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Remediation of PCB-contaminated soils - Risk analysis of biological *in situ* processes

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Remediation of PCB-contaminated soils – Risk analysis of biological *in situ* processes

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Remediation of PCB-contaminated soils – Risk analysis of biological *in situ* processes

by Arno Rein[1]

Abstract: Biological *in situ* measures can be efficient and cost effective options for the remediation of contaminated sites. However, the accepted application requires a detailed and reliable analysis of potential impacts. An important objective is to quantify the potential of contaminant degradation and metabolite formation. This thesis addresses a quantitative multimedia risk assessment. Methodologies and tools were developed for this objective and applied to evaluate *in situ* bioremediation of soils contaminated with polychlorinated biphenyls (PCBs). Soil bacteria in conjunction with plant roots were addressed (rhizoremediation) with a focus on the use of genetically modified microorganisms (GMOs).

PCBs are known to be harmful compounds that are ubiquitously distributed in the environment. PCB contaminations in soil and groundwater were identified as important problems. 209 different congeners are sterically possible, but not all are of environmental significance. PCB congeners of concern were evaluated with respect to their potential toxicity, environmental occurrence and mobility. For this objective, congener specific data on the toxicity potential and the frequency in environmental matrices were collected. To quantify the mobility potential, multimedia modelling was performed applying deterministic and probabilistic procedures. 56 PCB congeners of concern were evaluated, and multimedia risk assessments of PCB-contaminated soils should concentrate on this group.

Kinetics parameters were specified for degradation experiments with individual PCB congeners in solution and different bacterial strains. These laboratory assays were performed with wild-type *Burkholderia* sp. strain LB400 and the genetically modified *Pseudomonas fluorescens* strains F113pcb and F113L::1180. The F113 derivatives demonstrated a good survival ability in willow (*Salix* sp.) rhizosphere (mesocosm experiments). Therefore, and due to high depletion rates, rhizoremediation with F113L::1180 and willow plants might be a promising approach. Degradation kinetics in soil was estimated, but it is associated with a high uncertainty. The relation of degradation kinetics in laboratory (solution) to field conditions (soil) necessitates further research. Results of exemplary modelling were sensitive to estimated removal velocities, and especially to variable bacterial numbers in soil.

A multimedia model was set up to estimate biodegradation and metabolite formation, fate and transport of contaminants and risks arising from the exposure to contaminated media. With this model, deterministic and probabilistic calculations (performing Monte Carlo simulations) were carried out to generically evaluate rhizoremediation of PCB contaminated soil. Results indicate a clear potential for risk reduction associated to the use of F113L::1180 and willow plants. PCB was effectively reduced by the investigated strains but nonetheless, chlorobenzoic acids (CBAs) as degradation products of concern revealed a high importance for the aquatic pathway (leaching, groundwater transport, mixing with surface water) and the uptake into plants. Thus, drinking water wells should be located in a sufficient distance to the source (5 km at least as a conservative estimate for the studied scenario). However, high uncertainty remains for the degradation potential of PCB mixtures in soils.

Risks associated to the investigated GMOs are expected to be very low. Results of laboratory experiments with F113 derivatives and field release tests with non-GM F113 strains gave no significant hint on uncontrolled bacterial spreading. Observed gene transfer rates were very low, as the introduced *bph* trait is stably inserted into the chromosome of F113. Potential impacts of GMOs on microbial soil communities also were very low, but there was a shift in rhizosphere populations. Uncertainty is given for possible long-term effects, especially for gene transfer processes and impacts on soil bacteria, and for potential adverse effects on other soil organisms. Potential field release applications of *in situ* bioremediation using GMOs require performance control in the source zone (to ensure the functionality of the degradation process) and compliance monitoring, addressing contaminants, metabolites and GMOs. Detailed guidelines were compiled for respective tasks.

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Sanierung PCB-kontaminierter Böden – Gefährdungsabschätzung biologischer *in situ*- Verfahren

Kurzfassung: Biologische *in situ*- Sanierungsverfahren können effektive und kostengünstige Optionen darstellen. Die Akzeptanz entsprechender Maßnahmen setzt eine detaillierte und verlässliche Untersuchung möglicher Risiken voraus. Eine wichtige Aufgabe kommt hierbei der Quantifizierung des Abbaupotenzials bzw. der Metaboliten-Entstehung zu. Im Rahmen der vorliegenden Arbeit wurden Methoden und Modellwerkzeuge für eine quantitative multimediale Gefährdungsabschätzung erstellt. Damit wurde eine biologische *in situ*- Sanierung kontaminierter Böden bewertet, die eine erhöhte Konzentration von Polychlorierten Biphenylen (PCBs) aufweisen. Das untersuchte Verfahren beruht auf dem Einsatz aerober Bodenbakterien, die im Wurzelraum bestimmter Pflanzen leben (sog. Rhizoremediation). Einen Schwerpunkt hierbei bildete die Verwendung gentechnisch veränderter Mikroorganismen (GMOs).

PCBs sind eine wichtige Gruppe von Schadstoffen, die weit in der Umwelt verbreitet sind. PCB-Kontaminationen in Böden und Grundwasser haben sich als schwerwiegende Probleme herausgestellt. 209 unterschiedliche Kongenere sind sterisch möglich, jedoch nicht alle sind von Relevanz. Umweltrelevante Stoffe wurden hinsichtlich ihres toxischen Potenzial, ihrer Verbreitung in der Umwelt und ihrer Mobilität ermittelt. Dabei wurden kongener-spezifische Daten zur Toxizität und zur Häufigkeit in Umweltmedien gesammelt und das Mobilitätspotenzial mit Hilfe multimedialer Modellierung, basierend auf deterministischen und probabilistischen Ansätzen quantifiziert. Die Untersuchung ergab eine Gruppe von 56 relevanten PCB Kongeneren, die für Gefährdungsabschätzungen PCB-kontaminierter Standorte betrachtet werden sollten.

Für Abbauexperimente mit einzelnen PCB Kongeneren in Lösung und unterschiedlichen Bakterien-Stämmen wurden kinetische Parameter angepasst. Die Experimente erfolgten mit dem natürlich vorkommenden Stamm *Burkholderia* sp. LB400 und den GMOs *Pseudomonas fluorescens* F113pcb und F113L::1180. Die F113-Derivate erwiesen ein gute Überlebensfähigkeit in der Rhizosphäre von Weiden (*Salix* sp.; Ergebnisse von Mesokosmos-Experimenten). Dadurch, und durch die hohen Abbauraten erscheint die Feldverwendung von Rhizoremdiation mit F113L::1180 in Weidenwurzeln als ein vielversprechender Ansatz. Abbauprozesse im Boden wurden abgeschätzt, gehen jedoch mit einer hohen Unsicherheit einher. Hinsichtlich der Übertragung der Abbaukinetik von der Laborlösung auf Bodenverhältnisse besteht weiterer Forschungsbedarf. Die Ergebnisse einer exemplarischen Modellierung weisen eine hohe Sensitivität ermittelter Abbaugeschwindigkeiten und insbesondere variabler Bakterienzahlen im Boden auf.

Ein multikompartimentelles Schadstoffausbreitungs-, Expositions- und Risikoabschätzungsmodell wurde erstellt, das die Modellierung des Bioabbaus und der Metaboliten-Bildung berücksichtigt. Mit diesem Modell erfolgte eine generische Auswirkungsprognose hinsichtlich eines hypothetischen Feldeinsatzes von Rhizoremdiation mit F113L::1180 und Weidenpflanzen, für die Sanierung PCB-kontaminierten Bodens. Entsprechende Berechnungen erfolgten deterministisch und probabilistisch (Monte Carlo- Simulationen). Die Ergebnisse dieser Abschätzung sprechen für ein deutliches Risiko-Reduktionspotenzial durch das Verfahren. Dennoch konnte gezeigt werden, dass Chlorbenzoate als relevante PCB-Abbauprodukte von großer Bedeutung für den aquatischen Pfad (Versickerung, Grundwassertransport, Eintrag in Oberflächengewässer) und für die Aufnahme in Pflanzen sind. Deshalb sollten Trinkwasser-Brunnen eine ausreichende Distanz zum Reaktionsraum aufweisen (mindestens 5 km in einer konservativen Abschätzung für das betrachtete Szenario). Eine hohe Unsicherheit bleibt jedoch bezüglich des Reduktionspotenzials von PCB-Gemischen in Böden.

Risiken, die mit einer möglichen Freisetzung der untersuchten GMOs einhergehen erscheinen als sehr niedrig. Laborexperimenten mit F113-Derivaten und Freisetzungsversuche mit gentechnisch unveränderten F113-Stämmen gaben keine Hinweise auf eine unkontrollierte bakterielle Ausbreitung. Die beobachteten Gentransfer-Raten waren sehr gering, da die den PCB-Abbau induzierende Gensequenz stabil in das Chromosom der F113-Stämme eingefügt ist. Potenzielle Auswirkungen auf die Mikroflora im Boden sind ebenfalls sehr gering, allerdings wurde eine Veränderung in der Zusammensetzung mikrobieller Rhizosphären-Populationen festgestellt. Unsicherheiten bestehen bezüglich möglicher Langzeiteffekte, insbesondere für Gentransferprozesse und die Beeinträchtigung natürlicher Bodenbakterien, sowie etwaige Auswirkungen auf andere Bodenorganismen. Ein potenzieller Feldeinsatz von *in situ*- Verfahren mit gentechnisch veränderten Bakterien erfordert umfangreiche Maßnahmen zur Prozesskontrolle und Schutzgutüberwachung, die sowohl die Schadstoffe und deren Abbauprodukte als auch die GMOs umfassen. Für diese Aufgaben wurden detaillierte Richtlinien erstellt.

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Symbols and abbreviations

Symbols

A_γ	Correction factor for activity approximation	[-]
A	Area	[m^2]
a, b, c	Empirical correction factors between plant lipids and octanol	[-]
ADD_{ij}	Average daily dose	[mg kg^{-1} d^{-1}]
AFS	Fraction of apparent free space on total root volume	[m^3/m^3]
a_{Sc}	Empirical Schmidt exponent	[-]
AT	Averaging time	[yr]
B	Bacterial mass	[mg]
B_{MA}	Molecular diffusivity in air	[cm^2/s]
B_R	Width of stream channel	[m]
BW	Body weight	[kg]
B_{W4}	Molecular diffusion coefficient in sediment	[cm^2/s]
C	Concentration	[mass/volume]
CF	Conversion factor	[g/L]
$CFU_{lab,0}$	Initial bacterial numbers in laboratory	[cfu/L]
CFU_{Soil}	Bacterial numbers in soil	[cfu/kg]
$corr_{P,ion}$	Correction (biomembrane permeability for ions)	[log units]
C^S_L	Solubility, subcooled liquid state	[mol/m^3]
C^S_S	Solubility, solid state	[mol/m^3]
D	Intermedia transport D value	[m^2/s]
d_A	Atmospheric mixing height	[m]
D_{Aj}	Advection D value	[mol Pa^{-1} h^{-1}]
D_{CW}	Cell wall diffusion coefficient	[m^2/s]
d_{CW}	Thickness of cell wall	[m]
d_{GW}	Depth from source bottom to groundwater level	[m]
$D_{i,a}$, B_A	Molecular diffusion coefficient of compound i in air	[cm^2/s]
$D_{i,w}$, B_W	Molecular diffusion coefficient of compound i in water	[cm^2/s]
D_{Rj}	Degradation D value for bulk compartment j	[mol Pa^{-1} h^{-1}]
d_S	Average soil depth (Part II of the thesis)	[m]
d_S	Source thickness (Part IV of the thesis)	[m]
d_{Sed}	Average sediment depth	[m]
D_s^{eff}	Effective diffusion coefficient in soil	[m^2/s]
d_W	Average water depth	[m]
D_x, D_y, D_z	Dispersion coefficient (longitudinal, transverse and vertical direction)	[m^2/s]
E	Amount of water vapour leaving a leaf per unit area and per unit time	[kg s^{-1} m^{-2}]
E	Membrane potential	[V]
EEC_i	Estimated environmental concentration	[different units]
EF	Exposure frequency, housing	[d/yr]
E_{ij}	Exchange term, compartment i, j	[m^3/s]
ET	Evapo-transpiration level (Part II of the thesis)	[mm/yr]
ET	Exposure time (Part IV of the thesis)	[h/d]
E_V	Electrical potential vacuole	[V]
E_W	Saturation vapour pressure of water	[Pa]
F	Faraday constant, F = 96 485.3415	[C/mol]
f_{AX}	Fraction of xylem area on total root area	[m^2/m^2]
F_{eff}	Effective portion of the cross-sectional area for mixing	[-]
f_{Fish}	Volume fraction of fish in water	[-]
f_{fZ}	Free mobile fraction in the central cylinder	[-]
f_L, f_S	Liquid and solid fugacity	[-]
f_n, f_d	Fractions and of the neutral species and ionised species	[-]
f_{nf}, f_{df}	Fraction of the neutral free, dissociated free species	[-]
f_{OC}	Fraction soil organic carbon	[%]
f_R	Fraction of roots in soil	[g/g dry weight]
f_{RD}	Factor for reduced degradation performance under field conditions	[-]
f_{VX}	Fraction of xylem volume on total root volume	[m^3/m^3]
f_{VZ}	Fraction of central cylinder volume on total root volume	[m^3/m^3]
f_W	Fraction of surface water on total area	[%]
G	Conductance	[m/s]
G_{Inf}	Level of infiltration	[mm/yr]
G_j	Advective flow rate	[m^3/h]
H	Henry's law constant	[Pa m^3 mol^{-1}]
H	Stack height	[m]

h	Suction	[cm]
h_A	Total drainage	[mm/yr]
h_A/h_G	Drainage quotient	[-]
h_G	Infiltration rate	[mm/yr]
h_{GR}	Aquifer-river intersection height	[m]
HI	Hazard index	[-]
HQ_{ij}	Hazard quotient for chemical *i*, exposure route *j*	[-]
h_R	River depth	[m]
hu	Air humidity	[-]
i	Hydraulic gradient	[%]
I_A	Contaminant emission rate, subsurface soils to ambient air	[mg/s]
$IF_{A,adj}$	Ae-adjusted air inhalation factor	[m^3 yr d^{-1} kg^{-1}]
$IF_{W,adj}$	Ae-adjusted water ingestion factor	[L yr d^{-1} kg^{-1}]
IH	Inhalation rate	[m^3/h], [m^3/d]
IR	Ingestion rate (used for water ingestion)	[L/d]
IS	Ionic strength	[M]
J	Unit flux	[kg m^{-1} s^{-1}]
k^*_{max}	Maximum removal rate	[1/h]
K_{AW}	Air-water partition coefficient	[-]
K_{AW}	Air-water partition coefficient	[-]
K_d	Soil-water sorption coefficient	[cm^3 water/g soil]
k_{death}	First order rate describing the decline of active bacterial cells	[1/h]
k_f	Effective hydraulic conductivity	[m/s]
K_{io}	Equilibrium partition coefficient between the concentration inside and outside the membrane	[-]
k_j	First-order degradation rate constant	[1/h]
K_{LW}	Partition coefficient between leaves and water	[-]
K_M	Half-saturation constant	[mg/L]
K_M^*	Dimensionless half-saturation constant	[-]
K_n	Empirical partition coefficient between pure aqueous and pure liquid phase of the neutral molecule	[-]
K_{OA}	Octanol-air partition coefficient	[-]
K_{OC}	Organic carbon partition coefficient	[cm^3/g]
K_{OW}	Octanol-water partition coefficient	[-]
k_r	Relative permeability	[-]
K_{RW}	Partition coefficient between root and water	[-]
K_S	Half-growth concentration	[mg/L]
K_{SW}	Soil-water partition coefficient	[-]
k_T	MTC for liquid diffusion in sediment water	[m/h]
LAI	Leaf area index	[m^2 leaf / m^2 field]
L_d	Diffusive path length	[m]
L_{Fish}	Fish lipid content	[-]
L_L	Leaf lipid content	[g/g]
L_R	Root lipid content	[g/g]
L_S	Depth to subsurface source	[m]
L_Z	Lipid content of central cylinder	[g/g]
M	Molecular weight; or substrate mass	[g/mol]; [m]
m	Mass	[mass]
N	Nernst coefficient (Part IV of the thesis)	[-]
N	Measure of the pore-size distribution	[-]
N_A	Diffusive net flux between leaves and atmosphere	[mg/s]
n_e	Effective porosity	[-]
$NOAEC_i$	No-observed-adverse-effects-concentration	[different units]
N_{Xy}	Mass transport within the xylem	[mg/s]
OC_S	Organic carbon content in soil solid phase	[-]
OC_{Sed}	Organic carbon content in sediment solid phase	[-]
OC_{Sus}	Organic carbon content in suspended sediment	[-]
OD_{600}	Optical density of liquid medium at 600 nm	[-]
p	Level of significance (Pearson correlation)	[-]
P	Permeability	[m/s]
$PC_{,i}$	Sin permeability coefficient for chemical i	[cm/h]
pH_C	pH cytoplasm	[-]
pH_S	Soil pH	[-]
pH_V	pH vacuole	[-]
pH_X	pH xylem sap	[-]
pK_a	Dissociation constant	[-]
pK_{aH}	Acidity constant of the unsubstituted organic acid	[-]
P_L	Vapour pressure	[Pa]

P_L, P_A	Saturation concentration of water vapour in the leaf, atmosphere	[kg/m^3]
P^S	Saturation vapour pressure	[Pa]
Q	Scavenging ratio	[-]
Q/C	Dispersion factor	[(g m^{-2} s^{-1})/(kg/m^3)]
Q_{GW}	Groundwater flux into the river	[m^3/yr]
Q_{GW}	River flow rate	[m^3/yr]
Q_j	Equilibrium criterion of bulk compartment j	[Pa]
q_R	Rain rate	[mm/yr]
q_w	Infiltration rate	[mm/yr]
Q_W	Transpiration stream	[m^3 yr^{-1} ha^{-1} field]
Q_X	Translocation stream	[m^3/s]
R	Universal gas constant, R = 8.3145 kJ mol^{-1}K^{-1}	[kJ mol^{-1}K^{-1}]
R	Retardation factor	[-]
r	kinetic term	[mg m^{-3} s^{-1}]
R_{Aq}	Retardation factor in the saturated zone	[-]
RfD_{ij}	Reference dose	[mg kg^{-1} d^{-1}]
RL_{ij}	Cancer risk level for chemical *i*, exposure route *j*	[-]
RL_T	Total cancer risk level	[-]
s	Fraction of secondary and tertiary endodermis in root	[m^3/m^3]
S_A	Solubility in air	[mol/m^3]
SA	Eposed skin surface area	[cm^2]
$Sc_{i,A}$, $Sc_{i,w}$	Schmidt-number of compound i in air (A) and water (W)	[-]
SF_{ij}	Slope factor	[(mg kg^{-1} d^{-1})$^{-1}$]
$SFS_{S,adj}$	AG-adjusted dermal intake factor (dermal contact with water)	[cm^3 yr d^{-1} kg^{-1}]
SLA	Specific leaf area	[m^2 leaf / kg leaf]
S_O, S_{OL}	Solubility in octanol	[mol/m^3] or [mg/L]
S_{OW}, S_{WO}	Solubility in octanol saturated with water (OW), water saturated with octanol (WO)	[mol/m^3]
S_W, S_{WL}, S_L	Water solubility	[mg/L] or [mol/m^3]
S_{wat}	Concentration in water	[mg/L]
t	Time	[different units]
T, T_0	System and reference temperature	[K]
T_{Air}	Air temperature	[°C]
T_B	Boiling point	[K] or [°C]
T_M	Melting point	[K] or [°C]
T_S	Soil temperature	[°C]
$TSCF$	Transpiration stream concentration factor	[-]
u	Vertically averaged wind speed	[m/s]
U^*	Friction velocity	[m/s]
U_1 to U_{12}	Intermedia transport parameter	[m/h]
U_1, k_{VA}	Air side, air-water mass transfer coefficient (MTC)	[m/h]
u_{10}	Wind speed measured at 10 m height	[m/s]
U_{10}, U_{RS}	Sediment resuspension rate	[m/h]
U_{11}, U_{WW}	Soil water runoff rate from soil	[m/h] or [mm/yr]
U_{12}, U_{EW}	Soil-solids runoff rate solids runoff rate	[m/h]
U_2, k_{VW}	Water side air-water MTC	[m/h]
U_3	Rain rate	[m/h]
U_4	Dry deposition velocity of aerosols	[m/h]
U_5, k_{SA}	Soil-air phase MTC (vapour diffusion in soil air pores)	[m/h]
U_6, k_{SW}	Soil-water phase transport MTC (liquid diffusion in soil water)	[m/h]
U_7, k_{EA}	Air side MTC over soil (soil-air boundary layer)	[m/h]
U_8	Diffusive sediment-water MTC	[m/h]
U_9, U_{DP}	Sediment deposition rate	[m/h]
U_A	Wind speed above ground surface in ambient mixing zone	[m/s]
u_{Air}	Wind speed	[m/s]
u_R	River flow velocity	[cm/s]
V	Volume	[different units]
$\bar{v}$	Seepage velocity (or interstitial velocity)	[m/s]
v^*_{max}	Maximal removal velocity related to	[mg/h]
v, v_x	Contaminant velocity, advective groundwater velocity	[m/s]
V_C	Fraction of cytoplasm on total root volume root	[m^3/m^3]
$v_{i,a}$, $v_{i,w}$	Exchange velocity of substance i in air and water	[m/h]
v_{max}	Maximal substrate removal velocity per bacterial mass	[mg h^{-1} mg bacteria^{-1}]
v_Q	Volume fraction of aerosols	[-]
W_L	Leaf water content	[g/g]
W_{Plume}	Plume width at the plume-river intersection	[m]
W_R	Root water content	[g/g]

W_X, X	Source width, x-direction	[m]
W_Y, Y	Source width, y-direction	[m]
$x(T)$, x_0	Given property at temperature T, T_0	[property units]
Y_3	Diffusion path length in soil	[cm]
Y_4	Diffusion path length in sediment	[cm]
z	Distance below the source	[m]
z	Valency of the ion	[-]
Z_i	Z value of compartment i	[mol m^{-3} Pa^{-1}]
z_m	Distance from the source to the observation location	[m]
ΔH	enthalpy of phase change	[kJ/mol]
$\Delta_r G_j^0$	Standard free energy change of carboxyl group dissociation, substituent j	[J/mol]
ΔS_{fus}	Entropy of fusion	[J mol^{-1} K^{-1}]
ΔU	Internal energy change	[kJ/mol]
ΔU_{fus}	Enthalpy of fusion (solid to liquid)	[kJ/mol]
α	Parameter related to the inverse of air entry suction	[1/cm]
α_i, α_o	Ion activity on the inside i, outside o of the membrane	[-]
α_L	Longitudinal dispersivity	[m]
α_x, α_y, α_z	Longitudinal, transverse and vertical dispersivity	[m]
β_ι	Source zone depletion coefficient, pathway i	[-]
δ_A	Ambient air mixing zone height	[m]
γ	Pore size distribution parameter	[-]
γ_n, γ_d	Activity coefficient of the non-electrolyte, electrolyte	[-]
λ_G	Growth rate	[1/yr]
μ	First-order decay coefficient for chemical	[1/s]
μ_{max}	Maximum growth rate of bacteria	[1/h]
$\theta(h)$	Measured vol. water content at suction h	[cm^3/cm^3]
$\theta_{1/3\ bar}$	Measured vol. water content at 330 cm suction	[cm^3/cm^3]
θ_A	Vapour diffusion porosity	[cm^3/cm^3]
θ_{as}	Air-filled porosity	[cm^3/cm^3]
θ_r, θ_s	Residual and saturated water content	[cm^3/cm^3]
θ_{Sed}	Water content in sediment	[cm^3/cm^3]
θ_T	Total soil porosity	[-]
θ_W	Soil water content, water-filled porosity	[cm^3/cm^3]
$\theta_{w,m}$, θ_{WS}	*Calculated mean water saturation*	[cm^3/cm^3]
$\theta_{w,sed}$	Water-filled porosity in sediment	[cm^3/cm^3]
ρ_W	Density	[kg/m^3]
σ_j	Substituent constant, substituent *j*	[-]
σ_y	Lateral dispersion coefficient	[m]
σ_z	Vertical dispersion coefficient	[m]
$\tau_{,j}$	Advective residence time, compartment i (index A for air, Sed for sediment and W for water)	[h]

Abbreviations

1-D, 2-D, 3-D	One-, two, three-dimensional
A1016	Aroclor 1016
A1221	Aroclor 1221
A1232	Aroclor 1232
bph	Biphenyl
CBA	Chlorobenzoic acid
CFU	Colony forming units
CO_2	Carbon dioxide
COC	Contaminants and metabolites of concern
CSM	Conceptual site model
DWD	Deutscher Wetterdienst (German Weather Survey)
EC	Soil exchange capacity
EtOH	Ethyl alcohol
EU	European Union
FRET	Fluorescence resonance energy transfer

GC/ECD	Gas Chromatography/Electron Capture Detector
GIS	Geographical information system
GM	Genetically modified
GMO	Genetically modified microorganism
GW	Groundwater
ICN	Illinois Climate Network,
IUPAC	International Union of Pure and Applied Chemistry
LB	Luria Broth
LBE	Leitboden-Einheiten (representative soil profiles)
MC	3-methylcholanthrene
MFO	Mixed-function oxidase
MTC	Mass transfer coefficient
NA, ENA	Natural attenuation, enhanced natural attenuation
NOAEL, LOAEL	No/Lowest-Observed-Adverse-Effect-Levels
NOEC, LOEC	No/Lowest-Observed-Effect- Concentrations
OC	Organic carbon
OM	Organic matter
PAH	Polycyclic aromatic hydrocarbon
PB	Phenobarbital
PCB	Polychlorinated biphenyl
PCR	Polymerase Chain Reaction
PDF	Probability density function
POC	Points of compliance
PRG	Preliminary risk-based goal
RBSL	Risk Based Screening Level
SA	Salicylic acid
SPME	Solid phase microextraction
SSTL	Site-specific target level
SW	Surface water
SYBR	Synergy Brands Inc.
TGGE	Temperature Gradient Gel Electrophoresis
TPH	Total petroleum hydrocarbon
TSA	Trytpic Soy Agar
US EPA	U.S. Environmental Protection Agency
US HHS	U.S. Department of Health and Human Services
USDA	U.S. Department of Agriculture
USGS	U.S. Geological Survey
VCH	Volatile chlorinated hydrocarbon
WaBoA	Wasser- und Bodenatlas (water body and soil atlas)
WHO	World Health Organization

Part I General Introduction

1 Motivation

1.1 Background

Soil contamination by organic pollutants originating from industrial sites, landfills or tanks is a widespread problem in urban areas. Bioremediation with soil bacteria has extensively been investigated during the last few decades, as it might be an alternative and less expensive option compared to traditional cleanup techniques like soil excavation or soil vapour extraction. However, such biological *in situ* measures require a detailed and reliable analysis of potential risks. They need to be performed over long time periods and therefore necessitate accompanying activities, i.e. performance control (to ensure the functionality of the degradation process) and compliance monitoring. An important objective is to quantify the potential of contaminant degradation and metabolite formation.

Polychlorinated biphenyls (PCBs) have been identified as important contaminants frequently found in sediments and in soil of former landfills, and they also were detected in groundwater in considerable concentrations. PCBs are a complex group of synthetic organic compounds that have been produced in large amounts from 1930 to the late 1970s. Due to the thermal and chemical stability, and their dielectric properties they have been widely applied in a variety of industrial products and processes. Numerous toxic effects on different organisms have been identified for these compounds, and PCBs are known to be persistent and ubiquitously distributed in the global ecosystem (Safe 1994, McFarland and Clarke 1989, Meijer et al. 2003).

1.2 Microbial degradation of PCB in soil

Microbial degradation of PCB in contaminated soil has been subject of extensive research (e.g. Furukawa and Matsumura 1976, Unterman 1988, Leigh et al. 2006). In the environment, PCBs are degraded by aerobic bacteria through the biphenyl catabolic pathway, following a cometabolic process (Seeger et al. 1995, Abramowicz 1990). Most studies centred on *Burkholderia* sp. strain LB400 (formerly *Pseudomonas* sp. LB400) which was isolated from PCB contaminated soil (Bopp 1986). This strain is reported to oxidise a wide range of PCBs, including congeners containing up to 6 chlorines (Bedard et al. 1986, Bedard 1990, Gibson et al. 1993).
As a major problem for the application of microbes for *in situ* bioremediation, effective degrader strains revealed a decline in survival and degradation activity after introduction into soil. These difficulties can be met by periodic reinoculation or continuous addition of specific substrate (e.g. biphenyl) in order to impose positive selection (Barriault and Sylvestre 1993). The maintenance of such procedures might be limited, however, when applied in practise at contaminated sites. This accounts for technical difficulties (necessity of repeated application) or the potential toxicity and low water solubility of biostimulating substances such as biphenyl (e.g. Leigh et al. 2006).

1.3 Rhizoremediation using genetically modified PCB degraders

An alternative solution is to insert the genes encoding the biphenyl (*bph*) pathway into a host that is known to possess a high survival capability in specific soil compartments. As a natural environment for *in situ* bioremediation in soil, the rhizosphere has been identified as an ideal compartment. Among other factors, this can be assigned to cosubstrates that biostimulate degradation activitiy of microbes (e.g. Olson et al. 2001, Fletcher and Hedge 1995). In fact, the root zone of plants is a hot spot of bacterial activity (e.g. Aragno 2005, Walton and Anderson 1990). Plants may reduce off-site leaching of contaminants, aerate the soil and release compounds via the roots that selectively foster microorganisms (Amos and Younger 2003, Fletcher et al. 1995, Gibson et al. 1993). Furthermore, the dispersal of the introduced strain in soil is enhanced (Villacieros 2005). Thus, rhizoremediation, i.e. the use of microbes in conjunction with plants is a promising bioremediation strategy (Trapp and Karlson 2001, Leigh et al. 2006, Yee et al. 1998). Efforts have been undertaken to expand the degradation capacities of rhizosphere-competent bacteria (Villacieros 2005, Brazil et al. 1995, Yee et al. 1998). A number of plant-microbe consortia was tested recently (e.g. Ryslava et al. 2003, Demnerova et al. 2005).

Pseudomonas fluorescens F113 has originally been isolated from sugar beet rhizosphere (Shanahan et al. 1992). It is known as an excellent coloniser of several plant rhizospheres, such as those of sugar beet (Shanahan et al. 1992, Delany et al. 2001), tomato (Simons et al. 1996), pea (Naseby and Lynch 1999) and alfalfa (Villacieros et al. 2003). Derivatives of strain F113 with rhizoremediation ability were genetically constructed. In a first step, genes encoding the *bph* pathway were cloned from LB400 and inserted into in an environmental useful transposon (Dowling et al. 1993). Then the *bph*-cassette was chromosomally integrated into F113 to generate F113pcb (Brazil et al. 1995) and F113L::1180 (Villacieros 2005).

2 Objectives

The aim of this thesis is to develop strategies and tools for a quantitative risk assessment of *in situ* soil bioremedation, considering contaminations that are characterised by complex mixtures of organic compounds. As an important aspect, the use of genetically modified microorganisms (GMOs) is addressed (F113 derivatives), as potential impacts arising from the deliberate release of GMOs hardly have been analysed to date. The developed approaches are adopted for a preliminary estimation of impacts arsing from a potential field application of GMO-based rhizoremdiation for PCB contaminated soil. In this study, the following research questions are addressed:

- What are the criteria to determine target compounds within contaminant mixtures, i.e. constituents that are of environmental relevance? Which PCB congeners should be addressed for multimedia environmental risk assessments?

- How can contaminant breakdown and metabolite formation due to microbial activity be quantified and what are the key factors to estimate the time frame of the bioprocess? Which PCB congeners are degraded by the investigated bacterial strains and what are the kinetics parameters?

- Can risks associated to PCB contaminated soil efficiently be reduced by applying the projected rhizoremediation system? Will there be uncontrolled spreading of the GMOs or impacts on soil ecosystems? Which parameters are sensitive to an appropriate risk estimation and where are uncertainties?

- What has to be considered for preparing, controlling and monitoring field release applications of genetically modified bacterial strains used for *in situ* bioremediation?

3 Structure of the thesis

This thesis is divided into six main parts. **Part II** provides a strategy to evaluate environmentally relevant compounds present in contaminant mixtures, and this strategy is applied to identify PCB congeners of concern. Part II includes a literature review on toxicity and environmental frequency of PCBs and provides a dataset on physicochemical properties. Multimedia modelling is performed to estimate PCB mobility. **Part III** investigates the degradation of PCB congeners in laboratory experiments for different bacterial strains. It presents a methodology to quantify the bioprocess and exemplarily estimates degradation kinetics for lowly chlorinated PCB mixtures. **Part IV** develops a multimedia model to estimate contaminant degradation and metabolite formation, fate and transport (mass fluxes and concentrations in various environmental matrices) and risks for receptors exposed to contaminated media (human health and ecological receptors, different exposure routes). Chemical risks for a potential field application of GMO-based rhizoremediation are evaluated for a generic scenario. GMO dispersion, gene transfer and potential effects on indigenous microbial communities are investigated in laboratory experiments and a field release trial (non-GM F113 strains). **Part V** provides a monitoring guideline for the safe and efficient use of *in situ* soil bioremediation utilising GMOs. **Part VI** gives general conclusions of this thesis and an outlook on future studies, referring to the research questions posed in **Part I**. Cited literature is given in the **Overall references** list, except for resources referring to the physicochemical database (presented in Appendix A). An **Abstract** is provided in English and German (**Kurzfassung**) at the beginning of the present thesis, along with **Acknowledgements**.

Part II Identification of environmentally relevant PCB congeners – Considerations for a multimedia risk assessment in an uncertain and variable environment

Contents

Abstract

A strategy is presented to identify environmentally relevant compounds present in contaminant mixtures. This strategy was applied to the group of polychlorinated biphenyls (PCBs). PCBs are known to be harmful compounds that are ubiquitously distributed in the environment. 209 different congeners are sterically possible, but not all are of environmental significance. In this study, PCB congeners of concern were evaluated with respect to their potential toxicity, environmental occurrence and mobility. Congener specific data on the toxicity potential and the frequency in environmental matrices were derived from an extensive literature study. To understand the environmental fate of contaminants, multimedia fugacity modelling was performed concentrating on contaminant partitioning from soil into the air and water (deterministic and probabilistic calculations). Data on physicochemical properties and their temperature dependency were collected for all 209 congeners and adjusted to be internally consistent. Measurement uncertainty of physicochemical properties and variability due to their temperature dependency were found to significantly influence the modelled results. Also environmental input parameters such as advective residence times, soil properties and meteorological data revealed a high influence on the variance of estimated environmental concentrations. Considering potential toxicity, environmental frequency and the mobility potential as criteria, 56 PCB congeners of concern were evaluated. For multimedia environmental risk assessments of PCB-contaminated soils, it is recommended to focus on these congeners.

1 Introduction

In many cases, soil contaminations are characterized by complex mixtures of organic compounds. For the remediation of respective sites, biological *in situ* measures might be an option as they can offer an efficient degradation performance at comparatively low costs. An important task is to identify target constituents within the contaminant mixture present at a site (Part I). In this part of the thesis, an identification procedure for relevant compounds is presented that is based upon their toxicity potential, the environmental frequency and the mobility tendency. These compounds should be reduced by the applied clean-up measure in order to achieve a significant risk reduction. The strategy was applied for polychlorinated biphenyls PCBs, but it also can be used for other contaminant groups.
PCBs have attracted concern because of the ubiquitous distribution, their persistence in the environment and their potential for harmful effects on human health and ecosystems (Part I). Furthermore, many of those compounds bioaccumulate and biomagnify in environmental matrices (such as sediments, fat tissue, etc.; e.g. Campfens and Mackay 1997). PCBs have been shown to cause cancer in animals. In addition, a number of serious non-carcinogenic health effects in animals are reported (Safe 1994, US HHS 2000, WHO 1993). Few PCB congeners exhibit acute toxicity (McFarland and Clarke 1989, Bright et al. 1995), but exposure may result in chronic adverse effects on survival, growth and reproduction (Suedel et al. 1997). For the prediction of effects, congener-specific toxicities have to be considered (Schweitzer et al. 1997).

Among the 209 possible PCB congeners, not all are of environmental concern. In the past, PCBs were applied as technical mixtures with a different degree of chlorination and released into the environment. These mixtures are characterized by different congener patterns with 60 to 80 congeners being present in relevant amounts (e.g. Frame 1996). Natural aerobic biodegradation was observed to rapidly reduce lowly to moderately chlorinated PCBs (e.g. Furukawa 1986, Bedard et al 1986), and also dechlorination processes (in an anaerobic environment) might change the PCB congener pattern (e.g. Brown et al. 1987, Quensen et al. 1988).
However, some compounds potentially present at a contaminated site may be immobile whereas others readily partition from soil into other environmental media like the air or the hydrosphere where they pose a threat to human health or ecosystems. Multimedia environmental prediction is an essential approach for obtaining information on this issue, as measured results specific to the large amount of PCB congeners cannot be obtained with reasonable efforts. Among others, multimedia models based on the fugacity concept (Mackay et al. 1992) have variously been used by the scientific community and regulatory bodies, considering different compounds (e.g. Arp et al. 2005, Hsieh et al. 1994, Achten et al. 2002 and EUR 2002, US EPA 1998a).

In this study, toxicological data from various studies were compared and data sets on the concentration in different environmental media (e.g. soil, sediments and fat tissue of organisms) analysed. The fate and transport behaviour of PCBs were evaluated with multimedia environmental modelling. One focus of this investigation was aimed on the uncertainty and variability of the required input parameters. To account for measurement uncertainty of physicochemical properties, an extensive literature study was performed for all 209 PCBs to gather data on water solubility, vapour pressure, Henry's law constant and other parameters. The data were compared and adjusted to be internally consistent. In addition, the temperature dependency of these properties was studied, as varying temperatures can significantly influence the environmental behaviour of contaminants.
As a next step, detailed information on best estimate values and statistical characteristics for environmental input parameters was collected. These parameters cover spatial dimensions and properties of the modelled region and meteorological data (e.g. wind speed, rain rate, soil properties), which are subject to considerable measurement or estimation uncertainty and also may show temporal and/or spatial variability. For the estimation of related parameters like intermedia exchange velocities, several methodologies were compared.
Level III calculations following the fugacity approach were employed to evaluate general tendencies of PCB congeners to partition from soil into the air and into the water compartment (deterministic and probabilistic calculations). Generic modelling was performed with a data set of environmental parameters that is specific to the Upper Rhine region of South West Germany. This region was chosen as it is well characterized by a number of monitoring surveys. Thus, the considered database reflects natural parameter ranges and variations that can be observed under realistic conditions. Based on a probabilistic sensitivity analysis, the model was carefully parameterised. Finally, PCB congeners of concern were classified according to their environmental significance. Recommendations are given for the risk assessment of PCB contaminated sites.

2 Data and methods

2.1 Potential toxicity

Data on the potential toxicity of PCBs were derived from a literature review. The evaluation of PCB congeners of toxicological concern was based upon a study of McFarland and Clarke (1989) following the structure-activity relationship. Other investigations considered were those addressing acute or direct toxicity (McFarland and Clarke 1989, Bright et al. 1995, Suedel et al. 1997, Bergen et al. 1996), the potential to promote tumours and a number of other health effects (US HHS 2000).

2.2 Environmental occurrence

For some PCB congeners of toxicological relevance, very low quantities in environmental samples are reported. To identify congeners of concern with respect to environmental frequency, literature studies were performed. Data were collected for PCB congener patterns in different environmental matrices, such as soils, sediments and other environmental samples (animal tissues, human fat and milk).

2.3 Mobility and transport potential - physicochemical properties of PCBs

The behavior of organic compounds in the environment is largely controlled by their relative tendencies to partition into air, water and organic phases such as lipids, waxes and natural organics matter. These tendencies can be described by solubility in water, octanol-water partition coefficient, vapor pressure and Henry's law constant. Furthermore, values of solubility in octanol and the octanol-air partition coefficient are given for many compounds. For PCBs, physicochemical properties were derived from literature studies and estimations.
The following sources were used to gather data and further literature: a) database within the computer program EPI Suite 3.10 (US EPA 2003), b) online database CHEMFATE (see reference list), c) online resource Physical Chemical Property Data (see ERG database in the reference list). For some compounds without experimental data, approximated values are cited in the above databases. If more recent publications were found, these values were taken into consideration for the present study. In case that more than one measurement was found for a given property, either a typical value was chosen or the mean or median of all measurements were calculated. Additionally, and for compounds without any cited data, estimations were performed with EPI Suite 3.10 and (for vapor pressure estimations) according to Falconer and Bidleman (1994). Selected literature values and estimations for all 209 PCBs are provided in Appendix A, Tab. A1. Data for all PCB congeners were gathered in order to avoid data gaps (meeting the uncertainty given for environmental congener patterns).

2.3.1 Internal consistency

Taking into account all available data, inconsistencies are likely to occur. E.g., measured Henry's Law constants may deviate from those calculated from measured vapour pressure and water solubility. Therefore, values of vapour pressure, water solubility, solubility in octanol, Henry's Law constant, octanol-water and octanol-air partition coefficients were screened and adjusted using a procedure developed by Beyer et al. (2002), resulting in a consistent set of physicochemical data that considers all available information. Adjusted physicochemical properties for all PCB congeners, together with details on the deviation from selected literature values are presented in Tab. A2 (Appendix A). Evaluative steps for the adjustment are described in the following.

a) Transformation of measured and estimated values into units of [mol/m^3] or dimensionless partition coefficients

$$S_A = \frac{P^S}{R \times T} \quad (1)$$

$$S_W = \frac{S_{Wat}}{M} \quad (2)$$

$$K_{AW} = \frac{H}{R \times T} \quad (3)$$

S_A, S_W: solubility in air and water [mol/m^3]
R: universal gas constant, R = 8.3145 kJ mol^{-1} K^{-1}
T: absolute temperature [K]
P^S: saturation vapour pressure [Pa]
S_{wat}: concentration in water [mg/L]
M: molecular weight [g/mol]
K_{AW}: air-water partition coefficient [-]
H: Henry's law constant [Pa m^3 mol^{-1}]

b) Calculation of liquid state values as recommended by Mackay (2001)

Liquid or subcooled liquid properties were used in quantitative structure-property relationships. The subcooled liquid state is related to the solid state with the fugacity ratio F:

$$C_S^S = \frac{C_L^S}{F} \quad (4)$$

C^S_L: solubility of the compound in a subcooled liquid state [mol/m^3]
C^S_S: solubility of the solid [mol/m^3]

The fugacity ratio can be estimated from the melting point and the entropy of fusion (Reid et al. 1987):

$$F = \frac{f_L}{f_S} = \exp\left[\frac{-\Delta S_{fus}}{R}\left(\frac{T_M}{T} - 1\right)\right] \quad (5)$$

f_L, f_S: liquid and solid fugacity
ΔS_{fus}: entropy of fusion [J mol^{-1}K^{-1}]
T: system temperature [K]
T_M: melting point [K]

If no measured or correlated value was found, a value of 56.52 J/mol-K was assumed for the entropy of fusion (Yalkowsky 1979).

c) Relation and adjustment of properties

Fundamental thermodynamic relationships between physicochemical properties enable to derive properties from each other as follows (according to Cole and Mackay 2000):

$\log K_{AW} = \log S_A - \log S_W$ (6)
$\log K_{OA} = \log S_O - \log S_A$ (7)
$\log K_{OW} = \log S_{OW} - \log S_{WO}$ (8)
$\log S_O/S_W = \log S_O - \log S_W$ (9)

K_{OW}: octanol-water partition coefficient [-]
S_O: solubility in octanol [mol/m^3]
K_{OA}: octanol-air partition coefficient [-]
S_{OW}, S_{WO}: solubility in octanol saturated with water, solubility in water saturated with octanol [mol/m^3]

The ratio S_O/S_W in Eq. (9) can be regarded as the partition coefficient between pure octanol and pure water, which however is not necessarily equal to the K_{OW} (Beyer et al. 2002). Calculated values of K_{OA} that are derived from K_{OW} and K_{AW} were shown to consistently deviate from measurements (due to differences between pure and water-saturated octanol). A rough estimated is given by:

$\log S_O/S_W = \log K_{OW} - 0.117$ for $\log K_{OW} \leq 4$ (10)
$= 1.35 \times \log K_{OW} - 1.58$ for $\log K_{OW} > 4$

Inserting values for all three properties into one of Eq. (6) to (10) typically result in a deviation (e.g. inserting K_{AW}, S_A and S_W into Eq. 6). After calculating this deviation, a quantity for adjustment can be determined. In addition, uncertainty factors may be applied to properties which are known to be more accurate than others (see Beyer et al. 2002). When data for 3 or 4 of the six partitioning properties from Eq. (6) to (10) is available, all values can be related to each other in one constraining equation. If more than 4 values are available, two equations are necessary to relate all properties. For the latter case Beyer et al. (2002) developed a numerical iteration procedure and an analytical approach (presented as an spread-sheet based tool at (http://www.usf.uos.de/projects/elpos) along with a description; this tool was used in the present study).
In addition to adjusted properties, minimum and maximum values were evaluated for K_{AW}, S_W, S_A and K_{OW} according to Eq. (6) to (10) taking into account all selected literature values. The evaluated data set finally consists of adjusted (most probable) values and minima and maxima (Tab. A2).

2.3.2 Temperature dependency

Temperature is an important parameter influencing the environmental behaviour of contaminants. Most physicochemical data relate to a standard temperature of 25 °C, but also temperature dependent data sets have recently been compiled by several authors (e.g. Falcooner and Bidleman 1994, Bamford et al. 1999 and 2000, Shiu and Ma 2000a and b, Staudinger and Roberts 2001). In many cases, the relationship between physicochemical properties and temperature can be described by a modified van't Hoff equation (Boethling and Mackay, 2000):

$$\ln x(T) = \ln x_0 + \frac{\Delta H}{R \times \left(\frac{1}{T_0} - \frac{1}{T} \right)} \qquad (11)$$

$x(T)$, x_0: given property at temperature T, T_0
T, T_0: system and reference temperature [K]
ΔH: enthalpy of phase change [kJ/mol]

For calculations, ΔH is commonly kept constant over the entire considered temperature range. Nevertheless, it has to be noticed that it is applicable only within relatively small temperature variations (Shiu and Ma, 2000a, Boethling and Mackay, 2000). Shiu and Ma (2000a and b) discuss limitations of Eq. (11) and report alternative expressions for a range of organic chemicals.
For solubilities, the temperature dependency is better expressed in terms of internal energy change, ΔU (Atkinson and Curthoys 1978, Goss and Eisenreich 1996). Values found in literature for ΔH (enthalpy of solution in water and enthalpies of air-water, octanol-water and octanol-air phase changes) are assumed to be actually heats of solubilisation ΔU (Beyer et al. 2002). Heats of vapourisation ΔH_{VP} as obtained from Falcooner and Bidleman 1994 were transformed into heats of phase transition (ΔU_A) to be applicable to air solubility:

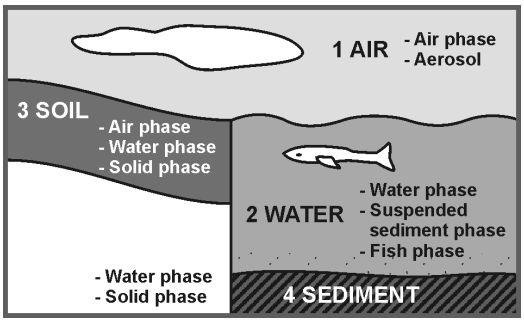
$\Delta U_A = \Delta H_{VP} - \Delta U_H$ (12) deviation ΔU_H = 2.391 J/mol

The difference between ΔH_{VP} and ΔU_A is temperature dependent but can be regarded nearly constant over a limited temperature range. A linear regression of ΔU_A versus 1/T showed a deviation of –2.391 J/mol from ΔH_{VP} over a temperature range from 0 to 30 °C. This value changes for a different temperature range, and the error of the regression increases for larger temperature ranges (Beyer et al. 2002).
Temperature coefficients of water solubilities applying to the solid phase have been converted to apply for the supercooled liquid state according to Dickhut et al. (1987):

$\Delta U_{WL} = \Delta U_{WS} - \Delta U_{fus}$ (13) ΔU_{fus}: enthalpy of fusion (solid to liquid) [kJ/mol]
$\Delta H_{fus} = T_M \times \Delta S_{fus}$ (14) T_M: melting point [K]
ΔS_{fus}: entropy of fusion [kJ $mol^{-1}K^{-1}$]

Similar to the physicochemical properties, heats of phase transfer can be related to each other (see Beyer et al. 2002 for further details). Adjustments have been made accordingly, using the spreadsheet tool cited in the previous section. When no measured data were found, an average value for PCBs of ΔU_W = 20 kJ/mol was assumed (according to Shiu et al. 1997) and ΔU_O set to zero (following Beyer et al. 2002).

2.4 Multimedia environmental modelling



The modelling of multimedia partitioning of PCBs was carried out with Level III calculations (Mackay 2001, Mackay et al. 1996a). This procedure accounts for partitioning kinetics, in addition to contaminant loss due to advection and degradation in the various phases. Calculations were performed in 4 bulk environmental compartments (air, water, soil and sediments) with subcompartments as shown in Fig. 1.

