	6
tri	14	$7.8x10^{-4}$	$3.9x10^{-3}$			1
tri	15	$3.0x10^{-4}$	$1.1x10^{-2}$			2
tri	21	$2.5x10^{-4}$	$7.3x10^{-3}$			1
tri	22	$2.5x10^{-4}$	$2.4x10^{-4}$			2