***Fig. 1**: Compartments considered for Level III modelling.*

Partitioning is described by *Z* values (fugacity capacities), which express the affinity of a chemical for each environmental phase (Mackay et al. 1996a). I.e., a partition coefficient can be described by the ratio of two *Z* values (Mackay 2001). For Type 1 chemicals (most organic compounds, including PCBs), the fugacity approach is followed. *Z* values [mol m^{-3} Pa^{-1}] must be defined for all environmental media. Bulk *Z* values are calculated using the *Z* values for the pure phases and the volume fractions of the subcompartments as decribed in detail by Mackay et al. (1996a). In general, fugacity is referred to as equilibrium criterion *Q* [Pa] which is related to the concentration *C* [mol/m^3] as follows:

$$C_i = Q_j \times Z_i \quad (15)$$

C_i, Z_i: concentration and *Z* value of compartment *i*
Q_j: equilibrium criterion of bulk compartment *j*

Situations are considered where a chemical is continuously discharged at constant emission rates *E* [mol/h] into the 4 bulk compartments. *Q* values are calculated specific to the bulk compartments as a function of *E* and so called *D* values (see Mackay et al. 1996a for respective mass balance equations). *D* values consist of parameters for intermedia transport (see Tab. 1) and for degradation and advection ($D_{R,j}$ and $D_{A,j}$). The latter are defined as follows:

$$D_{Rj} = V_j \times Z_j \times k_j \quad (16)$$

D_{Rj}: degradation *D* value for bulk compartment *j* [mol $Pa^{-1}h^{-1}$]
k_j: first-order degradation rate constant [1/h]

$$D_{Aj} = G_j \times Z_j \quad (17)$$

D_{Aj}: advection *D* value [mol $Pa^{-1}h^{-1}$]
G_j: advective flow rate [m^3/h]

with $$G_j = \frac{V_j}{\tau_j} \quad (18)$$

V_j: volume of bulk compartment j [m^3]
τ_j: advective residence time [h]

Tab. 1*: Intermedia transport D value equations according to Mackay (2001), A: interfacial area, Q: scavenging ratio, v_Q: volume fraction of aerosols, Z-value subscripts: A air, W water, Q aerosol, E soil, P sediment solids, S suspended sediment. U: intermedia transport parameter as defined in Tab. 8, U_4 denotes U_Q in Mackay (2001), other U-values denoted according to Mackay et al. (1996a).*

Compartments	Process	Intermedia transport D values
Air(1)-Water(2)	Diffusion	$D_V = 1/[1/(A_{12}U_1Z_A)+1/(A_{12}U_2Z_W)]$
	Rain dissolution	$D_{RW2} = A_{12}U_3Z_W$
	Wet deposition	$D_{QW2} = A_{12}U_3 \times Q \times v_Q \times Z_Q$
	Dry deposition	$D_{QD2} = A_{12}U_4 \times v_Q \times Z_Q$
	Transport Air-Water	$D_{12} = D_V+D_{RW2}+D_{QD2}+D_{QW2}$
	Transport Water-Air	$D_{21} = D_V$
Air(1)-Soil(3)	Diffusion	$D_E = 1/[1/(A_{13}U_7Z_A)+1/(A_{13}U_5Z_A+A_{13}U_6Z_W)]$
	Rain dissolution	$D_{RW3} = A_{12}U_3Z_W$
	Wet deposition	$D_{QW3} = A_{13}U_3 \times Q \times v_Q \times Z_Q$
	Dry deposition	$D_{QD3} = A_{13}U_4 \times v_Q \times Z_Q$
	Transport Air-Soil	$D_{13} = D_E+D_{RW3}+D_{QD3}+D_{QW3}$
	Transport Soil-Air	$D_{31} = D_E$
Soil(3)-Water(2)	Soil runoff	$D_{SW} = A_{13}U_{12}Z_E$
	Water runoff	$D_{WW} = A_{13}U_{11}Z_W$
	Transport Soil-Water	$D_{32} = D_{SW}+D_{WW}$
	Transport Water-Soil	$D_{23} = 0$
Sediment(4)-Water(2)	Diffusion	$D_Y = A_{24}U_8Z_W$
	Deposition	$D_{DS} = A_{24}U_9Z_P$
	Resuspension	$D_{RS} = A_{24}U_{10}Z_S$
	Transport Sediment-Water	$D_{24} = D_Y+D_{DS}$
	Transport Water-Sediment	$D_{42} = D_Y+D_{RS}$

The equation system for the Level III modelling was set up in a Microsoft Excel spreadsheet. Deterministic calculations with the most probable input parameters were performed and, in addition, a probabilistic approach (Monte Carlo simulations) was carried out using the software package Crystal Ball (Decisioneering 2001). Required input parameters comprise:

a) chemical specific input (physicochemical properties, first order degradation rate constants)
b) compartment dimensions and properties (area and depth, volume fractions of subcompartments, density, fraction of organic carbon, advective residence time)
c) intermedia transport parameters *U*

Methodologies to determine intermedia transport parameters *U* are presented in the following.

2.4.1 Air - water exchange

Mackay and Yeun (1983) performed experiments in a wind wave tank with 11 organic compounds of varying Henry's law constants to evaluate liquid- and vapour-phase mass transfer coefficients (MTC). They found the following relationships for the air side MTC over water k_{VA} **(U_1)** and water side MTC k_{VW} **(U_2)** [m/h]:

$$k_{VA} = 10^{-3} + 0.0462 \times U^* \times Sc_{i,A}^{-0.67} \quad (19)$$

$$k_{VW} = 10^{-6} + 0.0034 \times U^* \times Sc_{i,W}^{-0.5} \quad (20)$$

U^*: friction velocity [m/s]
$Sc_{i,A}$, $Sc_{i,W}$: Schmidt-number of compound *i* in air and water, respectively [-]

The friction velocity U^* can be estimated from the wind speed measured at 10 m height u_{10} [m/s] as follows (Mackay 2001):

$$U^* = 0.01 \times (6.1 + 0.63 \times u_{10})^{0.5} \times u_{10} \quad (21)$$

The Schmidt number in water $Sc_{i,W}$ is defined by the relation between the temperature dependent kinematic viscosity of water $\nu_W(T)$ [cm^2/s] (assumed to be approximately the dynamic viscosity of water) and the molecular diffusivity of compound i in water $D_{i,w}$ [cm^2/s] (Schwarzenbach et al. 2003):

$$Sc_{i,W} = \frac{\nu_W(T)}{D_{i,w}} \quad (22) \quad \text{with} \quad \nu_W(T) = 0.0175 \times e^{-0.075 \cdot T} \quad (23)$$

The Schmidt-number in air Sc_A ranges from 0.6 for water to about 2.5 (Mackay 2001). The relation of diffusivities D_i and D_j of two substances *i* and *j* in the same medium can be approximated from the relation of molar mass *M* (Tinsley 1979). Schwarzenbach et al. (2003) recommend to estimate $D_{i,w}$ from the diffusivity of CO_2 in water :

$$D_{i,W} = D_{CO_2,W} \times \sqrt{\frac{M_{CO_2}}{M_i}} \quad (24) \quad \text{with } D_{CO2,W} = 1.92 \times 10^{-5} \text{ cm}^2/\text{s}$$

Substituting typical values for the Schmidt number and taking into account other studies, Mackay (2001) suggest the following simplified correlations for k_{VA} and k_{VW}:

$$k_{VA} = 3.6 + 5 \times u_{10}^{1.2} \quad (25)$$

$$k_{VW} = 0.0036 + 0.01 \times u_{10}^{1.2} \quad (26)$$

An alternative approach is presented by Schwarzenbach et al. (2003) to estimate $v_{i,a}$ and $v_{i,w}$ (corresponding to k_{VA} and k_{VW}, respectively):

$$v_{i,a} = \left(\frac{D_{i,a}}{D_{water,a}}\right)^{0.67} \times v_{water,a} \quad (27)$$

$D_{water,a}$ = 0.257 cm^2/s, molecular diffusivity of water in air
$D_{i,a}$: diffusivity of compound *i* in air [cm^2/s]
$v_{water,a}$: exchange velocity of water in air [m/h]

with $D_{i,a} = D_{water,a} \times \sqrt{\frac{M_{water}}{M_i}}$ (28) and $v_{water,a} = 0.2 \times u_{10} + 0.3$ (29) u_{10} [m/s], $v_{water,a}$ [cm/s]

$$v_{i,w} = \left(\frac{Sc_{i,w}}{600}\right)^{-a_{Sc}} \times v_{CO_2,w} \quad (30)$$

$v_{CO2,w}$: exchange velocity of CO_2 in water [m/h]

with a_{Sc} = 0.67 if $u_{10} \leq 4.2$ m/s; 0.50 if $u_{10} > 4.2$ m/s (31)

and $v_{CO2,w}$ = 0.65×10^{-3} if $u_{10} \leq 4.2$ m/s; $(0.70 \times u_{10} - 2.68) \times 10^{-3}$ if 4.2 m/s < $u_{10} \leq 13$ m/s; $(1.64 \times u_{10} - 13.69) \times 10^{-3}$ if $4u_{10} > 13$ m/s (32)

Data on the rain rate **(U_3)** can be derived from climatological surveys. For the dry deposition velocity of aerosols **(U_4)**, 10.8 m/h is assumed by Mackay (2001). Trapp and Matthies (1998) suggest a velocity of 3.6 m/h, correlating to relatively fast deposition near the emitting source.

2.4.2 Air - soil exchange

Mackay and Stiver (1991) and Mackay (2001) consider 3 diffusive processes (based on the approach of Jury et al. 1983 and 1984): a) diffusion in the air boundary layer, b) vapour diffusion in soil air pores and c) liquid diffusion in soil water.

Mackay et al. (1992 and 1996a) consider the air side MTC over soil (boundary layer) k_{EA} **(U_7)** to be equal to the air side MTC over water U_1 (see above). In contrast, Mackay and Paterson (1991) and Mackay (2001) assume a lower velocity, with U_7 being one third of U_1.

Vapour diffusion in soil air pores k_{SA} **(U_5)** [cm/s] is calculated from molecular diffusivity in air B_{MA} [cm^2/s] and the diffusion path length in soil Y_3 [cm] according to Mackay et al. (1992) and Mackay (2001):

$$k_{SA} = \frac{B_{MA}}{Y_3} \qquad (33)$$

Y_3: diffusion path length in soil (1/2 soil depth) [cm]

Considering vapour diffusion porosity θ_A and tortuosity effects, B_{MA} is estimated with the model of Millington and Quirk (1961), as recommended by Jury et al. (1983):

$$B_{MA} = B_A \frac{\theta_A^{10/3}}{\theta_T^2} \qquad (34)$$

B_A: molecular diffusion coefficient in air [cm^2/s] (corresponding to $D_{i,a}$, as defined previously)
θ_T: total soil porosity [cm^3/cm^3]

Liquid diffusion in soil water k_{SW} **(U_6)** [cm/s] can be estimated similarly from molecular diffusivity in water B_{MW} [cm2/s] (Mackay et al. 1992 and Mackay 2001), again using the Millington-Quirk (1961) tortuosity model:

$$k_{SW} = \frac{B_{MW}}{Y_3} \qquad (35) \text{ with } \qquad B_{MW} = B_W \frac{\theta_W^{10/3}}{\theta_T^2} \qquad (36)$$

B_W: molecular diffusion coefficient in water [cm^2/s](corresponding to $D_{i,W}$)
θ_W: water-filled porosity [cm^3/cm^3]

Capillary flow of water will contribute to transport in soil, probably dominating over diffusion (Mackay et al. 1992). For evaluative purposes, the latter therefore suggest a factor of 5 to be applied to the liquid diffusion in water, calculated with Eq. (35). The authors recognise, however, that this assumption may be associated with a substantial error as actual capillary flow rates will vary with rain characteristics and soil type. Unfortunately, characteristic capillary flow rates are difficult to determine. Nevertheless, assuming that advection is the overall dominating process (following Mackay et al. 1992), the infiltration rate can be used as an upper bound estimate for the considered transport process. Dörhöfer and Josopait (1980) developed an empirical approach for estimating infiltration rates. The methodology was set up for Northern Germany (a topographically flat area), but is also applicable to hilly and mountainous regions (Röder 1994). For respective calculations, the studied area is characterised with respect to a) land use, b) hydromorphic classification, c) soil type and d) hill slope class. After determining the evapo-transpiration level *ET* and the drainage quotient h_A/h_G (according to Tab. 2 and 3, respectively), the level of infiltration G_{Inf} was evaluated as follows:

$$G_{Inf} = 1 + \frac{h_N - 312.5 - ET \times 25}{h_A/h_G \times 50} \qquad (37)$$

h_N: rain rate [mm/yr]

According to Dörhöfer and Josopait (1980), a value of 1 for G_{Inf} corresponds to an infiltration rate h_G of 0-50 mm/yr. All following levels are a multiple of this range (e.g. for a infiltration level G_{Inf} = 9, the resulting infiltration rate h_G is 401-450 mm/yr).

***Tab. 2**: Evapo-transpiration level ET as a function of soil class and land use. Level 2 corresponds to a evapo-transpiration rate of 351-375 mm/yr. For every following level, 25 mm/yr is added. T: terrestrial, SH: semi-hydromorphic, H: hydromorphic.*

Soil class	Open land			Forest		
	T	SH	H	T	SH	H
Sand	2	3	11	6	7	11
Loamy sand	4	5	11	7	8	11
Sandy loam	7	8	11	9	10	11
Loess	6	7	11	8	9	11
Loam	9	10	11	10	11	11
Clay	10	11	11	11	11	11

***Tab. 3**: Drainage quotient h_A/h_G as a function of hill slope and hydromorphic class, h_A: total drainage, h_G: infiltration to groundwater.*

Hydromorphic class	Hill slope class					
	0-0.5°	>0.5-3°	>3-7°	>7-12°	>12-25°	>25°
Terrestrial	1	1.2	1.5	1.7	1.7	2.3
Semi-hydromorphic	2	2	2	2	2	2.3
Hydromorphic	2.5	2.5	2.5	2.5	2.5	2.5

2.4.3 Soil - water transport

The water runoff rate from soil U_{WW} **(U_{11})** can be determined with the methodology of Dörhöfer and Josopait (1980), as described in the last section:

$$U_{WW} = h_A - h_G \quad \text{with} \quad h_A = h_A / h_G \times h_G \qquad (38)$$

U_{WW}: soil water runoff rate [mm/yr]
h_A: total drainage [mm/yr]
h_G: infiltration rate [mm/yr], determined from G_{Inf} (Eq. 36)
h_A/h_G: drainage quotient [-] (Tab. 3)

As an approximation, Mackay et al. (1992 and 1996a) suggest a water runoff rate U_{WW} of half the rain rate, whereas Mackay and Paterson (1991) and Mackay (2001) utilise a U_{WW} of 2/5 rain rate.

For the determination of the solids runoff rate U_{EW} **(U_{12})**, Mackay et al. (1992 and 1996a) assume that the runoff water contains 200 parts per million by volume of solids. Mackay and Paterson (1991) and Mackay (2001) consider a content of solids in runoff water that is about three times higher.

2.4.4 Water – sediment exchange

To estimate water-sediment transport, diffusion (in the water phase) and deposition are considered whereas for the sediment-water exchange process, diffusion and resuspension are treated. Mackay et al. (1992) address the diffusion part with the mass transfer coefficient k_T, Mackay and Paterson (1991) and Mackay (2001) additionally take into account the water side MTC over sediment k_{SW}. Following the latter concept, the diffusive MTC U_8 [m/h] is calculated as follows:

$$U_8 = \frac{1}{1/k_{SW} + 1/k_T} \qquad (39)$$

with $$k_T = \frac{B_{W4}}{Y_4} \qquad (40)$$

B_{W4}: molecular diffusion coefficient in sediment [cm^2/s]
B_W: molecular diffusion coefficient in water [cm^2/s]

and $$B_{W4} = B_W \times \theta_{W,sed}^{4/3} \qquad (41)$$

$\theta_{w,sed}$: water-filled porosity in sediment [cm^3/cm^3]
Y_4: diffusion path length in sediment (1/2 sediment depth) [cm]

Mackay and Paterson (1991) and Mackay (2001) chose a k_{SW} of 0.01 m/h. For sediment deposition, Mackay et al. (1992 and 1996a) select a rate U_{DP} **(U_9)** of 5 x 10^{-7} m/h, corresponding to 5000 m^3/h in a lake with 10^{10} m^2 surface area. This is equivalent to a sedimentation rate of 12 cm^3 m^{-2} yr^{-1} and correlates to an upper bound estimation for large lakes (Mackay et al. 1992) that can also be applied to a aquatic system of rivers and lakes (Mackay 2001). Mackay et al. (1992) assume that 40% of the sediment mass is buried, 40% is resuspended (resulting in a corresponding resuspension rate U_{RS} or U_{10}) and 20% is mineralised organic matter OM (approximate OM balance). Mackay and Paterson (1991) and Mackay (2001) prefer a sediment deposition rate that is about one order of magnitude lower and a smaller portion of resuspension (about 24%).

3 Results and discussion

3.1 Potential toxicity

Table 4 shows PCBs of toxicological concern evaluated from the structure-activity relationship, based upon the study of McFarland and Clarke (1989). This group encompasses 65 PCB congeners. Among PCBs stimulating the production of bioactivating enzyme systems, the most problematic are those responsible for the formation of aryl hydrocarbon metabolising mixed-function oxidases (MFOs). A result can be an increased capacity for bioactivation of otherwise non-toxic foreign compounds such as certain polycyclic aromatic hydrocarbons (PAH) to cytotoxic or genotoxic metabolites (McFarland and Clarke 1989). Respective PCBs are summarised in Group I (Tab. 4), representing mono-ortho and di-ortho congeners that closely resemble 2,3,7,8- tetrachlorodibenzo-*p*-dioxin in their structures and toxic effects. Di-ortho PCBs are the most important group for neurotoxic effects (US HHS 2000). Also included in the evaluated group are PCBs showing strong enrichment in the liver (Ahlborg et al. 1992) or the potential to promote tumours (US HHS 2000, US EPA 1996).
Compared to Group I, Phenobarbital-type (PB-type) inducers have a considerably less potential for contributing to toxic effects, whereas weak PB-inducers reveal the least potential for toxicity (Group II and III in Tab. 4, respectively).

Tab. 4*: PCB congeners of toxicological concern (IUPAC-number), 3-MC: 3-methylcholanthrene-type, MFO: mixed-function oxidase, PB: Phenobarbital-type.*

Group I	**a) pure-3-MC inducers** PCB 77, 126, 169
	b) mixed-type MFO inducers PCB 37, 81, 105, 114, 118, 119, 123, 128, 138, 156, 157, 158, 166, 167, 168, 170, 189
Group II	**PB-inducers** PCB 47, 66, 85, 87, 99, 100, 101, 133, 137, 139, 140, 153, 154, 163, 165, 171, 180, 181, 182, 183, 184, 190, 191,194, 195, 196, 197, 203, 204, 205, 206, 207, 209
Group III	**weak PB-inducers** PCB 11, 14, 15, 52, 54, 75, 80, 136, 146, 151, 155, 159

3.2 Toxic potential and environmental occurrence

Different PCB congener patterns are known for contaminated soils, sediments and other environmental samples (animal tissues, human fat and milk). Frequencies of PCB congeners in environmental matrices were analysed in terms of relative abundance (percent of total PCBs in a sample). Table 5 shows PCB congeners that meet the criteria of toxic potential and environmental relevance (group A to C). Furthermore, congeners are listed for which no toxicity data are available but a significantly high abundance is reported (group D). In total, 77 PCB congeners are assumed to be relevant with respect to potential toxicity and/or environmental occurrence.

Tab. 5*: PCB congeners of different toxic potential as a function of environmental frequency (data from Alford-Stevens et al. 1988, McFarland and Clarke 1989, Brannon et al. 1991, Hansen et al. 1997 and Meijer et al. 2003).*

Group A highest toxic potential	**1) reported frequency in environmental matrices: 0.5 % of total PCB or higher** PCB 37, 77, 105, 118, 123, 128, 138, 156, 158, 167, 170, 189
	2) low frequency (<0.5 %) PCB 81, 114, 119, 126, 157, 166, 168, 169
Group B high to moderate toxic potential	**frequency: 0.5% or higher** PCB 47, 66, 85, 87, 99, 101, 137, 153, 180, 183, 191, 194, 195, 196, 202, 203
Group C low toxic potential	**frequency: 0.5% or higher** PCB 15, 52, 75, 80, 136, 146, 155
Group D no toxic potential reported	**high frequency (> 5% of total PCB in one or more of the matrices soil, sediment, animal tissues and human fat and milk)** PCB 8, 16, 17, 18, 20, 22, 25, 26, 28, 31, 32, 34, 41, 42, 44,49,50, 56, 60, 64, 70, 71, 74, 82, 90, 95, 96, 110, 132, 149, 151, 177, 187, 201

3.3 Mobility and transport potential

3.3.1 Uncertainty of physicochemical properties

Considerable uncertainty is associated with physicochemical properties of PCBs. Figures 2 and 3 present value ranges of Henry's law constant, vapour pressure, water solubility and octanol-air partitioning coefficient at 10°C for the group of 77 PCB congeners evaluated in the previous section (Tab. 5). The temperature correction was calculated with Eq. (11), using adjusted internal energy changes ΔU listed in Tab. A2. Direct measurements in Fig. 2 represent selected literature values from Tab. A1. Maximum, minimum and adjusted values were determined according to the methodology described in section 2.3, assuming the same accuracy for each datum.

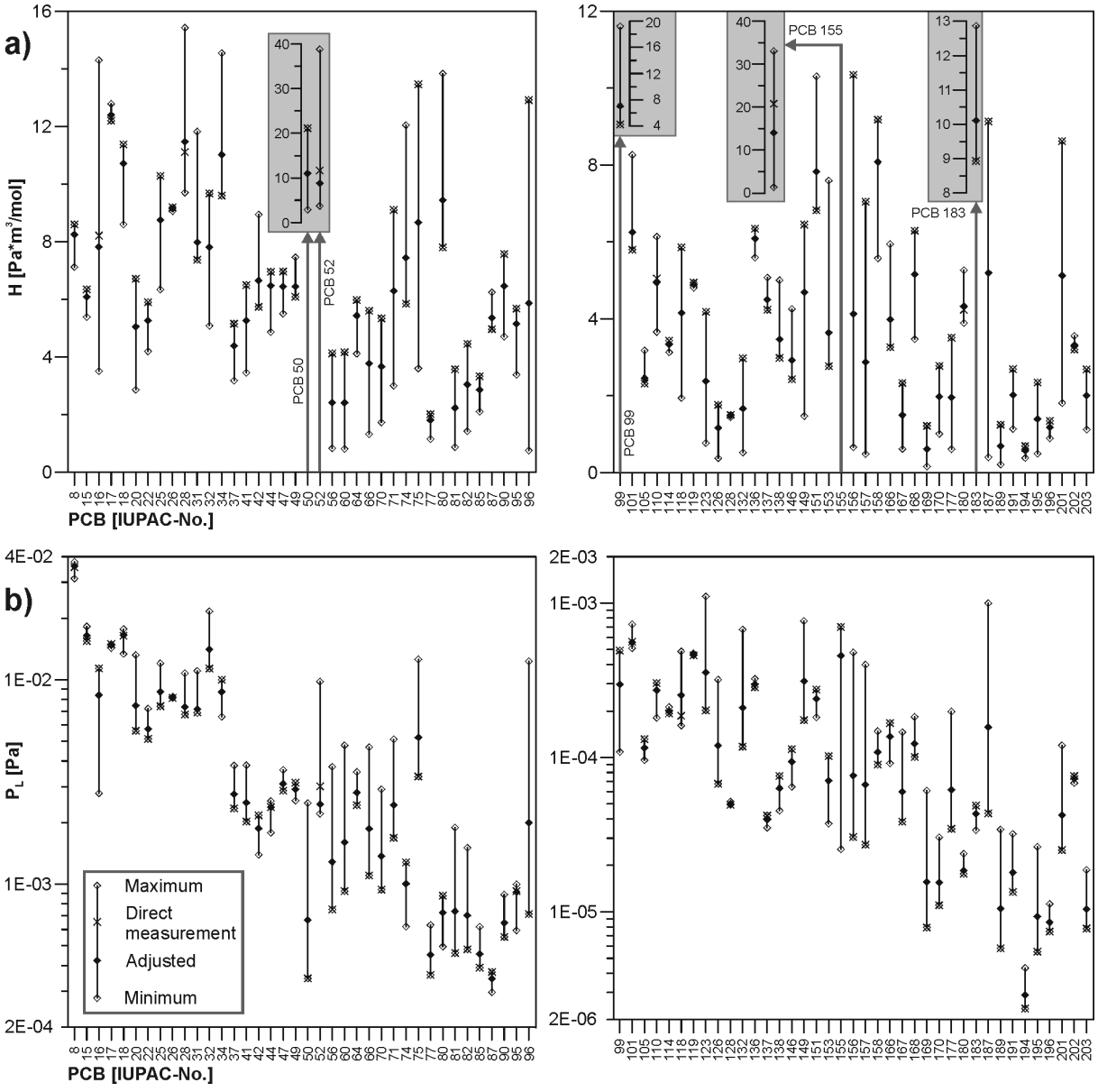


***Fig. 2**: Uncertainty of physicochemical properties for selected PCB congeners. Values of a) Henry's law constant, b) vapour pressure at a temperature of 10°C.*

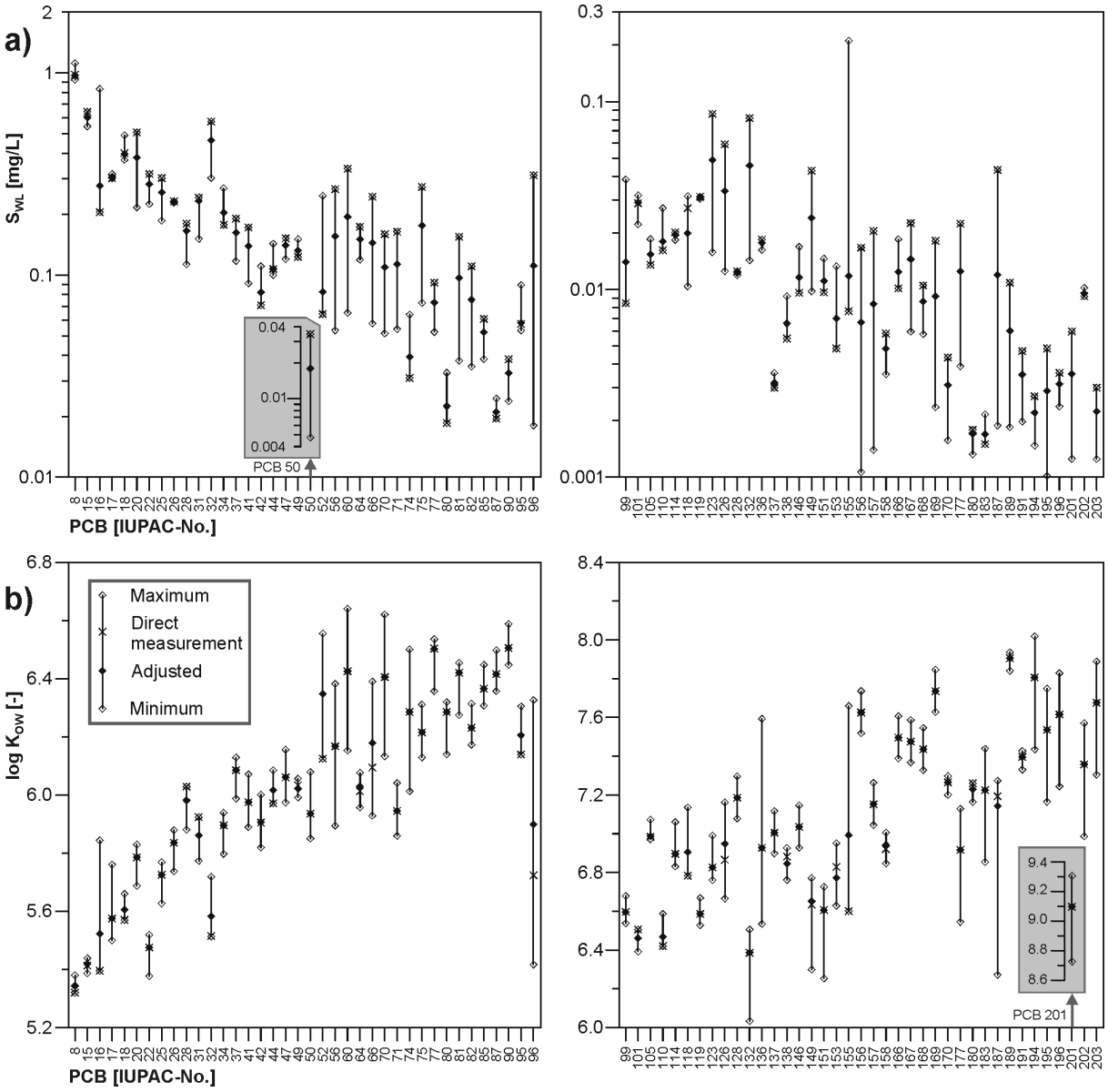


***Fig. 3**: Uncertainty of physicochemical properties for selected PCB congeners. Values of a) water solubility, b) log K_{OW} at a temperature of 10°C.*

Variations of Henry's law constants (maximum-minimum) are around 2-5 Pa m^3 mol^{-1} or 10-60% (referred to the adjusted, i.e. most probable value) for most PCBs. There are some congeners whose values vary between 80 and 150% and even variations up to a factor of 2 (PCB 96, 99, 155, 156, 157) and 4 (PCB 52) can be found (PCB congeners denoted with IUPAC-Numbers). Uncertainties for vapour pressure P_L and water solubility S_{WL} are in a similar range for the majority of PCBs. In contrast, maximal variations range up to a factor of 5 to 6 for P_L (PCB 96, 156, 157, 187) and 3.5 (PCB 187) respectively 17 (PCB 155) for S_{WL}. Most log K_{OW} values show a variability within 2-4%, however a group of 18 compounds is subject to 7-9% variation. Maximum variation in log K_{OW} is in the range of 14-16% (PCB 96, 136, 155, 187).

Internal energy changes ΔU are rarely reported for PCBs (except for ΔU_A, compare to Tab. A1). Data gaps were filled according to section 2.3.2. For the group of considered PCBs, uncertainty of ΔU can be quantified for PCB 15 only, revealing 9, 7 and 27% for ΔU_{AW}, ΔU_A and ΔU_{OW}, respectively (max.-min. referred to the adjusted value).

3.3.2 Temperature-dependency of physicochemical properties

Physicochemical properties as a function of temperature are plotted in Fig. 4 and 5. The aim of this study is to estimate possible variations occurring in soils. Temperature dependent values were calculated assuming an annual soil temperature range of 1-20°C (average value of 10°C) and seasonal variations of 1-5°C (3°C average) in winter and 15-20°C (18°C average) during summer. These temperature ranges were estimated from air temperatures observed at a variety of weather stations in Germany (monthly averages in the years 1961-1990, provided by the German Weather Survey DWD). Temperature variations in soil rapidly decrease with depth. Information on this aspect was obtained from a dataset including temperature measurements in the air and in soils at different depths (10.2 and 20.3 cm). These measurements were performed in the United States (Brownstown, Illinois) over a time period of 15 years (Illinois Climate Network, ICN 2004). Nevertheless, soil temperature ranges considered in this section correspond to the upper range of temperatures, as values of zero or below zero that can occur in winter are neglected (meeting the constraints associated to the chosen method, compare to section 2.3.2).

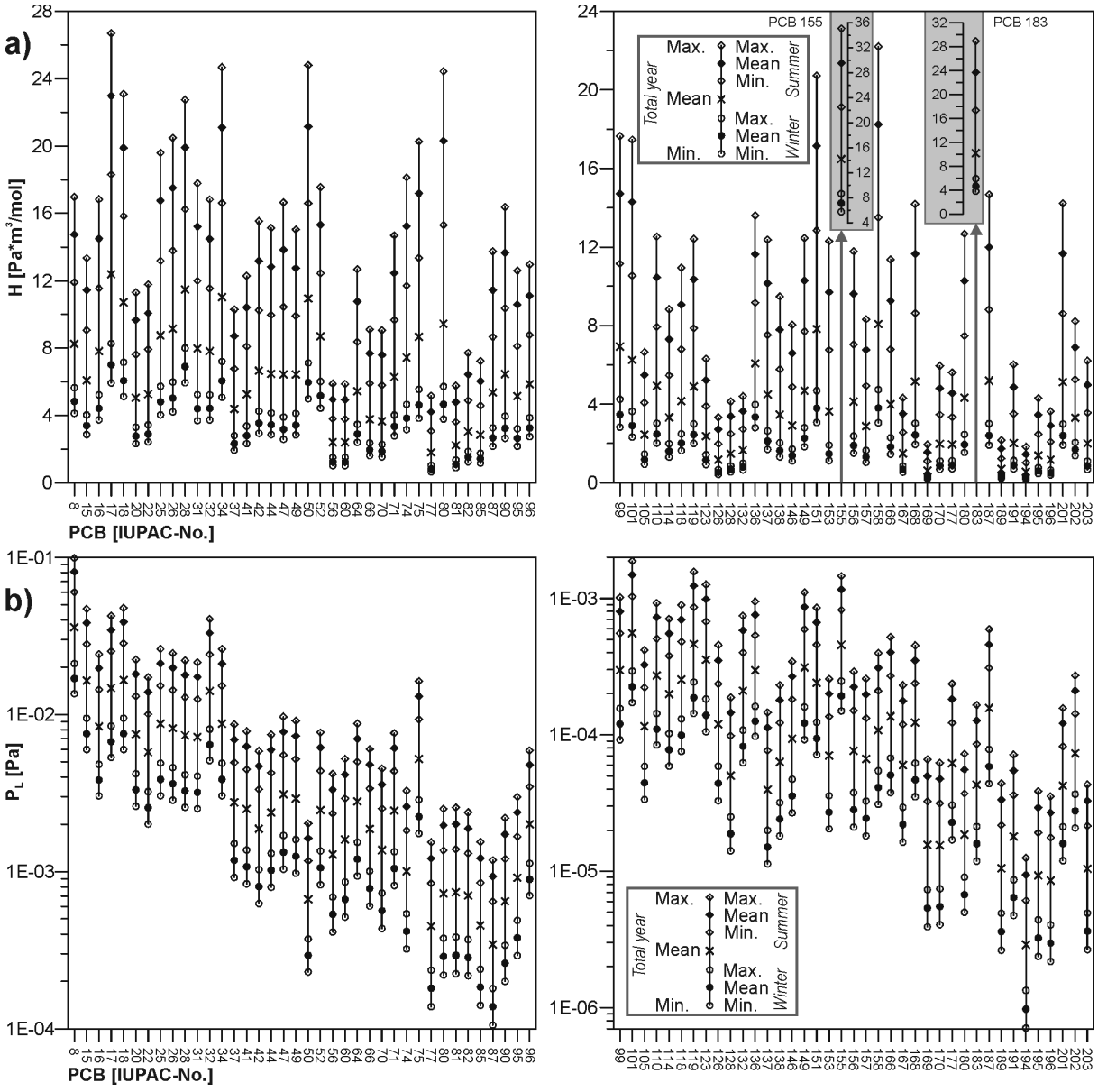


***Fig. 4**: Physicochemical properties of selected PCBs as a function of temperature (annual and seasonal variation). a) Henry's law constant, b) vapour pressure.*

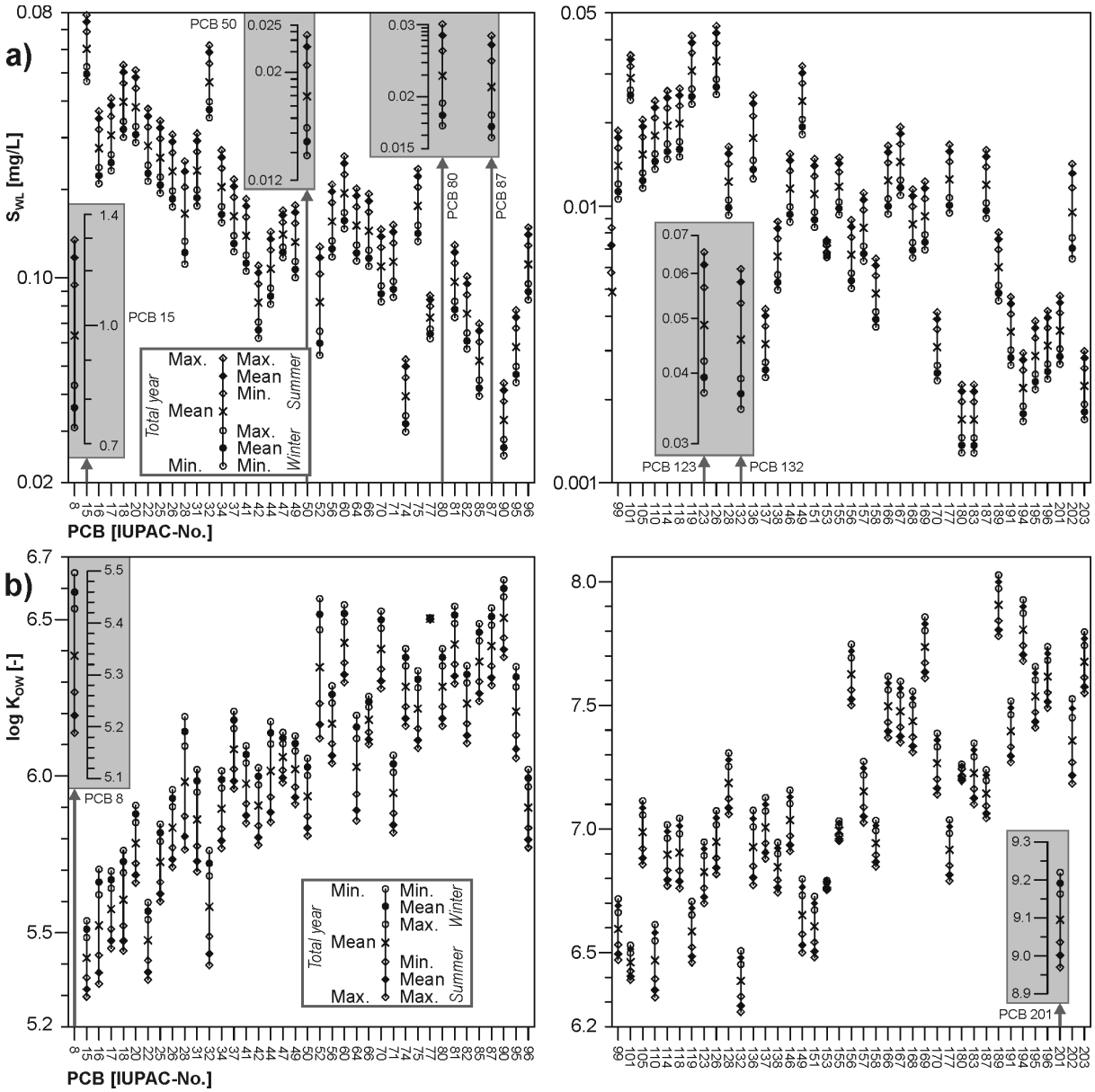


***Fig. 5**: Physicochemical properties of selected PCBs as a function of temperature (annual and seasonal variation). a) water solubility, b) log K_{OW}.*

As shown in Fig 4 and 5, temperature correlates directly with Henry's law constant H, vapour pressure P_L and water solubility S_{WL} (high summer, low winter values) and inversely with log K_{OW} (low values during summer and increased for winter temperatures). When comparing Fig. 2 and 3 to Fig. 4 and 5, respectively, it can be seen that parameter variations due to variable temperatures (assumed annual range) generally tend to exceed variation resulting from parameter uncertainty. Nevertheless, for some PCBs, parameter uncertainty is in the same range or even higher than temperature-dependent variations. This especially applies for water solubilities and, to a lower extent, for log K_{OW}. Annual variations (max.-min. referred to the value at 10°C) were found to be: H: 180-270% for most PCBs (maximal variation around 300%), P_L: 260-360% for the majority (up to 400%), S_{WL}: 60% is prevailing (based upon an average internal energy change ΔU_W for PCBs, see previous section), maximum variation around 90%, log K_{OW}: 3-5% (up to 7%).

3.3.3 Uncertainty of environmental parameters

High uncertainty is associated to almost every environmental parameter required as input for the Level III modelling. Tab. 6 to 8 summarise best estimates together with probable value ranges and statistical data.

As already mentioned in section 1, the modelling was performed for a model domain similar to the Upper Rhine region in South West Germany. Dimensions and properties were chosen accordingly, with a total area of 1000 km^2. Approximately 3% of this area consists of surface water bodies with an average depth of 3 m (Grathwohl et al. 2005, Valtchev et al. 2004). An average atmospheric mixing height of 1000 m with comparably stable conditions (variation between 700-1300 m) is assumed (see Tab. 6).
The chosen particulate matter concentrations in air and sediment represent typical values (with C_{Ae} = 5 $\mu g/m^3$ for rural areas and 100 $\mu g/m^3$ for polluted urban regions, C_{Sus} = 5 to 20 g/m^3 for natural waters). Clays and loamy soils are assumed to prevail in the model domain. Representative values for soil properties (including total porosity θ_T) have been derived from the estimation program ROSETTA (Schaap et al. 1998 and 2001) by calculating mean values from class average data for clays, loams and silts. Typical values for θ_W were estimated to be the average of residual water content and water content at 1/3 bar suction (or approximately field capacity), as often assumed (e.g. US EPA 2004a). The water content at 1/3 bar suction was calculated with van Genuchten's (1980) retention function as described by Schaap et al. (2001). The soil air content θ_A, which is required for the modelling was determined by $\theta_T - \theta_W$. Information on variation characteristics for θ_T and θ_W was obtained from a statistical analysis of the database that is included in ROSETTA.
A volume fraction of 10^{-6} for fish in water is often recommended as an approximation (Tab. 6). Mackay (2001) states however that this value might be overestimated. Therefore a range of 10^{-7} to 10^{-6} was chosen for the probabilistic modelling. For the process of aerosols being scavenged or swept out of the air, a scavenging ratio of 200,000 is commonly used. The mean, standard deviation and lognormal distribution stated in Tab. 6 was chosen by default, as detailed information on characteristic variation was not available.
Wind speed distributions were derived from a meteorological survey in Söllingen (located in the river Rhine valley near Karlsruhe, Germany). This survey was performed over a time period of 10 years (Traup and Kruse 1996). For average soil temperatures, 8-12 °C were assumed as a characteristic range for the modelled region. This assumption is based on air temperatures and on the fact, that temperature variations are lower in soil than in air. Air temperatures from selected weather observatory stations in Germany were considered (recorded in 1961-1990 by the DWD, see previous section).

Tab. 6*: Compartment dimensions and properties considered for the Level III modelling. Best est.: best estimate, St.dev.: standard deviation, Loc, Sc, Sh: Weibull parameters (Loc: location, Sc: scale, Sh: shape), Part.: particulate, Conc.: concentration, Sed.: sediment, Vol.: volume, a: site specific, b: Mackay (2001), c: Mackay et al. (1992 and 1996a), d: Mackay and Paterson (1991), e: specific to soil types, f: Traup and Kruse (1996), g: mean annual soil temperature range (see text for details).*

Input parameters	Best est.	Mean or Loc	St.dev. or Sc, Sh	Range	Distribtion
Fraction of SW on total area f_W [%] (a)	3			1.5-4.5	Uniform
Atmospheric mixing height d_A [m]	1000 (c)			700-1300	Uniform
Average water depth d_W [m] (a)	3			2.7-3.3	Uniform
Average soil depth d_S [m] (b)	0.15			0.1-0.2	Uniform
Average sediment depth d_{Sed} [m]	0.02			0.01 (c) -0.03 (b)	Uniform
Part. matter conc. in air C_{Ae} [$\mu g/m^3$] (b)	30			5-100	Uniform
Part. matter conc. in water C_{Sus} [g/m^3](b)	7.5			5-20	Uniform
Total soil porosity θ_T [cm^3/cm^3] (e)		0.44	0.08	0.3-0.7	Lognormal
Soil water content θ_W [cm^3/cm^3] (e)		0.17	0.04	0.02-0.3	Lognormal
Water content in sed. θ_{Sed} [cm^3/cm^3]	0.7 (d)			0.67 (b) -0.8 (c)	Uniform
Vol. fraction of fish in water f_{Fish} [-]	10^{-6} (b,c,d)			10^{-7}-10^{-6}	Uniform
Scavenging ratio Q [-]	200000 (b,c)	200000	20000		Lognormal
Wind speed u_{10} [m/s] (f)	2.9	Loc 2.9	Sc 3.3, Sh 1.5	2.2-3.6	Weibull
T soil T_S [°C] (g)	10			8-12	Uniform

For phase densities and organic carbon fractions, typical values were chosen and variations defined by default in most cases (see Tab. 7). For the soil solid phase density, variability assumptions are based on a statistical analysis of soil bulk densities (as compiled in the ROSETTA database, see above). Results reveal lognormally distributed values for loams, clays and silt with standard deviations

of 20% from the mean value. The variability of soil solid density ρ_S is assumed to be lower than the variability of bulk soil density ρ_b (where varying porosity has a strong influence). Therefore a standard deviation for ρ_S being half the value identified for ρ_b was chosen. Data on the fraction of soil organic carbon OC_S represent a typical range for the western Upper Rhine region, derived from digital soils maps (WaBoA 2004). However, the OC content can vary significantly higher within smaller areas, depending on the land use.
Advective residence time in air was calculated from wind speed (Tab. 6) and the length of the model domain in the main wind direction (i.e. parallel to the river Rhine valley, 50 to 55 km across the model domain). For advective residence times in water and sediment, typical estimates were considered that characterise aquatic systems consisting of rivers and lakes. Variations were assumed by default.

***Tab. 7**: Compartment properties considered for the Level III modelling. a: Mackay (2001), b: Mackay et al. (1992 and 1996a), c: Mackay and Paterson (1991), d: region specific (WaBoA 2004), other abbreviations according to Tab. 6.*

Input parameters	Best est.	Mean	St.dev.	Range	Distribtion
Phase Densities [kg/m^3]					
Aerosol ρ_{Ae}	1500 (a)	1500	150		Lognormal
Suspended sediment ρ_{Sus}	1500 (a,b)	1500	150		Lognormal
Soil solid phase ρ_S	2400 (b,c)	2400	240		Lognormal
Sediment solid phase ρ_{Sed}	2400 (b,c)	2400	240		Lognormal
Fish ρ_{Fish}	1000 (a,b,c)	1000	100		Lognormal
Fractions of organic carbon and lipid [-]					
Suspended sediment OC_{Sus}	0.2 (a,b)	0.2	0.02		Lognormal
Fish L_{Fish}	0.05 (a,b)	0.05	0.01		Lognormal
Soil solid phase OC_S (d)		0.023	0.01	0.01-0.04	Lognormal
Sediment solid phase OC_{Sed}	0.04 (a)	0.04	0.01		Lognormal
Advective residence times [h]					
Air τ_A	2.2			0.8-5.2	Triangular
Water τ_W	1000 (b)			500-1500	Uniform
Sediment τ_{Sed}	50000 (b)			25000-75000	Uniform

Intermedia transport velocities (Tab. 8) were determined according to section 2.4.1 to 2.4.4, where additional information on parameters can be found. Probability density functions for U_1, U_2, U_5 and U_8 were evaluated with Monte Carlo simulations (10000 trials) using the software package Crystal Ball and the required PDF (probability density function) input from Tab. 6. In addition, molar weights for the studied group of PCBs (di- to ortho-chloro biphenyls) were considered (uniform distribution of values). The chosen rain characteristic (U_3) was found to be typical for the area of Germany. A lognormal distribution was fitted to a dataset provided by the DWD (monthly average values for the years 1961-1990). For U_6, the infiltration rate was considered as an upper bound estimate. Infiltration was approximated from the rain rate under the assumption that clayey and loamy soils and low hill slopes prevail in the model domain (see section 2.4.2). A velocity of 5 x 10^{-7} m/h was chosen for U_9, corresponding to a typical deposition rate for aquatic systems that consists of rivers and lakes (Mackay 2001). The value range of 10^{-7} to 5 x 10^{-7} m/h was selected according to USGS 2003, reporting sedimentation rates in backwater areas of the Mississippi river.

***Tab. 8**: Intermedia exchange velocities. a: based on DWD, b: Trapp and Matthies (1998), c: Mackay (2001), d: corresponding to U1, e: Mackay et al. (1992 and 1996a), f: USGS (2003), g: 40% of the sediment mass, h: 10% of the rain rate, i: calculated from U11 (400 ppm by volume of solids), other abbreviations according to Tab. 6 (Loc, Sc and Sh are Weibull and Gamma parameters).*

Intermedia exchange velocities [m/h]	Best est.	Mean or Loc	St.dev. or Sc/ Sh	Range	Distribtion
Air side, air-water MTC U_1	11.1	Loc 11.1	Sc 22 Sh 1.2		Weibull
Water side, air-water MTC U_2	0.023	Loc 0.023	Sc 0.055 Sh 1.5		Weibull
Rain rate U_3 (a)		$9.1*10^{-5}$	$2.6*10^{-5}$	$4.6*10^{-5}$-$2.8*10^{-4}$	Lognormal
Dry deposition velocity U_4	3.6 (b)			3.6 (b) -10.8 (c)	Uniform
Soil-air phase diffusion MTC U_5	$2.7*10^{-2}$	Loc $6.5*10^{-4}$	Sc $1.4*10^{-2}$ Sh 2.5		Gamma
Soil-water phase transport MTC U_6		$2.6*10^{-5}$	$7.4*10^{-6}$	$1.3*10^{-5}$-$7.9*10^{-5}$	Lognormal
Soil-air boundary layer MTC U_7 (d,e)	11.1	Loc 11.1	Sc 22 Sh 1.2		Weibull
Sediment-water MTC U_8		$1.6*10^{-4}$		$1.3*10^{-4}$-$2.3*10^{-4}$	Triangular
Sediment deposition U_9	$5*10^{-7}$ (e)			10^{-7}- $5*10^{-7}$ (f)	Uniform
Sediment resuspension U_{10} (g)	$2*10^{-7}$			$4*10^{-8}$-$2*10^{-7}$	Uniform
Soil-water runoff U_{11} (h)		$9.1*10^{-6}$	$2.6*10^{-6}$	$4.6*10^{-6}$-$2.8*10^{-5}$	Lognormal
Soil-solids runoff U_{12} (i)		$3.6*10^{-9}$	$1.0*10^{-9}$	$1.8*10^{-9}$-$1.1*10^{-8}$	Lognormal

3.3.4 Sensitivity analysis

A sensitivity analysis was performed to identify the most important parameters. Crystal Ball calculates sensitivity by computing rank correlation coefficients between every input parameter and the forecast (Decisioneering 2001). The sensitivity analysis presented in Fig. 6 to 8 is based on the parameter values in Tab. 6 to 8 (PDF input to Level III modelling). The contribution of parameters to the variance of results are shown with respect to positive or negative influence (i.e. direct or inverse correlation). Correlation coefficients ≥0.1 resp. ≤-0.1 are indicated, assuming to represent the most significant contributions. Results for PCB 28, 52, 153 and 196 were chosen as examples for compounds of different chlorination. The probabilistic Level III modelling was performed with a constant emission rate of PCB into soil.

When comparing parameter sensitivities for the calculation of air, water and soil concentration, differences between the pathways and the considered compounds are obvious. Details are discussed in the following.

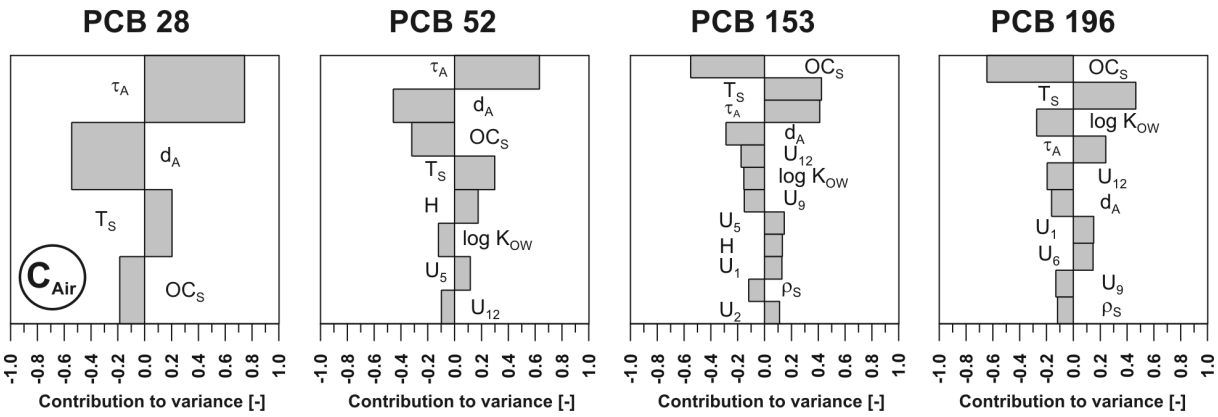


Fig. 6*: Sensitivity analysis for the Level III modelling. Parameter contributions to the variance of concentrations in air for PCB 28, 52, 153, 196. H: Henry's law constant, other parameter abbreviations according to Tab. 6 to 8.*

Uncertainty and variability of advective residence time τ_A and atmospheric mixing height d_A reveal the highest contribution to the variance of $\boldsymbol{C_{Air}}$ (Fig. 6). These findings reflect that advective processes are dominating, as also reported by Mackay et al. (1992). However, the influence is decreasing with chlorine content of the discussed compounds. Furthermore, soil temperature T_S and soil organic carbon OC_S are important, the latter especially for higher chlorinated PCBs. This can be assigned to a stronger sorption tendency compared to lower chlorinated compounds. Important as well are contributions given by Henry's law constant H and log K_{OW}, specific to the parameter uncertainty (compare to section 3.3.1) and the degree of chlorination, i.e. related to evaporation or sorption tendency. Vapour pressures P_L do not appear to be significant, as the Level III model uses P_L for the calculation of aerosol Z-values only (compare to Mackay et al. 1996a).

Contributions of U_5 and U_6 reflect the significance of soil to air phase diffusion (for lower chlorinated PCBs) and soil to water phase transport (for higher chlorinated compounds), respectively. Water to air partitioning (U_1 and U_2) can be seen as a secondary process, relevant for higher chlorinated PCBs. The influence of sediment deposition rate U_9 and soil-solids runoff rate U_{12} corresponds to compound removal by sediment deposition and run off (PCBs sorberd to solids) as significant processes. Soil particle density ρ_S is of influence for higher chlorinated PCBs, showing an inverse correlation which can be explained by the contribution of ρ_S for the calculation of soil-solids runoff transport (intermedia D value).

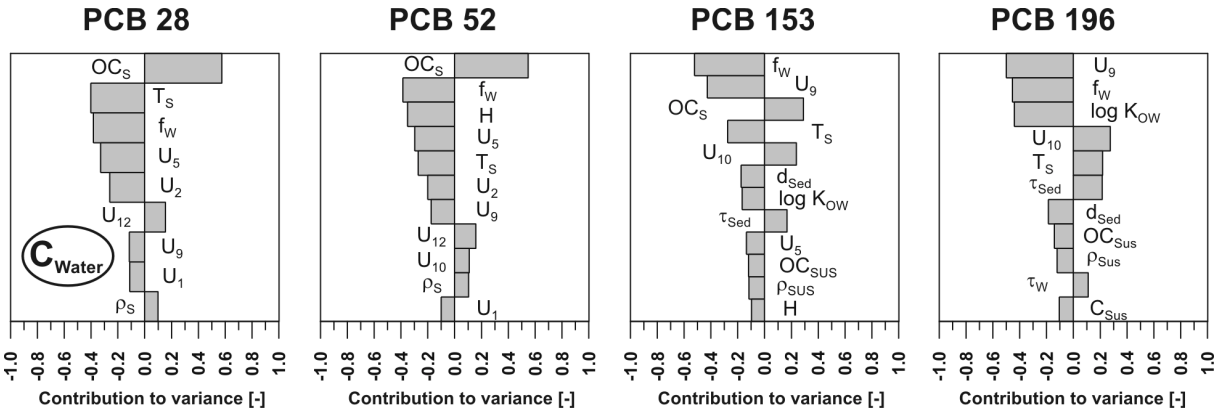


***Fig. 7**: Sensitivity analysis for the Level III modelling. Parameter contributions to the variance of concentrations in water for PCB 28, 52, 153, 196. H: Henry's law constant, other parameter abbreviations according to Tab. 6 to 8.*

For the variance of $\boldsymbol{C_{Water}}$ (Fig. 7), high contributions are given by OC_S, the fraction of surface water area on total area f_W and T_S. Sediment deposition and resuspension rate U_9 and U_{10}, sediment depth and advective residence time d_{Sed} and τ_{Sed}, log K_{OW}, furthermore OC_{Sus}, ρ_{Sus}, C_{Sus} (particulate matter concentration in water) and τ_W (advective residence time of water) show increasing influence with higher chlorine content, reflecting interactions with sediment and suspended matter (sorption, subsequent advective transport).

Contributions of U_{12} (direct correlation) can be assigned to soil-solids being transported into the water phase (via runoff), with subsequent contaminant diffusion (from soil-solids into the water phase). U_5, U_1, U_2, H (revealing negative contributions): significant especially for lower chlorinated compounds, this can be to related to processes of soil to air and water to air partitioning. The influence of ρ_S originates from the calculation of soil-water partitioning, showing direct correlation (significant for lower chlorinated PCBs).

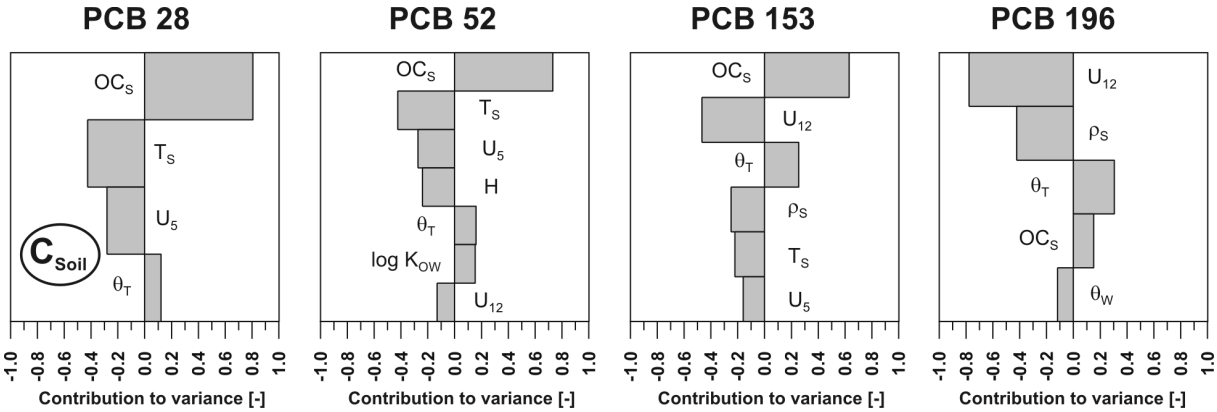


***Fig. 8**: Sensitivity analysis for the Level III modelling. Parameter contributions to the variance of concentrations in soil for PCB 28, 52, 153, 196. H: Henry's law constant, other parameter abbreviations according to Tab. 6 to 8.*

Significant contributions to the variance of $\boldsymbol{C_{Soil}}$ (Fig. 8) are obvious for OC_S, T_S and U_5 (T_S and U_5 especially for lowly and moderately chlorinated PCBs, U_5 corresponding to diffusive loss by evaporation). Furthermore θ_T (total soil porosity), θ_W (water saturation), ρ_S and U_{12} have to be mentioned: the contribution of soil properties and the removal of soil-solids with runoff water is most important for highly and moderately chlorinated PCBs (dominating over log K_{OW} in their influence).

3.3.5 Mobility and transport potential – Results of Level III modelling

Level III partitioning modelling was performed to evaluate partitioning tendencies specific to PCB congeners, concentrating on the soil to soil, soil to water and soil to air pathway. Constant emission rates of PCBs into soil were used for the group of the 77 PCBs shown in Tab. 5. Biodegradation was not considered for the modelling.
Deterministic calculations were performed with best estimates from Tab. 6 to 8 if available, otherwise mean values were taken. For the chemical input (i.e. Henry's law constant, log K_{OW} and vapour pressure), adjusted values were chosen (see Tab. A2). Probabilistic modelling was carried out with Monte Carlo simulations, using the probability density functions defined in Tab. 6 to 8. Triangular distributions were considered for the physicochemical properties (Henry's Law constant, log K_{OW} and vapour pressure), with adjusted (i.e. assumed likeliest) values, minima and maximum values from Tab. A2. The Monte Carlo simulations were performed running 10000 trials. This sample size ensures a high precision of estimated percentiles and demonstrates numerical stability of the tails of the output (Cullen and Frey 1999, Burmaster and Anderson 1994).

Results of the modelling are presented in Fig. 9. The shown concentrations are normalised to the maximum of the best estimates (be) in order to focus on differences between congeners. The plotted percentile values represent lower and upper bound estimations, respectively.

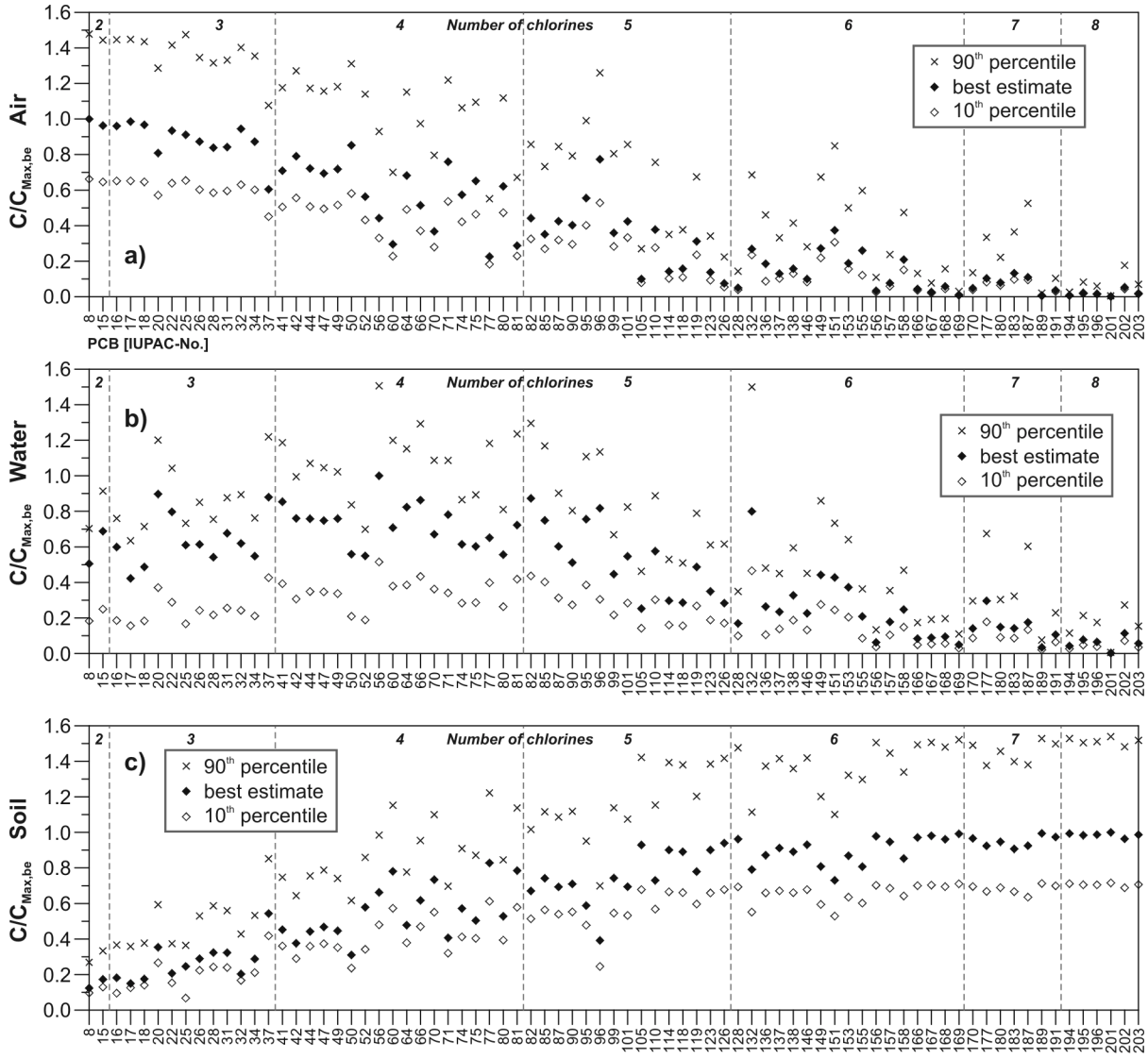


***Fig. 9**: Results of Level III partitioning modelling: relative concentration of PCB congeners in a) air, b) water and c) soil (normalised to the maximum of best estimates, be).*

Looking at Fig. 9, different trends are obvious. In the water and air compartment, lowly and moderately chlorinated PCBs show increased, highly chlorinated PCBs strongly decreased concentrations. Low water concentrations for low chlorinated PCBs are due an increased tendency of evaporation. In contrast, highly chlorinated PCBs are predominant in the soil. This general trend can clearly be seen from the best estimate values. It is obvious from the percentiles as well, but the values are more scattered in some areas. The variability of results (shown in Fig. 9 as the difference between the 10th and 90th percentile) is due to the uncertainty and variability of the input parameters being sensitive for the pathway and compound under consideration, as discussed in detail in the previous section. Differences between compounds when studied from the 90th percentile may be influenced by different uncertainties of physicochemical properties. This is the case e.g. for PCB 177, 183 and 187 which show a significantly higher variability of air and water concentration compared to other compounds adjacent in the graphs, resulting from a higher uncertainty with respect to log K_{OW} (see Fig. 9a and b).
It can be concluded, that lowly and moderately chlorinated PCBs possess the highest mobility potential whereas higher chlorinated compounds tend to be relatively immobile. Generally, the latter group is represented by congeners with 7 or more chlorines. Even some lower chlorinated compounds can be included (PCB 166, 167, 168 and 169). Exceptions should be made for PCB 177, 183 and 187, however, as these chemicals reveal peaks in air and water concentrations. This is especially the case when the 90th percentile is considered (compare to Fig. 9a and b).

3.4 Summary – PCB congeners of concern

PCB congeners of concern with respect to the toxic potential and environmental frequency encompass 77 PCB congeners (all compounds in Tab. 9). The group of relevant compounds diminishes when considering the mobility potential and natural biodegradation. In older contaminations, lowly chlorinated PCBs are likely to be reduced in large quantities by bioprocesses. As already mentioned in the introduction, the degradation of lowly and moderately chlorinated PCBs by aerobic microbes is reported by many authors (e.g. Furukawa 1986, Bedard et al 1986).
Though considerable uncertainty is associated both with the biodegradation activity and the transport potential at a given site, moderately chlorinated PCBs are suggested to be of greatest environmental concern for a multimedia environmental risk assessment. This group contains 51 congeners (see Tab. 9 without parentheses, plus PCB 37 and PCB 170). PCB 37 and 170 should be included because they are highly toxic. PCB 37 is potentially biodegradable but might be present at a given site, and the water concentrations of PCB 170 revealed a high variability (compare to Fig. 9b).
Following a more conservative approach, the 5 highly toxic compounds PCB 166, 167, 168, 169 and 189 may additionally be taken into account, to meet uncertainty under environmental settings that are different to those considered in this study.

***Tab. 9**: Evaluated PCB congeners of concern (IUPAC numbers). (a): high biodegradation potential in soil assumed for lowly chlorinated PCBs, (b): mobility potential for soil to air and soil to water pathways.*

Number of chlorines																*Classification*
2		*3*		*4*		*5*		*6*		*7*		*8*				
8	{D}	16	{D}	41	D	82	D	128	A1	170	[A1]	194	[B]			**Group A1)**
15	{C}	17	{D}	42	D	85	B	132	D	177	D	195	[B]			**highest toxic potential**
		18	{D}	44	D	87	B	136	C	180	[B]	196	[B]			**frequent (>0.5 % of total PCB)**
		20	{D}	47	B	90	D	137	B	183	B	201	[D]			**Group A2)**
		22	{D}	49	D	95	D	138	A1	187	D	202	[B]			**highest toxic potential**
		25	{D}	50	D	96	D	146	C	189	[A1]	203	[B]			**low freq. (<0.5 % of total PCB)**
		26	{D}	52	C	99	B	149	D	191	[B]					**Group B)**
		28	{D}	56	D	101	B	151	D							**high to moderate toxic pot.**
		31	{D}	60	D	105	A1	153	B							**frequent (>0.5 % of total PCB)**
		32	{D}	64	D	110	D	155	C							**Group C)**
		34	{D}	66	B	114	A2	156	A1							**low toxic potential**
		37	{A1}	70	D	118	A1	157	A2							**frequent (>0.5 % of total PCB)**
				71	D	119	A2	158	A1							**Group D)**
				74	D	123	A1	166	[A2]							**no toxic potential reported**
				75	C	126	A2	167	[A1]							**high freq. (>5 % of total PCB)**
				77	A1			168	[A2]							
				80	C			169	[A2]							**{}: high biodegrad. potential (a)**
				81	A2											**[]: low mobility potential (b)**

4 Conclusions

56 PCB congeners revealed relevance with respect to their toxicity and environmental frequency, and the mobility potential. Risk assessments of PCB-contaminated sites should concentrate on these congeners, not only for preliminary site investigations (impact analysis of a PCB contamination), but also for accompanying *in situ* measures (performance control and compliance monitoring) in order to evaluate the success of remedial actions. The author recommends analysing site samples for these 56 compounds. Congeners measured positively should be defined as target compounds for remediation, being subject of performance control and monitoring programs.

The procedure presented in this part of the thesis can be adapted to other groups of contaminants, such as polycyclic aromatic hydrocarbons (PAHs) or volatile chlorinated hydrocarbons (VCHs). Potential toxicity, frequency in environmental matrices and the mobility potential are suggested as criteria for the evaluation of constituents of concern.
For the modelling of contaminant partitioning, an internally consistent data set of physicochemical properties should be derived, including information on the temperature dependency of Henry's law constant and log K_{OW}. In order to meet uncertainty and/or variability of input parameters, probability density functions should be considered for Henry's law constant and log K_{OW}, temperature, soil properties (especially the content of soil organic carbon), meteorological parameters (wind speed, rain rate), advective residence times and sedimentation rates. Instructions are given for the derivation of probability density functions. For other parameters, best estimate values are supposed to be sufficient.
The detailed data collection provided in this study can be used for further investigations on PCBs. The dataset of environmental input parameters for Level III calculations can also be applied for the modelling of other compounds.

Part III Degradation of PCB congeners by bacterial strains – Determination of kinetic parameters and considerations for the modelling of rhizoremediation

Contents

Abstract

Biological *in situ* measures can be efficient and cost effective options for the remediation of contaminated sites. In Part III, a methodology to quantify biodegradation by soil bacteria was developed. The genetically modified *Pseudomonas fluorescens* strains F113pcb and F113L::1180 are known to be root colonisers capable to degrade polychlorinated biphenyls (PCBs). Wild-type *Burkholderia* sp. strain LB400 is the donor of PCB biodegradation genes included in the F113 derivatives. Laboratory (vial) assays were performed to investigate the potential and kinetics of strain LB400 and F113 derivatives to metabolise individual PCB congeners. Kinetics of metabolism was analysed according to the *Monod* model. In addition, mesocosm experiments were carried out with soil from a PCB contaminated site to elucidate survival and growth of F113 inoculants in willow (*Salix* sp.) rhizosphere.
Results revealed similar patterns of degradable PCB congeners for LB400 and F113L::1180. The degree of PCB degradation is comparable for LB400 and F113L::1180, but is much lower for F113rifpcb. In laboratory, microbial activity decreased with time. The evaluated maximal removal velocities correlate positively to the estimated rates of activity decline as a consequence of the cometabolic process. In the mesocosm experiments, the F113 derivatives demonstrated a good survival ability in willow rhizosphere over the observation period of seven months.
F113L::1180 in combination with willow plants is expected to degrade a large spectrum of PCB congeners in soil. The elaborated quantification method and the data from the experiments was used to estimate the time scale of the degradation process in a PCB-contaminated soil. High uncertainties are associated to the modelling due to the estimation of kinetics in soil (related from the laboratory vial experiments). In addition, considerable uncertainty is associated to the evaluated removal velocities, and especially to bacterial numbers in soil.

1 Introduction

The accepted implementation of biological *in situ* measures requires a detailed and reliable risk analysis. An important objective is to quantify the potential of contaminant degradation and metabolite formation (Part I). Requirements are data on the kinetics of the bioprocess, which can be utilised for an estimate of the time scale and for multimedia environmental modelling for risk assessment. In this part of the thesis, the performance of different bacterial strains to degrade PCBs was investigated. Methods for a quantification of contaminant breakdown by microbial activity were developed.

The degradation of individual PCB congeners was studied in laboratory experiments (pure culture assays in vials) utilising LB400 and derivatives of F113 (Part I). Substrate range and capacity of depletion (in terms of depleted percentage) and degradation as a function of time was evaluated. Results of experiments were analysed considering *Monod* kinetics. In addition, survival and growth of bacteria in willow rhizosphere was analysed in mesocosm experiments with contaminated soil. The potential and kinetics of the strains to metabolise the low chlorinated commercial PCB mixtures Aroclor 1016, 1221 and 1232 in soil was exemplarily estimated, based upon the results for individual PCB congeners and the methodology developed to quantify the bioprocess. Results were discussed concerning uncertainty associated to the modelling of contaminant breakdown.

2 Materials and Methods

The experiments described in section 2.1 and 2.3 were carried out by Ulrich Karlson and co-workers (National Environmental Research Institute NERI, Roskilde, Denmark; publication in preparation).

2.1 Biodegradation in vials

Experiments were performed with the wild-type *Burkholderia* sp. strain LB400, and with the genetically modified F113 derivatives *Pseudomonas fluorescens* F113L::1180, F113rifpcb and F113rif (compare to section 1). Strains F113rif and F113rifpcb are rifampicin resistant mutants. The bacterial cultures were pregrown on biphenyl, except strain F113rif (which serves as the negative control) on salicylic acid (SA) medium (minimal medium enriched with 20 g/L sucrose and 2 g/L asparagine). The bacteria were diluted in minimal medium to an OD_{600} (optical density at 600 nm) of around 0.4, corresponding to approximately 1.5 - $2x10^{11}$ cells/L. PCB was dissolved in acetone and spiked into the medium, to yield a final concentration of 5 µmol/L. Bacterial incubation was performed immediately following the PCB spike.
The disappearance of individual PCB congeners was measured versus time, using headspace-Solid Phase Microextraction (SPME) and a Gas Chromatography/Electron Capture Detector (GC/ECD). Prior to measurement, the reaction was stopped by mixing the culture sample with 20% ethyl alcohol (EtOH) + 0.1% Triton-X-100, and the vials were put in an autosampler tray. With the non-degrader, F113rif, being used as negative control, disappearance was assumed to signify abiotic degradation of the PCB substrate. Because of analytical constraints, production of metabolites was not determined in this assay. In total, the degradation of 29 PCB congeners was investigated.
12 to 16 measurements per assay were carried out with degrader bacteria (duplicates at the beginning and in the end for most experiments) and 6 for each negative control (3 duplicate measurements). For data analysis, contaminant loss due to processes other than biodegradation has to be taken into account, e.g. potential evaporation from the vial (especially for low chlorinated PCB congeners). Where necessary, concentrations measured in vials with degrader bacteria were corrected utilising information gained from the negative control. For corrections, the abiotic control was assumed to decline linearly.

2.2 Estimation of initial bacterial mass and bacterial numbers in vials

Initial bacterial mass B_0 was estimated from optical density (OD_{600}) measurements taken for the individual experiments:

$$B_0 = CF \times OD_{600} \qquad (1)$$

B_0: initial bacterial mass, total protein [g/L]
CF: conversion factor [g/L]
OD_{600}: optical density of liquid medium at 600 nm [-]

The conversion factor CF was established by analysing one experimental culture of each bacterial strain in triplicate, using a commercial protein determination kit and bovine serum albumin as a standard. Bacterial numbers were determined as colony forming units (CFU) on Luria Broth (LB) plates. Culture purity was ascertained by streaking on LB plates.

2.3 Bacterial survival and growth in mesocosm experiments

Plant-soil mesocosm studies were conducted in the laboratory in order to elucidate the fate of F113 derivatives in phytoremediation of contaminated soil. PCB-contaminated soil from a dump site near Lhenice, Czech Republic, was used for the experiments. The studies involved the inoculants F113rif, F113rifpcb and F113L::1180.
Two- to three-week old willow plants (*Salix* sp.) were inoculated by dipping the roots in bacterial suspensions for 1 hour. The number of bacteria in suspension was approximately 10^6 cfu/mL. The willows then were planted into zinc pots. Sieved soil material (2 kg soil per pot) was poured around the roots. Bulk soil and rhizosphere were sampled at 4-week intervals over a total period of 7 months. For bulk soil samples, undisturbed cores were taken. For rhizosphere samples, whole plants were removed from the mesocosms, soil adhering to the roots was shaken off and roots with residual soil were collected using sterile scissors and forceps. Except for total viable counts, all samples were frozen immediately and maintained at –20 ºC until analysis. Bacterial numbers were determined as CFU on SArif plates.

2.4 Evaluation of degradation capacity and kinetics

The PCB metabolism studied in the experiments is characterised by a cometabolic process. Cometabolism describes the transformation of a non-growth substrate while the microbes feed on a growth or energy substrate. Cometabolism therefore results from the lack of specificity to enzymes and cofactors (Horvath 1972, Dalton and Stirling 1982). In the above definition, substrates are electron donors providing reductive power and energy. A growth substrate enables cell growth and maintenance whereas an energy substrate does not by itself support growth. Experimental observations indicate that for growing cells, the rates of cometabolic transformations are linked to the consumption of a growth substrate. In the absence of a growth substrate (i.e. for resting cells), the transformation rates are coupled to the consumption of cell mass and/or energy substrate (Criddle 1993). Accordingly, the kinetics of the bioprocess can be described by *Monod* kinetics, considering bacterial growth or decay (e.g. Trapp et al. 2006):

$$\frac{dB}{dt} = \frac{\mu_{\max} \times C \times B}{K_S + C} - k_{death} \times B \quad (2)$$

B: bacterial mass [mg]
μ_{max}: maximum growth rate of bacteria [1/h]
C: substrate concentration [mg/L]
K_S: half-growth concentration (concentration where the growth is half of the maximum) [mg/L]
k_{death}: first order rate describing the decline of active bacterial cells [1/h]

During growth, the bacteria metabolise the substrate. The substrate mass balance is set up as follows (according to Trapp et al. 2006, Cornish-Bowden 1995):

$$\frac{dm}{dt} = -\frac{v_{\max} \times C}{K_M + C} \times B \quad (3)$$

m: substrate mass [mg]
v_{max}: maximal substrate removal velocity per bacterial mass [mg h^{-1} mg $bacteria^{-1}$]
K_M: half-saturation constant [mg/L]

Considering initial bacterial mass in experiment, Eq. (3) modifies to:

$$\frac{dm}{dt} = -\frac{v^*_{\max} \times C}{K_M + C} \times \frac{B}{B_0} \quad (4)$$

v^*_{max} [mg/h]: maximal removal velocity related to initial bacterial mass B_0 [mg], with $v^*_{max} = v_{max} \times B_0$

When no growth but decay of active microbes is presumed, μ_{max} is zero and the respective term in Eq. (2) eliminates:

$$\frac{dB}{dt} = -k_{death} \times B \quad (5)$$

From the data set consisting of measured and corrected concentrations, parameters for *Monod* kinetics were determined with Eq. (4) and (5). This model is consistent with an approach presented by Criddle (1993). Three unknown variables are required: v^*_{max}, K_M and k_{death}. The estimation of these variables was performed in two steps: a) approximation of v^*_{max} and K_M at the initial phase of the experiment, b) adjustment of k_{death} by least square fit. An iterative procedure was performed to adjust the parameters. Beside the evaluation of most probable model curves, uncertainty was addressed by fitting minimum and maximum curves to the measured data. Automated curve-fitting procedures included in the Life Science Workbench (LSW) Data Analysis Toolbox (add-in program for Microsoft Excel) were used.

2.5 Modelling of degradation under field conditions

To estimate degradation kinetics under field conditions, initial bacterial numbers from the laboratory (vial) experiments and bacterial numbers observed in rhizosphere (mesocosm test with contaminated soil) were considered (see Fig. 1). For a potentially reduced degradation performance under field conditions, a factor f_{RD} [-] is introduced. The *Monod* parameters v^*_{max} and K_M were scaled to initial experimental substrate mass and concentration to obtain k^*_{max} and K_M^*:

$$k^*_{max} = \frac{v^*_{max}}{m_0} \quad (6)$$

$$K^*_M = \frac{K_M}{C_0} \quad (7)$$

k^*_{max}: maximum removal rate [1/h]

m_0: initial experimental substrate mass [mg]
K_M*: dimensionless half-saturation constant [-]
C_0: starting concentration in laboratory [mg/L]

Inserting Eq. (6) and (7) into Eq. (4) (i.e., utilising *Monod* parameters that are scaled to dimensionless mass and concentration) and considering relative values for soil concentration (normalised units), the removal of substrate mass in soil can be calculated as:

$$\frac{dm_S}{dt} = -\frac{k^*_{max} \times C_S/C_{S,0}}{K^*_M + C_S/C_{S,0}} \times m_{S,0} \times \frac{B_{soil}}{B_0} \times f_{RD}^{-1} \quad (8)$$

B_0: initial bacterial mass in laboratory [mg]
m_S, $m_{S,0}$: mass, initial mass in soil [mg]
C_S, $C_{S,0}$: concentration, initial concentration in soil [mg/kg]

If microbial numbers are considered instead of bacterial mass, Eq (8) is rewritten:

$$\frac{dm_S}{dt} = -\frac{k^*_{max} \times C_S/C_{S,0}}{K^*_M + C_S/C_{S,0}} \times m_{S,0} \times \frac{CFU_{soil}}{CFU_{lab,0}} \times f_{RD}^{-1} \quad (9)$$

CFU_{Soil}: bacterial numbers in soil [cfu/kg]
$CFU_{lab,0}$: initial bacterial numbers in laboratory [cfu/L]

A f_{RD} of 1 indicates that the degradation performance of bacteria in the field is identical to that in the laboratory. In contrast, a f_{RD} > 1 corresponds to a slower bioprocess (e.g., reduced by a factor of 2 for f_{RD} = 2). Conditions resulting in a lower degradation performance might e.g. given by:

- interactions between different PCB congeners
- impact of toxic compounds present at a contaminated site
- reduced nutrient supply (e.g., oxygen, root exudates)
- reduced substrate availability (aging)

Equation (8) and (9) were suggested under the assumption, that the considered bacteria mainly settle on soil particles (in the rhizosphere) and on roots where they metabolise the contaminants. Nevertheless, this is a preliminary and highly uncertain assumption that probably substantially overestimates degradation kinetics in soil. It is based upon the consideration, that contaminant breakdown by microbes can be related to total mass in soil, i.e. PCB adsorbed to soil particles and dissolved in soil solution. Respective processes (i.e. bacterial access) are currently discussed by the scientific community, but it is more likely that only the contaminant mass in soil solution is available for bacteria. Given the high lipophilicity of PCBs, contaminant mass might be 10 to 1000 times lower in soil solution than in total soil (depending on the soil type, i.e. content of soil organic content and the PCB congener considered, i.e. the octanol-water partition coefficient).

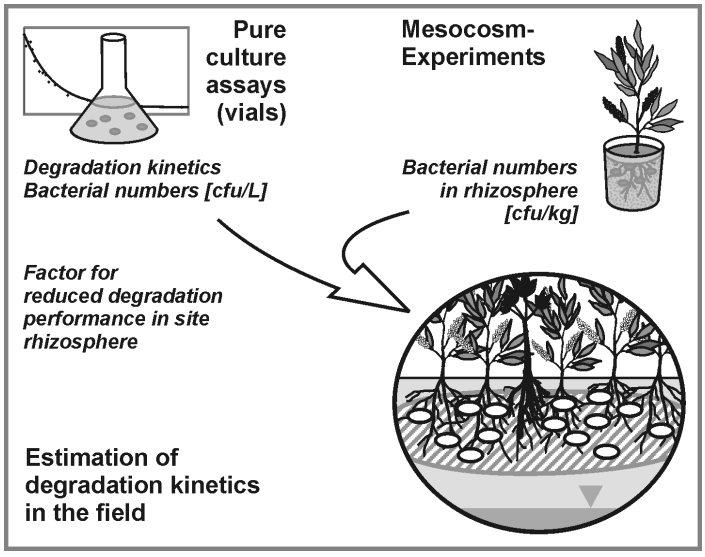


***Fig. 1**: Overview on the procedure to estimate degradation kinetics for field conditions.*

3 Results and discussion

3.1 Degradation capacity for PCB congeners

Table 1 gives an overview on the investigated PCB congeners and bacterial strains. Not all of the tested congeners were metabolised by all strains, but patterns were similar for LB400 and F113L::1180. From 25 congeners tested with LB400, 15 were depleted; 14 of 26 studied congeners were metabolised by F113L::1180 and 3 of 7 by F113rifpcb.

***Tab. 1**: PCB congeners and bacterial strains investigated in the laboratory experiments. X: congener was metabolised, 0: no degradation. The number of symbols corresponds to the number of experiments performed.*

PCB		LB400	F113L::1180	F113rifpcb
IUPAC No.	**Chlorine substitution**			
1	2	X	XX	
2	3		XX	
3	4	X	XX	
4	2,2’		XX	X
5	2,3	X	XXX	X
10	2,6	0	0	
15	4,4’	00	00	0
16	2,2’,3	X	X	
17	2,2’,4	X0	X0	X
18	2,2’,5	X	XX	
20	2,3,3’	X	X	
25	2,3’,4	X	0	00
28	2,4,4’	0	0	
31	2,4’,5	X	X	
34	2,3’,5’	X	X	
37	3,4,4’	000	00	00
41	2,2’,3,4	X	X	
47	2,2’,4,4’	00	00	
52	2,2’,5,5’	X0	X	
66	2,3’,4,4’	00	00	
69	2,3’,4,6	X	0	
70	2,3’,4’,5	X00	00	0
74	2,4,4’,5	00	0	
77	3,3’,4,4’	0	0	
87	2,2’,3,4,5’	0		
101	2,2’,4,5,5’	X	X	
153	2,2’,4,4’,5,5’	0	0	

Figure 2 shows the percentage of PCB-depletion observed at the end of the experiments. The indicated ranges (minimum and maximum) result from measurement uncertainty (duplicate measurements at the beginning and at the end of the assay). Measured and corrected values are given. In cases where the negative control showed a clear decreasing tendency, degradation experiments were corrected accordingly (compare to section 2.1). Contaminant loss observed for the negative control was up to 26%.

Most results reflect either clear biodegradation or clear absence of the bioprocess. In 4 experiments, depletion rates (uncorrected values) were between 10 and 20%. This loss of contaminant cannot exclusively be assigned to biodegradation. As can be seen from Fig. 2, corrections were required for lower chlorinated PCBs, which is in accordance to the assumption of compound loss by evaporation. In Tab. 2, corrected values (i.e. in cases where corrections were necessary) and ranges for the percentage of depletion are listed. Depletion of the abiotic control is indicated in Tab. 2, as well. Corrections were made as follows, shown for the example of PCB 4 (degradation with strain F113L::1180): initial concentration C_0 = 1 mg/L, C (measured) after 17.8 h = 0.06 mg/L; depletion of the abiotic control = 12% (17.8 h); C (corrected) after 17.8 h = 0.06 mg/L x 1.12 = 0.07 mg/L. Accordingly, the corrected percentage of depletion (Depl. In Tab. 2) is 93%.

Comparing the degradation capacity specific to the tested strains, LB400 and F113L::1180 exhibited similar ranges, whereas F113rifpcb generally showed lower depletion percentages. Differences between LB400 and F113L::1180 were within 3 and 17% of depletion in most cases (see Fig. 2). Variations between tests with one given strain were up to 16%. Accordingly, large differences between strains could only be seen for PCB 41 (better performance of F113L::1180, by 46%) and PCB 52 (higher rate for LB400, by 60% of depletion). Differences from mean to maximum and minimum, respectively range from 1 to 9%, except for one assay with strain F113rifpcb (difference of 26%).
Comparing the results with those obtained by Villacieros et al. (2005), the latter found in their experiments with the technical mixture Delor 103 that F113L::1180 degrades most PCB congeners to a greater extent than LB400. The lower degradation capacity for F113rifpcb can be assigned to a lower *bph* gene expression (Villacieros et al. 2005).

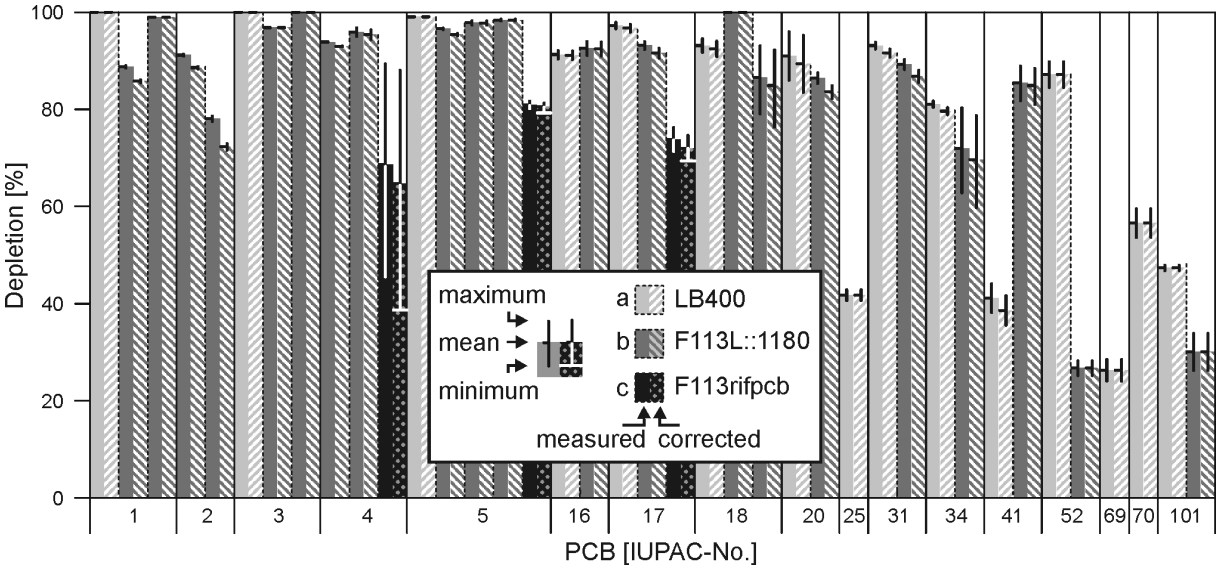


***Fig. 2**: Depletion of PCB congeners with the strains LB400, F113L::1180 and F113rifpcb observed at the end of experiments. (compare to Tab. 1 and 2).*

3.2 Degradation potential for PCB mixtures

In the past, PCBs were applied as technical mixtures for different applications and released into the environment. These mixtures were produced with different degrees of chlorination, designed for specific applications (e.g. Frame 1996, WHO 1993). As low and moderately chlorinated PCBs were readily degraded by the studied microbes, the potential to metabolise the commercial mixtures Aroclor 1016, 1221 and 1232 was analysed (low degree of chlorination). Table 3 lists percentages of individual PCB congeners that were measured in these mixtures by different authors. Appendix B (Tab. B) presents weight fraction of all 209 PCB, and in addition for Aroclor 1242, 1248, 1254, 1260 and 1262.

As can be seen from Fig. 3,

- About 30 to 45% of the PCB congeners reported for Aroclor 1016 (A1016) could potentially be degraded by the strains, whereas PCB congeners representing about 10 to 25 % of A1016 were not able to be depleted by LB400 and F113L::1800. For the remaining percentage, i.e. PCB congeners that are present in A1016 but were not analysed in experiments, no information is available.
- 60-70% of A1221 and 44-50% of A1232 potentially are metabolised versus 5-6% and 13-15% of respective mixtures being recalcitrant for the considered strains (lower values for LB400).

The variations for A1016 and A1232 reflect ranges of percentage that are reported in the literature (see Tab. 3). F113L::1180 shows a slightly enhanced degradation potential compared to strain LB400.

***Tab. 3**: Weight % of PCB congeners in Aroclors (IUPAC-No.) investigated in the degradation experiments. Minimum and maximum values were taken from Albro and Parker (1979) and Frame et al. (1996); mv: mean value.*

PCB	A 1016			A 1221	A 1232			PCB	A 1016			A 1221	A 1232		
	min	max	mv		min	max	mv		min	max	mv		min	max	mv
1	0.52	0.59	0.55	35.80	15.21	15.84	15.53	**34**	0.03	0.03	0.03	0.00	0.01	0.01	0.01
2	0.02	0.07	0.05	3.81	1.94	1.98	1.96	**37**	1.01	1.91	1.46	0.19	1.12	1.15	1.13
3	0.15	0.74	0.45	20.44	10.20	10.36	10.28	**41**	0.76	2.29	1.52	0.03	0.35	0.36	0.35
4	3.62	3.81	3.71	6.19	5.32	5.38	5.35	**47**	1.24	2.06	1.65	0.05	0.49	0.49	0.49
5	0.15	0.17	0.16	0.74	0.49	0.50	0.49	**52**	4.61	4.97	4.79	0.22	1.83	1.86	1.84
10	0.17	0.23	0.20	0.80	0.58	0.60	0.59	**66**	0.16	0.39	0.27	0.21	1.71	1.74	1.73
15	0.93	2.49	1.71	4.18	3.19	3.24	3.21	**69**	0.004	0.005	0.004	0	0	0	0
16	3.53	3.88	3.70	0.31	1.79	1.79	1.79	**70**	0.00	0.59	0.30	0.24	1.90	1.90	1.90
17	3.17	3.98	3.58	0.34	1.82	1.83	1.83	**74**	0.33	1.54	0.93	0.12	0.92	0.92	0.92
18	10.75	10.96	10.85	0.78	4.83	4.89	4.86	**77**	0	0	0	0.01	0.16	0.17	0.16
20	0.88	4.02	2.45	0.07	0.42	0.42	0.42	**87**	0	0	0	0.04	0.22	0.22	0.22
25	0.72	1.80	1.26	0.09	0.37	0.37	0.37	**101**	0	0.04	0.02	0.07	0.32	0.33	0.32
28	8.50	14.60	11.55	0.62	3.89	3.92	3.91	**153**	0	0	0	0.001	0.05	0.05	0.05
31	4.76	9.32	7.04	0.60	4.11	4.17	4.14								

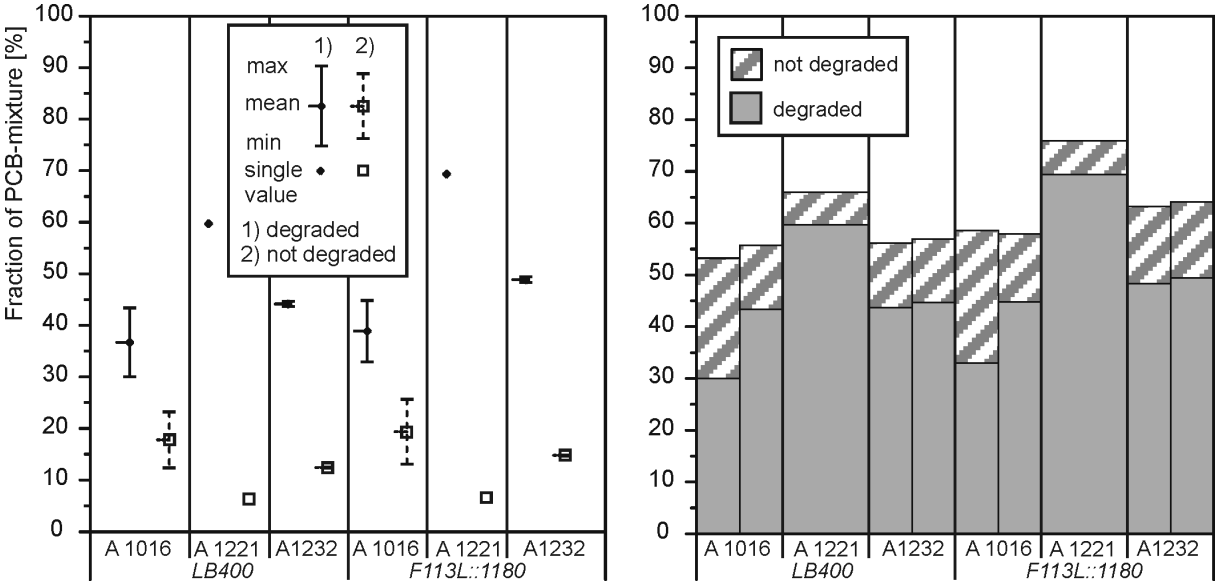


***Fig. 3**: Potential of LB400 and F113L::1180 to metabolise Aroclors 1016, 1221 and 1232. a) minimum, maximum and mean resp. single values for fractions of PCB-mixture, b) summary: percentage of fractions being depleted and not depleted (compare to Tab. 3).*

3.3 Degradation kinetics in the laboratory

Experimental results indicate biphasic kinetics with declining bacterial activity. Figure 4 shows an example (degradation of PCB 4 with strain F113L::1180). After the compound is rapidly degraded in the first phase, the process slows down (see Fig. 4a and c). The mass of active bacteria is assumed to decrease accordingly (see Fig. 4b), as discussed later.

Data from the performed assays are summarised in Tab. 2. Adjusted v^*_{max} and K_M values from the initial assay phase yielded lower estimates (compare to section 2.4). In some cases, better results were obtained by preliminary estimation of v^*_{max} from initial removal velocities and subsequent fitting of K_M (removal velocities versus concentrations), compared to the evaluation of v^*_{max} and K_M in one single step. However, for some assays, the latter possibility was not given due to a low number of measurements or large scattering of values.

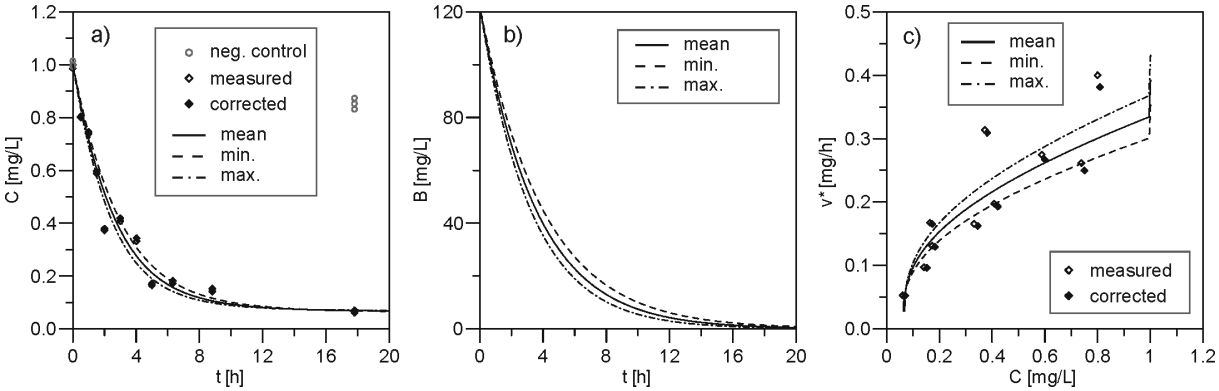


***Fig. 4**: Degradation of PCB 4 with strain F113L::1180: results of experiments and Monod modelling. a): contaminant concentration versus time, b): bacterial mass per litre versus time, c): removal velocity against concentration (compare to Tab 2). Neg. control: negative control.*

***Tab. 2**: Results from the degradation experiments and calculated kinetic parameters. OD_{600}: optical density at the start of experiment; c_0: initial PCB concentration; Depl.: percentage of depleted PCB after $t_{depl.}$; $t_{depl.}$: time period of experiment; Contr.: depletion of abiotic control at $t_{depl.}$; v^*_{max}: maximum PCB removal velocity; K_M: half-saturation constant; k_{death}: first-order rate describing the decline of active microbes; R2: R-squared of the mean Monod curve fit (modelled with mean v^*_{max} , K_M and mean K_{death}) to corrected measurements.*

PCB	OD_{600} [-]	c_0 [mg/L]	Depl. [%]	Contr. [%]	$t_{depl.}$ [h]	v^*_{max} [mg/h] mean	min.	max.	K_M [mg/L]	k_{death} [1/h] mean	min.	max.	R2 [-]
Strain LB400													
1	0.400	0.94	100 ± 0	-	24.0	2.85	2.71	3.00	0.17	1.50	1.30	1.70	0.999
3	0.400	0.94	100 ± 0	-	22.7	4.53	4.25	4.62	0.24	2.40	2.15	2.70	0.996
5	0.395	1.12	99 ± 0	-	20.8	3.50	3.15	3.85	0.16	2.00	1.60	2.15	0.994
16	0.395	1.29	91 ± 1	1	20.2	0.65	0.55	0.71	0.26	0.35	0.30	0.38	0.976
17	0.386	1.29	97 ± 1	17	22.2	2.11	2.01	2.22	0.30	1.03	0.95	1.09	0.991
18	0.395	1.29	92 ± 2	9	19.8	0.77	0.71	0.84	0.29	0.35	0.30	0.41	0.979
20	0.397	1.29	89 ± 7	15	21.6	0.90	0.81	1.03	0.39	0.38	0.32	0.47	0.957
25	0.400	1.29	42 ± 1	-	23.4	0.16	0.14	0.18	0.21	0.17	0.14	0.20	0.907
31	0.395	1.29	92 ± 2	18	20.8	1.55	1.39	1.70	0.39	0.72	0.64	0.80	0.981
34	0.400	1.29	80 ± 2	7	22.2	0.33	0.28	0.38	0.25	0.25	0.21	0.29	0.950
41	0.404	1.46	39 ± 5	4	22.5	0.071	0.05	0.092	0.36	0.08	0.035	0.12	0.972
52	0.397	1.46	87 ± 3	-	22.5	0.44	0.42	0.48	0.26	0.23	0.22	0.26	0.830
69	0.404	1.46	26 ± 2	-	23.0	0.18	0.14	0.23	0.16	0.38	0.30	0.49	0.555
70	0.397	1.46	57 ± 3	-	22.1	0.19	0.15	0.22	0.31	0.17	0.13	0.21	0.920
101	0.397	1.63	47 ± 1	-	21.9	0.15	0.10	0.19	0.44	0.13	0.08	0.18	0.948
Strain F113L::1180													
1	0.400	1.00	86 ± 3	21	8.0	0.70	0.67	0.74	0.20	0.52	0.49	0.57	0.991
1	0.400	0.94	99 ± 0	-	24.0	1.17	1.11	1.22	0.27	0.50	0.40	0.60	0.996
2	0.400	1.00	91 ± 3	21	9.2	1.81	1.63	2.08	0.20	1.40	1.25	1.60	0.971
2	0.400	1.00	77 ± 6	23	9.2	0.85	0.78	0.91	0.25	0.80	0.73	0.86	0.992
3	0.400	1.00	97 ± 0	-	4.0	2.88	2.67	3.10	0.25	1.50	1.30	1.70	0.994
3	0.400	0.94	100 ± 0	-	22.7	2.80	2.52	3.01	0.24	1.00	1.05	0.95	0.965
4	0.400	1.00	93 ± 1	12	17.8	0.39	0.35	0.43	0.17	0.28	0.25	0.31	0.968
4	0.400	1.12	95 ± 1	13	22.4	0.48	0.46	0.51	0.25	0.24	0.22	0.26	0.987
5	0.400	1.00	95 ± 1	26	20.1	1.25	1.12	1.37	0.26	0.80	0.70	0.90	0.977
5	0.400	1.12	98 ± 0	2	22.1	2.16	2.00	2.38	0.28	1.00	0.90	1.15	0.980
5	0.408	1.12	98 ± 0	-	21.6	1.49	1.41	1.64	0.36	0.60	0.55	0.72	0.989
16	0.400	1.29	92 ± 2	2	25.6	0.31	0.29	0.34	0.23	0.17	0.15	0.20	0.974
17	0.400	1.29	92 ± 2	19	24.6	0.37	0.39	0.39	0.26	0.22	0.19	0.24	0.925
18	0.400	1.00	100 ± 0	-	17.6	0.26	0.24	0.28	0.22	0.14	0.11	0.16	0.990
18	0.400	1.29	85 ± 8	12	25.4	0.40	0.36	0.46	0.32	0.26	0.23	0.31	0.923
20	0.400	1.29	84 ± 4	17	25.2	0.16	0.15	0.18	0.44	0.082	0.065	0.085	0.970
31	0.408	1.29	87 ± 3	19	21.3	0.19	0.17	0.20	0.35	0.071	0.060	0.095	0.988
34	0.400	1.29	70 ± 11	8	23.8	0.15	0.13	0.18	0.16	0.16	0.12	0.19	0.937
41	0.401	1.46	85 ± 4	4	22.0	0.23	0.21	0.25	0.26	0.11	0.10	0.13	0.981
52	0.400	1.46	27 ± 1	-	24.8	0.035	0.028	0.044	0.36	0.06	0.035	0.080	0.983
101	0.406	1.63	30 ± 4	-	27.0	0.098	0.069	0.13	0.33	0.15	0.090	0.20	0.841
Strain F113rifpcb													
4	0.400	1.12	65 ± 25	11	21.1	0.17	0.14	0.19	0.29	0.17	0.14	0.21	0.822
5	0.400	1.12	81 ± 1	2	21.4	0.45	0.40	0.49	0.28	0.34	0.30	0.38	0.983
17	0.400	1.29	72 ± 4	6	23.4	0.17	0.16	0.19	0.39	0.12	0.10	0.13	0.971

The procedure of keeping K_M constant and varying v^*_{max} with subsequent adjustment of k_{death} proved appropriate to evaluate reasonable ranges for model curves. This is due to a higher sensitivity of v^*_{max} compared to K_M (Eq. 4). Upper and lower bound estimates for the degradation kinetics were defined by maximum and minimum values for v^*_{max} and k_{death}, respectively, and K_M as given in Tab. 2. An example is shown in Fig. 4 (point-dotted and dashed graphs). In addition to first-order decline of active bacterial cells (Eq. 5), linear decay was analysed. Nevertheless, best curve fits were obtained by using the first-order assumption.

When analysing the results, it is obvious that k_{death} increases with v^*_{max}. A highly significant linear correlation exists (level of significance $p < 0.001$, based upon Pearson correlation). The data is more scattered for F113L::1180 compared to LB400, but the general trend is very similar (see Fig. 5a). Considering data for all bacterial strains, the regression between k_{death} and v^*_{max} is (compare to Fig. 5b):

$k_{death} = 0.059 + 0.50 \times v^*_{max}$ (10) (N = 39, $R^2 = 0.935$)

To obtain consistent results, the correlations were adjusted iteratively. For some experiments with high measurement uncertainty (scattered data), the estimation of *Monod* parameters was repeated considering the dependence between k_{death} and v^*_{max}. The findings indicate that active cells decline as a consequence of the reaction, i.e. the faster the bioprocess, the higher the rate of bacterial depletion. The depletion could be explained by the cometabolic process, i.e. lack of energy after consumption of biphenyl that the microbial cells were grown on prior to the assay. Furthermore, toxic effects of metabolites have to be taken into account.

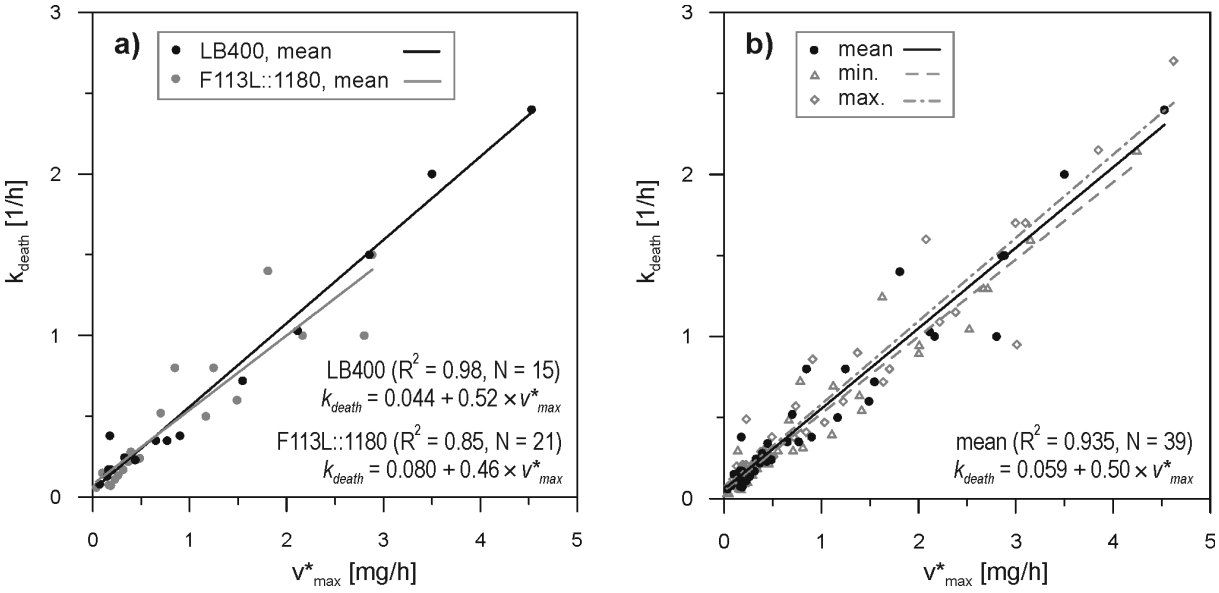


***Fig. 5**: Bacterial decline rate k_{death} (active cells) as a function of maximal removal velocity v^*_{max}. a) mean values specific to strain LB400 and F113L::1180, b) mean, minimum and maximum for all experiments. N: number of values.*

3.4 Bacterial survival and growth

3.4.1 Resting cell assays

Initial bacterial mass B_0 and bacterial numbers CFU_0 are indicated in Tab. 4. Bacterial mass B_0 was estimated from the conversion factor *CF* according to Eq. (1), for an OD_{600} of 0.400, which is an average optical density value for all assays. However, actual values of OD_{600} were recorded with a precision of 3 decimal units for each individual experiment (see Tab. 2) and utilised for modelling. Results presented in Tab. 4 are specific to the utilised bacterial strains.

***Tab. 4**: Conversion factor CF, initial bacterial mass B_0 and bacterial number $CFU_{lab,0}$ specific to bacterial strains.*

	CF [g/L]	Mean B_0 at OD_{600} = 0.4 [g/L]	Mean $CFU_{lab,0}$ [cells/L]
LB400	0.263 ± 0.003	0.105	1.43×10^{11}
F113L::1180	0.305 ± 0.002	0.122	1.52×10^{11}
F113rifpcb	0.232 ± 0.005	0.093	1.50×10^{11}
F113rif	0.308 ± 0.003	0.123	1.96×10^{11}

3.4.2 Mesocosm experiments

The studied F113 derivatives showed good survial ability. Bacterial plate counts revealed that the inocula were present in willow rhizosphere throughout the experiment. Numbers of bacterial cells per pot at the beginning of experiments are given in Tab. 5.

***Tab. 5**: Number of bacterial cells inoculated per pot, determined at the beginning of experiment by plate counts on SA medium.*

Inoculum	[CFU/pot]
F113L::1180	0.96×10^6
F113rifpcb	0.25×10^6
F113rif	1.89×10^6

Results of bacterial plate counts in the rhizosphere over the time period of observation are summarised in Fig. 6 (root samples, i.e. root material and residual soil within fine roots). With time, the roots formed dense mats at the bottom and the sides of the pot. A problem was that the leaves were beginning to turn yellow after 1 month, suggesting nutrient deficiency in the soil. Soil analysis revealed that the utilised soil was poor in phosphate. The problem was alleviated by fertilization.
Looking at the development of bacterial plate counts (CFU) in rhizosphere (root samples) during the course of the study, high fluctuations are obvious. Fig. 6a indicates plate counts for the total population of heterotrophic microbes, Fig. 6b reports observations specific to the investigated F113 derivatives. The variations are difficult to explain, they might be assigned to uncertainty associated with sampling (i.e. reflecting the heterogeneity of microbial density in the rhizosphere). Bacterial numbers counted in soil samples were lower than those observed in rhizosphere (root samples) by a factor of around 4, 5 and 20 for F113rif, F113rifpcb and F113L::1180, respectively (sampling at the end of experiment, i.e. after 224 days).

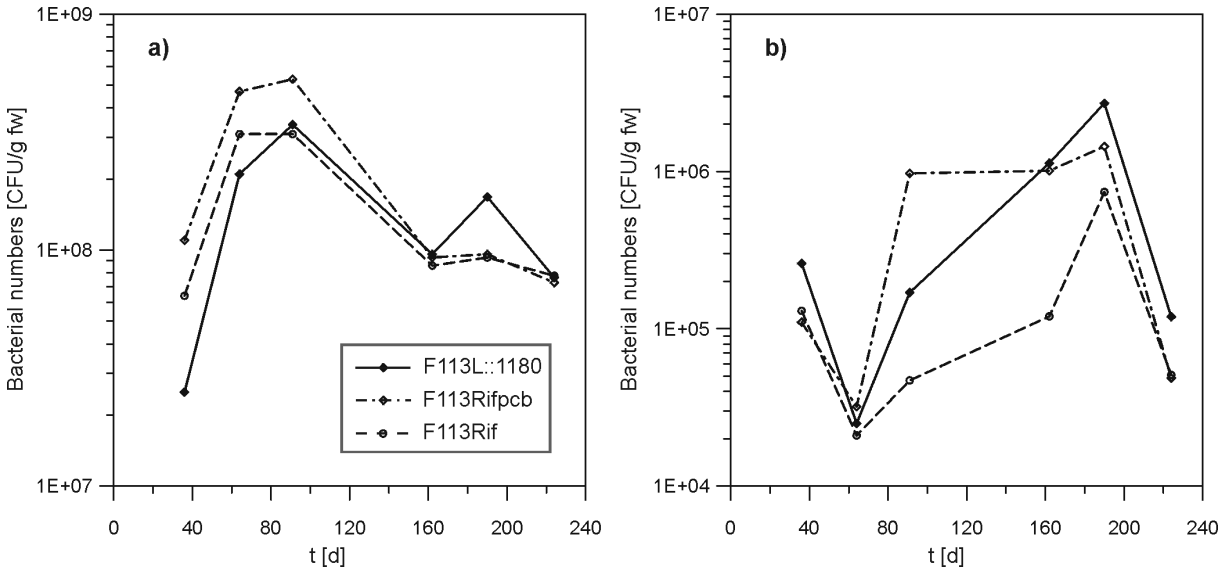


***Fig. 6**: Counted bacterial numbers in the willow rhizosphere (root samples) as a function of time, a) total heterotrophic bacteria on 10% Trytpic Soy Agar (TSA), b) F113-like colonies on SA medium.*

3.5 Modelling of PCB degradation in soil

In order to estimate degradation kinetics at a contaminated site (hypothetical rhizoremediation), the bioprocess was modelled according to Eq. (9) for PCB congeners that were shown to be degradable. Results of a rough estimation are presented in this section, considering biodegradation only (i.e. neglecting other contaminant loss processes like leaching or volatilisation). The model is based on the *Monod* parameters determined in section 3.3 and the findings on microbial survival in willow rhizosphere (section 3.4).
For the calculations, maximal removal velocities v^*_{max} and half saturation constants K_M from Tab. 2 were normalised to initial PCB mass and concentration to derive k^*_{max} and K_M^* (according to Eq. (6) and (7), specific to experiment). Initial bacterial numbers in laboratory $CFU_{lab,0}$ were taken from Tab. 4. Constant bacterial mass in soil was presumed, as no clear decline or growth tendency could be deduced from the mesocosm experiments (section 3.4).
The average bacterial number in willow rhizosphere (root samples, mesocosm experiments) was approximately 5×10^5 cfu/g root fw (fresh weight) for strain F113L::1180 (compare to Fig. 6b). In pure soil, the number of microbes was around 20 times lower (see section 3.4.2). The pots were filled with 2 kg soil fw and contained approximately 100 g roots (upper estimate). In real soil, the portion of roots is expected to be much lower. Sitte et al. (1991) estimate 10 tons of roots per ha (dry weight) for a Central European deciduous forest dominated by oaks and beech-trees. Thus, assuming a mass ratio root to soil for a Central European forest of about 1: 1000 and applying the observed bacterial numbers in root and soil samples from the mesocosm experiments, an average value for bacterial cells of 2.6×10^7 cfu/kg fw was determined (bacteria on roots plus bacteria in soil material):

5×10^5 cfu/g root fw x 0.001 + 2.5×10^4 cfu/g soil fw x 0.999 = 2.55×10^4 cfu/g

= 2.55×10^7 cfu/kg

This can be seen as an upper estimate. In comparison, for the sum of naturally occurring PCB degraders at a PCB-contaminated site, Leigh et al. (2006) determined microbial numbers in the rhriosphere of willows (*Salix caprea*) that were about one order of magnitude lower.

In the following, results for the degradation of Aroclor (A) 1016, 1221 and 1232 are presented (optimum conditions with f_{RD} = 1). The scenario of a fresh soil contamination was considered for the modelling, i.e. an unaltered congener composition. The modelling was performed on a congener by congener basis, considering 100 mg/kg for the total concentration of commercial PCB mixture in soil. Initial concentrations of individual congeners were used according to their reported portion in the mixture (Table 3).

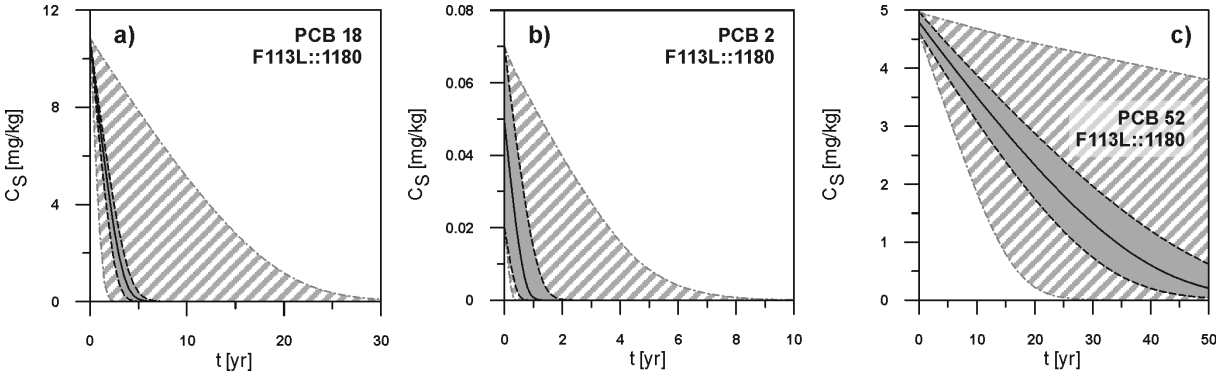


***Fig. 7**: Estimated depletion of PCB congeners with strain F113L::1180 in soil, as a function of uncertainty (rhizoremediation using willow plants).*

Fig. 7 shows soil concentrations over time, modelled for the congeners PCB 18, 2 and 52 (IUPAC-No.) in 100 mg/kg A1016 (degradation with strain F113L::1180). As depicted in Fig. 7a, PCB 18 (the main component in A1016) is degraded after around 5 years (straight black line). This is an average estimation, based on mean values for starting concentration C_0, for v^*_{max} and CFU_{soil}. Taking into account uncertainty due to the estimation of v^*_{max} and the measurement of C_0, the required time for the depletion is between 4 and 6 years (see grey area, defined by minimum and maximum curves). Calculations were performed by putting in observed and reported ranges for v^*_{max} and C_0, respectively

(Tabs. 2 and 3). Facing in addition the uncertainty inherent to bacterial numbers in soil, the hatched area is obtained. Under these assumptions, the compound is degraded after approximately 2 to 30 years. PCB 2 (Fig. 7b) is depleted much faster (after 1.2 years by mean estimation), the uncertainty of C_0 is higher than for PCB 18. In contrast, PCB 52 is metabolised very slowly.

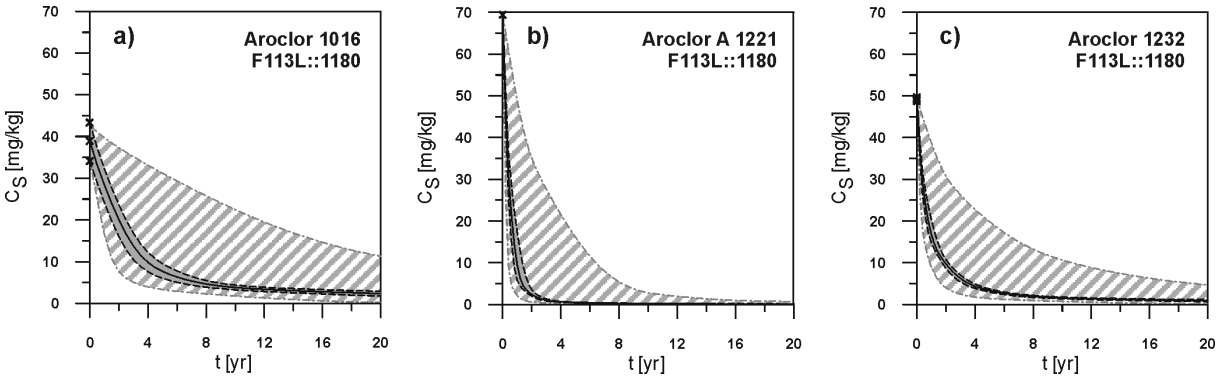


***Fig. 8**: Modelled breakdown of Aroclor mixtures (degradable fraction only) with strain F113L::1180 in willow rhizosphere.*

Depletion kinetics estimated for total mixtures (i.e. the degradable fraction of Aroclors) are presented in Fig. 8 for strain F113L::1180. Around 4 mg/kg of the degradable fraction in A1016 will still remain after 20 years (average estimation, see Fig. 8a). This is due to congeners that are slowly degraded (e.g. PCB 52, see Fig. 7c). In general, A1221 reveals the highest potential of being metabolised by the strains, followed by A1232 and A1016. However, A1221 and A1232 are technical mixtures that were rarely applied, whereas A1016 was frequently used (1%, <1% and 13%, respectively of total PCB production in the United States 1957-1977, according to Brown 1994).

4 Conclusions

Low and moderately chlorinated PCB congeners were readily metabolised by the investigated strains. LB400 and F113L::1180 showed a similar degradation capacity whereas the percentage of PCB depletion was generally lower for F113rifpcb. A procedure to quantify contaminant breakdown, and to estimate the time scale of microbial biodegradation was developed. Biphasic kinetics could be observed in the pure culture assays (vials) as bacterial activity was decreasing with time. A significant positive (linear) correlation was found between maximal removal velocities and decline rates of active cells (data estimated specific to PCB congeners). This finding can be seen as a consequence of the cometabolic process.

F113-like inoculants revealed a good survival ability in willow rhizosphere (mesocosm experiments with PCB contaminated soil material). Numbers of F113L::1180, F113rifpcb and F113rif strains observed over a time period of 7 months fluctuated more than one order of magnitude. These variations can mainly be assigned to sampling uncertainty (heterogeneity of microbial colonisation in the willow root zone).

Modelling of rhizoremediation, i.e. biodegradation with strain F113L::1180 in conjunction with willow plants (utilising *Monod* parameters from the laboratory assays and bacterial numbers from the mesocosm experiments) showed that an efficient performance in soil can be expected. More than 90% of the degradable fraction of Aroclor 1016, the most frequently applied PCB mixture among those studied, potentially is depleted after 20 years (mean estimation for a fresh contamination, i.e. unaltered congener composition). This assumptions is highly uncertain, however, and might be an considerable overestimation as it assumes bacterial contaminant breakdown not only in soil solution, but also for PCB mass adsorbed to soil particles (that might not be accessible for the microbes).

Considerable uncertainty is further associated a) to the initial concentration, i.e. the portion of individual PCB congeners in the mixture, b) to the maximal removal velocity, and c) to the number of bacterial cells expected in soil. The latter contribution is dominating by far. In fact, the maintenance and frequency of microbial degraders in soil is a crucial aspect for the assessment of the biodegradation potential. The data on degradation kinetics and bacterial numbers and the information obtained on uncertainty can be used for multimedia environmental modelling. Further investigations are required to elucidate kinetics in contaminated soil. Efforts should especially be focussed on bacterial numbers and the heterogeneity of microbial populations in soil and rhizosphere. The evaluated methodology can also be used to quantify microbial biodegradation of other contaminants.

Part IV Rhizoremediation of PCB contaminated soil – Multimedia environmental impact assessment and risk analysis

Contents

Abstract

A multimedia model was developed to estimate biodegradation and metabolite formation, fate and transport of contaminants and risks arising from the exposure to contaminated media. Mesocosm experiments with F113 derivatives and a field release trial with non-GM F113 strains were performed to evaluate microbial spreading. Gene transfer rates were investigated *in vitro* and *in vivo* (microcosm). Potential impacts of GMOs on indigenous microbial communities in soil and rhizosphere were analysed in additional experiments.

Results of generic modelling revealed a clear potential for risk reduction for rhizoremediation of PCB contaminated soil, using F113L::1180 and willow plants. Non the less, chlorobenzoic acids (CBAs) as the degradation products of concern are mobile compounds showing significance for the aquatic pathway and plant uptake. Groundwater water wells for drinking water supply should be located at a sufficient distance downstream to the source, i.e. more than 5 km as a preliminary, conservative estimate. Considerable uncertainty is associated to the degradation potential for Aroclor 1016, as kinetics data for a large number of PCB congeners present in this mixture were not available. Probabilistic modelling is recommended to identify the magnitude of potential risk, as a high uncertainty and/or variability was found to be relevant for a large number of model input parameters. Especially of importance were bacterial numbers in soil, the content of soil organic carbon, and hydraulic conductivity and effective porosity in an aquifer.

There was no significant hint on bacterial spreading into leaves, root free soil and leachate. Observed gene transfer rates were very low, as the introduced *bph* trait was stably inserted into the chromosome of the F113 strains. Potential impacts of GMOs on microbial soil communities also were very low, but there was a shift in rhizosphere populations. Uncertainty is given on long-term effects (especially for gene transfer and impacts on soil bacteria) and on potential impacts on soil organisms other than microbes.

1 Introduction

Biological *in situ* remediation is an emerging technology that bears the potential for an efficient and comparatively inexpensive treatment of contaminated sites. An accepted implementation of such measures requires a detailed and reliable assessment of associated risks. The time frame of the biodegradation process needs to be evaluated and potential new impacts assessed, such as those induced by the production of environmentally harmful metabolites, or by utilised organisms (e.g. degrader bacteria). In this investigation, strategies and tools were developed that can be used to estimate contaminant degradation and metabolite formation in soil (based upon the findings of Part III), chemical fate and transport, and risks for receptors exposed to contaminated environmental media. Furthermore, potential impacts by genetically modified (GM) bacteria were addressed.

The developed methodologies and modelling procedures were applied for a preliminary risk estimation of rhizoremediation of PCB contaminated soil, based upon the use of (GM) F113 strains in conjunction with willow (*Salix* sp.) plants (Part III). Biodegradation with strain F113L::1180 (Part I) was investigated in more detail, based upon results from Part III, where degradation capacities and kinetics were compared and microbial survival and growth were studied. The considered bioprocess follows the biphenyl (*bph*) pathway with a series of intermediates and chlorobenzoates resp. chlorobenzoic acids (CBAs) as stable end products (Novakova et al. 2002, Ahmed and Focht 1973, Furukawa et al. 1978a and b, Bedard 1990, Seeger 1999).

Beside chemical risk, the dispersal of GM inoculants (and resulting impacts) and the fate of the modified genes are important concerns. In an open environment, inoculants are competing and interacting with a diverse community of organisms that can have profound effects on the survival and performance of the introduced strain (Morrissey et al. 2002, Sayler and Ripp 2000, Walsh et al. 2001). The *bph* genes introduced into the chromosome of the investigated F113 strains only confer a selective advantage as long as the PCB substrate is available (Brazil et al. 1995, Villacieros 2005). Furthermore, these bacteria are root colonisers specialised to the rhizosphere of specific plants (Part III). Thus, it was hypothesised that the studied GM strains could have a low potential of uncontrolled spreading, being therefore restricted to PCB contaminated rhizospheres (potentially resulting in a biological containment). To verify this hypothesis, microbial dispersion was studied in macrocosm experiments (F113 derivatives) and a field release test (non-GM F113rif). Impacts on indigenous soil and rhizosphere bacteria, and gene transfer were investigated in additional studies.

The organisation of Part IV is given in the following. In section 2, scopes and strategies for the risk evaluation of the projected rhizoremediation system (potential field application) are discussed. Section 3.1.1 indicates pathways of contaminant partitioning, section 3.2.1 specifies exposure scenarios that were considered for the modelling. Then, a detailed description of the multimedia model is presented, that was set up in the present study. Methods applied for the calculation of mass balances and contaminant concentrations (section 3.1.2), and for the exposure modelling and risk evaluation (3.2.2. and 3.2.3) are deduced and discussed.
Input parameters considered for the modelling of this study are provided in section 3.1.3 and 3.1.4 (chemical input and environmental data) and 3.2.4 and 3.2.5 (exposure parameters and toxicity values). Similarly to Part II, one focus was aimed on the uncertainty and/or spatial and temporal variability of the required model input, so that best estimate values along with possible value ranges and statistical information were collected. Instructions are given for the derivation of appropriate probability density functions. Data and methods used to elucidate the fate and potential impacts of the genetically modified microorganisms (GMOs) are indicated in section 3.3.
Generic modelling was performed deterministically and probabilistically, addressing contaminant partitioning and subsequent exposure. Contaminant mass fluxes from soil into various environmental media and resulting concentrations are presented and discussed in section 4.1. Scenarios without biodegradation were compared to those where the bioprocess (strain F113L::1180 and willow plants) is active. Based upon the obtained receptor point concentrations, potential risks for human health and ecological receptors were analysed (section 4.2). Results on evaluated fate and behaviour of GMOs, their impacts and gene transfer rates are given in section 4.3. Uncertainty and sensitivity was analysed for contaminant fate and transport and estimated risks, and for the impact analysis of GMOs. The findings on chemical risks and potential impacts of GMOs is summarised in section 4.4.
Conclusions concerning the risk reduction potential of rhizoremediation with GMOs were drawn in section 5. There, recommendation for further investigations and potential applications are given (such as field test trials and real case studies).

2 Objectives and strategy

2.1 Conceptual site model

One aim of the present study was to evaluate potential impacts arising from the GMO-based rhizoremediation system (section 1) and to estimate associated risks in a base-line approach. To determine the focus and scope of the assessment and to identify major factors, conceptual site models (CSM) were set up. The CSM is a common tool to characterise contaminants, pathways and receptors of concern and other features that are relevant for assessment objectives (e.g. US EPA 1999, AFCEE 2005). An example for the conceptual site model at an early stage is shown in Fig. 1. In an iterative process (e.g. after identification of relevant pathways), the conceptual site model was further refined.

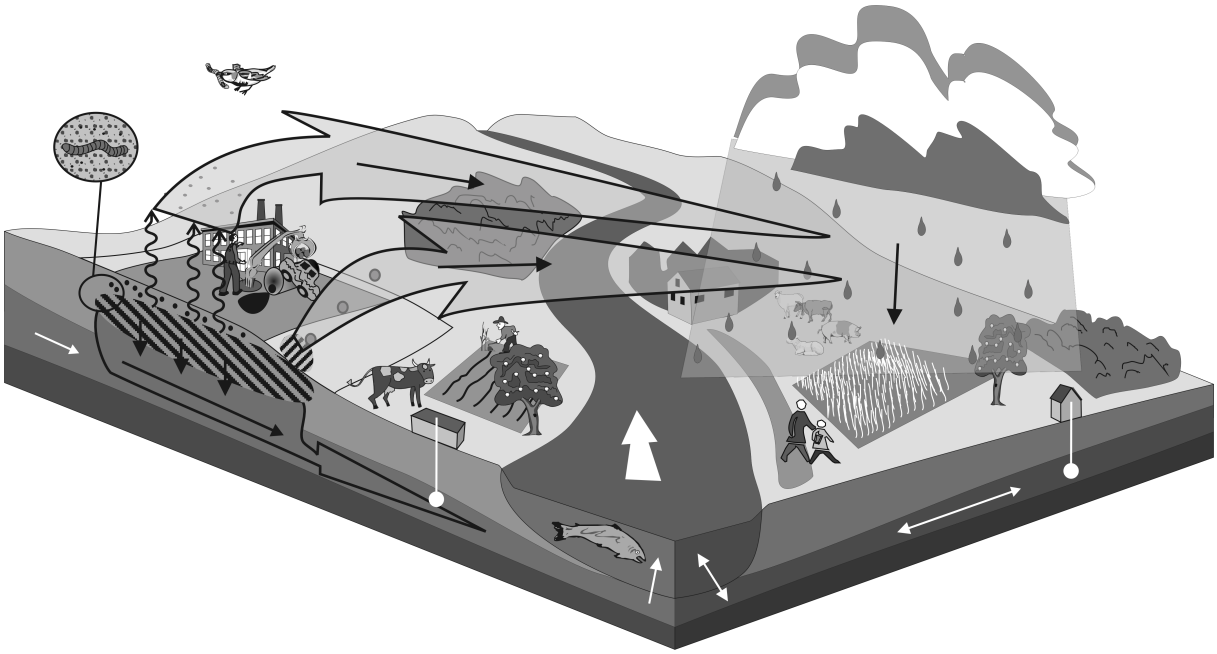


***Fig. 1**: Contaminated site with potential pathways and potential receptors (general overview).*

Subject of the analysis was a potential field application of *in situ* rhizoremediation of PCB-contaminated soil, using genetically modified bacteria in conjunction with plant roots (section 1). A qualitative and quantitative assessment of potential effects was performed, addressing:

a) PCB congeners of concern
b) GMOs utilised for *in situ* bioremediation (derivatives of *Pseudomonas* fluorescens strain F113)
c) CBAs as degradation products of concern (section 1)

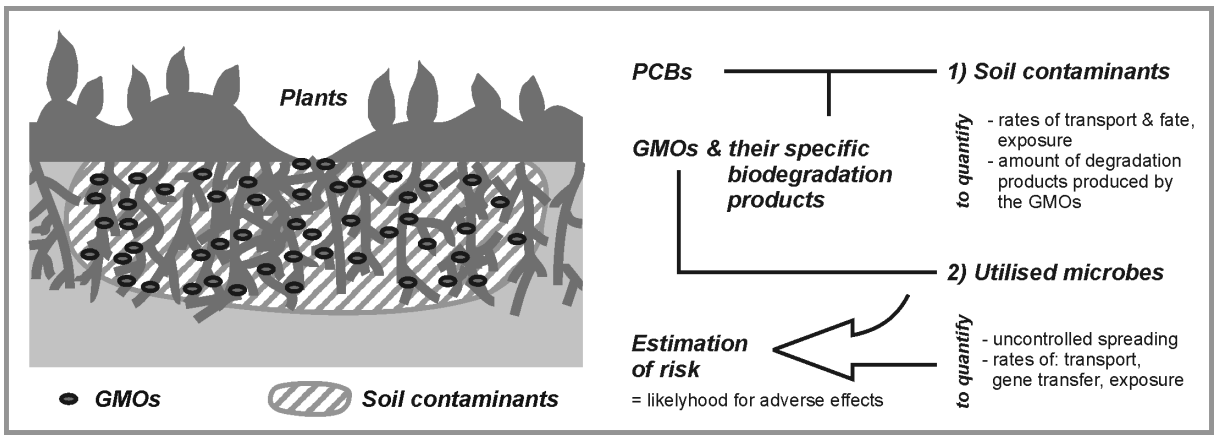


***Fig. 2**: Risk assessment objective for the GMO-based rhizoremediation system.*

2.2 Potential transport mechanisms and exposure scenarios

The concept of identifying contaminants, pathways and receptors of significance was applied both for chemicals (PCBs and CBAs) and GMOs. Potential primary transport routes for site contaminants are volatilisation and leaching, resulting in secondary contaminant sources (such as ambient air and groundwater, Fig. 3 A and B). Also plant uptake and exchange processes between leaves and air may be of importance. The relevance of further transport routes depend upon site characteristics and the environmental setting (e.g. receptors might be exposed by contaminants being transported with groundwater and surface water or by dry and wet deposition, Fig. 3 B).
Exposure routes for site contaminants are ingestion (e.g. soil particles and groundwater), dermal contact to contaminated media and inhalation of polluted air. Potential receptors are ecosystems (at the site and near the site) and human health (e.g. workers at the site, residents, farmers, trespassers, or the public via contaminated drinking water; Fig. 1).

Potential dispersal mechanisms for the GMOs encompass uncontrolled spreading and furthermore, transport via groundwater, air or soil organisms (Fig. 3 A and C). These processes might occur in case that the biological containment (section 1) is not maintained. Both on-site and off-site, gene transfer and direct exposure might be of concern (e.g. ingestion of GMOs by soil organisms). Respective mechanisms could result in impacts on the biodiversity (e.g. shift in species composition of microbial communities) and on soil organisms.

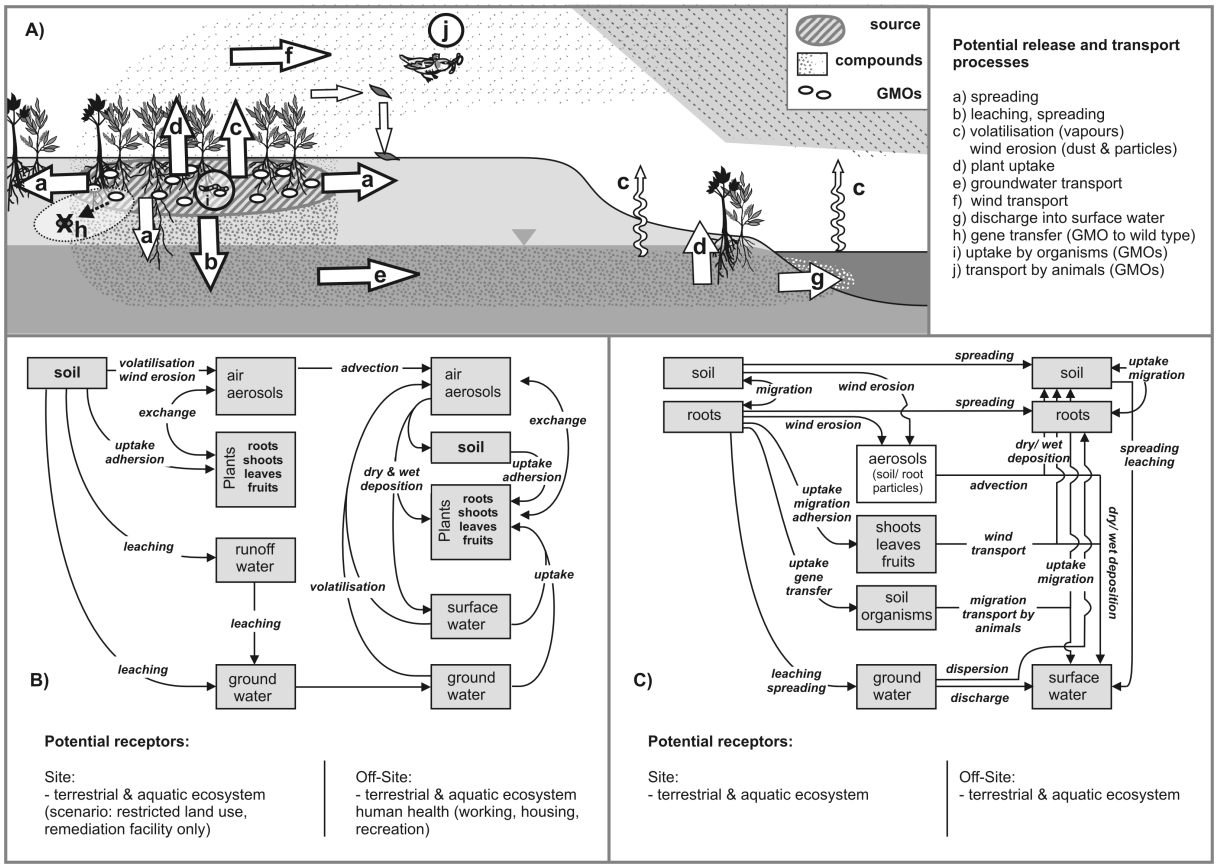


***Fig. 3**: Potential transport routes and receptors (generic level). a): general overview, b): site contaminants, c): GMOs.*

3 Data and methods

3.1 Contaminant fate and transport modelling

3.1.1 Considered pathways

Multimedia environmental computer modelling was performed to generically estimate PCB and CBA partitioning. Compound mass fluxes from soil into air, with leachate into groundwater, and the uptake into plants were calculated. Concentrations were estimated in respective media, including surface water (application of a water mixing model). In addition, a mass balance was set up, including gains and losses for the considered compartments (Fig. 4).

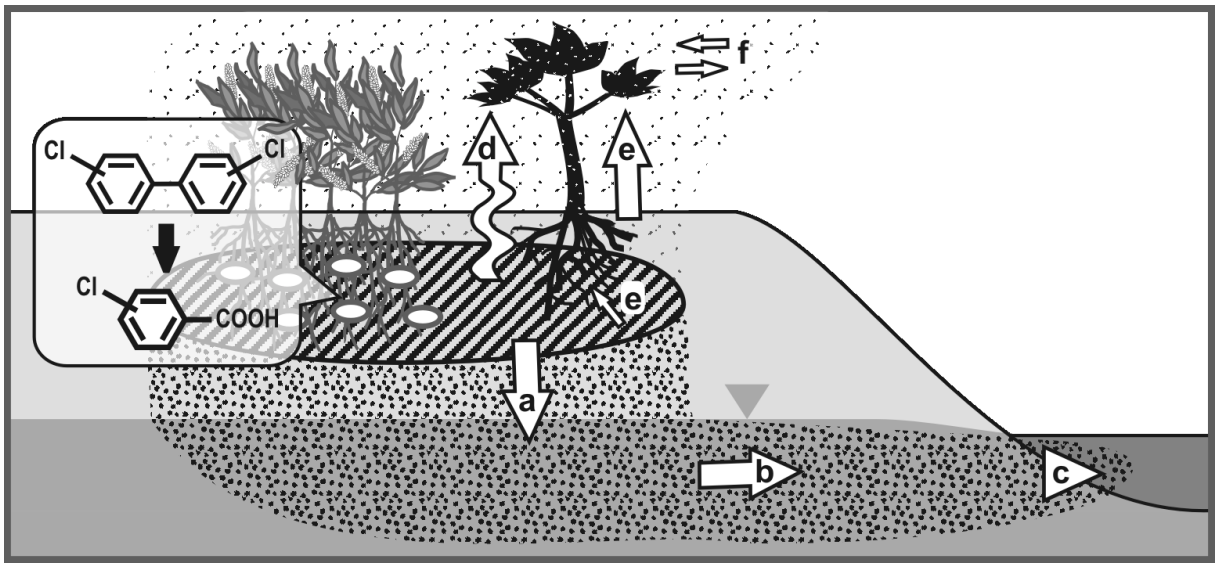


***Fig. 4**: Fate and transport modelling of PCBs and CBAs. a) leaching, b) groundwater transport, c) surface water mixing, d) volatilisation, e) uptake into plants, f) exchange between air and leaves.*

3.1.2 Applied model for multimedia contaminant partitioning

The multimedia modelling applied in this study was intended for a base-line investigation, in order to obtain upper estimates on a screening level to be used for risk assessment. For this task, a number of analytical, semi-analytical and numerical codes exist to date (compare to Part V). Unfortunately, the studied software were found to either lack a sufficient resolution (i.e. too large time steps) or they did not implement *Monod* kinetics for biodegradation. As another problem, some of the studied procedures were not suited to model weak acids (which is required to address CBAs). Thus, in this part of the thesis, an adequate tool was set up based upon Microsoft Excel spreadsheets and Visual Basic programming. The applied algorithms correspond to a number of widely utilised procedures and were combined and adjusted to allow consistent, mass balance-based calculations. They are based upon strongly simplified considerations and homogeneous conditions. The chosen model structure allows to perform probabilistic modelling (Monte Carlo simulations) by implementing the software package Crystal Ball (Decisioneering 2001). Details on the model are given in the following.

3.1.2.1 Soil compartment

The mass balance in soil was maintained as follows:

change of chemical mass in soil = – loss by biodegradation – gaseous flux into air – flux with leachte – – uptake into plants

$$\frac{dm_S}{dt} = -\frac{dm_B}{dt} - \frac{dm_V}{dt} - \frac{dm_W}{dt} - \frac{dm_P}{dt} \quad (1)$$

m_S: mass in soil [mg]
m_B: biodegraded mass [mg]
m_V: volatilised mass [mg]
m_W: leached mass [mg]
m_P: mass taken up by plants [mg]
t: time [s]

Contaminant mass and concentrations were calculated specific to compartments and for every time step. Soil concentration was obtained from contaminant mass in soil and the soil volume:

$$C_S = \frac{m_S}{V_S} \quad (2)$$

C_S: soil concentration [mg/m^3]
V_S: soil volume [m^3]

For the different phases in the soil compartment, a simple three phase linear partitioning model was adopted. This model is based upon the assumption that at any time point within the system, an equilibrium is established between contaminant concentrations within each of the phases (adsorbed, dissolved and soil vapour). Accordingly, when no residual phase hydrocarbon is present, the relation between soil concentration C_S and soil water concentration C_{SW} is given by the soil-water partition coefficient:

$$K_{SW} = \frac{C_S}{C_{SW}} \quad (3)$$

K_{SW}: soil-water partition coefficient [-]

$$K_{SW} = \rho_b K_d + \theta_{ws} + \theta_{as} K_{AW} \quad (4)$$

ρ_b: bulk soil density [g/cm^3]
K_d: soil-water sorption coefficient [cm^3 water/g soil]
θ_{ws}: water-filled porosity [cm^3/cm^3]
θ_{as}: air-filled porosity [cm^3/cm^3], with $\theta_{as} = \theta_T - \theta_{ws}$
θ_T: total porosity [cm^3/cm^3]

The vapour/dissolved phase equilibrium was assumed to be governed by Henry's law. This approach is consistent with that used by most base-line volatilisation models:

$$C_{SV} = C_{SW} \times K_{AW} \quad (5)$$

C_{SV}: soil vapour concentration [mg/m^3]
K_{AW}: air-water partition coefficient (dimensionless Henry's law constant) [-]

Adsorption of contaminants was treated to be governed by a linear organic carbon relationship (assumed hold as an approximation for most moist soils, e.g. Fetter 1994). Accordingly, following the Freundlich model, the soil-water sorption K_d was calculated as:

$$K_d = K_{OC} \times f_{OC} \qquad (6)$$

K_d: Soil-water sorption coefficient [cm^3 water/g soil]
K_{OC}: organic carbon partition coefficient [cm^3/g]
f_{OC}: fraction of organic carbon in soil [-]

The K_{OC} correlates with the octanol-water partition coefficient K_{OW}. A variety of regressions are given in the literature. For a number of non-polar organic compounds including PCB, Schwarzenbach and Westall (1981) found the following relationship:

$$\log K_{OC} = 0.72 \times \log K_{OW} + 0.49 \qquad (7)$$

For CBAs as polar compounds, the simplifying assumption was made that only the neutral species is subject to the sorption on soil particles and to volatilisation, as detailed in the following subsection.

3.1.2.2 PCB-biodegradation and CBA-formation

Biodegradation was calculated with the *Monod* model, according to Part III (section 2.5):

$$\frac{dm_B}{dt} = -\frac{k^*_{\max} \times C_S / C_{S,0}}{K^*_M + C_S / C_{S,0}} \times m_{S,0} \times \frac{CFU_{soil}}{CFU_{lab,0}} \times f_{RD} \qquad (8a)$$

m_B: biodegraded mass in soil [mg]
$m_{S,0}$: initial mass in soil [mg]
k^*_{max}: maximal removal rate [1/h]
K_M*: dimensionless half-saturation constant [-]
C_S, $C_{S,0}$: concentration, initial concentration in soil [mg/kg]
CFU_{Soil}: bacterial numbers in soil [cfu/kg]
$CFU_{lab,0}$: initial bacterial numbers in laboratory (vial) [cfu/L]
f_{RD}: factor for potentially reduced degradation performance under field conditions [-]

with $k^*_{\max} = \frac{v^*_{\max}}{m_0}$ (8b)

and $K^*_M = \frac{K_M}{C_0}$ (8c)

v^*_{max}: maximal removal velocity [mg/h]
K_M: half-saturation constant [mg/L]
m_0, C_0: initial substrate mass [mg] and concentration [mg/L] in degradation assay

It has to be noticed that this assumption might substantially overestimate microbial biodegradation, as it implies that microbes could access contaminants adsorbed to soil particles. Respective processes are not verified to date. Contrarily, it seems to be more likely that bacteria only can metabolise PCB mass in soil solution (Part III, section 2.5).

In the applied approach, the mass of depleted PCB corresponded to the mass of CBA that was produced by the bioprocess. Thus, a flux of CBA into soil was generated originating from PCB breakdown. Full (equimolar) conversion of a PCB congener into the corresponding CBA was considered as a worst case scenario, as will be discussed in detail in section 3.1.3.

CBAs are weak organic acids and therefore undergo proton transfer reactions. These reactions result in the formation of charged species (i.e. anions). Properties and reactivities of these charged species are fundamentally different to their neutral counterparts. Thus, the extent to which the molecules may form ions has to be determined for the considered environmental system. The fraction of the neutral species $\Theta_{n,acid}$ is depending on soil *pH* and on the dissociation constant pK_a (according to the Henderson-Hasselbalch equation, e.g. Trapp and Matthies 1998):

$$\Phi_{n,acid} = \frac{1}{1 + 10^{(pH - pKa)}} \qquad (9)$$

Ions are hydrophilic in principle as they interact with water dipoles. Accordingly, partition coefficients addressing lipophilic processes refer to neutral molecules, only. In the present study, neither sorption to soil particles nor volatilisation was assumed for the dissociated species. This approach is commonly followed for the modelling of polar compounds (e.g. modules included in CemoS1, Trapp and Matthies 1998).

3.1.2.3 Volatilisation and wind transport

A buried source was considered for the modelling, with the volatilised mass dm_V given as follows:

$$dm_V = D_S^{eff} \times \frac{C_{SV}}{L_d} \times A \times dt \quad (10)$$

D_s^{eff}: effective diffusion coefficient in soil [m^2/s]
L_d: diffusive path length [m]
A: effective cross section area [m^2]

with $L_d = L_S + 0.5 \times d_S$ (11)

L_S: depth of subsurface source [m]
d_S: source thickness [m]

and $A = W_X \times W_Y$ (12)

W_X, W_Y: source width parallel and perpendicular to the main wind direction, respectively [m]

$$D_s^{eff} = D_{air} \frac{\theta_{as}^{10/3}}{\theta_T^2} + D_{water} \frac{1}{K_{AW}} \frac{\theta_{ws}^{10/3}}{\theta_T^2} \quad (13)$$

D_{air}, D_{water}: molecular diffusion coefficient for the compound in air and water [m^2/s]

The relation of molecular diffusion coefficients for two substances in the same medium can be approximated from the relation of molecular weight M (Tinsley 1979; see Part II, section 2.4.1). D_{air} and D_{water} were calculated accordingly:

$$D_{air} = 2.57 \times 10^{-5} \times \sqrt{\frac{18}{M}} \quad (14)$$

diffusion coefficient of air in water = 2.57x 10^{-5} m^2/s
molecular weight of H_2O = 18 g/mol

$$D_{water} = 2 \times 10^{-9} \times \sqrt{\frac{32}{M}} \quad (15)$$

diffusion coefficient of water in air = 2 x 10^{-9} m^2/s
molecular weight of O_2 = 32 g/mol

Ambient air concentrations can be determined with a simple box model as e.g. used within the risk estimation program RISC 4.02 (Spence and Walden 2001) or as recommended by ASTM (2002) to derive volatilisation factors. This model assumes that emissions into a hypothetical box will be distributed uniformly throughout the box. The width of the box is given by W_Y, the length is based on the wind speed in the mixing zone U_A, and the height is defined by the diffusion height or ambient air mixing zone height δ_A:

$$C_A = D_S^{eff} \times \frac{C_{SV}}{L_d} \times \frac{W_Y}{U_A \delta_A} \quad (16)$$

U_A: wind speed above ground surface in ambient mixing zone [m/s]
δ_A: ambient air mixing zone height [m],
δ_A = 2 m is commonly assumed as a default value for risk modelling, corresponding to the height of a person (upper estimate)

The US EPA (1996b) states, however, that the assumptions and mathematical treatment of dispersion in the box model may not be applicable to a broad range of site types and meteorology. Thus, a revised dispersion analysis was performed for 29 U.S. locations selected to be representative for the national range of meteorological conditions (EQ 1993 and 1994). This investigation included numerical modelling for both volatile and particulate matter contaminants. Results are a set of dispersion coefficients *Q/C* specific to U.S. regions and for different source extensions, presented by the US EPA (1996b). The *Q/C* term describes the inverse of the mean concentration at the centre of a square source normalised to the volatile emission rate. The US EPA (1996b) recommends to select a *Q/C* value that best represents the size and meteorological condition of the investigated site. Alternatively, a site-specific *Q/C* can be determined with the Industrial Source Complex Model platform in the short-term mode (ISCST3), presented by the US EPA Support Center for Regulatory Air Models (SCRAM, see reference list). Under consideration of *Q/C*, Eq. (16) modifies to:

$$C_A = D_S^{eff} \times \frac{C_{SV}}{L_d} \times (Q/C)^{-1} \times 10^3 \frac{g}{kg} \quad (17)$$

Q/C: dispersion coefficient [(g m^{-2} s^{-1})/(kg/m^3)]

For receptor points located downwind to the source zone, air concentrations can be calculated as follows (e.g. Trapp and Matthies 1998; Technical Guideline for Air Pollution Control, TA-Luft 1986):

$$C_A(x,y,z,H) = \left[\frac{I_A}{2\pi\sigma_y\sigma_z u}\right] \times \exp\left[-\frac{y^2}{2\sigma_y^2}\right] \times \left\{\exp\left[-\frac{(z-H)^2}{2\sigma_z^2}\right] + \exp\left[-\frac{(z+H)^2}{2\sigma_z^2}\right]\right\} \qquad (18)$$

x, y: receptor distance from the source in wind direction, lateral to wind direction [m]
z: receptor elevation from the source [m]
H: stack height [m]
u: vertically averaged wind speed [m/s]
I_A: contaminant emission rate, subsurface soils to ambient air [mg/s]
σ_y: lateral dispersion coefficient [m]
σ_z: vertical dispersion coefficient [m]

Considering concentrations in main wind direction (y = 0), Eq. (18) simplifies to:

$$C_A(x,0,z,H) = \left[\frac{I_A}{2\pi\sigma_y\sigma_z u}\right] \times \left\{\exp\left[-\frac{(z-H)^2}{2\sigma_z^2}\right] + \exp\left[-\frac{(z+H)^2}{2\sigma_z^2}\right]\right\} \qquad (19)$$

with $$I_A = \frac{dm_V}{dt} \qquad (20)$$

and $$\sigma_y = a \cdot x^p \qquad (21)$$

$$\sigma_z = b \cdot x^q \qquad (22)$$

a, *b*: empirical linear coefficients [-]
p, *q*: empirical exponents [-]

For *a*, *b*, *p* and *q*, values for different meteorological conditions are reported by the TA-Luft (1986). If neutral stability is prevailing (in terms of Pasquill's stability classes), *a* = 0.640, *p* = 0.784, *b* = 0.215 and *q* = 0.885. These values were determined by Vogt (1980) in the area of Karlsruhe, Germany (cited by Trapp and Matthies 1998) and were used for the modelling in the present study.

3.1.2.4 Leaching

The contaminant mass being subject to leaching dm_L was calculated from soil water concentration, infiltration rate and the source area:

$$dm_L = q_W \times C_{SW} \times A \times dt \qquad (23)$$

q_W: infiltration rate [m/s]
A: source area (plan view) [m^2], $A = W_X$ x W_Y

Leachate concentrations were estimated according to a procedure that is adopted by RISC 4.02 (Spence and Walden 2001) and recommended by the New Zealand Ministry for the Environment (NZ ME 1999). Accordingly, the source zone was treated as a well-mixed (homogeneous) finite source that depletes with time. The vadose zone beneath the source was considered as being one-dimensional and at pseudo-steady state. In the applied concept, solute transport with leachate occurs via advection and dispersion, addressing mass loss by a first-order degradation reaction. An appropriate one-dimensional solute transport equation (including adsorption) is reported by van Genuchten and Alves (1982):

$$R\frac{\partial C_W}{\partial t} = D_z\frac{\partial^2 C_W}{\partial z^2} - \bar{v}\frac{\partial C_W}{\partial z} - \mu C_W \qquad (24)$$

C_W: dissolved phase concentration of chemical [mg/L] (corresponding to soil water concentration C_{SW})
$\bar{v}$: seepage velocity (or interstitial velocity) [m/s]
D_z: dispersion coefficient [m^2/s]
μ: first-order decay coefficient for chemical [1/s]
z: distance below the source (measured positively downwards) [m]
t: time [s]
R: retardation factor [-]

In Eq. (24), dispersion is considered in downward direction only (longitudinal dispersion). For the following boundary conditions,

$C_W(z,0) = 0$ (25) (concentrations below the source are zero at time t = 0)

$C_W(0,t) = C_{W,0}e^{-\beta \times t}$ (26) (the leachate concentration leaving the source zone decays exponentially with time)
β: source zone depletion coefficient (loss term) [1/s]

$\frac{\partial C_W}{\partial z}(\infty,t) = 0$ (27) (long distance below source: concentration gradient is zero)

equation (24) can be solved as follows (van Genuchten and Alves 1982):

$C_w(z,t) = C_{W,0}e^{-\beta \times t}B(z,t)$ (28) C_w(z,t): dissolved phase concentration [mg/L] at time t [s] and depth z [m] below the source
$C_{W,0}$: dissolved phase concentration in the source zone at the beginning of the simulation [mg/L]

with

$$B(z,t) = \frac{1}{2}\exp\left[\frac{(\bar{v}-w)z}{2D_z}\right]erfc\left[\frac{Rz-wt}{2\sqrt{D_zRt}}\right] + \frac{1}{2}\exp\left[\frac{(\bar{v}+w)z}{2D_z}\right]erfc\left[\frac{Rz+wt}{2\sqrt{D_zRt}}\right] \quad (29)$$

and

$$w = \bar{v}\sqrt{1+\frac{4D_z}{\bar{v}^2}[\mu - R\beta]} \quad (30)$$

Contaminant loss by volatilisation, leaching and plant uptake was treated with the source zone depletion coefficient β:

$\beta = \beta_w + \beta_v + \beta_P$ (31) β_W: leachate loss term [1/s]
β_V: vapour loss term [1/s]
β_P: plant uptake loss term [1/s]

$$\beta_v = \frac{D_{eff}K_{aw}}{(\rho_b K_d + \theta_w + \theta_a K_{aw})d_S L_d} \quad (32)$$

$$\beta_w = \frac{q_W}{(\rho_b K_d + \theta_w + \theta_a K_{aw})d_S} \quad (33)$$

$$\beta_P = \frac{Q_W \times TSCF}{V_S \times K_{SW}} \quad (34)$$

Q_W: transpiration stream [m^3/s]
TSCF: transpiration stream concentration factor [-]

Plant uptake (Eq. 34) will be discussed in section 3.1.2.7. The dispersion coefficient D_z was determined from longitudinal dispersivity and seepage velocity:

$D_z = \alpha_L \times \bar{v}$ (35) α_L: longitudinal dispersivity [m]

$$\bar{v} = \frac{q_W}{\theta_w} \quad (36)$$

The longitudinal dispersivity α_L can be estimated as a function of vertical distance (according to Gelhar et al. 1985):

$\ln\alpha_L = -4.933 + 3.811\ln z_m$ (for $z_m \le 2$ m) (37a)
$\ln\alpha_L = -2.727 + 0.584\ln z_m$ (for $z_m \ge 2$ m) (37b)
α_L: longitudinal dispersivity [m]
z_m: distance from the source to the observation location [m]

Finally, the retardation factor R [-] for the unsaturated zone is defined as:

$$R = 1 + \frac{\rho_b K_d}{\theta_w} \quad (38)$$

Equation (28) was used to calculate aqueous-phase concentrations as a function of depth below the source. Respective results (concentrations expected at the water table) were considered as input for the groundwater transport modelling.

3.1.2.5 Groundwater transport

Multidimensional transport involves both longitudinal and transverse dispersion in addition to advection. The most complex form of the dispersion-advection equation that is amenable to an analytical solution includes three dispersive components (D_x, D_y, D_z), a constant advective velocity v_x and one kinetic term r (Domenico and Schwartz 1990):

$$D_X \frac{\partial^2 C_W}{\partial x^2} + D_y \frac{\partial^2 C_W}{\partial y^2} + D_z \frac{\partial^2 C_W}{\partial z^2} - v_x \frac{\partial C_W}{\partial x} - \frac{r}{n_e} = \frac{\partial C_W}{\partial t} \quad (39)$$

n_e: effective porosity [cm^3/cm^3]

For a continuous source, a closed form solution for Eq. (39) is given by Domenico & Robins (1985), addressing advection and dispersion:

$$C_{GW}(x,y,z,t) = \left(\frac{C_{w,0}}{8}\right) \times erfc\left[\frac{x - vt}{2\sqrt{\alpha_x vt}}\right] \times \left\{erf\left[\frac{y + Y/2}{2\sqrt{\alpha_y x}}\right] - erf\left[\frac{y - Y/2}{2\sqrt{\alpha_y x}}\right]\right\} \times \left\{erf\left[\frac{y + Z}{2\sqrt{\alpha_z x}}\right] - erf\left[\frac{y - Z}{2\sqrt{\alpha_z x}}\right]\right\}$$

(40) $C_{GW}(x,y,z,t)$: groundwater concentration as a function of time t and receptor point location (x: distance in groundwater flow direction, y: lateral direction, z: vertical distance from the source)
Y: source width [m] (corresponding to W_Y)
Z: source thickness [m] (corresponding to d_S)
v: contaminant velocity [m/s]
α_x, α_y, α_z: longitudinal, transverse and vertical dispersivity [m]

Neglecting vertical dispersion and considering a receptor point that is located at z = 0, Eq. (40) simplifies accordingly. Respective analytical solution was applied for the modelling of contaminant transport in groundwater:

$$C_{GW}(x,y,0,t) = \left(\frac{C_{w,0}}{4}\right) \times erfc\left[\frac{x - vt}{2\sqrt{\alpha_x vt}}\right] \times \left\{erf\left[\frac{y + Y/2}{2\sqrt{\alpha_y x}}\right] - erf\left[\frac{y - Y/2}{2\sqrt{\alpha_y x}}\right]\right\} \quad (41)$$

with

$$v = \frac{K_f \times i}{n_e \times R_{Aq}} \quad (42)$$

K_f: effective hydraulic conductivity [m/s]
i: hydraulic gradient [m/m]
R_{Aq}: retardation factor in the saturated zone [-]

and

$$R_{Aq} = 1 + \frac{\rho_b \times K_d}{n_e} \quad (43)$$

Gelhar (1992) and Fetter (1994) define the longitudinal dispersivity α_x to be 1/10 of the plume length L_P. Alternatively, Xu and Eckstein (1995) found a correlation of the form $\alpha_x = 0.83 (\log_{10} L_P)^{2.414}$. The transversal dispersivity α_y is often assumed to be 1/10 α_x (Lege 1996); Kobus et al. (1992) recommend a range of ¼ to 1/20 α_x.

Eq. (40) and (41) utilise a constant initial solute concentration $C_{W,0}$. In contrast, the scenarios modelled in the present study implied time-varying values for $C_{W,0}$ (leachate concentrations at the groundwater level, e.g. decreasing with time due to biodegradation in the source zone, leaching, volatilisation and plant uptake). This problem can solved by applying the principle of superposition to the solute concentration input (e.g. Häfner 1993), as illustrated in Fig. 5. By applying a constant concentration $C_{W,0}$ for $t \geq t_0$ and adding the negative value of $C_{W,0}$ for $t \geq t_1$ (Fig. 5a), a pulse input of C_W for $t_0 < t < t_1$

can be generated (Fig. 5b). Respective procedure was adapted to obtain a rectangular fit to input concentration data ("real" C_W in Fig. 5c and d), consisting of 10 steps for superposition. In fact, 10 constant input concentrations were considered that are mean values of "real" C_W for each time interval ($t_0 \le t < t_1$, $t_1 \le t < t_2$, etc., see Fig.5d).

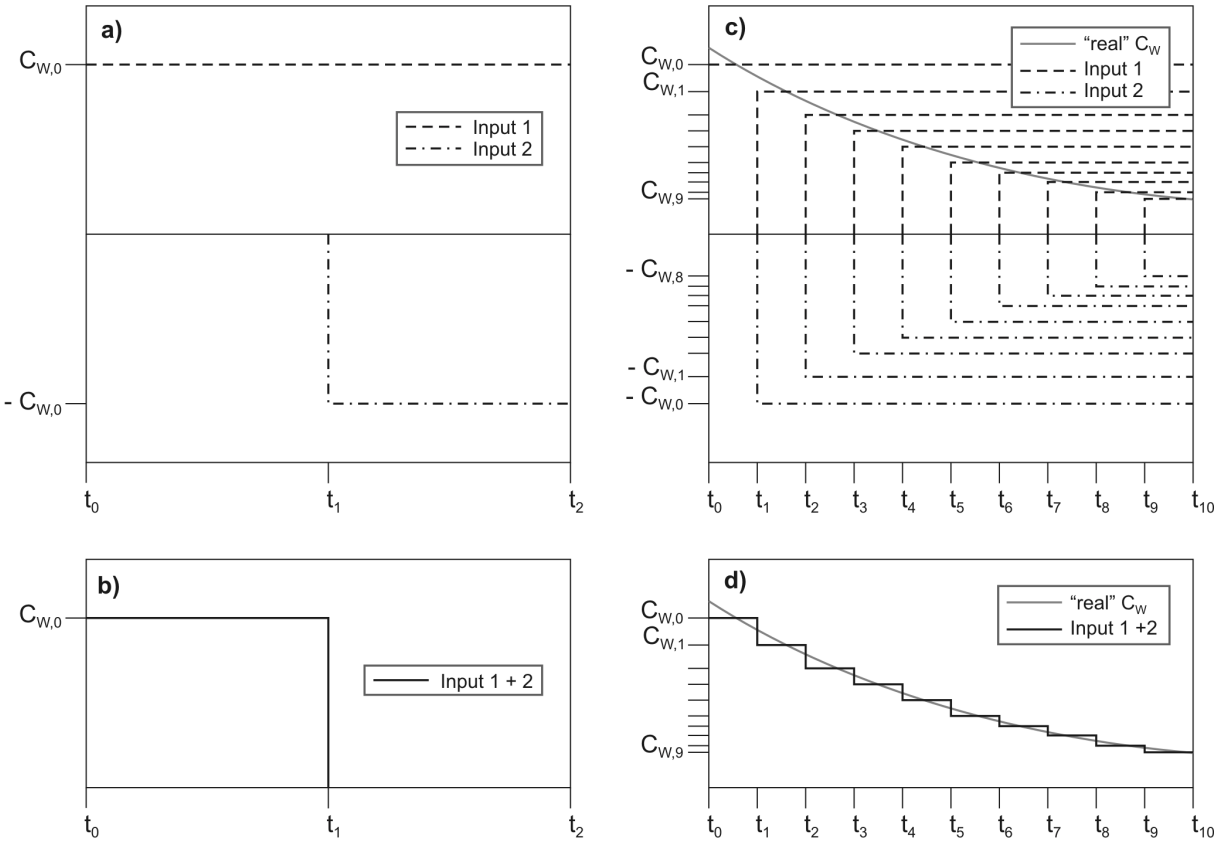


Fig. 5*: Principle of superposition applied to solute concentration (C_W) input. a) and b): generation of a pulse input (example); c) and d): rectangular input fitted to C_W data ("real" C_W); $C_{W,0}$; $C_{W,1}$; …; C_{W9}: mean solute concentration for $t_0 \le t < t_1$; $t_1 \le t < t_2$; …; $t_9 \le t < t_{10}$.*

Based upon the superposition principle, Eq. (41) was modified to:

$$C_{GW}(x,y,0,t) = \left\{ erf\left[\frac{y+Y/2}{2\sqrt{\alpha_y x}}\right] - erf\left[\frac{y-Y/2}{2\sqrt{\alpha_y x}}\right] \right\} \times \left\{ \left(\frac{C_{w,0}}{4}\right) \times erfc\left[\frac{x-vt}{2\sqrt{\alpha_x vt}}\right] + D \right\} \qquad (42a)$$

with

$D = 0$ if $t_0 \le t < t_1$ (42b)

$$D = \left(\frac{C_{w,1}-C_{w,0}}{4}\right) \times erfc\left[\frac{x-v(t-t_1)}{2\sqrt{\alpha_x v(t-t_1)}}\right] \quad \text{if } t_1 \le t < t_2 \qquad (42c)$$

$$D = \left(\frac{C_{w,1}-C_{w,0}}{4}\right) \times erfc\left[\frac{x-v(t-t_1)}{2\sqrt{\alpha_x v(t-t_1)}}\right] + \left(\frac{C_{w,2}-C_{w,1}}{4}\right) \times erfc\left[\frac{x-v(t-t_2)}{2\sqrt{\alpha_x v(t-t_2)}}\right] \quad \text{if } t_2 \le t < t_3 \qquad (42d)$$

$$D = \sum_{i=1}^{n} \left\{ \left(\frac{C_{w,i}-C_{w,(i-1)}}{4}\right) \times erfc\left[\frac{x-v(t-t_i)}{2\sqrt{\alpha_x v(t-t_i)}}\right] \right\} \quad \text{if } t_{(i-1)} \le t < t_i \qquad (42e)$$

n: number of steps for superposition [-]
$C_{W,i}$: input concentration, step i [mg/L]
t_i: time, step i [s]

3.1.2.6 Surface water mixing

For contaminant discharge from groundwater into a river, a simplified water mixing model was used according to the code G3CTM (developed by the North Carolina Department of Environment and Natural Resources, NCDENR 1997), assuming C_{River} = 0 upstream to the discharge area:

$$C_{River} = C_{GW} \times \frac{Q_{GW}}{Q_{GW} + Q_{River}} \quad (43)$$

C_{River}: contaminant concentration in the river [mg/L]
Q_{GW}: groundwater flux into the river [m^3/yr]
Q_{GW}: river flow rate [m^3/yr]

with

$$Q_{GW} = K_f \times i \times W_{Plume} \times h_{GR} \times F_{eff} \quad (44)$$

W_{Plume}: plume width at the plume-river intersection [m]
h_{GR}: height of the plume-river intersection [m]
F_{eff}: effective portion of the cross-sectional area for mixing [-]

and

$$Q_{River} = u_R \times B_R \times h \quad (45)$$

u_R: river flow velocity [m/s]
B_R: river width [m]
h: river depth [m]

The mixing model of Eq. (43) considers concentrations that are homogeneously mixed throughout the water body and is also used by RISC 4.01 (Spence and Walden 2001). The groundwater plume was assumed to intersect the river body at a right angle. In the present study, constant groundwater concentrations across the plume width were considered (centre line concentrations with y = 0, see Eq. 42), with a plume width W_{Plume} that corresponds to the source width W_Y.

3.1.2.7 Contaminant plant uptake

Relevant processes for the uptake of neutral organic compounds into plants include lipophilic sorption, dilution by growth and advection in the vascular system. For dissociating compounds, also electrochemical interactions and ion trap mechanisms have to be accounted for (Trapp 2000, 2004). Details on the applied model approach are given in the following. The presented methodology was used to determine root and leaf concentrations and to set up mass balances.

3.1.2.7.1 Uptake from soil into roots

For fine roots, diffusive exchange with soil solution is high (due to an extremely large surface area), and near-equilibrium can be assumed, expressed by the partition coefficient between root and water K_{RW} (e.g. Trapp and Matthies 1998):

$$C_{Root} = C_S \times \frac{K_{RW}}{K_{SW} \times \rho_R} \quad (46)$$

C_{Root}: root concentration [mg/kg]
C_S: soil concentration [mg/m^3]
K_{RW}: partition coefficient between root and water [-]
ρ_R: root density [kg/m^3]

Root concentrations were determined with Eq. (46). For thicker roots, however (e.g. taproots and storage roots), equilibrium is an upper limit, and the kinetics of uptake control the concentration (Trapp and Matthies 1995, 1998). Plant tissue consists of lipoid and aqueous phases. Neutral organic compounds are subject to the sorption on lipids. For these substances, the partition coefficient between plant tissue and water K_{PW} is given by a regression to the K_{OW} (Trapp and Matthies 1995, erratum):

$$K_{PW} = \left(W_P + L_P \times a \times K_{OW}^{b}\right) \frac{\rho_P}{\rho_W} \quad (47)$$

W_P: water content of the plant tissue [g/g]
L_P: lipid content [g/g]
ρ_P: density of the plant tissue [kg/m^3]
ρ_W: water density [kg/m^3]
a, b: empirical correction coefficient and exponent for differences between plant lipids and octanol [-],
$a = \rho_W/\rho_{Octanol}$ ($\rho_{Octanol}$ = 822 kg/m^3; ρ_W = 1000 kg/m^3)

For neutral organic compounds, the partition coefficient between root and water K_{RW} is calculated with Eq. (47), using root water and lipid content and root density, and applying adequate *b* exponents. E.g., *b* = 0.75 was found for cut bean roots and stems (Trapp and Pussemier 1991); for mazerated barley roots it was 0.77 (Briggs et al. 1982). The latter authors introduced the root concentration factor *RCF* for equilibrium (ratio of root concentration to concentration in solution). In fact, the *RCF* corresponds to the term (W_P + L_P x a x K_{OW}^{b}) in Eq. (47), considering root water and root lipid content (e.g. Trapp 2000).

For polar compounds, a multi-compartment model was applied in the present study to determine the K_{RW}, as will be described in section 3.1.2.7.5.

3.1.2.7.2 Translocation with the transpiration stream

Water containing dissolved compounds is taken up by roots with the transpiration stream. The uptake into roots not necessarily results in a translocation into the shoot (Shone and Wood 1974). In fact, for most xenobiotics, the concentration ratio between xylem sap and external solution (soil water) is smaller than one (Shone and Wood 1974, Briggs et al. 1982), expressed by the transpiration stream concentration factor *TSCF*. Compounds cannot move from root to shoot by a completely apoplastic pathway because the latter is blocked at the endodermis, between cortex and stele, by the Casparian strip. To reach the vascular system and thus the shoot, compounds must cross the plasmalemma (the membrane separating the apoplast and symplast) and the *TSCF* is thus a measure of the ability of a compound to do this (Bromilow and Chamberlain 1995). Accordingly, the compound mass flux from soil water into above-ground plant parts is (Trapp and Matthies 1995):

$$N_{xy} = Q_W \times TSCF \times C_{SW} \qquad (48)$$

N_{Xy}: mass transport within the xylem [mg/s]
Q_W: transpiration stream [m^3/s]
TSCF: transpiration stream concentration factor [-]

In the mass balance equation (Eq. 1), N_{XY} was considered as dm_P/dt for the contaminant uptake from soil into plants. For non-dissociating organic compounds, the *TSCF* is related to the K_{OW} as follows (Briggs et al. 1982):

$$TSCF = 0.784 \exp\left[-\frac{(\log K_{OW} - 1.78)^2}{2.44}\right] \qquad (49)$$

Respective studies were carried out with barley plants and two series of non-ionised compounds spanning a wide range of log K_{OW} values. Literature values for the *TSCF* of a number of systemic pesticides were also found to match the correlation of Eq. (49) reasonably well, even though several plant species were involved (Trapp and Mc Farlane 1995). Hsu et al. (1991) found an equation of similar form but with different values (translocation of cinmethylin and related compounds in detopped soybean plants):

$$TSCF = 0.7 \exp\left[-\frac{(\log K_{OW} - 3.07)^2}{2.78}\right] \qquad (50)$$

For substances with intermediate K_{OW}, Eq. (49) and (50) work satisfactorily well (Trapp and Matthies 1995, Bromilow and Chamberlain 1995, Mc Farlane et al. 1990, Trapp and Pussemier 1991). From the comparison of both empirical equations it can be seen that the *TSCF* is an uncertain parameter, in particular for very lipophilic substances.

For poplar trees (*Populus* sp.) and 12 organic compounds commonly found at hazardous waste sites, Burken and Schnoor (1998) report a correlation that is approximately in between Eq. (49) and (50):

$$TSCF = 0.756 \exp\left[-\frac{(\log K_{OW} - 2.50)^2}{2.58}\right] \qquad (51)$$

This correlation was used by Trapp et al. (2003) to calculate contaminant uptake into fruit trees and was also considered for the modelling of neutral organic compounds in the present study. Like for the K_{RW}, a different approach was used to calculate the *TSCF* for dissociating substances (section 3.1.2.7.5).

3.1.2.7.3 Gaseous exchange between leaves and atmosphere

Due to their large surface area, leaves posses a high potential for gaseous exchange with the atmosphere. Resistance against volatilisation is composed of parallel resistances through stomata and cuticles and a series resistance through the atmosphere (mainly determined by the air boundary layer resistance, Thompson 1983). The conductance is the inverse to the resistance. The total conductance G was calculated as follows, according to the Plant module in CemoS1 (Trapp and Matthies 1998) and Trapp (1995):

$$G = G_c + G_s \quad (52)$$

G_s: conductance of the stomatal pathway [m/s]
G_c: total conductance of the cuticle pathway [m/s]

$$G_c = \frac{1}{\frac{1}{G_k} + \frac{1}{G_a}} \quad (53)$$

G_k: cuticle conductance [m/s]
G_a: conductance of the air boundary layer (atmosphere) [m/s]

The cuticle consists of waxy material and is subject to diffusion for lipohpilic compounds (Schönherr and Riederer 1989). Using the permeance P [m/s], the cuticle conductance G_k can be determined:

$$G_k = \frac{P}{K_{AW}} \quad (54)$$

Kerler and Schönherr (1988) showed that P for isolated *Citrus* cuticles is closely related to the K_{OW}:

$$\log P = -11.2 + 0.704 \times \log Kow \quad (55)$$

A chemical volatilising from the leaf additionally has to overcome the air boundary layer. An estimate of the conductance between leaf surface and free atmosphere G_a is 0.005 m/s for chemicals with a molecular weight M of 300 g/mol (Thompson 1983). For other molecular weights this value can be adjusted (Trapp 1995):

$$G_a = 0.005\sqrt{\frac{300}{M}} \quad (56)$$

The exchange of water vapour takes place via the stomatal pathway, as the cuticle of the leaf is nearly impermeable for water. Respective conductance G_{wv} was calculated according to Gates (1980):

$$G_{WV} = \frac{E}{P_L - hu \times P_A} \quad (57)$$

G_{WV}: stomatal conductance of water vapour [m/s]
E: amount of water vapour leaving a leaf per unit area and per unit time [kg s^{-1} m^{-2}]
P_L: saturation concentration of water vapour in the leaf at leaf temperature [kg/m^3]
P_A: saturation concentration of water vapour in the atmosphere at air temperature [kg/m^3],
hu: relative air humidity [-]

with

$$E = \frac{Q_W \times \rho_W}{A_L} \quad (58)$$

ρ_W: water density [kg/m^3]
A_L: leaf area [m^2]

P_L is assumed to be approximately equal to P_A. Temperature dependent values for P_A are tabulated, or they can be calculated from the empirical Magnus equation (Möller 1973), as done automatically in the program PlantX (Trapp et al. 1994) and optionally in the Plant module of CemoS1:

$$P_A = \frac{E_W}{461 \times T} \quad (59)$$

E_W: saturation vapour pressure of water [Pa]
T: temperature [K]

with

$$E_W = 610.7 \times 10^{\frac{7.5 \times (T - 273.15)}{273 + (T - 273.15)}} \quad (60)$$

From stomatal conductance of water vapour G_{WV}, the conductance of any substance G_S can be approximated by the ratio of molecular weights M (M of water = 18 g/mol):

$$G_S = G_{WV}\sqrt{\frac{18}{M}} \qquad (61)$$

Even when air concentrations are very low, leaves can be heavily contaminated, as the partition coefficient between leaves and air K_{LA} may be very high (resulting in a high concentration gradient):

$$K_{LA} = \frac{K_{LW}}{K_{AW}} \qquad (62)$$

K_{LW}: partition coefficient between leaves and water [-]

The K_{LW} was determined analogously to Eq. (47) by using leaf water and lipid content, and leaf density. For the exponent b, e.g. 0.95 is reported by Briggs et al. (1983) for barley shoots and b = 0.97 for isolated citrus cuticles (Kerler and Schönherr 1988).

Finally, the diffusive net flux between leaves and atmosphere (gaseous dry deposition) N_A can be deduced from Fick's 1st law of diffusion (according to Trapp and Matthies 1995):

$$N_A = A_L \times G \times \left(C_A - \frac{C_L}{K_{LA}}\right) \qquad (63)$$

N_A: diffusive net flux between leaves and atmosphere [mg/s]
C_A: contaminant concentration in air [mg/m^3]
C_L: contaminant concentration in leaves [mg/m^3]

3.1.2.7.4 Equations for the uptake in above-ground plant parts

For the calculation of leaf concentrations, a generic model was considered that treats the aerial plant part as one single compartment. Respective procedure was developed by Trapp and Matthies (1995) who set up the mass balance as follows:

Change of chemical mass in the aerial plant parts =
+ flux from soil via xylem to the shoots N_{XY} ± gaseous flux from/to air N_A
– metabolism – dilution by growth

$$\frac{dm_L}{dt} = V_L \frac{dC_L}{dt} = Q_W \times TSCF \times C_W + A_L \times G \times \left(C_A - \frac{C_L}{K_{LA}}\right) - \lambda_E \times C_L \times V_L - \lambda_G \times C_L \times V_L \qquad (64)$$

where m_L is the chemical mass in aerial plant parts [mg] and λ_E and λ_G [1/s] denote first-order rate constants for metabolism and growth, respectively. Assuming constant conditions, an analytical solution can be obtained. Eq.(64) may be rearranged to:

$$\frac{dC_L}{dt} + \left[\frac{A_L \times G}{K_{LA} \times V_L} + \lambda_E + \lambda_G\right] \times C_L = \frac{Q_W \times TSCF \times C_W}{V_L} + \frac{A_L \times G \times C_A}{V_L} \qquad (65)$$

With C_A and C_W being constant, a linear differential equation of first order is yielded:

$$\frac{dC_L}{dt} + a \times C_L = b \qquad (66)$$

a: sink term (left side of Eq. 65, term in squared brackets)
b: source term (right side of Eq. 65)

The analytical solution of Eq. (66) is given as follows (Trapp and Matthies 1995):

$$C_L(t) = C_L(0) \cdot e^{-a \cdot t} + \frac{b}{a} \cdot \left(1 - e^{-a \cdot t}\right) \qquad (67)$$

$C_L(0)$: initial leaf concentration [mg/m^3]

The steady state concentration ($t \rightarrow \infty$, $dC_L/dt \rightarrow 0$) is:

$$C_L(\infty) = \frac{b}{a} \qquad (68)$$

3.1.2.7.5 Model for the plant uptake of dissociating compounds

For the uptake of dissociating compounds into roots and subsequent translocation to shoots, the following processes might be relevant: chemical accumulation due to the electrical potential at the membrane (Nernst effect), the ion trap mechanism, lipophilic sorption, dilution by growth and advection in the vascular system. The approach presented in this section was taken from Trapp (2000, 2004).

Soil-solution-cell system

A model for the soil-solution-cell system is proposed by Trapp (2000), consisting of the following units that are assumed to be relevant for the exchange of dissociating compounds: a) soil and soil solution, b) apoplast, c) cell wall and plasmalemma, d) cytoplasm, e) tonoplast, f) vacuole (see Fig. 6). The plasmalemma and the tonoplast are biomembranes, they are crossed faster by a neutral molecule than by an ion.

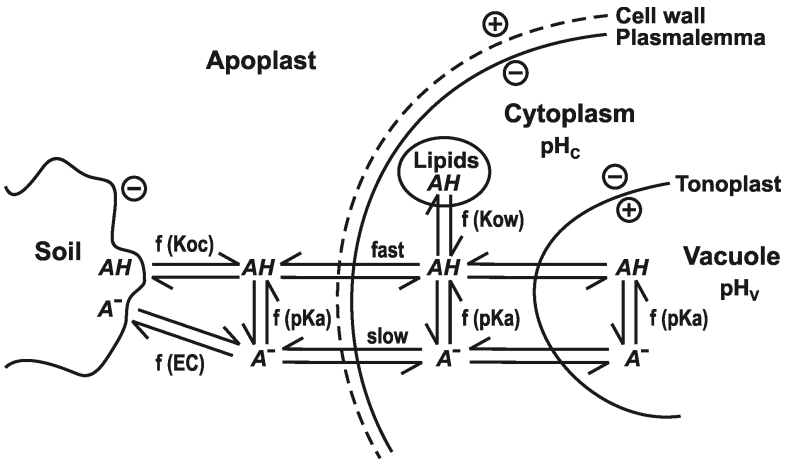


***Fig. 6**: Molecule species in the soil-solution-cell system (for weak acids).* AH*: neutral molecule;* A-*: dissociated anion; f( ): function of;* EC*: exchange capacity of the soil;* K_{OC} *and* pK_a*: given in section 3.1.2.1 and 3.1.2.2, respectively; plus and minus symbols: positive and negative membrane potential;* pH_C, pH_V*: pH of cytoplasm and vacuole (according to Trapp 2000).*

Weak electrolytes

Under physiologically relevant conditions, molecules of weak electrolytes exist in neutral and ionic form or as a complex (Trapp 2004), whereas the latter was not considered in the present study. The activity ratio K_D between the neutral [*neutral*] and ionic species [*ion*] is described by the Henderson-Hasselbalch equation (e.g. Trapp and Matthies 1998):

$$K_D = \frac{[ion]}{[neutral]} = 10^{i(pH-pKa)} \qquad (69) \qquad i = 1 \text{ for acids and } -1 \text{ for bases}$$

The fractions f_n and f_d of the neutral species and ionised species, respectively, at a given pH is:

$$f_n = \frac{1}{1+K_D} \qquad (70) \qquad f_d = 1 - f_n \qquad (71)$$

The molecule species can exist in the following forms:

- neutral fraction: sorbed to soil, dissolved in soil solution, dissolved in cytoplasma or vacuole, or sorbed to cell lipids
- dissociated fraction: same states as for the neutral fraction, except that lipohpilic sorption is usually not relevant

The ratio between the different fractions is determined by the electrochemical conditions (see Fig. 6). The (measurable) total concentration C_t of a compound in each compartment is the sum of at least three different molecule species: 1) the "free" (dissolved) neutral molecule with activity α_{nf}, 2) the sorbed neutral molecule with concentration C_{ns} and 3) the free dissociated molecule with activity α_{df}. The species are related by the partition and the dissociation constant:

$$C_{ns} \overset{K_n}{\Longleftrightarrow} \alpha_{nf} \overset{K_D}{\Longleftrightarrow} \alpha_{df}$$

K_n: empirical partition coefficient between pure aqueous and pure liquid phase of the neutral molecule [-]

The activities are found from

$$\alpha_{nf} = f_{nf} \times C_t \quad (72)$$

f_{nf}: fraction of the neutral free (not sorbed) species

$$\alpha_{df} = f_{df} \times C_t = K_D \times f_{nf} \times C_t \quad (73)$$

f_{df}: fraction of the dissociated free species

where

$$f_{nf} = \frac{1}{\frac{W}{\gamma_n} + L \times K_n + \frac{K_D \times W}{\gamma_d}} \quad (74)$$

W: water content [g/g]
L: lipid content [g/g]
γ_n: activity coefficient of the non-electrolyte [-]
γ_d: activity coefficient of the electrolyte [-]

with

$$K_n = c \times K_{OW}^b \quad (75)$$

c, b: empirical constants to correct differences between plant lipids and octanol [-], c corresponds to a in Eq (47), b is chosen specific to the considered plant tissue

and $$f_{df} = 1 - f_{nf} \quad (76)$$

Actually, K_n in Eq. (75) was determined from sorption experiments between water and macerated roots (Briggs et al. 1982). Ionic strength of water is likely to be negligible, giving an activity coefficient near one. Inside cells, the ionic strength is between 0.3 and 0.5 moles, and γ_n differs from one. Therefore, Eq. (75) has to be multiplied with γ_n (Trapp 2004). Thus, γ_n in Eq. (74) is omitted and the obtained expression $W + L \times K_n$ is analogue to Eq. (47).

The ion activity coefficient γ_d can be calculated with the modified Debye-Hückel equation. Several approximations exist, among them the Davies equation (Stumm and Morgan 1996):

$$\log \gamma_d = A \times z^2 \left(\frac{\sqrt{IS}}{1 + \sqrt{IS}} - 0.2 \times IS \right) \quad (77)$$

IS: ionic strength [M]
A_γ[-]: correction factor depending on ambient pressure and temperature (A = 0.5 for 15–20°C, 1 atm)
z [-]: valency of the ion (for a monovalent acid, z = -1)

Eq. (77) is valid for $IS \leq 0.5$ M; for plant saps, $IS \approx 0.5$ M (0.3-0.5 M) can be assumed (Trapp 2000).

Relevant processes

The flux of non-electrolytes across a semi-permeable membrane is described by Fick's 1st law of diffusion. For electrically charged molecules, the electrochemical potential at the membrane is the driving force of diffusion and the flux across the membrane is described by the Nernst-Planck equation (see Trapp 2000 for details). When the electrical potential gradient at the membrane is constant, the net current is zero and each ion flux is at steady state. In this case, a suitable analytical solution for the flux of the ion is (Briggs et al. 1961, see Trapp 2000 for additional information):

$$J = P \frac{N}{e^N - 1} \left[\alpha_o - \alpha_i \times e^N \right] \quad (78)$$

J: unit flux [kg m^{-1} s^{-1}]
P: permeability [m/s]
N: Nernst coefficient [-]
α_i, α_o: ion activity on the inside i, outside o of the membrane [-]

with

$$N = \frac{z \times E \times F}{R \times T} \quad (79)$$

E: membrane potential [V]
F: Faraday constant, F = 96 485.3415 [C/mol]
R: universal gas constant, R = 8.314 [J mol^{-1} K^{-1}]
T: temperature [K]

Only the free fractions of the molecule take part at the exchange processes. The total flux of the compound (neutral, free molecule and free ion) across the membrane from outside, *o*, to the inside, *i*, is the sum of both fluxes:

$$J = P_d \frac{N}{e^N - 1}\left[f_{dfo}C_o - f_{dfi}C_i \times e^N\right] + P_n\left[f_{nfo}C_o - f_{nfi}C_i\right] \quad (80)$$

P_d, P_n: permeability, dissociated and neutral species [m/s]

Under steady-state conditions, the flux is constant, and the concentration ratio between inside and outside is:

$$\frac{C_i}{C_o} = \frac{f_{nfo}P_n + f_{dfo}P_d \times N/\left(e^N - 1\right)}{f_{nfi}P_n + f_{dfi}P_d \times e^N \times N/\left(e^N - 1\right)} = K_{io} \quad (81)$$

K_{io}: equilibrium partition coefficient between the concentration inside and outside the membrane [-]

Permeabilities

Before a chemical can enter the cytoplasm, it must cross the cell wall and the plasmalemma. The cell wall may be considered as an unstirred aqueous layer with polysaccharides providing additional resistance. The diffusion coefficient was assumed to be somewhat lower than in pure water, i.e. about 10^{-10} m^2/s (Schönherr and Riederer 1989). The thickness of the cell wall is about 0.4 μm (Boersma et al. 1988). Accordingly, the permeability of the cell P_W is 2.5 x 10^{-4} m/s and was considered for all compounds. The permeability of biomemebranes P_M for neutral organic compounds is positively correlated to compound lipophilicity. Based upon a study from Collander (1954, permeation of 70 compounds through *Nitella* cell membranes) and other data, Grayson and Kleier (1990) and Hsu and Kleier (1996) recommend the following regression:

$$\log P_M = 1.20 \log K_{OW} - 7.50 \quad (82)$$

For the permeability of the tonoplast, the cell wall resistance is omitted. The overall permeability from external solution into the cell P_C is the sum of the resistances of cell wall and plasmalemma membrane:

$$P_C = \frac{1}{1/P_W + 1/P_M} \quad (83)$$

Kleier (1988) state for a regression similar to Eq. (82) that assumptions are also valid for ions, but with a log K_{OW} reduced by 3.5 log units ($corr_{P,ion}$). Similarly, Briggs et al. (1987) report log K_{OW} measurements of ions which were on average 3.24 log units smaller (n = 4) than those of the corresponding neutral molecules. Accordingly, P_M of the ion is 15849 times lower than P_M of the neutral molecule. If a chemical is neutral outside and dissociated inside the cell, it can be trapped. This process is named “ion trap” (Briggs et al. 1987).
There are indications that the log K_{OW} is not a good predictor for the membrane permeability of very lipophilic compounds so that Eq. (82) may underestimate the permeability for ions (see Trapp 2000 for details). To account for this aspect, the minimum value for organic ions is taken to be P_{min} = 10^{-10} m/s, a value that is consistent with the permeability ratios found by Briggs et al. (1987).

Distribution between cytoplasm and vacuole

A pre-study with a data set of chemicals (including acids, bases and neutral compounds) revealed that equilibrium is reached quickly for most compounds and a time period of 12 days (Trapp 2000). Thus, to simplify the modelling, immediate equilibrium between cytoplasm and vacuole was assumed for all chemicals. Although the vacuole may accumulate the major portion of a chemical, it is not taking part in the transport processes in the symplast (Sitte et al. 1991). Therefore, the only change in the flux equation is that the mobile fractions in the cytoplasm need to be recalculated for the cell:

$$f_{Cell} = f_{Cytoplasm} \times \frac{C_C}{C_C + C_V} = f_{Cytoplasm} \times \frac{1}{V_C + K_{VC} \times V_V} \quad (84)$$

C_C, C_V: concentration in cytoplasm, vacuole [mg/m^3]
V_C, V_V: volume fractions of cytoplasm and vacuole [-] (0.1 and 0.9, Trapp 2000)
$K_{VC} = C_V/C_C$ in equilibrium (Eq. 81)

Equilibrium approach

Eq. (80) can be rewritten for the exchange between solution and roots to give the mass balance

$$\frac{dm_R}{dt} = E_{SR}C_{SW} - E_{RS}C_R \qquad (85)$$

C_{SW}: concentration in external (soil) solution [mg/m^3]

and for the xylem

$$\frac{dm_X}{dt} = E_{RX}C_R - E_{XR}C_X \qquad (86)$$

where *S*, *R* and *X* are indices for external solution, root and xylem sap, E_{ij} are exchange terms [m^3/s]:

$$E_{SR} = A_R\left\{f_{nfS}P_{nC} + f_{dfS}P_{dC}\,N/\left(e^N - 1\right)\right\} \qquad (87)$$

A_R: root surface area [m^2]
N: from Eq. (79)

$$E_{RS} = A_R\left\{f_{nfR}P_{nC} + f_{dfR}P_{dC}\,e^N N/\left(e^N - 1\right)\right\} \qquad (88)$$

$$E_{RX} = A_X\left\{f_{nfR}P_{nC} + f_{dfR}P_{dC}\,e^N N/\left(e^N - 1\right)\right\} \qquad (89)$$

A_X: xylem surface area [m^2]
$A_X = A_R/5$ is assumed (Boersma et al. 1988)

$$E_{XR} = A_X\left\{f_{nfX}P_{nC} + f_{dfX}P_{dC}\,N/\left(e^N - 1\right)\right\} \qquad (90)$$

The equilibrium given in Eq. (81) can also be expressed in the form

$$K_{RS} = \frac{E_{SR}}{E_{RS}} \qquad (91) \qquad \text{and} \qquad K_{XS} = K_{RS} \times \frac{E_{RX}}{E_{XR}} \qquad (92)$$

Detailed root model – calculation of K_{RW} and TSCF

Within the root, three compartments were considered: the apparent free space, the root cortex and the central cylinder. In the root cortex, cell walls between the cells are porous, and the chemical can move freely from solution to the interior before it reaches the endodermis. This area where free solute movement occurs is called “apparent free space” (Mc Farlane 1995). It occupies between 8% and 25% of the root volume (Sitte et al. 1991). The model assumes 20% of the water of the root to be in the apparent free space (Trapp 2000). The chemical concentration in this free space is the same as in the external solution.
Uptake of water and compounds occurs mainly via root hairs that are located closely behind the tip of the root (5-50 mm; Sitte et al. 1991, Börner 1995). The xylem sap flows in the central cylinder, which is separated from the root cortex and the apoplast by the endodermis. It can be assumed that the endodermis in its primary state is still permeable for water and solutes (see Trapp 2000 for more details). Accordingly, the xylem was separated in two distinct compartments: a) the portion of the root with secondary and tertiary endodermis, denoted *s* (*s* = 90%) and b) the root tip (1 – *s*). The uptake of water and solutes was limited to the root tip. In addition, the apoplastic pathway was considered by specifying a portion ε of the translocation stream Q_X with solute concentration C_S that directly enters the xylem (ε = 5%, according to Trapp 2000). The xylem volume V_X was supposed to be 0.0233 times the total root volume V_R (Boersma et al. 1988).

For the modelling of dynamic uptake into roots, dilution by growth, first-order sink terms and exchange with the xylem have to be accounted for:

$$\frac{dC_R}{dt} = \frac{E_{SR}C_{SW} - E_{RS}C_R + E_{XR}C_X - E_{RX}C_R}{V_{RR}} - kC_R \qquad (93)$$

V_{RR}: root volume without the central cylinder [m^3], $V_{RR} = V_R - V_Z$
k: sum of first-order rate constants (dilution by exponential growth plus sinks, e.g. metabolism) [1/s]

$$\frac{dC_X}{dt} = \frac{(1-s)E_{RX}C_R - (1-s)E_{XR}C_X + \varepsilon \times Q_X C_{SW} - Q_X C_X}{V_X} - kC_X \qquad (94)$$

Q_X: translocation stream (Q_X = transpiration stream Q_W) [m^3/s]
V_X: xylem volume [m^3]

The transpiration stream enters the upper central cylinder (index *Z*) with the chemical concentration C_X. The chemical can either sorb or flow upwards. The mass balance is given by:

$$\frac{dC_Z}{dt} = \frac{Q_X (C_X - f_{fZ} C_Z)}{V_Z} - kC_Z \quad (95)$$

f_{fZ}: free mobile fraction in the central cylinder [-]
V_Z: volume of central cylinder [m3], $V_Z = 0.1 V_R$ *(Trapp 2000)*

The chemical may be retained in the cells (with partition coefficient K_{RX}) or sorb to the lipophilic material that surrounds the xylem vessels and the cell walls in the endodermis with partition coefficient K_{nZ}. Assuming instant equilibrium gives

$$f_{fZ} = \frac{1}{K_{RX} + K_{nZ}} \quad (96)$$

Only the neutral fraction in the xylem f_{nfX} sorbs. Therefore,

$$K_{nZ} = f_{nfX} \times L_Z \times c \times K_{OW}^{1.0} \quad (97)$$

f_{nfX}: neutral fraction in the xylem [-], calculated according to Eq. (70) (xylem pH of 5.5, Briggs et al. 1987*)*

The amount (L_Z) and composition of the material which forms the incrustations of the central cylinder varies with species and age (Zeier at al. 1999). L_Z = 5% was assumed for the modelling (Trapp 2000). Data for sorption were not available but probably correspond to those for cutin (the main component of the cuticle) which has nearly the same sorption capacity as octanol (Schönherr and Riederer 1989).

The equations for the dynamic uptake were solved analytically for steady state. The solution scheme and steady-state solutions for Eq. (93) to (95) are indicated in Tab. 1 (Trapp S and co-workers, Danish Technical University, Copenhagen, Denmark; personal communication, unpublished FORTRAN code). The concentration of the xylem sap when it leaves the central cylinder (i.e. the central cylinder solution) is given by:

$$C_{ZS} = f_{fZ} \times C_Z \quad (98)$$

The transpiration stream concentration factor is calculated as:

$$TSCF = \frac{C_{ZS}}{C_{SW}} \quad (99)$$

Finally, the partition coefficient between root and soil solution is determined as a function of the three considered root compartments:

$$K_{RW} = \frac{C_{Root}}{C_{SW}} = \left[\frac{C_R \times (f_Z - 1) + C_Z \times f_Z + f_{AFS} \times C_{SW}}{C_{SW}} \right] \times \frac{\rho_R}{\rho_W} \quad (100)$$

The total root concentration C_{Root} is the sum of the contributions from the root cortex including xylem (C_R x (f_z – 1)), the central cylinder (C_Z x f_Z) and the apparent free space (C_{SW} x f_{AFS}). In the latter, the concentration corresponds to soil solution concentration, actually.

Tab. 1*: Analytical steady state solutions for Eq. (93) to (95) after substitution. i): Eq. (93), ii): Eq. (94), iii): Eq. (95). According to Trapp S and co-workers (personal communication).*

Substitution	**Inflow rates I [mg m^{-3} s^{-1}]**	**Rate constants a [1/s]**	
i) $\frac{dC_R}{dt} = I_1 + C_R a_{11} + C_X a_{12}$	$I_1 = C_{SW} \frac{E_{SR}}{V_{RR}}$	$a_{11} = -\frac{E_{RS}}{V_{RR}} - \frac{E_{RX}}{V_{RR}} - k$	$a_{12} = \frac{E_{XR}}{V_{RR}}$
ii) $\frac{dC_X}{dt} = I_2 + C_R a_{21} + C_X a_{22}$	$I_2 = C_{SW} \frac{\varepsilon Q_X}{V_X}$	$a_{21} = \frac{(1-s) E_{RX}}{V_X}$	$a_{22} = -\frac{(1-s) E_{XR}}{V_X} - \frac{Q_X}{V_X} - k$
iii) $\frac{dC_Z}{dt} = I_3 + C_Z a_{33}$	$I_3 = C_X \frac{Q_X}{V_Z}$	$a_{33} = -\frac{f_{fz} \times Q_X}{V_X} - k$	
Steady state solutions	i) $C_R = \frac{I_1}{a_{12}\, a_{21}/a_{22} - a_{11}}$	ii) $C_X = -\frac{a_{21}}{a_{22}} - C_R \frac{I_2}{a_{22}}$	iii) $C_Z = -\frac{I_2}{a_{33}}$

3.1.3 Considered compounds and their physicochemical properties

3.1.3.1 PCB congeners

The fate of a fresh Aroclor 1016 soil contamination (unaltered composition) was generically modelled in this study. This lowly chlorinated mixture has widely been applied in the past (Part III, section 3.5). Unfortunately, data that allow a quantification of the biodegradation process with strain F113L::1180 is available only for a part of PCB congeners present in Aroclor 1016. Accordingly, two groups of PCB congeners were considered for the modelling (Tab. 2):

1) **Group I**: PCB congeners that were metabolised by strain F113L::1180 (Part III experiments)
2) **Group II**: approximated total compound inventory of (fresh) Aroclor 1016

Modelling of Group I corresponds to an estimation specific to those compounds that are involved in the bioprocess (as known to date). Results for Group II will yield a worst case approximation of biodegradation performance (assuming all PCB congeners to be recalcitrant except for PCBs measured positively in Part III).

The modelling was performed on a congener by congener basis, i.e. each PCB congener included in the groups was modelled separately. Subsequent summation yielded group specific results for every calculated time step. Initial soil concentrations of 39 mg/kg (Group I) and 98 mg/kg (Group II) were chosen (best estimate, based upon congener specific weight fractions in Tab. 2 and considering 100 mg/kg of Aroclor 1016). Group II includes all PCB congeners shown to be degradable with strain F113L::1180 (i.e. Group I) and additional congeners with weight percentages ≥ 0.5%. Making up about 98% of Aroclor 1016 in total (Tab. 2), Group II was assumed to be representative for this mixture.

***Tab. 2**: Weight % of PCB congeners in Aroclor 1016 (IUPAC-No.). Group 1: PCBs that were degraded in the degradation experiments, Group 2: representative for Aroclor 1016 in total. Minimum and maximum values were taken from Albro and Parker (1979) and Frame et al. (1996), mv: mean value*.

Group 1				Group 2											
PCB	**min**	**max**	**mv**	**PCB**	**min**	**max**	**mv**	**PCB**	**min**	**max**	**mv**	**PCB**	**min**	**max**	**mv**
1	0.52	0.59	0.55	**1**	0.52	0.59	0.55	**22**	2.82	3.51	3.17	**47**	1.24	2.06	1.65
2	0.02	0.07	0.05	**2**	0.02	0.07	0.05	**25**	0.72	1.80	1.26	**48**	1.59	1.61	1.60
3	0.15	0.74	0.45	**3**	0.15	0.74	0.45	**26**	0.63	1.59	1.11	**49**	3.35	3.98	3.66
4	3.62	3.81	3.71	**4**	3.62	3.81	3.71	**28**	8.50	14.60	11.55	**52**	4.61	4.97	4.79
5	0.15	0.17	0.16	**5**	0.15	0.17	0.16	**31**	4.76	9.32	7.04	**53**	0.94	1.22	1.08
16	3.53	3.88	3.70	**6**	1.20	1.69	1.44	**32**	2.33	2.37	2.35	**64**	1.84	1.87	1.85
17	3.17	3.98	3.58	**7**	0.29	1.01	0.65	**33**	3.11	6.21	4.66	**69**	0.004	0.005	0.004
18	10.75	10.96	10.85	**8**	8.29	9.00	8.64	**34**	0.03	0.03	0.03	**70**	0.00	0.59	0.30
20	0.88	4.02	2.45	**15**	0.93	2.49	1.71	**37**	1.01	1.91	1.46	**71**	1.16	1.17	1.17
31	4.76	9.32	7.04	**16**	3.53	3.88	3.70	**39**	0	1.09	0.54	**74**	0.33	1.54	0.93
34	0.03	0.03	0.03	**17**	3.17	3.98	3.58	**41**	0.76	2.29	1.52	**75**	0.06	2.74	1.40
41	0.76	2.29	1.52	**18**	10.75	10.96	10.85	**42**	1.59	1.59	1.59	**101**	0	0.04	0.02
52	4.61	4.97	4.79	**19**	0.99	1.09	1.04	**44**	1.30	4.48	2.89				
101	0	0.04	0.02	**20**	0.88	4.02	2.45	**45**	1.14	1.23	1.19				
Sum	32.94	44.87	38.90	**Sum (Group 2 in total)**					78.31	117.32	97.81				

3.1.3.2 CBA formation

Full (equimolar) conversion of PCB into the corresponding CBA was considered as a worst case scenario for biodegradation. Preferential ring fission at the non- or lower chlorinated ring was presumed for the breakdown of PCB congeners (following Furukawa 1978a and 1978b). In cases where two alternative metabolites were possible (e.g. degradation of a PCB with one chlorine at each ring), the more water soluble CBA was accounted for (worst case assumption). Table 3 presents PCBs that were degradable in laboratory experiments with strain F113L::1180 (Part III) and corresponding CBAs chosen for the modelling. In the considered experiments, CBA concentrations were not measured due to analytical constraints (Part III).

***Tab. 3**: PCB congeners and corresponding CBAs.*

PCB [IUPAC-No.]	Corresponding CBA	PCB [IUPAC-No.]	Corresponding CBA
1	2-CBA	18	2,5-CBA
2	3-CBA	20	2,3-CBA
3	4-CBA	31	2,5-CBA
4	2-CBA	34	3,5-CBA
5	2,3-CBA	41	2,3,4-CBA
16	2,3-CBA	52	2,5-CBA
17	2,4-CBA	101	2,4,5-CBA

3.1.3.3 Physicochemical properties

The methodology to derive internally consistent physicochemical properties for PCBs (Part III) was also adopted for CBAs. Respective data for PCBs and CBAs are given in Tab A1 to A3 in Appendix A (for all 209 PCB congeners and all 19 possible CBAs). Literature data and adjusted properties are indicated there, whereas adjusted data and evaluated ranges were used as input parameters for the modelling. Physicochemical data are rarely reported for CBAs. Thus, many properties were estimated with the program EPI Suite 3.10 (US EPA 2003, Part II). This program approximates physicochemical properties from molecule structures (such as hydroxyl radicals, specific molecule groups, bonds, etc.), using a variety of methods. High measurement and estimation uncertainties can be seen (especially for vapour pressures, Tab. A3). Information on the temperature dependence of physicochemical properties of CBAs (e.g. internal energy changes) were not found in the literature (the evaluated data refer to a temperature of 25°C).

For a large number of CBAs, no measured or estimated dissociation constant pK_a are reported. In these cases, pK_a-values were estimated from structural features as described in the following. Hammett (1940) investigated the effect of substituents on the standard free energy change of carboxyl group dissociation $\Delta_r G^0$. He recognised that this effect (for constituents in *meta* or *para* position) could be expressed as the sum of $\Delta_r G_H^0$ (free energy change of unsubstituted compound dissociation) and contributions of substituents $\Delta_r G_j^0$:

$$\Delta_r G^0 = \Delta_r G_H^0 + \sum_j \Delta_r G_j^0 \qquad (101)$$

To express the effect of substituent *j* on the *pKa*, Hammett introduced a constant σ_j that is defined as:

$$\sigma_j = \frac{-\Delta_r G_j^0}{2.303 \cdot RT} \qquad (102)$$

R: universal gas constant, $R = 8.314$ J mol^{-1} K^{-1}
T: temperature [K]

Since $\Delta_r G^0 = -2.303\, RT \log K_a$, Eq. (101) can be written in terms of acidity constants:

$$\log \frac{K_a}{K_{aH}} = \sum_j \sigma_j \quad \text{or} \quad pK_a = pK_{aH} - \sum_j \sigma_j \qquad (103)$$

pK_{aH}: acidity constant of the unsubstituted organic acid [-]

A set of $\sigma_{j,meta}$ and $\sigma_{j,para}$ values is given by Dean (1985) and Shorter (1994 and 1997) for some common substituent groups. For chlorine as a substiuent in benzoic acid, values are $\sigma_{Cl,meta} = 0.37$ and $\sigma_{Cl,para} = 0.22$. Because of proximity effects that are difficult to be separated from electronic factors, no generally applicable σ_j values can be derived for *ortho* substitution. Proximity effects arise from the influence of substituents that are physically close to the acid or base function under consideration (interactions of intramolecular hydrogen bonding and steric effects, e.g. Anslyn and Dougherty 2006). Instead, for *ortho* substitution, apparent $\sigma_{j,ortho}$ values can be determined for a specific type of reaction. This was done for the dissociation of CBA, i.e. $\sigma_{Cl,ortho}$ was calculated from pK_a reported for *ortho* substituted compounds (Tab. 4). The average of calculated values (i.e. $\sigma_{Cl,ortho} = 1.28$) was used to estimate pK_a according to Eq. (103).

***Tab. 4**: Calculation of $\sigma_{Cl,ortho}$ for CBAs. o: ortho; m: meta; p: para; a: Bykova et al. 1970; b: Serjeant and Dempsey 1979; c: Weber 1972 (approximated data).*

Compound	Chlorine substitution	Calculation pK_{aH} (benzoic acid) = 4.19 $\sigma_{Cl,meta}$ = 0.37, $\sigma_{Cl,para}$ = 0.22	pK_a reported [-]		$\sigma_{Cl,ortho}$ calculated [-]
2-CBA	**o**	$\sigma_{Cl,ortho} = pK_{aH} - pK_a$	2.89	a	1.3
2,3-CBA	**o,m**	$\sigma_{Cl,ortho} = pK_{aH} - pK_a - \sigma_{Cl,meta}$	2.55	b	1.27
2,4-CBA	**o,p**	$\sigma_{Cl,ortho} = pK_{aH} - pK_a - \sigma_{Cl,para}$	2.68	b	1.29
2,5-CBA	**o,m**	$\sigma_{Cl,ortho} = pK_{aH} - pK_a - \sigma_{Cl,meta}$	2.47	b	1.35
2,6-CBA	**o,o**	$\sigma_{Cl,ortho} = (pK_{aH} - pK_a)/2$	1.59	b	1.3
2,3,6-CBA	**o,m,o**	$\sigma_{Cl,ortho} = (pK_{aH} - pK_a - \sigma_{Cl,meta})/2$	1.50	c	1.16
2,4,6-CBA	**o,p,o**	$\sigma_{Cl,ortho} = (pK_{aH} - pK_a - \sigma_{Cl,para})/2$	1.40	c	1.29

3.1.4 Environmental input parameters

Site characteristics and environmental input parameters that are required for the modelling are subject to considerable uncertainty and might also be temporal and/or spatial variable. This section discusses the derivation of a dataset consisting of best estimate values together with possible ranges and probability density functions (PDF).

3.1.4.1 Source dimensions and location

The modelling was performed for a generic site with a contaminated zone of 45 x 45 m and 1 m thickness, located at a depth of 0.3 m in average (Tab. 5). Two scenarios were investigated for the groundwater pathway: 1) groundwater level (GWL) directly below the source, 2) GWL at a mean depth of 0.5 m below the source bottom.
To account for the uncertainty of the source extension (area and thickness) and depth, lognormal distributions were assumed as recommended by Ott (1995; with a standard deviation of 10% from the mean value selected by default). The groundwater level (second scenario) was presumed to vary between 0.4 and 0.6 m below the source bottom.

***Tab. 5**: Source dimensions and location considered for the modelling (generic site). Best est.: best estimate, St.dev.: standard deviation, GWL: groundwater level.*

Source dimensions and location		Best est.	Mean	St.dev.	Range	Distribution
Source width, x-direction W_X [m]		45	45	4.5		Lognormal
Source width, y-direction W_Y [m]		45	45	4.5		Lognormal
Source thickness d_S [m]		1	1	0.10		Lognormal
Depth to subsurface source L_S [m]		0.30	0.30	0.03	0.2-0.4	Lognormal
Depth from source bottom to GWL d_{GW} [m]	1)	0				
	2)	0.5			0.4-0.6	Uniform

3.1.4.2 Soil properties and aquifer parameters

Soil and aquifer properties considered for the modelling are summarised in Tab. 6, and Appendix C presents additional information. The data on total soil porosity θ_T, volumetric water content θ_{WS} and soil bulk density ρ_S are based upon class average values and a statistical analysis of the soil property database included in the estimation program ROSETTA (Schaap et al. 2001). Respective values and distributions were assumed to be characteristic for sands and loamy sands and were chosen to account for an upper estimate of contaminant mobility in soil (see Appendix C for details on the derivation). The values of θ_T correspond to the values of saturated water content, evaluated for sand and loamy sand (θ_S in Appendix C). Volumetric water content was estimated from residual water content and van Genuchten parameters (ROSETTA) and the infiltration rate (see next section). The data on soil bulk density was evaluated from information contained in the ROSETTA database and average values reported by Ley et al. (1994).
The chosen values and distribution for the fraction of soil organic carbon f_{OC} are characteristic for an aquifer in northern Germany (Boorboor 2004). Respective data were considered for soil, the vadose zone and the aquifer. Although very low, the applied f_{OC} is assumed to be valid as a low estimate among observations reported for lower soil units (Appendix C). The best estimate and value range for

pH_S (soil pH) represent rather low values for soils (US EPA 1996b). A low pH yields a high fraction of dissociated CBA species (Eq. 9), characterised by a high mobility potential for the aqueous pathways.
The applied soil temperature range is based upon air temperatures observed by the German Weather Survey (DWD) for a number of weather stations in south western Germany (annual averages in the years 1961-1990). Soil temperatures were approximated from these observations, accounting for reduced temperature variations in soil. For respective estimation, data on soil and air temperatures measured by the Illinois Climate Network (ICN 2004) were utilised (analogously to Part II, section 3.3.2).The considered soil temperature range is an upper estimate.
Concerning the aquifer parameters, values and distributions on the effective hydraulic conductivity K_f and the hydraulic gradient *i* were taken from Boorboor (2004). The best estimate for effective porosity n_e is given by Boorboor (2004) for the same aquifer. The considered range is reported to be typical for grain sizes of gravels and sands (Langguth and Voigt 1980 and de Marsily 1986, see Appendix C).

Tab. 6*: Soil and aquifer properties. a: soil type specific data (see text for details), b: site Buchholz/Nordheide, northern Germany (Boorboor 2004), c: selected by default, d: estimated mean range (see text for details), e: typical range for gravels and sands (Langguth and Voigt 1980, de Marsily 1986). Loc, Sc, Sh: Weibull parameters (Loc: location, Sc: Scale, Sh: Shape), other abbreviations according to Tab. 5.*

Soil and aquifer properties	Best est.	Mean or Loc	St.dev. or Sc, Sh	Range	Distribution
Total soil porosity θ_T [-] (a)		0.383	0.039	0.26-0.51	Lognormal
Volumetric soil water content θ_{WS} [-] (a)		0.128	0.026	0.06-0.27	Lognormal
Soil bulk density ρ_S [mg/km] (a)		1.64	0.138	1.13-1.965	Lognormal
Fraction soil organic carbon f_{OC} [%] (b)	0.1	0.1	0.19	0.01-0.39	Lognormal
Soil pH pH_S [-] (c)	6			5.75-6.25	Uniform
Soil temperature T_S [°C] (d)	13.5			12-15	Uniform
Effective hydraulic conductivity k_f [m/s] (b)	4.23×10^{-4}	4.23×10^{-4}	3.12×10^{-4}	$(1.29\text{-}1.02) \times 10^{-4}$	Lognormal
Hydraulic gradient *i* [%] (b)	0.15	Loc 0.0364	Sc 0.111, Sh 15	0.125-0.157	Weibull
Effective porosity n_e [-]	0.21 (b)			0.13-0.30 (e)	Uniform

3.1.4.3 Meteorological parameters and related properties

Data on the rain rate q_R (Tab. 3) were obtained from a dataset provided by the German Weather Survey (DWD) that is assumed to be representative for the area of Germany (derivation according to Part II, section 3.3.3). The infiltration rate q_W was estimated from the rain rate according to the methodology of Dörhöfer and Josopait (1980, Part III, section 2.4.2). For respective calculation, a flat area (i.e. no water runoff) and evapo-transpiration levels typical for sand and loamy sand were considered.
Selected air temperatures are in accordance to observed averages for southern Germany (based upon DWD data, see previous section). An air humidity *hu* of 50% was accounted for by default, varying between 25% and 75%. For the wind speed U_{air} , distributions reported by Traup and Kruse (1996) for Söllingen near Karlsruhe, Germany were considered. The best estimate selected for the dispersion factor *Q/C* is recommended by the US EPA (1996b) as a reasonable conservative default value for generic calculations (approximately the 90th percentile value for 29 analysed sites, section 3.1.2.3). In fact, this value was obtained for a site in Los Angeles, CA with a 0.5 acre square source (about 2023 m^2, i.e. similar to the model area considered in this study). The chosen *Q/C* range reflects lower and upper estimations given by the US EPA (1996b) for 0.5 acre sites throughout the U.S.

Tab. 7*: Meteorological parameters and related properties. a: based upon DWD data, b: from the rain rate according to Dörhöfer and Josopait (1980), c: mean annual temperature range, d: Traup and Kruse 1996, e: US EPA 1996b. Abbreviations according to Tab. 5 and 6.*

Meteorological parameters and related properties	Best est.	Mean or Loc	St.dev. or Sc, Sh	Range	Distribution
Rain rate q_R [mm/yr] (a)	800	800	230	400-2450	Lognormal
Infiltration rate q_w [mm/yr] (b)	440	440	126	125-1210	Lognormal
Air temperature T_{Air} [°C]	15			10-15 (c)	Uniform
Air humidity *hu* [-]	0.5			0.25-0.75	Uniform
Wind speed u_{Air} [m/s] (d)	2.9	Loc 0	Sc 3.3, Sh 1.5		Weibull
Dispersion factor *Q/C* [(g m^{-2} s^{-1})/(kg/m^3)] (e)	69			62-100	Uniform

3.1.4.4 Characteristics of the riverine system

A generic scenario was established for a river that is 10 m wide and 1.5 m deep in average, flowing at a velocity of 5 cm/s as best estimate (i.e. moderate velocity). A wide range of potential flow velocities was considered (1-10 cm/s). The chosen Intersection height h_{GR} is varying between 1.5 and 2 m (comparably high estimation). The whole cross sectional area was assumed to be available for mixing (F_{eff} = 1). Uniform distributions were selected by default.

***Tab. 8**: River characteristics and parameters for aquifer-river water mixing (see text for details).*

River characteristics	Best estimate	Range	Distribution
Width of stream channel B_R [m]	10	8-12	Uniform
River depth h_R [m]	1.5	1-2	Uniform
River flow velocity u_R [cm/s]	5	1-10	Uniform
Aquifer-river intersection height h_{GR} [m]	1.75	1.5-2.0	Uniform

3.1.4.5 Input parameters for the modelling of contaminant plant uptake

The chosen leaf area index *LAI* and the specific leaf area *SLA* (best estimates) are consistent to the findings of Sitte et al. (1991). The latter authors estimate 4 tons of leaves per hectare in a Central European *Quercus-Carpinus* deciduous forest, i.e. 0.4 kg leaves per m^2 area. The same value is obtained from the ratio *LAI* to *SLA*. The value range for *LAI* and *SLA* is approximated for willow trees. Around 3000 $m^3\ yr^{-1}\ ha^{-1}$ can be assumed for typical transpiration rates occurring in the environment and was used by Trapp et al. (2003) for the modelling of contaminant uptake into fruit trees. The average growth of an oak forest with 240 tons of stem per ha is 2.5 tons of stem per year (Sitte et al. 1991), corresponding to a growth rate of 0.01 1/yr. This value is presumed to be rather at the lower end for willows, which are known to grow comparatively fast.

***Tab. 9**: Plant properties. Best est.: best estimate, a: Schaeffer et al. 2000, b: Schaff et al. 2003, c: Trapp et al. 2003, d: see text, e: based upon Sitte et al. 1991, f: typical value, g: default, h: Trapp and Matthies 1998, i: reported range (see text), j: Trapp and Matthies 1995 , k: Briggs et al. 1982, l: Briggs et al. 1983, m: Trapp 2000, n: Boersma et al. 1988, o: Rubery and Sheldrake 1973, p: Briggs et al. 1987, q: Larcher 1995, r: Schönherr and Riederer 1989, s: Kleier 1988, t: Stumm and Morgan 1996. pH vacuole, pH xylem sap, E_C and E_V: the best estimates are upper approximations (Trapp 2000). Uniform distributions were chosen as no information on statistical characteristics were available.*

Plant properties	Best est.	Range	Distribution
Leaf area index *LAI* [m^2 leaf / m^2 field]	2 (a)	2-3.5 (a)	Uniform
Specific leaf area *SLA* [m^2 leaf / kg leaf]	5 (b)	4-6 (b)	Uniform
Transpiration stream Q_W [$m^3\ yr^{-1}\ ha^{-1}$ field]	3000 (c)	2000-4000 (d)	Uniform
Growth rate λ_G [1/yr]	0.01 (e)	0.01-0.05 (d)	Uniform
Density root ρ_R [kg/m^3 wet]	1000 (f)	1000-1200 (g)	Uniform
Density leaf ρ_L [kg/m^3 wet]	500 (f)	400-600 (g)	Uniform
Fraction of roots in soil f_R [g/g dry weight]	0.001 (e)	0.001-0.01 (d)	Uniform
Root water content w_R [g/g]	0.8 (h)	0.8-0.942 (i)	Uniform
Leaf water content w_L [g/g]	0.8 (j)	0.73-0.90 (i)	Uniform
Root lipid content L_R [g/g]	0.03 (j)	0.02 (k) - 0.03 (j)	Uniform
Leaf lipid content L_L [g/g]	0.02 (j)	0.02 (j) - 0.03 (k)	Uniform
Correction exponent *b* for K_{RW} [-]	0.77 (k)	0.75-0.77 (i)	Uniform
Correction exponent *b* for K_{LW} [-]	0.95 (l)	0.95-0.97 (i)	Uniform
Plant properties – Modelling of dissociating compounds			
Fraction of apparent free space on total root volume *AFS* [m^3/m^3]	0.2 (m)	0.08-0.25 (e)	Uniform
Fraction of cytoplasm on total root volume root V_C [m^3/m^3]	0.1 (m)	0.05-0.15 (g)	Uniform
Fraction of secondary and tertiary endodermis in root *s* [m^3/m^3]	0.9 (m)	0.85-0.95 (g)	Uniform
Fraction of xylem area on total root area f_{AX} [m^2/m^2]	0.2 (n)	0.15-0.25 (g)	Uniform
Fraction of xylem volume on total root volume f_{VX} [m^3/m^3]	0.0233 (n)	0.02-0.03 (g)	Uniform
Fraction of central cylinder volume on total root volume f_{VZ} [m^3/m^3]	0.1 (m)	0.05-0.15 (g)	Uniform
pH cytoplasm pH_C [-]	7 (o)	7.0-7.5 (m)	Uniform
pH vacuole pH_V [-]	5.5 (e)	5.25-5.5 (g)	Uniform
pH xylem sap pH_X [-]	5.5 (p)	5.25-5.5 (g)	Uniform
Electrical potential cytoplasm E_C [V]	-0.12 (m)	(-0.12)-(-0.10) (e)	Uniform
Electrical potential vacuole E_V [V]	0.02 (q)	0.01-0.02 (g)	Uniform
Lipid content of central cylinder L_Z [g/g]	0.05 (m)	0.04-0.06 (g)	Uniform
Cell wall diffusion coefficient D_{CW} [m^2/s]	10^{-10} (r)	5×10^{-11} - 5×10^{-10} (g)	Uniform
Thickness of cell wall d_{CW} [m]	4×10^{-7} (n)	9×10^{-8} - 9×10^{-7} (g)	Uniform
Correction (biomembrane permeability for ions) $corr_{P,ion}$ [log units]	3.5 (s)	3.24-3.50 (p,s)	Uniform
Correction factor for activity approximation A_γ [-]	0.5 (t)	0.45-0.55 (g)	Uniform

The selected best estimates for root and leaf density are typically used for plant modelling (e.g. Trapp and Matthies 1998), the value ranges were chosen by default. Sitte et al. (1991) estimate 10 tons of roots per ha (dry weight) for an oak forest, so that the fraction of root in soil is approximately 0.1%. In upper soil areas, root penetration may be more intensively. Thus, 1% was chosen as an upper value.
Water content in root was found to be between 0.8 and 0.942 (0.8 used as typical value by Trapp and Matthies 1998; 0.82 determined by Briggs et al. 1982 for barley roots; 0.85 for bean roots, Trapp and Pussemier 1991; 0.89 for carrots, Wang and Jones 1994; 0.942 for soybeans, Trapp and Matthies 1994). The value of 0.8 was selected as best estimate because the water content in roots of trees might be at the lower end of the reported range. Similarly, Trapp et al. (2001b) consider the value of 0.82 for the modelling of contaminant uptake into oak wood.
For the water content in leaves, 0.727 is reported by Trapp et al. (1994) for soybeans, 0.85 for bean shoots by Trapp and Pussemier (1991). Water contents of 0.8 and 0.9 are considered as typical values by Trapp and Matthies 1995 and Trapp et al. 2001b, respectively. The selected lipid contents in root and leaf also correspond to typical estimates. Concerning the correction exponents *b*, the value of 0.77 was evaluated for mazerated barley roots (Briggs et al. 1982) and 0.75 for cut bean roots and stems (Trapp and Pussemier 1991). b = 0.95 accounts for barley shoots (Briggs et al. 1983) and b = 0.97 for isolated citrus cuticles (Kerler and Schönherr 1988).
The additional parameters required for the modelling of dissociating compounds were taken from Trapp (2000). In most cases, parameter ranges were chosen by default as no information on variability and/or uncertainty was available. This was done in order to theoretically investigate the sensitivity of these properties for plant modelling.

3.2 Exposure modelling and risk analysis for PCBs and metabolites

3.2.1 Studied exposure scenarios

Based on modelled receptor point concentrations in different environmental media, exposure was estimated for generic scenarios. Risks were analysed for human health and for ecological receptors. The following scenarios were considered (Fig. 7):

a) human health:

- ingestion of drinking water (housing scenario)
  - a) leachate ingestion (hypothetical risk)
  - b) groundwater ingestion
- inhalation of outdoor air
  - 1) housing scenario (residential area)
  - 2) sports activity scenario (e.g. recreational area, sports facility)
- dermal contact to/ ingestion of surface water while swimming

b) aquatic ecosystem, exposure of fish to:

- leachate water (hypothetical risk)
- groundwater (hypothetical risk)
- surface water

For the modelling it was assumed that the land use at the contaminated site is restricted to remediation facilities. Ingestion of leachate water for drinking purpose is a hypothetical pathway that was analysed in order to evaluate potential maximum impacts arising from the leaching pathway. The same intention was followed when estimating hypothetical risks for fish species that are exposed to leachate and groundwater.

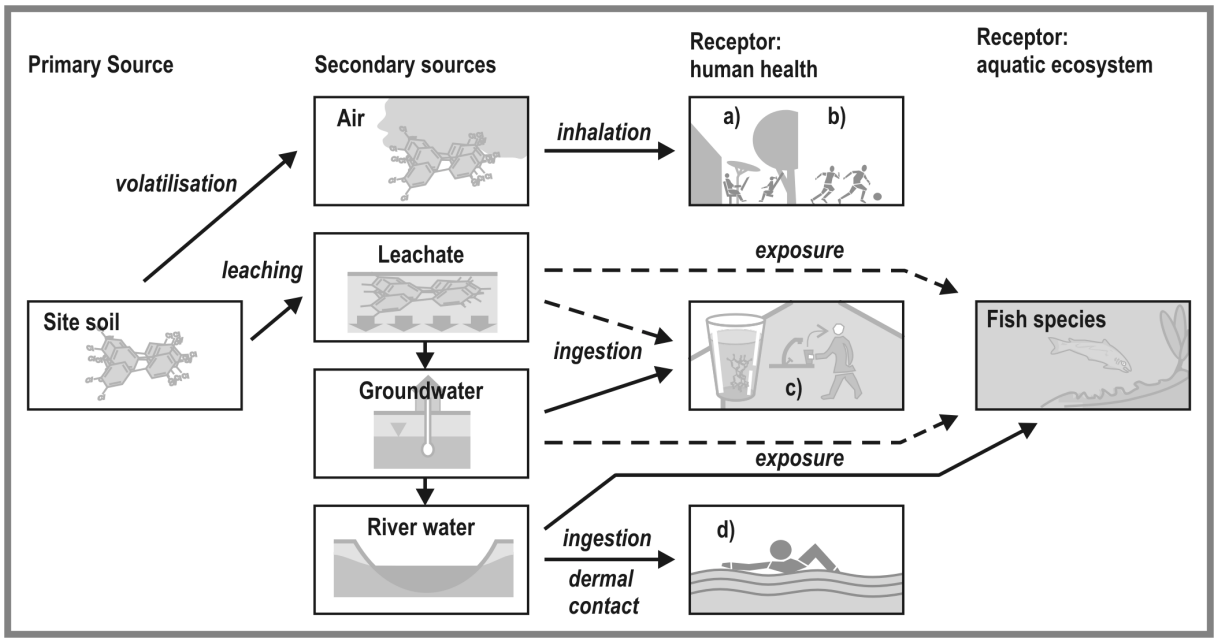


Fig. 7*: Analysed exposure scenarios. a): inhalation outdoors at home, b): inhalation at outdoor activity, c): ingestion of drinking water (housing scenario), d) exposure while swimming. Dashed arrows: hypothetical pathways.*

3.2.2 Human health risk evaluation

PCBs are classified as non-carcinogenic and as probable human carcinogens (e.g. WHO 1993, US HHS 2000, online database IRIS), CBAs are non-carcinogenic compounds (e.g. RAIS online resource). Therefore, both carcinogenic and non-carcinogenic impacts were analysed, using the hazard quotient *HQ* and cancer risk level *RL* (e.g. US EPA 1989, Paustenbach 2002):

$$HQ_{ij} = \frac{ADD_{ij}}{RfD_{ij}} \quad (104)$$

HQ_{ij}: hazard quotient for chemical *i*, exposure route *j* [-]
ADD_{ij}: average daily dose [mg kg^{-1} d^{-1}]
RfD_{ij}: reference dose [mg kg^{-1} d^{-1}]

$$RL_{ij} = ADD_{ij} \times SF_{ij} \quad (105)$$

SF_{ij}: slope factor [(mg kg^{-1} d^{-1})$^{-1}$]
RL_{ij}: cancer risk level for chemical *i*, exposure route *j* [-]

The non-carcinogenic hazard quotient *HQ* assumes that there is a level of exposure (represented by the *RfD*) below which it is unlikely for even sensitive populations to experience adverse health effects. If the exposure exceeds this threshold (i.e. *HQ* > 1), non-cancer effects are expected. As a rule, the greater the value of *HQ* above unity, the higher the level of concern. The level of concern does not increase linearly as the *RfD* is approached or exceeded because *RfD* values do not have equal accuracy or precision and are not based on the same severity of toxic effects (US EPA 1989). Thus, the slopes of the dose-response curve in excess of the *RfD* can range widely depending on the substance.

For carcinogens, risks are estimated as the incremental probability of an individual developing cancer over a lifetime as a result of exposure to the potential carcinogen (i.e. incremental or excess individual lifetime cancer risk, e.g. US EPA 1989, Paustenbach 2002). The slope factor *SF* converts estimated daily intakes averaged over a lifetime of exposure directly to incremental risk of an individual developing cancer. This linear dose-response relationship (Eq. 105) is valid for relatively low intakes (compared to those experienced by test animals), as can be expected for most contaminated sites. If the estimated cancer risk exceeds 0.01, an alternative calculation equation should be applied instead (see US EPA 1989 for details). In many cases, the slope factor is an upper (95th percentile) confidence limit of the probability of response so that the carcinogenic risk estimate corresponds to an upper-bound estimate (US EPA 1989). For some carcinogens, there may be sufficient information on the mechanism of action, so that a modification of the approach above is warranted.

The hazard index *HI* determines the overall potential for non-carcinogenic effects (US EPA 1986b), the total cancer risk level RL_T sums up risk levels specific to the considered chemicals and pathways:

$$HI = \sum_{ij} HQ_{ij} \quad (106)$$

HI: hazard index [-]

$$RL_T = \sum_{ij} RL_{ij} \quad (107)$$

RL_T: total cancer risk level [-]

The hazard index approach assumes that simultaneous sub-threshold exposures to several chemicals could result in an adverse health effect. It also assumes that the magnitude of the adverse effect will be proportional to the sum of the ratios of the sub-threshold exposures to acceptable exposures (US EPA 1989). When the hazard index exceeds unity, there may be concern for potential health effects. While any single chemical with an exposure level greater than the toxicity value will cause the hazard index to exceed unity, for multiple chemical exposures, the hazard index can also exceed unity even if no single chemical exposure exceeds its *RfD*.

Equation (107) is used to estimate the incremental individual lifetime cancer risk for simultaneous exposure to several carcinogens (based on US EPA 1986a and b). This equation represents an approximation of the precise equation for combining risks. The precise methodology accounts for the joint probabilities of the same individual developing cancer as a consequence of exposure to two or more carcinogens. The difference between the precise equation and the approximation described in Eq. (107) is negligible for total cancer risks less than 0.1 (US EPA 1989). Thus, the simple additive equation is appropriate in most cases (see US EPA 1989 for more details).

The average daily dose represents the most common dose measure (Paustenbach 2002). Average daily doses are calculated specific to the considered pathway, e.g. for **drinking water ingestion**:

$$ADD_i = \frac{IR_w \times EF \times ED \times C_{i,w}}{BW \times AT \times 365 \frac{d}{yr}} \qquad (108)$$

IR_W: water ingestion rate [L/d]
EF: exposure frequency [d/yr]
ED: exposure duration [yr]
$C_{i,W}$: concentration of contaminant i in water [mg/L]
BW: body weight [kg]
AT: averaging time [yr]

For the assessment of non-carcinogenic effects of a chemical, *AT* is the time period over which the dose is averaged. When the primary health risk posed by a chemical is cancer, the biological response is usually described in terms of lifetime probabilities (as described above). In this case, lifetime is considered for *AT*. Therefore, for the prediction of cancer risk, the term lifetime average daily dose *LADD* instead of *ADD* is often used in literature (e.g. US EPA 1992a cited by Paustenbach 2002).

Generally, differences are obvious for two exposure groups - children and adults. When exposure is expected throughout childhood and into adult years, age-adjusted factors can be applied to account for specific chemical ingestion or intake rates, body weights and exposure durations. Accordingly, Eq. (108) modifies to (based on US EPA 1991):

$$ADD_i = \frac{IF_{w,adj} \times EF \times C_{i,w}}{AT \times 365 \frac{d}{yr}} \qquad (109)$$

$IF_{W,adj}$: age-adjusted water ingestion factor [L yr d^{-1} kg^{-1}]

with

$$IF_{s,adj} = \frac{IR_{w,c} \times ED_c}{BW_c} + \frac{IR_{w,a} \times ED_a}{BW_a} \qquad (110)$$

In Eq. (110), the indices *c* an *a* denote child and adult, respectively. Other pathways can be calculated similarly, as shown in the following for air inhalation and dermal contact with water (based on EPA 1989).

Air inhalation

$$ADD_i = \frac{IH \times EF \times ET \times ED \times C_{i,A} \times \frac{1}{24}\frac{d}{h}}{BW \times AT \times 365 \frac{d}{yr}} \qquad (111)$$

IH: inhalation rate [m^3/d]
$C_{i,A}$: concentration of contaminant i in air [mg/m^3]
ET: exposure time [h/d]

$$ADD_i = \frac{IF_{air,adj} \times EF \times C_{i,A}}{AT \times 365 \frac{d}{yr}} \qquad (112)$$

$IF_{A,adj}$: age-adjusted air inhalation factor [m^3 yr d^{-1} kg^{-1}]

$$IF_{air,adj} = \frac{IH_c \times ED_c \times ET_c \times \frac{1}{24}\frac{d}{h}}{BW_c} + \frac{IH_a \times ED_a \times ET_c \frac{1}{24}\frac{d}{h}}{BW_a} \qquad (113)$$

Above, time-activity patterns were further specified by applying the exposure time *ET* as an additional factor. E.g. when outdoor air inhalation while playing soccer is considered, *EF* indicates the number of days per year and *ET* the hours per day spent for this activity.

Dermal contact with water

$$ADD_i = \frac{SA \times PC_i \times EF \times ET \times ED \times C_{i,w} \times 10^{-3} \frac{L}{cm^3}}{BW \times AT \times 365 \frac{d}{yr}} \quad (114)$$

SA: exposed skin surface area [cm^2]
PC_i: skin permeability coefficient for chemical i [cm/h]

$$ADD_i = \frac{SFS_{w,adj} \times EF \times C_{i,w} \times 10^{-3} \frac{L}{cm^3}}{AT \times 365 \frac{d}{yr}} \quad (115)$$

$SFS_{S,adj}$: age-adjusted dermal intake factor (dermal contact with water) [cm^3 yr d^{-1} kg^{-1}]

$$SFS_{w,adj} = \frac{SA_c \times PC_i \times ED_c \times ET_c \times \frac{1}{24}\frac{d}{h}}{BW_c} + \frac{SA_a \times PC_i \times ED_a \times ET_a \times \frac{1}{24}\frac{d}{h}}{BW_a} \quad (116)$$

The skin surface area parameter *SA* describes the amount of skin exposed to the contaminated medium. For populations in which both body weight *BW* [kg] and height *H* [m] are known, the skin surface area *SA* [m^2] can be estimated according to US EPA 1997a, based upon a study of Murray and Burmaster (1992):

$$SA = 0.0239 \times H^{0.417} \times BW^{0.517} \quad (117)$$

However, combined body weight and height data for individuals within a population are limited. In most cases, body weight data are readily available. ECETOC (2001) recommends the following equations to approximate skin surface area from body weight alone, with *SA* in [m^2] and *BW* in [kg]:

$$SA = \frac{4 \times BW + 7}{BW + 90} \quad (118)$$ Costeff (1966)

where

$$SA = a \times BW^c \quad (119)$$ Burmaster (1998)

or $\ln SA = \ln a \times c \ln BW$

with ln *a* = -2.2781, *c* = 0.6821 (both genders)
ln *a* = -2.2752, *c* = 0.6868 (males)
ln *a* = -2.2678, *c* = 0.6754 (females)

Equation (118) gives a better estimate of central tendency than Eq. (119), but overestimates *SA* at values exceeding the median. Thus, ECOTOC (2001) recommends the Burmaster (119) equation for single central estimates and the Costeff (118) equation to generate skin surface area distributions for adults. The amount of exposed skin also depends upon the exposure scenario. Parts of the skin may be protected by clothing. Scenario-specific *SA* values can be determined according to the US EPA (1997a and 2001) or ECETOC (2001).

Skin permeability constants PC_i reflect chemical movement across the skin to the *stratum corneum* and into the bloodstream. The dependency of permeability coefficients on lipophilicity and on molecular size of compounds is evident from a number of studies (see US EPA 1992b for details). Kasting et al. (1987) and Potts and Guy (1992) performed statistical analyses of various permeability coefficient data and found the following relationship between octanol-water partition coefficient K_{OW} and molecular weight *M* [g/mol] of a chemical:

$$\ln PC = -2.72 + 0.71 \times \log K_{OW} - 0.0061 \times MW \quad (120)$$

PC: Skin permeability constant [cm/h]

3.2.3 Risk calculation for ecological receptors

Risks for ecological receptors were estimated on a screening level (conservative, base-line estimate) by comparing exposure point concentrations with ecotoxicity values (according to US EPA 1997b):

$$HQ_i = \frac{EEC_i}{NOAEC_i} \qquad (121)$$

HQ_i: hazard quotient for contaminant i [-]
EEC_i: estimated environmental concentration [e.g. mg/L water, mg/kg food]
$NOAEC_i$: no-observed-adverse-effects-concentration [units that match the *EEC*]

In case that multiple contaminants of potential ecological concern are present, it might be appropriate to sum the *HQ* values for receptors that could be simultaneously exposed to contaminants inducing effects by the same toxic mechanism (US EPA 1986b):

$$HI = \sum_i HQ_i \qquad (122)$$

HI: hazard index [-]

A *HI* less than one indicates that the group of contaminants is unlikely to cause adverse ecological effects. A *HQ* or *HI* less than one does not indicate the absence of ecological risk. Rather, it should be interpreted based on the severity of the effect reported (i.e. the effect which the considered NOAEC is related to) and the magnitude of the calculated quotient (US EPA 1997b). Similarly, as discussed above for the *HQ* in human health risk assessment, the level of concern (due to an increasing quotient) does not increase linearly with the *NOAEC* but as a function of the chemical-specific dose-response curve which may has a different characteristic.

The US EPA (1997b) recommends screening level evaluations as a conservative estimate. Results can be used to decide whether ecological threats are negligible or the process should continue to a more detailed ecological risk assessment. If the process continues, the screening-level assessment serves to identify exposure pathways and preliminary contaminants of concern by eliminating those contaminants and exposure pathways that pose negligible risks (see e.g. US EPA 1997b, US EPA 1998b for further information).

3.2.4 Exposure parameters

Tab. 10 shows values and probability density functions that were used as input for the exposure modelling. Details on the derivation of these data and criteria for their choice are discussed in the following subsections. Main sources have been the Exposure Factors Sourcebook for European Populations (with a focus on UK data, ECETOC 2001) and the US EPA Exposure Factors Handbook (US EPA 1997a).

***Tab. 10**: Parameter input for exposure modelling. Best est.: best estimate, St.dev.: standard deviation, (sw): swimming, a: age 15-65+ yr, b: age <1-8 yr, c: age 20-64 yr, d: age 1-10 yr, e: adult and child, f: age 16+ yr, g: age <1-10 yr. See text for details.*

Exposure parameters	Best est.	Mean	St.dev.	Range	Distribution
Short-term IH (high activity), adult $IH_{act,a}$ [m^3/h]	3.2			3.0-3.6	Triangular
Short-term IH (high activity), child $IH_{act,c}$ [m^3/h]	1.9			1.1-2.5	Triangular
Long-term inhalation rate, adult IH_a [m^3/d] (a)	15			11.3-17	Uniform
Long-term inhalation rate, child IH_c [m^3/d] (b)	7.5			4.5-10.0	Uniform
Drinking water ingestion rate, adult $IR_{GW,a}$ [L/d] (c)	1.27	1.27	0.66		Lognormal
Drinking water ingestion rate, child $IR_{GW,c}$ [L/d] (d)	0.70	0.70	0.37		Lognormal
Surface water ingestion rate (sw) IR_{SW} [L/d] (e)	0.05			0.01-0.1	Uniform
Exposure frequency, housing *EF* [d/yr]	337			316-365	Triangular
Exposure time outdoors at home, adult $ET_{out,a}$ [h/d]	2			0.8-2.4	Triangular
Exposure time outdoors at home, child $ET_{out,c}$ [h/d]	3			1.2-3.6	Triangular
Exposure frequency, outdoor activity EF_{act} [d/yr]	270			180-365	Uniform
Exposure time, outdoor activity ET_{act} [h/d] (e)	0.75			0.5-1.0	Uniform
Exposure frequency, swimming EF_{sw} [d/yr] (e)	150			30-180	Uniform
Exposure time, swimming ET_{sw} [h/d] (e)	0.5			0.25-1.0	Uniform
Body weight, adult BW_a [kg] (f)	73.7	73.7	13.1		Lognormal
Body weight, child BW_c [kg] (b)	18.6	18.6	3.1		Lognormal
Body weight, child BW_c [kg] (g)	21.4	21.4	3.86		Lognormal
Averaging time (life time) AT_{canc} [yr]	75			70-78	Uniform

3.2.4.1 Inhalation rates

Inhalation rates (also referred to as ventilation rates) vary depending upon age, gender, weight, health status and level of activity (e.g. Paustenbach 2002, ECETOC 2001). Tab. 11 shows mean short-term and long-term inhalation rates reported by Layton (1993) and recommended by US EPA (1997a) and ECETOC (2001).
The short-term data are supposed to be reasonably representative for people of any nationality. For a given activity, a similar inhalation rate would be expected for a person of similar body size and same gender (ECETOC 2001).This is supported by the similarity of the short-term values to reference inhalation rates reported by Snyder et al. (1975). Detailed age- and gender specific data on short-term inhalation is provided by US EPA (1997a).
Data on the long-term rates are based upon the development of metabolically consistent breathing rates by Layton (1993). Respective methods (i.e. inhalation rates sustained upon food consumption and long-term energy expenditure data) appear to be more appropriate than those applied for short-term inhalation (ventilation rates related from heart rates measurements, Layton 1993). This is possibly due to differences in long-term vs. short-term activity patterns (ECETOC 2001). The long-term estimates may show considerable difference among populations, as a result of varying lifestyles and activity levels. The estimate of Layton (1993) was performed in the US, and it is probably reasonably representative for European populations, as well (ECETOC 2001).

Inhalation rate data are considered to be inadequate for estimating distributions for inhalation rates (US EPA 1997a). As an alternative, McKone and Daniels (1991) developed equations relating inhalation rate to body weight *BW* for the data of Snyder et al. (1975). Accordingly, inhalation rates (in units of m^3/h) are obtained by multiplying the body weight [kg] with an empirical factor *a* (*a* = 0.011 and 0.030 for resting and active children respectively, and *a* = 0.006 and 0.018 for resting and active adults). This approach is suggested with caution, however, as it is based on very limited data (number of samples *N* = 2 for children, *N* = 9 for adults). Any inhalation distributions should be cross-checked with the range of inhalation rates reported in the literature for similar levels of activity (ECETOC 2001).

For the exposure modelling in the present study, values for heavy activity level were selected as best estimate for short-term inhalation (scenario of sports activity), the chosen range corresponds to lower and upper bound short-term inhalation rates specific to sport activities (as reported by the US EPA 1997a). Triangular distributions were considered, as recommended by AIHC (1994) and used by the program RISC 4.02. For long-term inhalation, minimum and maximum values from Tab. 11 were taken (uniform distribution, chosen by default).

***Tab. 11**: Mean long-term and short-term inhalation rates IH (according to Snyder et al. 1975).*

Activity level	Short-term *IH* [m^3/h]			Age	Long-term *IH* [m^3/d]		
	Adults	Children	Outdoor workers	[yr]	Males	Females	Both genders
Rest	0.4	0.3	-	**<1**			4.5
Sedantary	0.5	0.4	-	**1-2**			6.8
Light	1	1	1.1	**3-5**			8.3
Moderate	1.6	1.2	1.5	**6-8**			10
Heavy	3.2	1.9	2.5	**9-11**	14	13	
Hourly average			1.3	**12-14**	15	12	
				15-18	17	12	
				19-65+	15	11.3	

3.2.4.2 Water ingestion rates

Drinking water ingestion rates are reported by the US EPA (1997a), based on a survey of Ershow and Cantor (1989) on data collected by the USDA 1977-1978 Nationwide Food Consumption Survey (NFCS). In this study, calculated daily intake rates for tapwater and total water are presented for various age groups for males, females and both genders combined. Roseberry and Burmaster (1992) fit lognormal distributions to the Ershow and Cantor (1989) dataset and estimated population-wide distributions for total fluid and total tapwater intake based on proportions of the population in each age group. Results are shown in Tab. 12. There, the simulated balanced population SBP represents an adjustment for differences in the age distribution of the US population between 1978 (survey period)

and 1988, when Ershow and Cantor prepared their study. Data representative of Great Britain are available from a survey performed by Hopkins and Ellis (1980). As a limitation of this study, investigations were performed in September and October and do not cover seasonal variation in water intake.
Data are very rare to estimate the amount of contaminated water ingested while swimming. The US EPA (1988) assumes a rate of 50 mL/h. This value was used as best estimate for the exposure modelling, minimum and maximum were chosen by default.

***Tab. 12**: Best-fit lognormal distributions for tapwater intake rates: summary statistics, estimated means, standard deviations (Stdev.) and quantiles (according to Roseberry and Burmaster 1992). SBP: simulated balanced population.*

Age [yr]	Tapwater intake rate IR [mL/d]									
	μ	σ	R2	Mean	Stdev.	Percentile distribution				
						2.5	25	50	75	97.5
>1	5.59	0.62	0.97	323	219	80	176	267	404	891
1-10	6.43	0.50	0.98	701	372	233	443	620	867	1644
11-19	6.67	0.54	0.99	907	522	275	548	786	1128	2243
20-64	7.02	0.49	0.96	1265	657	430	807	1122	1561	2926
65+	7.09	0.48	0.98	1341	676	471	869	1198	1651	3044
All	6.9	0.53	0.98	1108	631	341	674	963	1377	2721
SBP	6.87	0.58	1.00	1129	707	310	649	957	1411	2954

Mean IR = $\exp [\mu + 0.5 \times \sigma^2]$
Stdev. IR = $\{ \exp [2\mu + 2\sigma^2] - \exp [2\mu + \sigma^2] \}^{0.5}$

2.5 percentile IR = $\exp [\mu - 1.96 \times \sigma]$
25 percentile IR = $\exp [\mu - 0.6745 \times \sigma]$
50 percentile IR = $\exp [\mu]$
75 percentile IR = $\exp [\mu + 0.6745 \times \sigma]$
97.5 percentile IR = $\exp [\mu + 1.96 \times \sigma]$

3.2.4.3 Exposure frequency and exposure time

Exposure frequency and duration are used to estimate the total time of exposure for a given site. In many approaches, an exposure frequency *EF* of 350 d/yr is used for the time spent at home (housing scenario). This conservative value suggests 2 weeks of holidays and is consistent to the EPA policy (US EPA 1991). Smith (1994) suggests a triangular distribution for exposure frequency in a residential scenario. For the time spent at home, 345 d/yr is assumed as the likeliest value (20 days of holiday), 365 d/yr as the maximum (no absence from home) and 180 d/yr as the minimum (half-year absence). Instead, for exposure modelling in the present study, 4 weeks of absence from home were considered as best estimate, 7 weeks as maximum and no absence as minimum (see Tab. 10). The chosen values fit better to observations made by Gershuny (1995) for European countries, while the considered minimum and maximum are conservative assumptions. In fact, Gershuny (1995) analysed time budget data for a number of countries (European states, USA, Canada and Australia). He developed a model to estimate the effect of gender, employment status, age and family status and country on the minutes per day spent in each of several activities. Evaluated time budgets can be used as a rough estimate to indicate the relative amount of time spent at work, at home or in away-from-home leisure activities by country (see ECETOC 2001 for details).

For the time spent outside at home, 2 h/d was assumed for adults (as recommended by ECETOC 2001 as an average for the UK population) and 3 h/d for children as best estimate. The value of 2 h/d is based upon the study of Gershuny (1985), citing a time budget survey performed 1983/84 by the Economic and Social Research Council (ESRC). Unfortunately, no data for children is specified in this study. However, it is likely that the frequency (days per year) spent in outdoor recreation is greater for children, regarding typical age related behavioural patterns (ECETOC 2001). Triangular distributions were used as recommended by AIHC (1994). The chosen estimates are in accordance with other studies and can be seen as upper bound approximations. E.g., Ott (1989) reports 2-3 h/d spent outdoors in total (including travel) for European countries, the US EPA (1997a) estimates 1.5 h/d outdoors and 1.5 h/d for travelling. The considered range for adults corresponds to results presented by Gershuny (1985) and was correlated for children, given the assumption of longer times spent outside.

Concerning the activity pattern for outdoor recreation, a scenario of playing sports (e.g. at a sports facility near the site) was set up. The exposure frequency corresponds to 9 months per year being

active outside (half a year and the whole year as possible range). 0.75 hours per day were assumed in average to correspond to an upper bound estimate (e.g. playing soccer every second day during the playing season). For the swimming scenario, 5 months per year were considered with half an hour per day staying in surface water as mean assumption.

The aim of the modelling in this study was to estimate upper bound risk possibly arising from activities in an polluted environment. Therefore, the chosen scenarios are conservative, both for playing sports outdoors and swimming in surface water. E.g., Gershuny (1985) estimates an average daily value of 0.3 hours for outdoor recreation in the whole year (long-term approximation). In this study, outdoor leisure activities (away from home) are reported to take place at the same location each day. Different categories are specified as a function of gender and employment status, such as playing sports, walking and watching sports (see ECETOC 2001 for details). These estimations are long-term averages and therefore include zero values for days without recreational activity and for adults who did not participate in outdoor leisure. Unfortunately, data on the number of days per year spent with outdoor recreation or on the percentage of the population participating is not available within this study.
Results of a survey performed by the National Human Activity Pattern Survey NHAPS (Tsang and Klepeis 1996, presented by US EPA 1997a) between 1992 and 1994 indicate that for individuals who reported outdoor recreational activity, a 50^{th} percentile of 2.5 h/d can be approximated. Respective study provides detailed information and statistical data on a multitude of different activities and criteria of gender, age, employment status, education, region, day of week (weekday and weekend) and season. However, the number of occurrences per year of outdoor activity is not given. Only about 3% of the respondents indicated participating in outdoor recreational activities during the survey period. For days in which outdoor recreation occurred, adults (aged 18-64 years) exhibited higher daily median times in outdoor recreation than children.
Data for swimming frequency and duration in freshwater pools are reported by the NHAPS study (Tsang and Klepeis 1996, see US EPA 1997a for details). Only about 7% of the participants answered that they were swimming in the last month. From this group, the highest number of respondents (147 persons or 23%) reported that they swam one time per month. Thus, the US EPA (1997a) recommends a swimming frequency of one event per month for the general population and a swimming duration of 60 minutes (50th percentile value).

3.2.4.4 Body weight and lifetime

ECETOC (2001) recommends the use of lognormal distributions for body weight. This assumption is based upon an investigation carried out by Burmaster and Crouch (1997) on body weight data from the US 1976-1980 National Health and Nutrition Examination Survey II (NHANES II, see US EPA 1997a for details on this survey). Mean values and standard deviation in Tab. 10 (with the mean value as the chosen best estimate) were determined for different age groups and both genders, representative for the English population (ECETOC 2001). Respective data consider the Health Survey for England (HSE, Prescott-Clarke and Primatesta 1998). The chosen mean body weight for adults is consistent with the NHANES II study (71.8 kg) and with the commonly used default of 70 kg (US EPA 1997a). ECETOC present also country specific data (mean body weight for adults) based upon a survey from the WHO (1999a).

The averaging time for carcinogenic risk calculation (lifetime) was chosen according to upper and lower life expectancies reported for European countries (WHO 1999b, cited by ECETOC 2001). The best estimate of 75 years corresponds to a mean approximation and is slightly higher than the value of 70 yr that is commonly applied (US EPA 1997a).

3.2.5 Toxicity values

3.2.5.1 Human health

Concerning PCBs, reference doses and cancer slope factors are reported for Aroclor mixtures and for PCB in total (Tab. 13). The toxicity values are based upon assays with test animals (oral administration of PCB) and the application of appropriate uncertainty factors, as described in detail by the US HHS (2000) and the online resource IRIS (see reference list). The following characterisation is recommended by the US HHS (2000) for chronic oral slope factors: SF_o= 2, 0.4 and 0.07 per (mg kg^{-1} d^{-1}) for high, low and lowest risk and persistence of PCB, respectively (see US HHS 2000 for details).

Oral slope factors specific to PCB mixtures are commonly derived from this finding (Tab. 13). Oral references doses RfD_o are reported for Aroclor 1016 and 1254, for other PCB mixtures they are not verified to date. The US HHS (2000) assumes that the oral toxicity values can also be applied for the inhalation pathway (no specific SF_i and RfD_i values were derived from experimental data on the inhalation route). For dermal intake, reported toxicity values are deduced from SF_o and RfD_o as well, i.e. by applying a gastrointestinal absorption factor of 0.9 (online resource RAIS, Tab. 13).

The US EPA (2004b) presents a Preliminary Remediation Goals (PRG) table along with detailed toxicity information on a large number of contaminants (US EPA Region 9, see Tab. 13). This resource recommends the lowest risk characteristics to be used for Aroclor 1016 (due to the low degree of chlorination) and the upper estimate for all other Aroclor mixtures and PCB in total (values based upon SF_o = 0.07 and 2 per (mg kg^{-1} d^{-1}), respectively). In contrast, RAIS recommends to use constant values for all PCB mixtures but to differentiate between the exposure medium. Thus, an oral/inhalation *SF* of 2 and 0.4 per (mg kg^{-1} d^{-1}), and a dermal *SF* of 2.22 and 0.44 per (mg kg^{-1} d^{-1}) is used by RAIS for exposure to soil/food (high estimates) and water (low estimates), respectively.

For the cancer risk calculation in the present study, the lowest estimate for SF_o and SF_i of 0.07 per (mg kg^{-1} d^{-1}) was considered for Aroclor 1016 (US EPA 2004b). Indeed, when comparing PCB congeners present in Aroclor 1016 (see Tab. 4) with those elaborated to be of toxicological concern (Part III, section 3.4), only a very small portion possess a high or moderate toxic potential (about 3% by weight). Thus, the assumption of US EPA (2004b) that the lowest bound estimate can be used for Aroclor 1016 is justified. For dermal contact with water while swimming, the RAIS slope factor (0.44 per (mg kg^{-1} d^{-1})) was used.

***Tab. 13**: Toxicity values for PCB (chronic exposure). SF: Cancer slope factor, RfD: reference dose, with indices o (oral), i (inhalation) and d (dermal), (1): corresponding to oral intake toxicity values (see text), (2) estimated from oral intake (see text), a: PRG table (US EPA 2004b based upon IRIS), b: US EPA classification, # lowest, ## low, ### high risk and persistence (US HHS 2000), c: RAIS online resource, exposure to soil or food (S) and exposure to water (W).*

Compound	CAS-No.	Oral intake		Inhalation (1)		Dermal contact (2)	
		SF_o [1/(mg $kg^{-1}d^{-1}$)]	RfD_o [mg $kg^{-1}d^{-1}$]	SF_i [1/(mg $kg^{-1}d^{-1}$)]	RfD_i [mg $kg^{-1}d^{-1}$]	SF_d [(mg $kg^{-1}d^{-1}$)$^{-1}$]	RfD_d [mg $kg^{-1}d^{-1}$]
PCB (total)	001336-36-3	2.0 (a)		2.0 (a)			
PCB #	001336-36-3	0.07 (b,c)		0.07 (c)		0.078 (c)	
PCB ##	001336-36-3	0.4 (b,c)		0.4 (c)		0.44 (c)	
PCB ###	001336-36-3	2.0 (b,c)		2.0 (c)		2.22 (c)	
Aroclor 1016	012674-11-2	0.07 (a) 2.0 (c,S) 0.4 (c,W)	7.0 x 10^{-5}(a,c)	0.07 (a) 2.0 (c,S) 0.4 (c,W)	7.0 x 10^{-5} (a)	2.22 (c,S) 0.44 (c,W)	6.3 x 10^{-5}(c)
Aroclor 1221	011104-28-2	2.0 (a)(c,S) 0.4 (c,W)		2.0 (a)(c,S) 0.4 (c,W)		2.22 (c,S) 0.44 (c,W)	
Aroclor 1232	011141-16-5	2.0 (a)(c,S) 0.4 (c,W)		2.0 (a)(c,S) 0.4 (c,W)		2.22 (c,S) 0.44 (c,W)	
Aroclor 1242	053469-21-9	2.0 (a)(c,S) 0.4 (c,W)		2.0 (a)(c,S) 0.4 (c,W)		2.22 (c,S) 0.44 (c,W)	
Aroclor 1248	012672-29-6	2.0 (a)(c,S) 0.4 (c,W)		2.0 (a)(c,S) 0.4 (c,W)		2.22 (c,S) 0.44 (c,W)	
Aroclor 1254	011097-69-1	2.0 (a)(c,S) 0.4 (c,W)	2.0 x 10^{-5}(a,c)	2.0 (a)(c,S) 0.4 (c,W)	2.0 x 10^{-5} (a)	2.22 (c,S) 0.44 (c,W)	1.8 x 10^{-5}(c)
Aroclor 1260	011096-82-5	2.0 (a)(c,S) 0.4 (c,W)		2.0 (a)(c,S) 0.4 (c,W)		2.22 (c,S) 0.44 (c,W)	

For CBAs, references doses are reported for 4-CBA only (Tab. 14). Additional information on CBA toxicity was derived from the NIOSH online resource, consisting of LD50 values for rats and mice. These data include CBAs other than 4-CBA which are likely produced in the considered bioprocess. Albeit it is problematic to compare LD50 data that are based upon different species and different toxicant applications, the higher chlorinated CBAs in Tab. 14 seem to be more toxic for the tested animals than the lower chlorinated compounds. As a rough estimation, considering these differences, a *RfD* of 0.01 mg/kg-d was derived for the total CBA inventory and for all pathways. I.e. an uncertainty factor of 20 (RfD_o and RfD_i) and 10 for (RfD_d) was applied to the 4-CBA reference doses.

***Tab. 14**: Toxicity values and lethal dose data for CBAs. RfD subscripts: o (oral), i (ingestion), d (dermal contact). a: RAIS online resource, b: NIOSH data, LD50: lethal dose (dose at which 50% of the test population is killed), toxicant applications: c: intraperitoneal, d: oral, e: subcutaneous.*

Compound	CAS-No.	Reference doses [mg $kg^{-1}d^{-1}$] (a)			LD50 [mg/kg] (b)			
		RfD_o	RfD_i	RfD_d	rat		mouse	
2-CBA	118-91-2				2300 (c)	6460 (d)		
3-CBA	535-80-8				750 (c)			
4-CBA	74-11-3	0.2	0.2	0.1	1000 (c)			
2,4-CBA	50-84-0						830 (d)	1200 (e)
2,5-CBA	50-79-3						237 (c)	1200(e)
2,6-CBA	50-30-6						316 (c)	1500 (e)

3.2.5.2 Ecological receptors

No-observed-adverse-effect-concentrations (NOAEC) for ecological receptors were derived from the ECOTOX online database (maintained by the US EPA), providing information on reported effects specific to a large number of chemicals and organisms. The fish species bluegill (*Lepomis* macrochirus) and fathead minnow (*Pimephales* promelas) were chosen for the modelling. These are the only species for which data specific to Aroclor 1016 as well as to CBA were found. Table 15 shows NOAECs for mortality and other effects arising from contaminant exposure, such as impacts on the behaviour or observed accumulation of compounds (see US EPA 2002 for details).

Minimum values were chosen to follow a worst case scenario (Aroclor 1016: 0.39 μg/L for bluegill, 0.087 μg/L for fathead minnow). One value was considered for the whole CBA inventory (90 μg/L for bluegill, i.e. lowest value for reported CBAs, and 6800 μg/L for fathead minnow).

***Tab. 15**: No-observed-adverse-effect-concentrations (NOAEC) for the fish species blue-gill (Lepomis macrochirus) and fathead minnow (Pimephales promelas), derived from the ECOTOX database. MORT: mortality, BEH, STRS: behaviour, observed stress, ACC, GACC: accumulation, general. a: related to fresh water.*

Compound	CAS-Nr.	NOAEC Bluegill			NOAEC, Fathead Minnow		
		Min. [μg/L]	Max. [μg/L]	Effect	Min. [μg/L]	Max. [μg/L]	Effect
PCB (total)	001336-36-3						
Aroclor 1016	012674-11-2	0.39 (a)	0.54 (a)	MORT	0.087	0.087	ACC, GACC
Aroclor 1221	011104-28-2						
Aroclor 1232	011141-16-5						
Aroclor 1242	053469-21-9	0.125	1.64	MORT	0.0086	0.51	MORT
Aroclor 1248	012672-29-6	0.1	10	MORT	0.047	0.047	MORT
Aroclor 1254	011097-69-1	0.0023	5	BEH, STRS	0.0023	0.033	MORT
Aroclor 1260	011096-82-5	0.01	4	BEH, STRS	0.033	0.033	MORT
2,6-CBA	50-30-6	120		MORT			
2,3,5-CBA	50-73-7	90	180	MORT			
2,3,6-CBA	50-31-7	1750	1800	MORT	6800	17100	MORT

3.3 Fate and impact of genetically modified microbes

Horizontal spreading, transport from soil into other environmental media, gene transfer and potential impacts on microbial communities in soil and rhizosphere were investigated for F113 microbes. Figure 8 gives an overview on the studied processes.
Data on microbial dispersal were obtained from mesocosm experiments (F113 derivatives) and a field release test (with non-GM F113rif), carried out by Karlson U and co-workers (National Environmental Research Institute NERI, Roskilde, Denmark; personal communication, publication in preparation). Information on gene transfer rates of F113pcb was gathered from Brazil GM and Dowling DN (Institute of Technology Carlow, Ireland; unpublished data), who performed *in vitro* (vial) and *in vivo* (microcosm) studies. Potential impacts on microbial communities were investigated by Aguirre de Carcer M, Rivilla R et al. (Universidad Autónoma de Madrid, Spain; unpublished data), whose results were considered in the present study. Some details on experimental set up and methods are given in the following subsections.

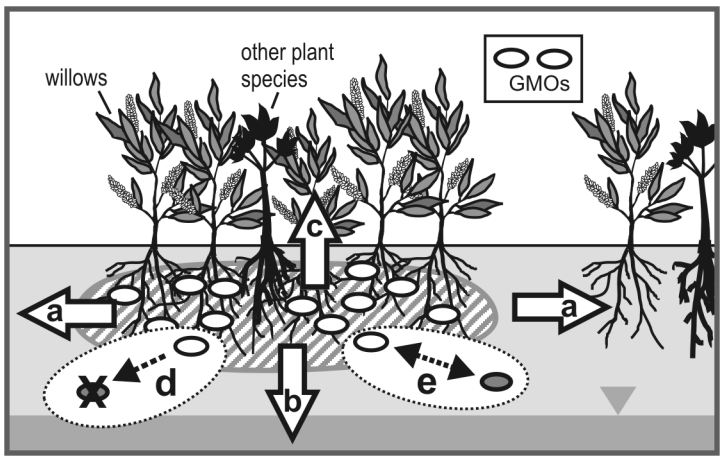


Fig. 8*: Fate and dispersion of GMOs: studied processes. a) horizontal spreading, b) leaching, c) plant uptake, d) gene transfer (GMO to wild type), e) potential impacts on microbial communities.*

3.3.1 Microbial dispersal in mesocosm

Potential dispersal of F113rif, F113rifpcb and F113L::1180 was analysed in mesocosm. For respective experiments, roots of willow plants were inoculated with bacteria, and the willows planted into pots of different size containing PCB-contaminated soil (according to Part III, section 2.3). Beside bulk soil and rhizosphere samples (Part III), other media were analysed for the presence of GMOs, such as living and dead willows leaves, roots and shoots of weeds growing in the pots. Furthermore, leachate samples were collected underneath the pots (upon flushing the soil with excess water). Sampling was performed at the conclusion of the experiment (on day 224), except for roots (monthly sampling interval) and bulk soil (sampling at the beginning and on day 224). Bacterial numbers were determined as colony forming units (CFU) on salicylic acid (SA, with and without rifampicin) and tryptone soya agar (TSA) plates.

3.3.2 Field release test with non-GM bacteria

A field release test with F113rif (non-GM derivative) was conducted in order to investigate survival and potential spreading. The experiment was carried out at a PCB-contaminated site near Århus, Denmark. The test site covers approximately 45 x 45 m and was planted with willows (*Salix* sp.). At three spots within this plantation, willow cuttings were dip-inoculated in bacterial suspension, immediately before planting. About four years (51 months) after the release, bacteria were counted on roots and leaves of willows and other pant species, and in soil samples. Samples were taken within the plantations and at various locations in the vicinity (Fig. 7). Soil and root sampling was carried out at different depths (up to 100 cm below surface). Molecular identification methods for F113rif were used to monitor the released inoculants, based on PCR fingerprinting using appropriate molecular primers. With these methods, plate counts on selective media were double-checked to ascertain the identity of the colonies counted.

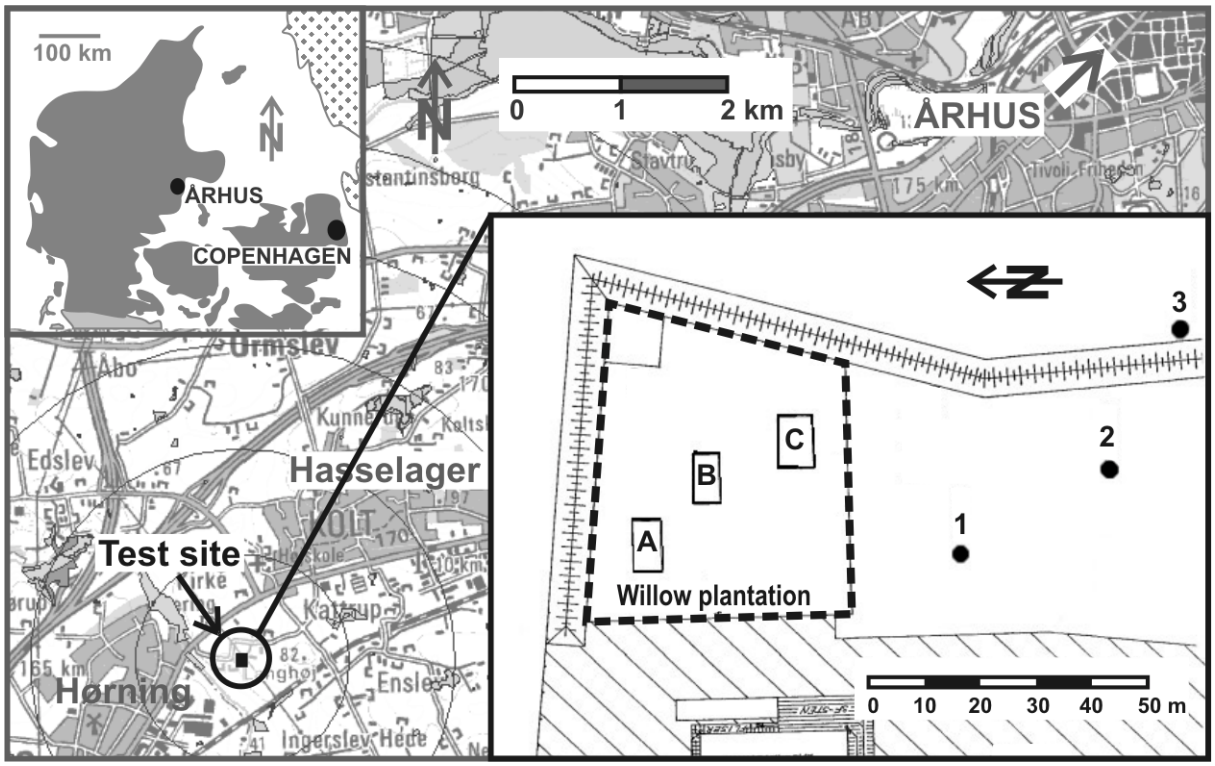


***Fig. 9**: Location and map of the test site. A, B, C: release site of microbes. 1, 2, 3: sample points outside the willow plantation.*

3.3.3 Gene transfer rates

Possible lateral transfer of the chromosomally introduced *bph*-trait (responsible for PCB degradation; Part III, section 1) was estimated for strain F113pcb. As a model system, a homologous recipient was used for *in vitro* and *in vivo* transfer studies. Experiments *in vivo* (microcosms) were conducted in the rhizosphere of sugarbeet plants (*Beta vulgaris* L.). Two possible mechanisms for lateral transfer were tested: a) transposition of the disabled element promoted by a transacting active transposon elsewhere in the genome and b) chromosomal mobilisation of the *bph* cassette promoted by a chromosomal mobilising plasmid.

3.3.4 Impacts of GMOs on microbial communities

Potential impacts of F113 derivatives on indigenous microflora were investigated focussing on a) shifts in the genetic structure, and b) impacts on the function of the microbial community. Such effects might occur due to the release of GMOs, but also the introduction of the host plant can be of influence. Further contributions might be given by the remediation process (reduction of PCB in soil and formation of toxic metabolites) or other factors, such as seasonal changes (Aguirre de Cárcer D, personal communication).
The studies were performed in microcosm experiments with PCB contaminated soil from a dump site near Lhenice, Czech Republic. Unplanted soil samples (negative control) and planted samples, i.e. soil and rhizosphere (roots plus residual soil) were analysed. Willow (*Salix* viminalis) was used as a suitable host plant for rhizoremediation. The planted samples involved the following treatments:

- untreated willows
- willows inoculated with F113rif (wild type)
- willows inoculated with F113pcb and F113L::1180

For the plant assays, willow cuttings (pregrown for two weeks) were planted into iron pots (three plants per pot) filled with 1.9 kg of PCB contaminated soil. In the experiments involving F113 derivatives, the willows were inoculated into bacterial suspension prior to be planted. After six months, the plants were removed and soil and roots samples analysed.

First, microbial populations that develop naturally in the rhizosphere of PCB-contaminated soil were investigated (negative controls). Then, possible structural changes occurring in the soil ecosystem after the introduction of willow plants were evaluated. Populations and phylogenetic distributions of key bacterial groups (α- and β- *Proteobacteria*, *Acidobacteria* and *Actinobacteria*) were studied in soil and rhizosphere. This was done by combining the construction of group-specific 16S rDNA libraries (i.e. primers, obtained from soil and rhizosphere samples, respectively) with the use of Temperature Gradient Gel Electrophoresis (TGGE) for library screening. I.e. the pooled DNA obtained from the samples was used to generate (via the PCR-TGGE approach) a genetic fingerprint using group-specific primers of the key bacterial communities for each treatment and sampling time. Similarly, structural changes due to the introduction of F113 derivatives were analysed, using appropriate molecular primers for these microbes. The resulting banding patterns were analysed according to band position and relative intensity, and were reduced by principal component analysis to obtain two-dimensional images.

In order to elucidate functional diversity and how it is affected by the introduction of willows or specific bacteria, community catabolic profile analyses were performed using ECOlog plates (according to Garland and Mills 1991, Glimm et al. 1997). Each ECOPlate contains 31 response wells with different sole carbon sources and a negative control (well without carbon source). A tetrazolium redox dye is included, which turns purple when it is reduced by microbial respiration. Thus, profiles were obtained for each community consisting of consumption rates for each carbon source. Prior to the application, the capacity of the ECOlog plates to discern among different microbial communities and its reproducibility was assayed by comparing forest and lawn soils.

4 Results and discussion

4.1 Fate and transport of PCBs and CBAs

Contaminant mass fluxes and receptor point concentrations were estimated deterministically and probabilistically. Respective calculations were performed for Group I and II (section 3.1.3.1), considering a) conditions without biodegradation and b) biodegradation with strain F113L::1180 and subsequent formation of CBA (Tab. 3). For the probabilistic approach, 1000 Monte Carlo simulations were run for the modelling of each compound. This sample size is 10 times lower than that used for the Level III modelling in Part II and was chosen due to constraints given by the applied procedure (long computing times). A high degree of simulation accuracy might not be necessary given the considerable empirical uncertainty associated to the input parameters (following Cullen and Frey 1999). Thus, the sample size of 1000 trails is assumed to be adequate for the estimations in this study.

Group I is representing the "degradable fraction" of Aroclor 1016 (i.e. verified for strain F113L::1180), Group II corresponds to Aroclor 1016 in total (section 3.1.3.1). For the probabilistic approach, uncertainty in initial soil concentration was addressed by considering two contributions:

a) uncertainty of total Aroclor 1016 concentration (lognormal distribution as recommended by Ott 1995, with 100 mg/kg as mean value, and 10 mg/kg as standard deviation chosen by default)
b) uncertainty of congener fractions included in Aroclor 1016 (ranges from Tab. 2, uniform distribution)

A generic environment was considered as defined in section 3.1.4. Deterministic calculations were performed with best estimate values from Tab. 5 to 9 if available, otherwise mean values were taken. Probabilistic calculations were conducted with the probability density functions (PDF) specified in Tab. 5 to 9.

Data on *Monod* parameters (v^*_{max}, K_M) and bacterial numbers in laboratory ($CFU_{lab,0}$) were taken from Part III, Tab. 2 and 4, respectively. An average microbial number in soil (CFU_{Soil}) of 2.6×10^7 cfu/kg was considered, varying within one order of magnitude (Part III, section 3.4.2 and 3.5). For the probabilistic modelling, uniform distributions were used for v^*_{max} (minimum and maximum from Part III, Tab. 2) and CFU_{Soil} (5×10^6 to 5×10^7 cfu/kg), as no information on statistical characteristics was available. The half saturation constant K_M was kept constant (single value used for probabilistic calculations) due to its low sensitivity compared to v^*_{max} (Part III, section 3.3). It was assumed that the degradation performance of bacteria in the field is identical to that in the laboratory ($f_{RD} = 1$ in Eq. 8).

4.1.1 Contaminant partitioning

4.1.1.1 Mass fluxes

a) Group I

Results for Group I ("degradable fraction" of Aroclor 1016) are given in Fig. 10. For conditions without biodegradation, the contaminant mass in soil is slowly depleted (Fig. 10a). Partitioning of PCB from soil with leachate, into ambient air and into plants can be seen. After 25 years, about 76% of PCB mass remains in soil, 19% and 4% are distributed into leachate and air, respectively and a very small portion (< 1%) is taken up by plants (mass in roots and leaves; the portion of leaves is < 0.1%).
In contrast, considering biodegradation with the studied microbes, the mass of the "degradable fraction" is significantly reduced in soil, leachate and air (Fig 10b). The portion of degraded mass is 29% after one year, 81% after five, 89% after ten and 94% after 25 years.

Looking at the mass of CBA produced by the microbes (Fig 10c), only a small fraction is remaining in soil (peak in the first months) whereas high mass fluxes with leachate and into plants occur. After 5 years, about 94% of the CBA mass is transported with leachate, and 5% is taken up by plants. Approximately 1% is retained in soil, and the portion in ambient air is negligibly low (about 3×10^{-5}%).

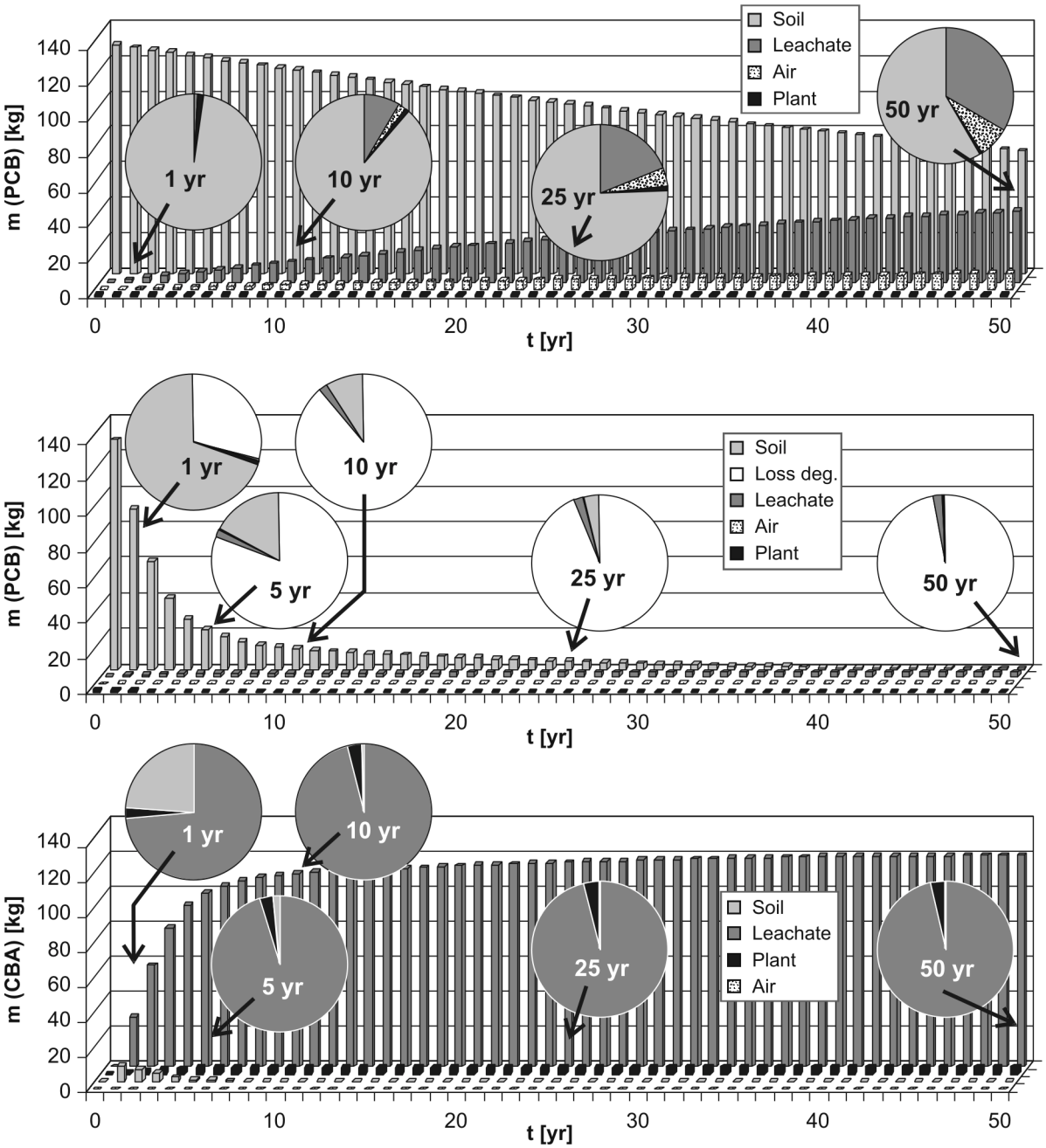


***Fig. 10**: Contaminant mass fluxes, Group I ("degradable fraction" of Aroclor 1016). PCB mass for conditions without biodegradation (a) and considering biodegradation (b), and CBA mass (c) in soil, leachate, air and plant (root and leaf).*

b) Group II

Fig. 11 shows the mass balance for Group II, i.e. Aroclor 1016 in total. Not surprisingly, the contribution of biodegradation (strain F113L::1180) to the PCB mass reduction is lower (compare Fig. 10b to Fig. 11b), as the "degradable fraction" accounts only for about 39 % by weight of Aroclor 1016 (section 3.1.3.3). As detailed previously (Part III, section 3.2), the remaining 61% consist of PCBs shown to be recalcitrant for the investigated strain (18%) and congeners that were not investigated (43%). Accordingly, Fig. 11b follows as a worst case scenario for the degradation capacity (substrate range) of F113L::1180.

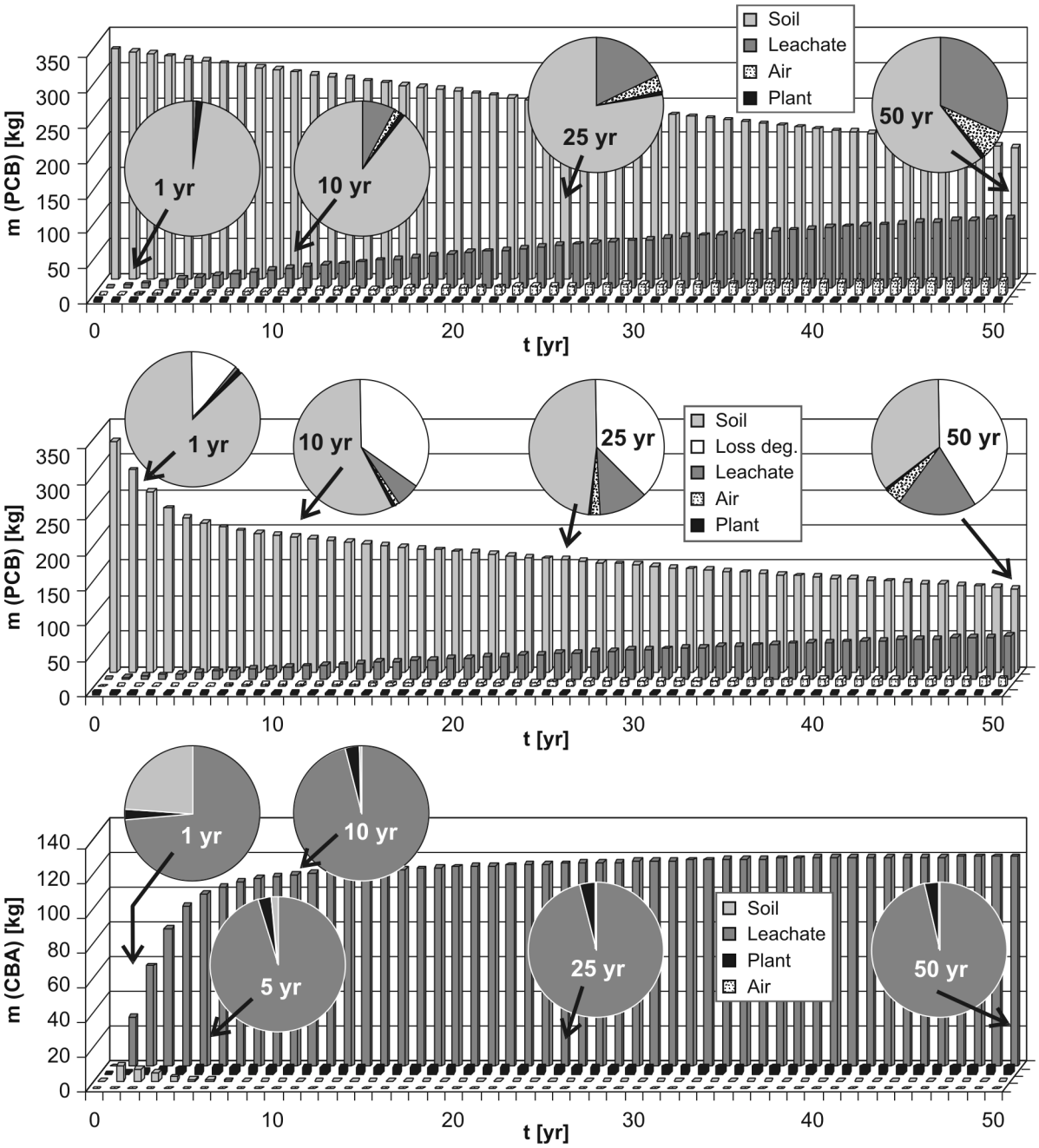


***Fig. 11**: Mass balance, Group II (Aroclor 1016 in total). PCB mass for conditions without biodegradation (a) and considering biodegradation (b) and CBA mass (c) in soil, leachate, air and plant (root and leaf).*

4.1.1.2 Concentrations

Contaminant concentrations in different environmental media as a function of time, specific to Group I and II are discussed in the following. Results of deterministic modelling (i.e. best estimates) are presented there. Concentrations derived from the probabilistic approach are given in Appendix E, specifying 5th, 10th, 50th, 90th and 95th percentile values together with best estimates. Analogously to the previous section, conditions without biodegradation are compared to those where the bioprocess (degradation with strain F113L::1180) is active.

a) Group I

Soil and air concentrations for the "degradable fraction" are plotted in Fig. 12a to 12c. Initial soil concentrations relate to the portion of PCB congeners in Aroclor 1016 that was shown to be degradable by strain F113L::1180. As already observed for the contaminant mass, PCB concentrations slowly decrease in the scenario without degradation. Rapid reduction is obvious when microbial activity is considered. There is a small peak of CBA concentration in soil occurring after about one year (Fig. 12c). Air concentrations are very low for CBA (below 10^{-8} mg/m^3) as the dissociated species is dominating by far for the considered soil pH range (pH = 6 in average, Tab. 6), and the dissociated species is assumed to be involatile (section 3.1.2.2). The presented air concentrations were determined using the dispersion coefficient *Q/C* (section 3.1.2.3). For comparison, calculations were performed with the box model (Eq. 16), yielding concentrations that are approximately a factor of two higher. This finding is in accordance to the US EPA (1996b) who recommends the Q/C approach, whereas the application of the box model was shown to result in overly conservative estimates.

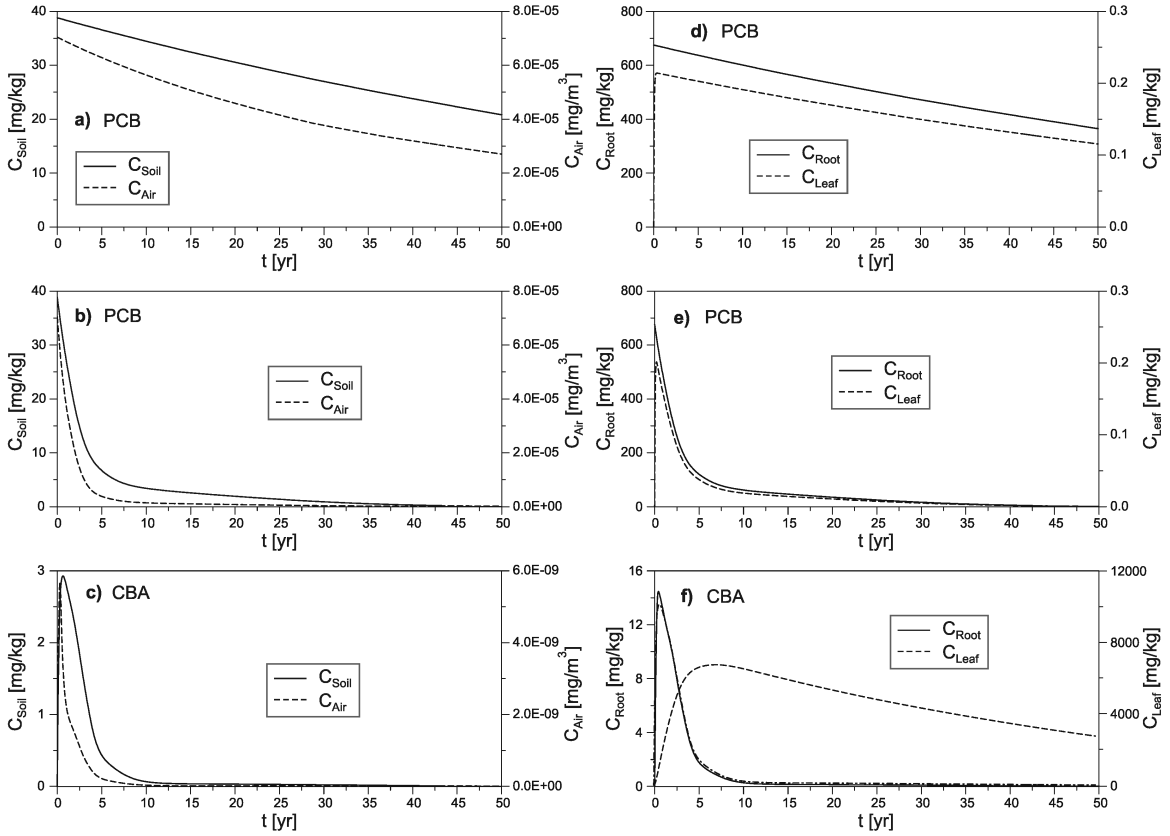


***Fig. 12**: Compound concentrations (Group I). a) to c): soil and air; d) to f): root and leaf; a), d): PCB for conditions without biodegradation; b), e): PCB considering biodegradation; c), f): CBA.*

Results for root and leaf concentration are shown in Fig. 12d to 12f, assuming that neither PCB nor CBA is subject to biodegradation in the plant (worst case modelling). Root concentrations behave similar like soil concentrations, as they were calculated from equilibrium partitioning between soil and roots (Eq. 46). For PCB, root concentrations are about 20 times higher than soil concentrations. For

CBA, this factor is lower (about 5) due to the fact that the major portion is translocated from the roots with the transpiration stream. Accordingly, only parts of the ions (ion trap) and neutral species (lipophilic sorption) are subject to retention in the roots (section 3.1.2.7.5).

Leaf concentrations are low for PCB but considerably high for CBA. The dashed curves in Fig.12d to 12f were obtained numerically with Eq. (64), applying a one-step Euler solution scheme. This approach was compared with a procedure using the analytical solution for steady state conditions (Eq. 68). Results are in a similar range for PCB (slightly enhanced concentrations with steady state) as concentrations in soil water and air on the one side and leaf on the other side are near equilibrium within the considered resolution (time step of 12 days between the steady state estimates). Results differed for CBA, where the steady state procedure led to large overestimations (equilibrium was not reached within the applied time step). The numerical approach revealed a peak of 6500 mg/kg after 8 years that is slowly decreasing (Fig. 12f). This characteristic is influenced by a very low sink term (dilution by growth as the only significant process contributing to CBA reduction).
The obtained curve might be an overestimation as accumulation over the total model period of 50 years is implied (no exchange of leaves during season was considered). Furthermore, there is evidence for CBA metabolism in plants, at least for lowly chlorinated compounds (Mackova et al. 2006a and b), probably resulting in leave concentrations that are substantially lower than those modelled in this study.

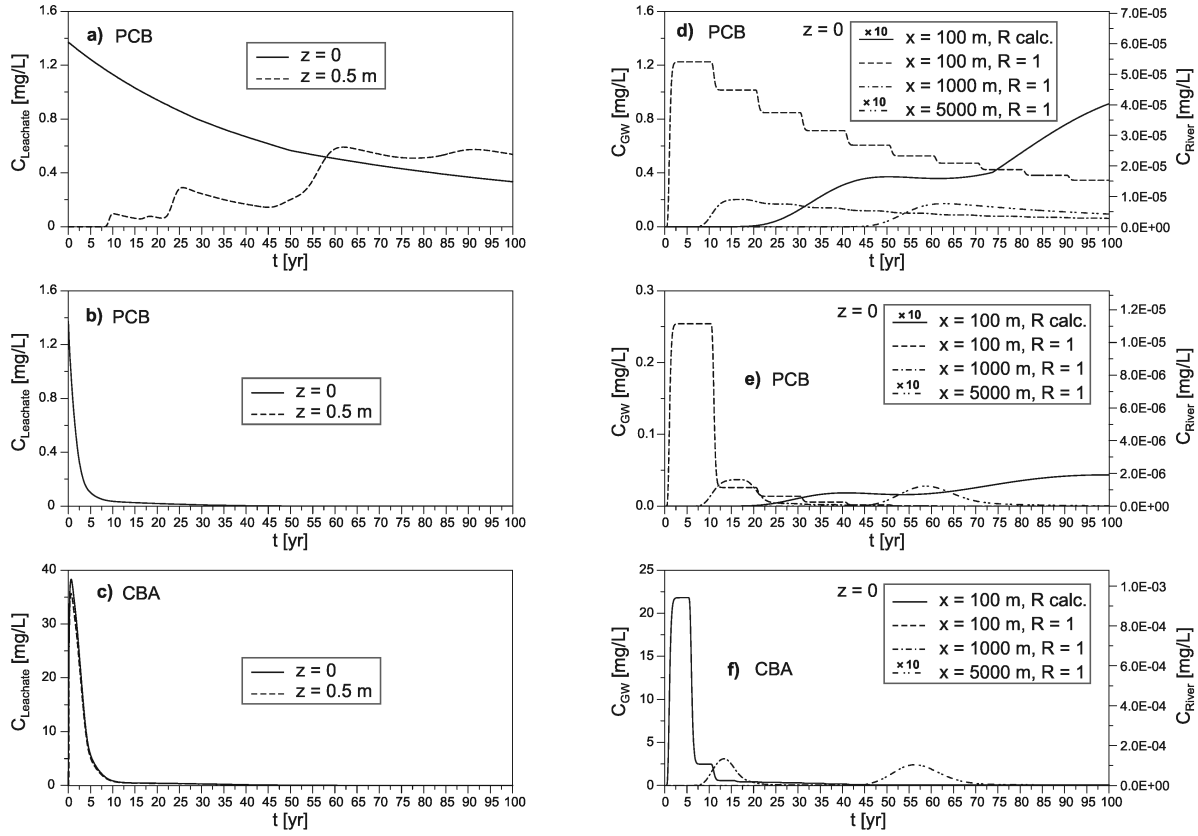


Fig. 13*: Compound concentrations (Group I). a) to c): leachate at the source bottom (z = 0) and at a depth z = 0.5 m beneath the source; d) to f): groundwater and river water (referring to z = 0); a), d): PCB for conditions without biodegradation; b), e): PCB considering biodegradation; c), f): CBA; x: downstream distance from the source; R: retardation coefficient, calc.: calculated; x 10: curves are 10 fold exaggerated.*

Figures 13a to 13c show leachate concentrations directly below the source (depth z = 0) and half a meter below the source bottom (z = 0.5 m). The results correspond to an upper bound estimate for contaminant leaching based upon a very low f_{OC} and a low *pH* in soil (section 3.1.4.2).
In the scenario without biodegradation, PCB will reach the receptor point at z = 0.5 m after about 6 years as best estimate. The plateau-like structure in Fig. 13a (dashed curve) originates from differences in leaching capacity between PCB congeners. Low chlorinated compounds will leach faster than high chlorinated PCBs (mainly controlled by the log K_{OW}, see section 3.1.2.1). For the

modelling of complex mixtures it has to be ensured that the simulation period is not too short, otherwise substantial underestimations can occur (compare to the plateau occurring after 60 years).
PCB concentration in leachate is rapidly reduced by degradation with strain F113L::1180, whereas a significant peak for CBA is induced (up to 40 mg/L in the first months, see Fig. 13c). Receptor point concentrations of PCB at z = 0.5 m are negligibly low. There is no significant difference between z = 0 and z = 0.5 m for CBA, as the dominating dissociated species is not assumed to sorb to soil material (section 3.1.2.2).

Groundwater and river water concentrations are given in Fig. 13d to 13f for different receptor point locations (at distances of x = 100, 1000 and 5000 m from the source, in groundwater flow direction). The presented results correspond to a groundwater level directly below the source (z = 0). For the straight lines in Fig. 13d to 13f (i.e. x = 100 m), retardation in the aquifer material was calculated. In addition, for x = 100 m, and for the other considered distances, the retardation coefficient was set to one in order to enable studies on contaminant concentrations within the modelled time frame of 100 years. These studies focussed on concentration as a function of the distance from the source (dilution by dispersion processes), in terms of potential maximum effects.
As it can be seen, considering retardation, PCB will reach the receptor point (e.g. a groundwater well) at x = 100 m after about 20 to 25 years (best estimate) when no biodegradation is treated. Concentration is slowly increasing. Neglecting retardation, a peak of 1.2 mg/L will be reached (Fig. 13d). This peak is reduced with the distance of the potential groundwater well from the source (C_{GW} = 0.3 mg/L for x = 1000 m and 0.04 mg/L for x = 5000 m). Considering biodegradation with strain F113L::1180, the concentration peaks are decreased by a factor of about 5. Again, this applies for z = 0. For a source that is located at z = 0.5 m, concentrations are reduced to negligible values (as observed for the leachate). CBA concentration curves calculated with and without aquifer retardation show the same shape, indicating no significant sorption to aquifer material (Fig. 13f). High peaks are obvious (22, 4.4 and 0.6 mg/L for x = 100, 1000 and 5000 m respectively).

The rectangular-like structures in Fig. 13d to 13f are due to the superposition procedure, applied for groundwater transport modelling (10 mean concentrations fitted to the leachate concentration input, see section 3.1.2.5).
The calculated groundwater concentrations are assumed to correspond to upper bound estimates. Comparative studies with the program RISC 4.02 (Spence and Walden 2001) yielded groundwater concentrations that are 3 and 8 times lower for x = 1000 m and 5000 m, respectively, due to different model codes (treatment of dispersion). Respective calculations were based upon the same dispersivities (section 3.1.2.5, longitudinal dispersivity α_x according to Xu and Eckstein 1995 and transversal dispersivity of 1/10 α_x). Using instead the dispersivity estimation method inherent to RISC 4.02, modelled groundwater concentrations are even lower.

River water concentrations (determined with the dilution factor approach, section 3.2.1.6) are a factor of approximately 23,000 lower than groundwater concentrations (Fig 13d to 13f). Scenarios are considered where a river is located 100, 1000 and 5000 m downstream of the source (in groundwater flow direction), and impacted by contaminated groundwater. Receptor points are located within the river, near the area where the contaminated groundwater flows in (concentrations are homogenously mixed in the water body). Modelling with RISC 4.02, performed to verify the applied approach for river water mixing gave similar results for a hydraulic gradient of 0.05% between groundwater and surface water.

b) Group II

As discussed above for contaminant mass, the results obtained for Group II refer to a worst case scenario for bioremediation with strain F113L::1180. Initial soil concentrations account for total A1016 (Appendix D, Fig. D1a and b). The studied microbes will breakdown the “degradable fraction” only (i.e. Group I as a subgroup of Group II), so that that a large portion of PCB (about 37 mg/kg) will still remain in soil after 50 years (Fig. D1b). PCB concentrations in other environmental media will be enhanced, accordingly. The CBA concentrations (Fig. D1c and f, Fig. D2c and f) are the same as for Group I (this group contains all PCB congeners, for which degradation and subsequent CBA formation was calculated).

4.1.2 Uncertainty and sensitivity analysis

Uncertainty refers to lack of knowledge about specific factors, parameters or models (US EPA 1997c). The latter study specifies scenario uncertainty (such as descriptive errors or incomplete analysis), model uncertainty (e.g. uncertainty due to necessary simplification of real-world processes) and parameter uncertainty (such as measurement or sampling errors). Sensitivity accounts for the variation in model output with respect to changes in the values of the model input (US EPA 1997c).

4.1.2.1 Model uncertainty

Uncertainty is given by the constraints inherent to the applied model procedures. Long time periods (50 to 100 years) and generic scenarios were modelled, in order to yield long-term (upper bound) estimates. The modelling of receptor point concentrations were intended for a subsequent preliminary assessment of potential risks (screening level evaluations). Thus, strongly simplified calculations were performed referring to homogeneous conditions.
Applying such methods for a real case study, a number of important processes might be neglected, such as preferential flow (percolation of water along soil fissures or root tubes). Furthermore, the assumption of a homogenous and isotropic distribution of soil organic carbon may yield misleading results. Layered structures of organic matter can be expected for alluvial domains (river valleys) or glacial deposits (e.g. Riser 2002), and such horizontal layers might act as barriers for organic compounds in leachate.
Similarly, spatial heterogeneity of hydraulic conductivity in an aquifer is known to largely influence contaminant transport (e.g. Fetter 1994). A high uncertainty is also associated to the estimation of dispersivity. Estimated groundwater concentrations were found to vary with a factor of 8, due to different methods in dispersivity approximation (section 4.1.1.2). Generally, results deviate largely between applicable model codes.

4.1.2.2 Uncertainty in estimating the biodegradation potential under field conditions

In this study, the microbial performance in soil was assumed to be identical to the laboratory. High uncertainties are associated to the modelling due to the estimation of kinetics in soil (related from the laboratory vial experiments). Furthermore, under field conditions, a number of biological and geochemical factors and processes might influence bacterial activity (such as substrate availability, reduced nutrient supply, toxic effects of contaminants and metabolites, etc.; Part III, section 2.5). The influence of uncertainties associated to specific parameters for biodegradation modelling will be discussed in section 4.1.2.3.
The degradation potential for Aroclor 1016 (by strain F113L::1180) is highly uncertain. Data that allow a quantification of the bioprocess are available for a small group of PCB congeners, only (Group I, about 39% of Aroclor 1016). However, Villacieros et al. (2005) found that F113L::1180 can degrade about 85% of Delor 103 (a technical mixture similar to Aroclor 1242) after 14 days (laboratory assays in vials). Aroclor 1242 is higher chlorinated than Aroclor 1016 (e.g. Frame 1996), so that the latter might posses the same (or even a higher) potential to be degraded. Thus, probably more than 39% of Aroclor 1016 (Group I) is degradable, and the Group II modelling (61% are recalcitrant to the bioprocess) is likely to be overly conservative.

Furthermore, scenario uncertainty is given, as a fresh Aroclor 1016 soil contamination (chosen for the modelling) might be unlikely under realistic conditions. At a given site (mature spill), the PCB congener pattern will be subject to considerable uncertainty.

4.1.2.3 Parameter uncertainty and sensitivity

High uncertainties are obvious for many environmental input parameters and physicochemical properties. In addition, many parameters are spatial and/or temporal variable (section 3.1.4). Thus, a sensitivity analysis was carried out in order to identify the most important parameters contributing to the variance of probabilistic results. Sensitivity was evaluated with the program Crystall Ball (Desicioneering 2001) by computing rank correlation coefficients between every input parameter and the forecast. Like in Part II, direct and inverse correlation was specified. Correlation coefficients ≥ 0.1 resp. ≤ -0.1 are presented in the following (assuming to represent the most significant contributions).

The results refer to the probabilistic concentrations shown in Appendix E. Sensitivities were found to be specific to the considered pathways and compounds, and they also differed between time steps.

Details are discussed in this section, concentrating on PCB 4, 18 and 52 and on 2,5-CBA. The PCB congeners were chosen as examples for compounds of different chlorination, accounting for high portions in Aroclor 1016 (Tab. 2). 2,5-CBA originates from degradation of PCB 18, 52 and other congeners, and it is the most frequent CBA formed by the bioprocess (Tab. 3).
Sensitivity charts were studied for different time steps. In some cases, for the initial phase of modelling, a low number of parameters was found to significantly contribute to the variance of result. This number increased with time (e.g. in soil, when contaminant loss processes like leaching gained importance).

Generally, the charts shown for PCB refer to the scenario without biodegradation. In contrast, considering biodegradation, also the number of soil bacteria B_S and (to a lower extent and compound-specific) the maximal removal velocity v_{max} had a high influence. This accounts for all pathways, and also for CBA (as they are formed by the bioprocess; B_S is most significant, throughout).

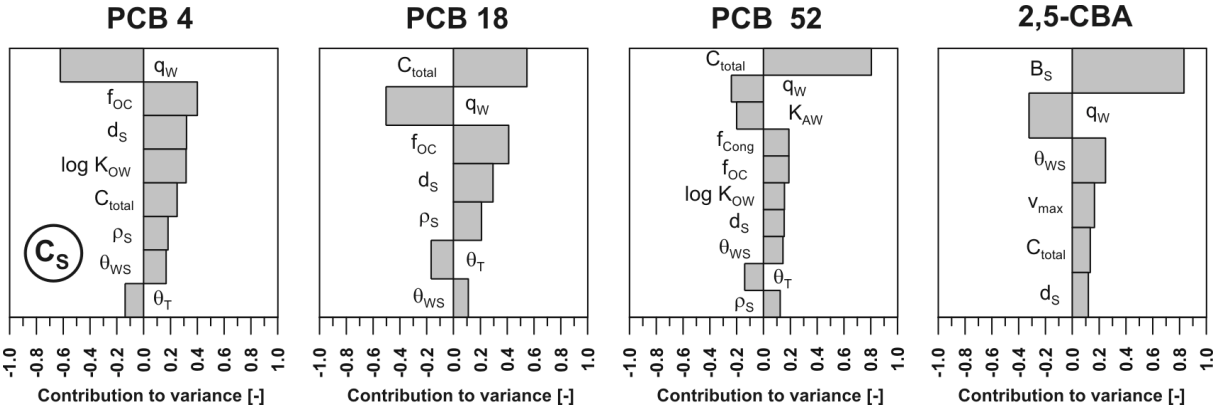


***Fig. 14**: Sensitivity analysis (modelling of contaminant partitioning). Parameter contributions to the variance of soil concentration for PCB 4, 18 and 52 and 2,5-CBA. See text for abbreviations.*

The variance of modelled **soil** concentrations C_S is a function of the initial estimate on uncertainty (C_{total}, f_{Cong}), but also other parameters revealed high contributions (Fig. 14). In fact, the uncertainty of initial soil concentration is based upon two components: the initial soil concentration of PCB in total (C_{total}), and the fraction of each modelled congener on total PCB (f_{Cong}). The first is generally more significant, but the latter is also of influence for PCB 52.
Furthermore, the infiltration rate q_w is important, as leaching significantly reduces PCB concentration in soil. This accounts for the presented compounds which are comparatively water soluble. In contrast, for higher chlorinated compounds such as PCB 101, q_w is negligible. Also important are the fraction of soil organic carbon f_{OC}, other soil parameters (total and saturated water content θ_T and θ_W, soil density ρ_S) and the source thickness d_S. Contributions given by the log K_{OW} and the dimensionless Henry's law constant K_{AW} are specific to the parameter uncertainty (Part II, section 3.3.1) and the degree of chlorination, i.e. related to evaporation or sorption tendency. Especially high contributions for the variance of CBA concentrations are given by the uncertainty of the bacterial number in soil B_S and (to a lower extent, varying between compounds) to the maximal removal velocity v_{max} .

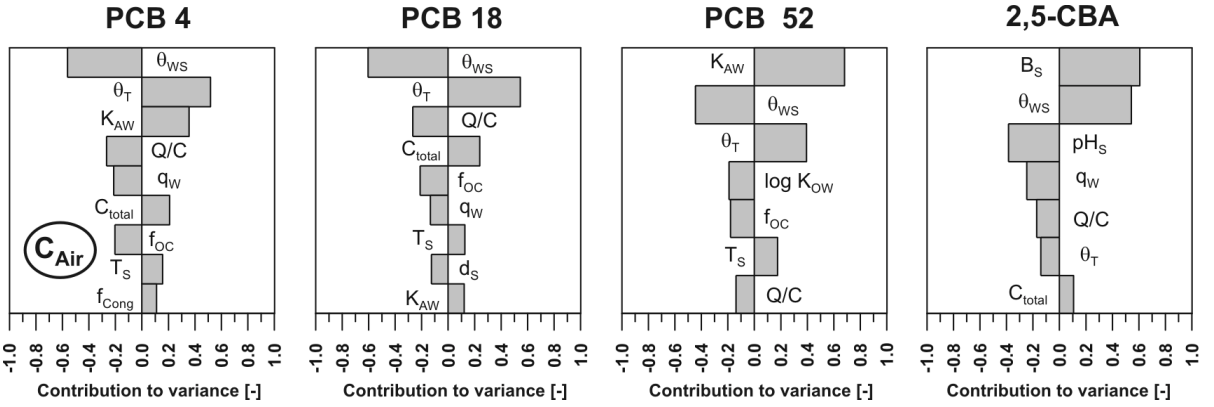


***Fig. 15**: Sensitivity analysis (modelling of contaminant partitioning). Parameter contributions to the variance of air concentration for PCB 4, 18 and 52 and 2,5-CBA. See text for abbreviations.*

Uncertainty and spatial variability of soil parameters (θ_W, θ_T and f_{OC}) show high contributions to the variance of **air** concentrations C_{Air} (Fig. 15). Also of importance is K_{AW} (especially for PCB 52, due to a high parameter uncertainty) and log K_{OW}. Further contributions are given by the dispersion factor Q/C (especially for low chlorinated PCBs) and C_{total} resp. f_{Cong}. The soil temperature T_S and source thickness d_S, and furthermore the infiltration rate q_w might contribute considerably, as well. The uncertainty of bacterial numbers in soil most significantly contributes to the variance of CBA air concentrations, and also a variable pH in soil pH_S is of importance.

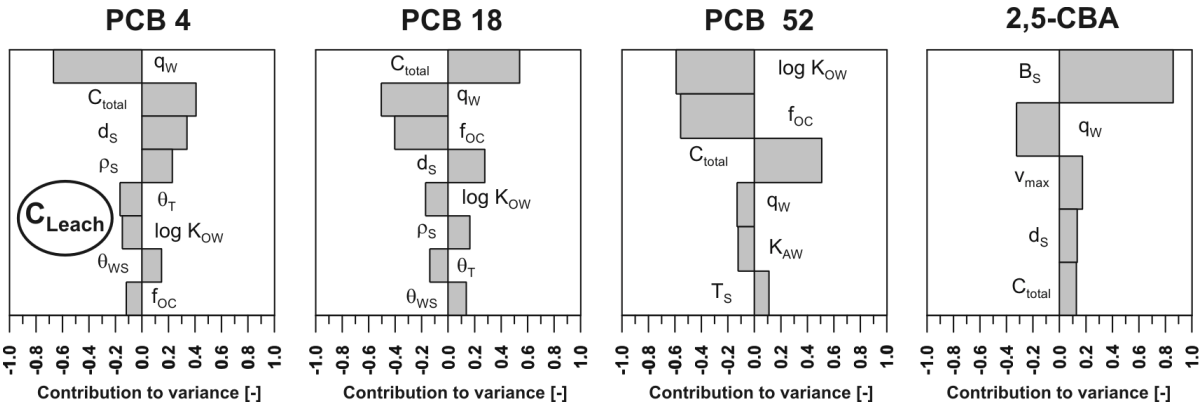


***Fig. 16**: Sensitivity analysis (modelling of contaminant partitioning). Parameter contributions to the variance of leachate concentration for PCB 4, 18 and 52 and 2,5-CBA. See text for abbreviations.*

For the variance of **leachate** concentrations C_{Leach} (Fig. 16), high contributions are given by q_w. This is especially the case for low chlorinated PCBs and for CBA, correlating to an enhanced leaching capacity. C_{total} and f_{OC} are also of influence, the latter increasingly with chlorine content of the considered compound. The source thickness d_S, the soil parameters θ_W, θ_T and ρ_S, and log K_{OW} resp. K_{AW} might be important, as well.
A much lower number of parameters significantly contribute to the variance of **groundwater** and **river water** concentrations. For groundwater concentrations, especially effective hydraulic conductivity k_f and effective porosity n_e, furthermore f_{OC}, q_W , ρ_S and (for some PCBs) log K_{OW} are of importance (and B_S, v_{max} for CBA, plus for the biodegradation scenario). For river water, in addition the flow velocity u_R has to be considered.

The parameters identified to contribute significantly to the variance of soil concentrations were also found to be important concerning **root** concentrations. Additionally, uncertainties of the root lipid content L_R and the correction factor b_{KRW} are of influence (for PCB only), and the fraction of apparent free space in root *AFS* plus the soil pH (pH_S) for CBA.

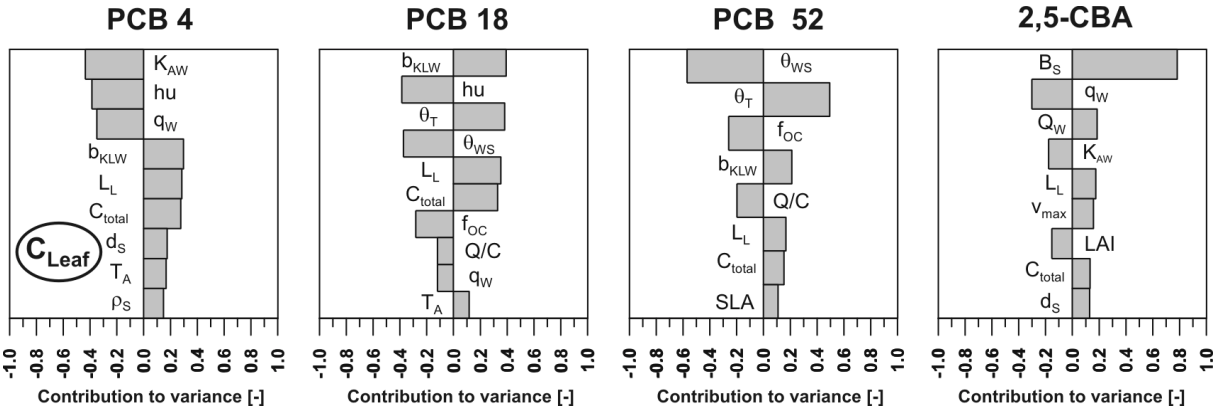


***Fig. 17**: Sensitivity analysis (modelling of contaminant partitioning). Parameter contributions to the variance of leaf concentration for PCB 4, 18 and 52 and 2,5-CBA. See text for abbreviations.*

Figure 17 shows sensitivity charts for the probabilistic modelling of **leaf** concentration C_{Leaf}. The air humidity *hu*, the K_{AW} (for PCB 4) and, to a lower extent, the dispersion factor *Q/C* contribute considerably for the PCBs. These findings reflect the importance of air-leaf exchange process, especially for the low chlorinated PCB 4 and 18 (indicated also by the influence of variable air temperature T_A). Further contributions are given by the correction factor b_{KLW} and the lipid content in leaf L_L, soil parameters (f_{OC}, θ_T, θ_W, ρ_S), C_{total} and the thickness of contamination d_S. High contributions of the infiltration rate q_W and the transpiration stream Q_W, as observed for CBA, can be assigned to the fact that plant uptake from soil water is the pathway of concern for these compounds. Finally, also the uncertainty inherent to the estimation of leaf area and volume (specific leaf area *SLA* and leaf area index *LAI*) can be of influence.

Trapp (2000) expects low to moderate variations of ratios between plant parameters (such as surface area, volume, growth rates and fluxes) for plants from the same ecosystem type. This assumption is based upon the fact that water use efficiency, leaf area index, growth rates, etc., are within a small range in which the plants are able to survive and compete (Larcher 1995).
Whereas for neutral compounds, the theory of plant uptake and transport appears to be almost fully understood, in contrast, for weak electrolytes, gaps in knowledge are much broader (Trapp 2004). The parameter supposed to have the largest influence on the fate of electrolytes in plants is the membrane permeability. It is very unclear whether the empirical relations between membrane permeability and log K_{OW} (Eq. 82 and other regressions) are accurate for ions. For this reason, Trapp (2004) pronounces the necessity to determine adequate membrane permeabilities for organic acids and bases, in order to improve the quality of model predictions.

4.2 Risk evaluation for PCBs and CBAs

Risks were calculated for generic exposure scenarios (section 3.2.1) based upon the receptor point concentrations presented in the previous section, and the input parameters provided in Tab. 10. Toxicity values were considered as described in section 3.2.5. Deterministic and probabilistic calculations were performed, as done for the contaminant concentrations (concentrations and risk values were determined within the same model run). In the following, best estimates and values of the 95th percentile are discussed (the latter assuming to represent reasonable conservative estimate). Concerning cancer risk, target risks levels of 10^{-6} (US legislation for residential areas, e.g. US EPA 1996b) and 10^{-5} (as proposed by many EU member states such as Germany, e.g. FoBiG 1992) were considered.

4.2.1 Non-carcinogenic effects

Concerning non-carcinogenic effects potentially arising from the inhalation of contaminated ambient air, hazard quotients and indices below one were found for all modelled scenarios. Considering biodegradation with strain F113L::1180, reduction of risk corresponds to the decrease in air concentration, as the influence of CBA is negligibly low. A higher risk potential (factor 1.5) can be expected for the housing scenario (inhalation of outdoor air in the garden, see Fig. 18) than for the activity scenario (playing sports outside, see Appendix F).

Figure 18 shows results specific to Group I and Group II, based upon ambient air concentrations directly at the contaminated site (corresponding to an upper estimate for receptors points located adjacent to PCB contaminated soil). Exposure times *ET* of 2 h/d for adults and 3 h/d for children spending their time outside in the garden were chosen (section 3.2.4.3). However, referring to these calculations alone, risks from air inhalation cannot be excluded in total for residential areas near the site. In addition, indoor air has to be considered that potentially could be mixed with outdoor air while ventilation. The result might be additional risk perceived by residents. This pathway was not modelled in this study. As a rough and conservative estimate, assuming *ET* = 24 h/d, hazard quotients and indices might be a factor of 12 higher than shown in Fig. 18 (neglecting age-adjustment in exposure characteristics). Thus, values for *HQ* and *HI* around three can be obtained for Group II in maximum (e.g. multiplying the 95th percentile *HI* of 0.23 in Fig. 21d with 12). This value is expected to be rapidly reduced for receptors located more distant to the site. As a consequence of air dispersion, hazard quotients and indices clearly below one can be expected for receptors located 100 m downwind to the site (dilution factor around 0.17, estimated with Eq. 19; generic assumption with neutral stability class, stack height *H* of zero and receptor elevation *z* of 2 m).

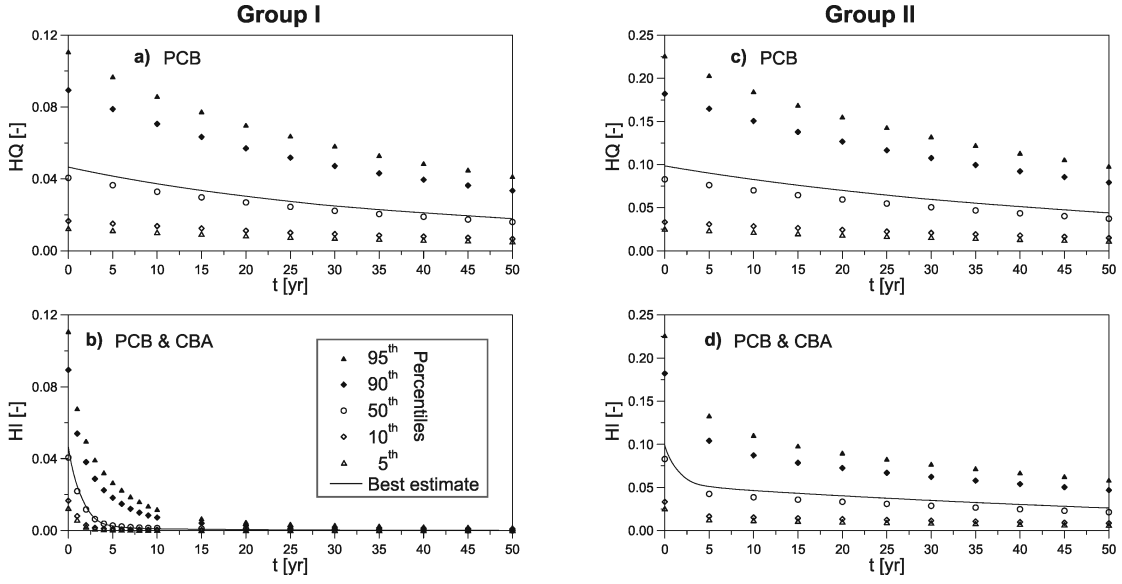


***Fig. 18**: Non-carcinogenic effects from ambient air inhalation, housing scenario. a), b): Group I, c), d): Group II; a), c): hazard quotient (PCB, no biodegradation); b), d): hazard index (PCB and CBA, biodegradation).*

Non-carcinogenic effects due to ambient air inhalation can be excluded for sports activities adjacent to the site (e.g. recreational area or sports facility). This accounts for a conservative scenario (section 3.2.4.3), where 95th percentiles of *HQ* resp. *HI* do not exceed 0.14 (Fig. F1c and d).

High hypothetical risks are obvious for the ingestion PCB contaminated leachate (Fig. F2a and c, Fig. F3a and c). Risks decrease as a result of biodegradation (Fig. F2b and d, Fig. F3b and d), but the amount of produced CBA significantly contributes to the hazard index. This is due to high CBA concentrations (the considered toxicity values of CBA are actually about 160 times lower than those for PCB, see section 3.2.5). The contribution of CBA can be viewed from Fig. F3b, where the influence of PCB on the *HI* is negligibly low (receptor point at a depth *z* = 0.5 m beneath the source). For the "degradable fraction" (Group I), potential impacts are lowered substantially, but the *HI* remains above one for the 95th percentile and the whole modelled period (Fig. F2b, F3b). For Aroclor 1016 in total (Group II) and a receptor point at a depth *z* = 0.5 m beneath the source, there is a peak in the beginning, then risks are lowered for a short time period until they rise again, due to the portion of PCB that is not biodegraded (Fig. F3d).

Potential impacts due to the ingestion of contaminated groundwater were analysed for different positions of the groundwater level relative to the source (directly below the source and at a mean depth *z* of 0.5 m, respectively), and as a function of distance *x* (groundwater well to site). In Fig. 19 and 20, retardation in the aquifer was neglected (retardation coefficient *R* = 1). These are deterministic values, Fig. F4 and F5 in Appendix F present probabilistic modelling results (calculated with retardation in the aquifer, for a groundwater well in 100 m downstream distance to the source).

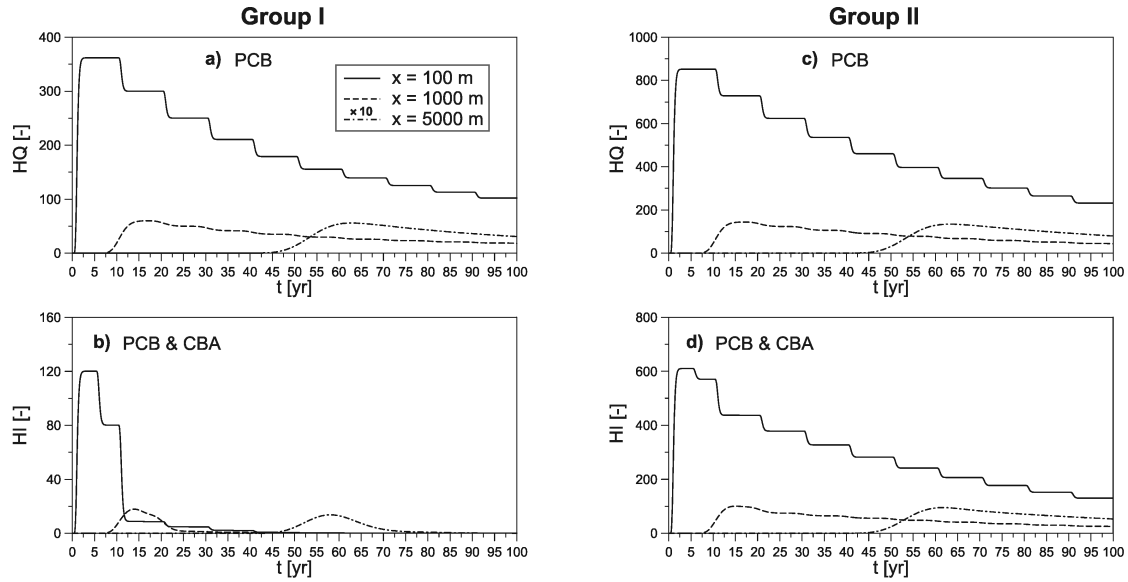


Fig. 19*: Non-carcinogenic effects from groundwater ingestion (domestic use as drinking water). For different groundwater wells (downstream distance x from the source), groundwater level at the source bottom (z = 0); neglecting retardation in the aquifer; a), b): Group I, c), d): Group II; a), c): hazard quotient (PCB, no biodegradation); b), d): hazard index (PCB and CBA, biodegradation). Curves for x = 5000 m are 10 fold exaggerated (x 10).*

Estimated PCB concentrations in groundwater revealed a considerable threat to drinking water for all scenarios without biodegradation (Fig. 19 and 20, a and c). Strain F113L::1180 could significantly reduce the impact potential, but only for Group I (Fig. 19b and 20b). The PCB mass reduction was insufficient for Group II, i.e. Aroclor 1016 in total (hazard quotients and indices are enhanced throughout, see Fig. 19d and 20d). Analogously as observed for the leachate, high contributions of CBA are obvious (see Fig. 20b, where the influence of PCB is negligible).
At a distance *x* of 100 m from the source (downstream direction), for Group I and considering biodegradation, the *HI* is expected to remain above one for 45 years (groundwater level GWL directly below the source, Fig. 19b) and 16 years (GWL half a meter below the source bottom, Fig. 20b). A hazard index below one was only achieved for Group I and a drinking water well at x = 5000 m, with a GWL located half a meter below the source (peak of *HI* = 0.4, Fig. 20b). For a GWL directly at the source bottom, the HI slightly exceeds unity due to contributions given by PCB (*HI* = 2 for *x* = 5000 m, Fig. 19b).

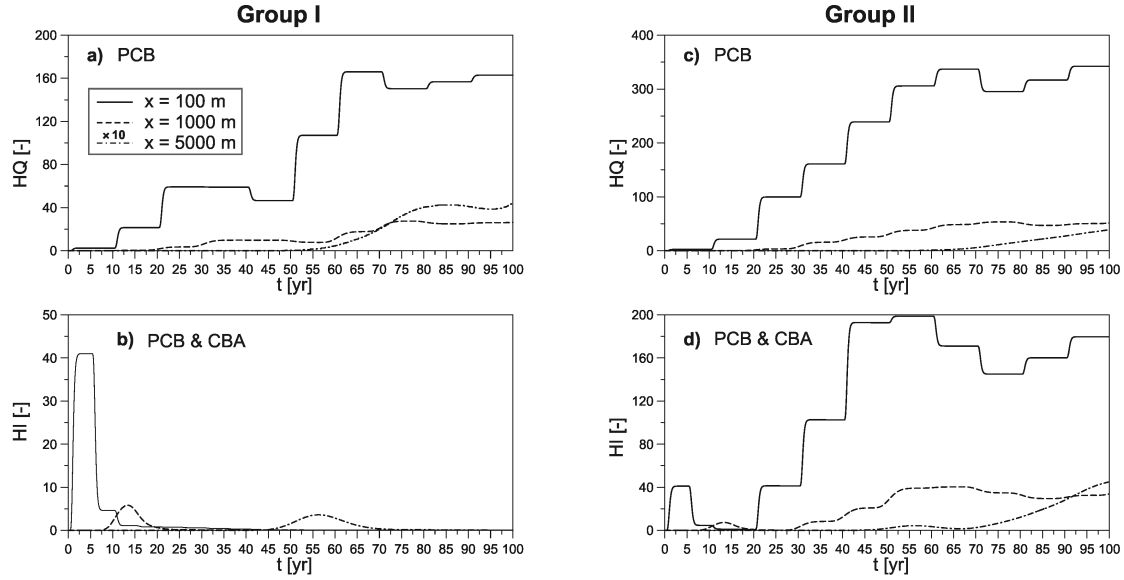


***Fig. 20**: Non-carcinogenic effects from groundwater ingestion (domestic use as drinking water). For different groundwater wells (downstream distance x from the source), groundwater level at a depth z = 0.5 m beneath the source; neglecting retardation in the aquifer; a), b): Group I, c), d): Group II; a), c): hazard quotient (PCB, no biodegradation); b), d): hazard index (PCB and CBA, biodegradation). Curves for x = 5000 m are 10 fold exaggerated (x 10).*

The results shown in Fig. 19 and 20 are based upon deterministic calculations. Taking into account potential uncertainty of these estimates, hazard indices might exceed unity, even for groundwater wells at x = 5000 m (scenario given in Fig. 20b, Group I). E.g., Fig. F5 reveals 95th percentile values that are up to 5 times higher than the deterministic results. On the other hand, the applied procedure is assumed to yield upper estimates. As discussed above (section 4.1.1.2), comparative modelling with RISC 4.02 yielded groundwater concentrations that are a factor of 8 lower for x = 5000 m.

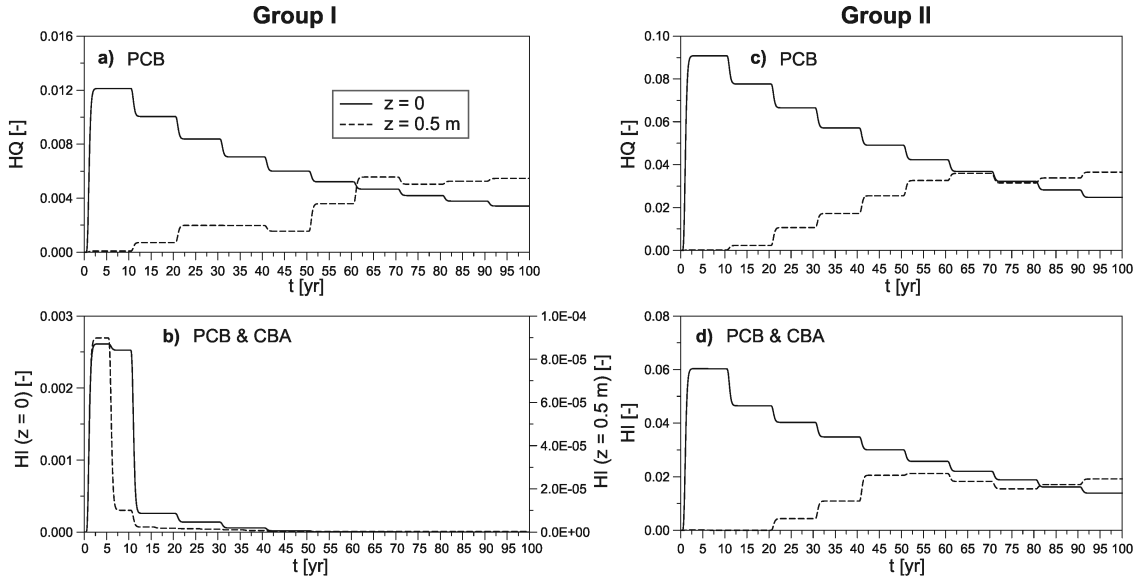


***Fig. 21**: Non-carcinogenic effects from exposure to river water while swimming (river water mixing with groundwater). Based upon groundwater level GWL at the source bottom (z = 0), and GWL at z = 0.5 m below the source); receptor point at x = 100 m downstream of the source; neglecting retardation in the aquifer; a), b): Group I, c), d): Group II; a), c): hazard quotient (PCB, no biodegradation); b), d): hazard index (PCB and CBA, biodegradation).*

For the swimming scenario (i.e. exposure to river water through dermal contact and accidental water ingestion), non-carcinogenic effects can be excluded. Hazard quotients and indices are more than one order of magnitude below one for all scenarios (Fig. 21). Probabilistic results (considering retardation in the aquifer) are shown in Fig. F6.

4.2.2 Carcinogenic effects

The decrease of PCB receptor point concentrations corresponds to the reduction of total cancer risk as CBAs are non-carcinogenic compounds.

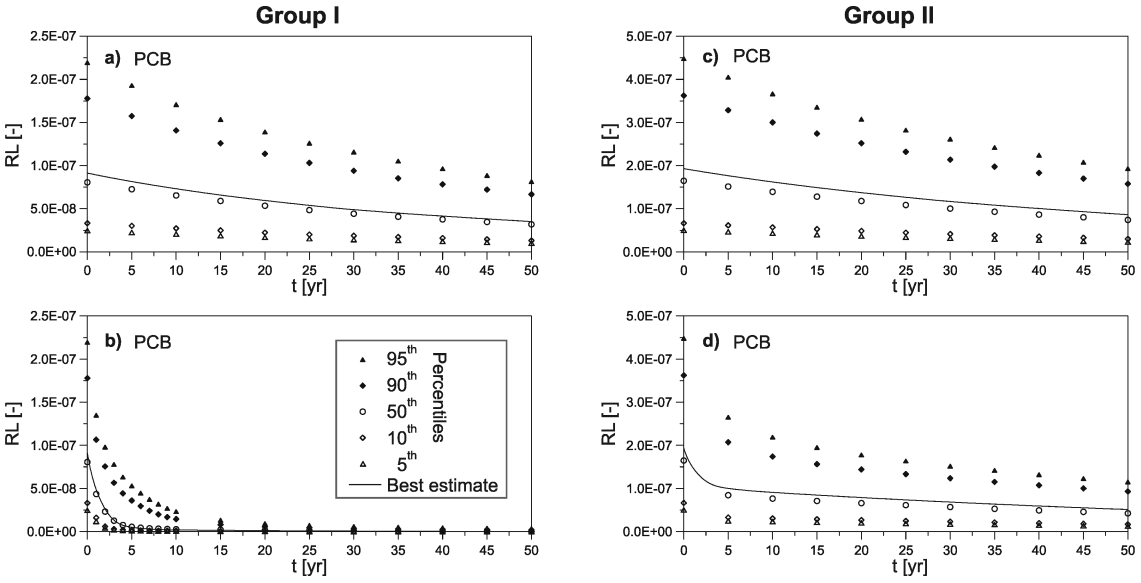


***Fig. 22**: Carcinogenic effects from ambient air inhalation, housing scenario: cancer risk levels for PCB. a), b): Group I, c), d): Group II; a), c): no biodegradation; b), d): biodegradation.*

For air inhalation, risk levels were below 10^{-6} for the modelled scenarios. Therefore, the criteria for residential areas are met (target risk level of 10^{-6} in US legislation, 10^{-5} for EU member states, see beginning of section 4.2). Fig. 22 shows cancer risk levels for the residential scenario (inhalation of outdoor air in the garden). As already described for non-carcinogenic effects (section 4.2.1), the risk potential is higher compared to the sports activity scenario (shown in Fig. F7). Accounting for uncertainties with respect to inhalation of contaminated indoor air that might occur with residential land use (i.e. applying a factor of 12 according to section 4.2.1), the maximum *RL* would be $4.5 \times 10^{-7} \times 12 = 5.4 \times 10^{-6}$ (4.5×10^{-7} is the maximum 95th percentile *RL*, see Fig. 22c and d). At a distance *x* of 100 m (downwind from the side), the risk level for potential receptors will be below 10^{-6} considering air dispersion (dilution factor of 0.17, section 4.2.1).

Risk levels for leachate ingestion (hypothetical domestic use as drinking water) reached high values for conditions without biodegradation (Fig. F8 and F9, a and c). A significant decrease by the bioprocess can only be expected for Group I ("degradable fraction", Fig. F8b and F9b). Here, the risk level remained above 10^{-5} for the 95th percentile (for a receptor point at the source bottom Fig. F8b), but it was lowered to a negligibly range for receptor points located half a meter below the source (Fig. F9b).

For the scenario without biodegradation, PCB in groundwater poses a clear cancer risk (domestic use as drinking water, Fig. 23 and 24, a and c). As for the leachate, risk levels are reduced effectively for Group I only (due to PCB breakdown by the investigated microbes), i.e. reaching negligibly low values for z = 0.5 m (Fig. 24b). For z = 0 m and Group I, risk levels will remain considerably high for long time periods, as can be seen from Fig. 23b (deterministic estimation, x = 100 m: 22 years above 10^{-5}, 42 years above 10^{-6}; for x = 1000 and 5000 m, peaks exceeding 10^{-5} are expected). Results of probabilistic calculations are shown in Fig. F10 and F11, for x = 100 m (considering retardation in the aquifer).

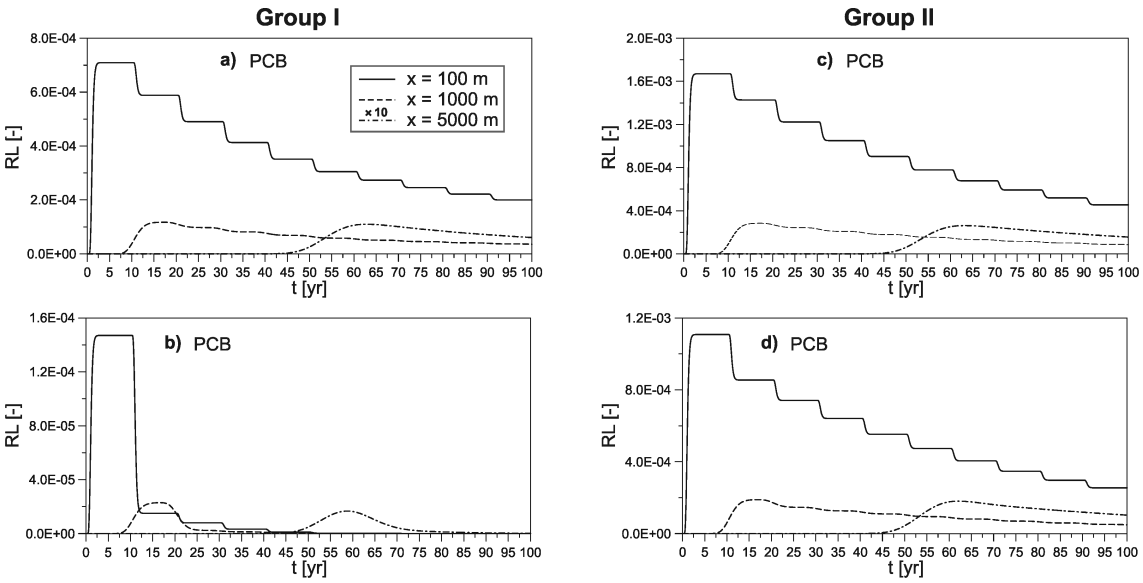


***Fig. 23**: Carcinogenic effects from groundwater ingestion (domestic use as drinking water), cancer risk levels for PCB. For different groundwater wells (downstream distance x from the source), groundwater level at the source bottom (z = 0); neglecting retardation in the aquifer; a), b): Group I; c), d): Group II; a), c): no biodegradation; b), d): biodegradation. Curves for x = 5000 m are 10 fold exaggerated (x 10).*

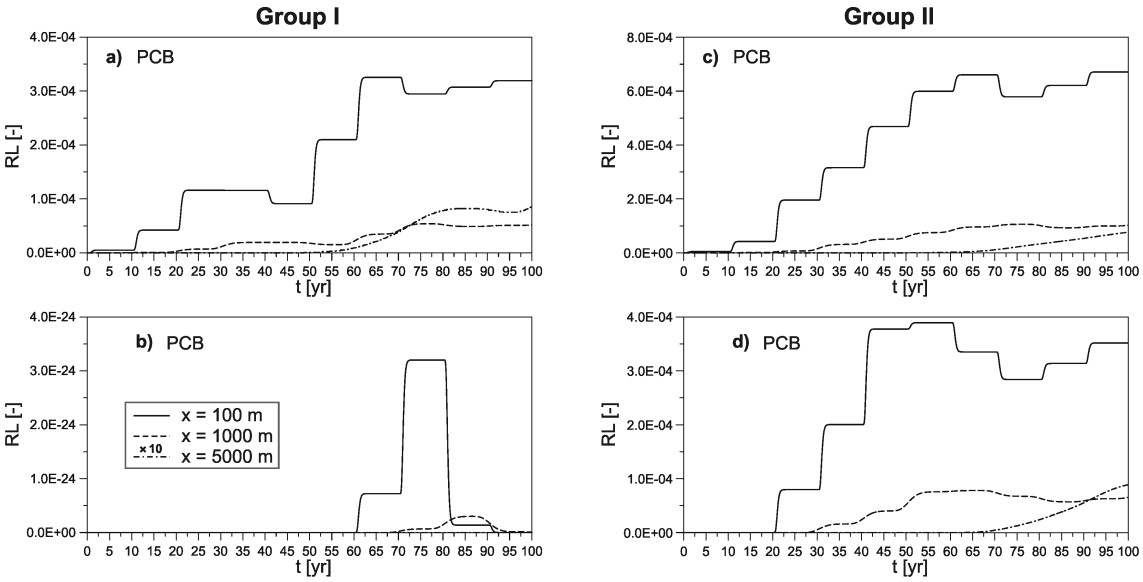


***Fig. 24**: Carcinogenic effects from groundwater ingestion (domestic use as drinking water). For different groundwater wells (downstream distance x from the source), groundwater level at a depth z = 0.5 m beneath the source; neglecting retardation in the aquifer; a), b): Group I; c), d): Group II; a), c): no biodegradation; b), d): biodegradation. Curves for x = 5000 m are 10 fold exaggerated (x 10).*

For potential exposure to contaminated river water while swimming (ingestion and dermal contact), cancer risk levels were significantly below 10^{-6} for all studied scenarios (Fig. 25; for probabilistic results, refer to Fig. F12).

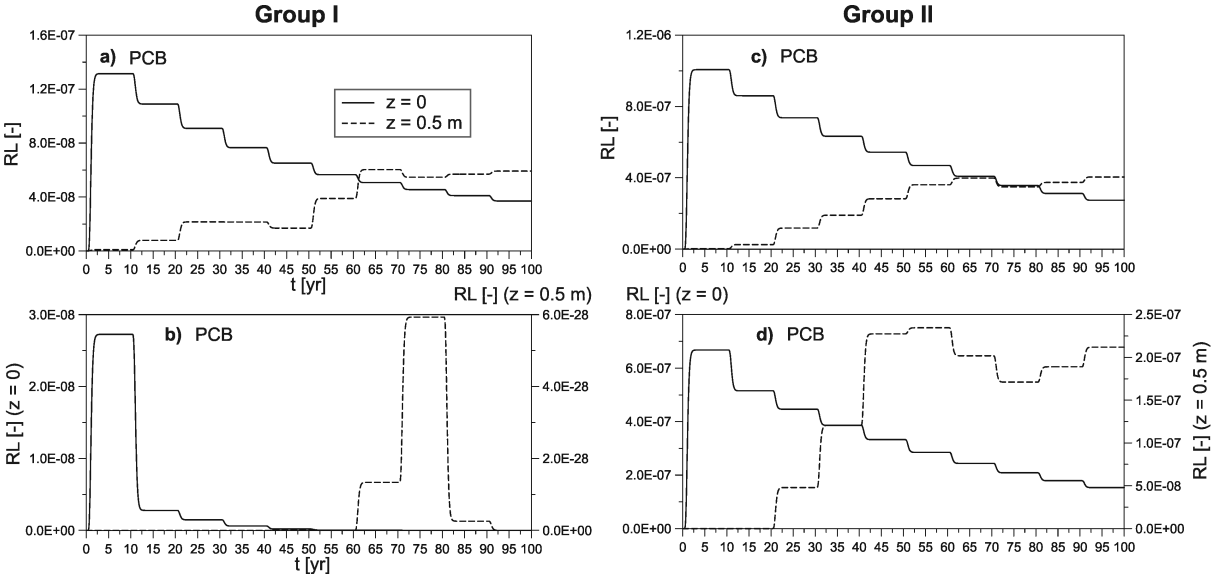


***Fig. 25**: Carcinogenic effects from exposure to river water while swimming (river water mixing with groundwater). Based upon groundwater level GWL at the source bottom (z = 0), and GWL at z = 0.5 m below the source); receptor point at x = 100 m downstream of the source; neglecting retardation in the aquifer; a), b): Group I; c), d): Group II; a), c): no biodegradation; b), d): biodegradation.*

4.2.3 Impacts on ecological receptors

Potential impacts on ecological receptors were studied for the fish species bluegill (*Lepomis* macrochirus) and fathead minnow *(Pimephales* promelas). For bluegill, no-observed-adverse-effect-concentrations (NOAECs) selected from literature refer to mortality (Tab. 15). Unfortunately, for fathead minnow, reported data are related to different effects, i.e. mortality for CBA and general accumulation for Aroclor 1016. Thus, hazard indices were determined for bluegill only (as required for the scenario of biodegradation, i.e. to estimate potential impacts of PCB and produced CBA). For exposure to CBA, bluegill is the more sensitive species. Lowest NOAECs from Tab. 15 were selected (worst case scenario, section 3.2.5.2).

In case that more than one NOAEC was available (Tab. 15), the lowest value was chosen in order to follow a worst case scenario. A NOAEC of 90 µg/L was selected for the whole group of CBA. Hazard quotients and indices for leachate and groundwater discussed in this section correspond to hypothetical risk, actually, as they relate to fish (toxicity data were not found for organisms typically expected to live in the vadose zone or aquifer that might be exposed to PCB and CBA).

Hazard quotients for exposure to PCB-contaminated leachate are very high, when no biodegradation is considered (Fig. F13 and F14, a and c). With biodegradation, risks are lowered remarkably for Group I, but the hazard index is greater than one during the whole modelling period (for all studied scenarios). Similarly as observed above (non-carcinogenic effects on human health), CBA reveals a significant contribution (visible from Fig. F14b, where the amount of PCB reaching the receptor point is nearly zero).

For potential exposure to groundwater and river water, deterministic values are shown in Fig. 26 and 27. Probabilistic results are provided in Fig. F15 to F17. Risks are clearly enhanced for the exposure to PCB-contaminated groundwater (Fig. 26 and 27, a and c). Considering PCB breakdown due to the use of the studied microbes, hazard indices reduce fast for Group I (slow decrease for Group II). Nevertheless, at receptor points located 100 m downstream of the source, the HI is greater than one for a long time (62 years for z = 0, 46 years for z = 0.5 m), and at x = 1000 m and x = 5000 m, peaks with high values are expected (Fig. 26b and 27b). These results were derived neglecting retardation. In comparison, probabilistic calculations (considering retardation) revealed hazard indices (95th percentiles) remaining above one for all scenarios with x = 100 m (F15 and F16, b and d).

Concerning the exposure to river water, hazard indices are very low throughout (Fig. 26 and 27, compare to Fig. F17). The presented results account for a river of moderate dimension and flow rate (Tab. 8). When a smaller river is considered, impacts will be enhanced. For a river with a flow rate that is 10 times lower (e.g. river width of 1 m instead of the 10 m modelled), risks will be approximately a factor of 10 higher (Eq. 43). In this case, a threat by PCB will be given for the studied fish species that potentially could be reduced applying the bioprocess (hazard indices below one for Group I, and for Group II with $x \geq 1000$ m; insufficient reduction for Group II with $x = 100$ m).

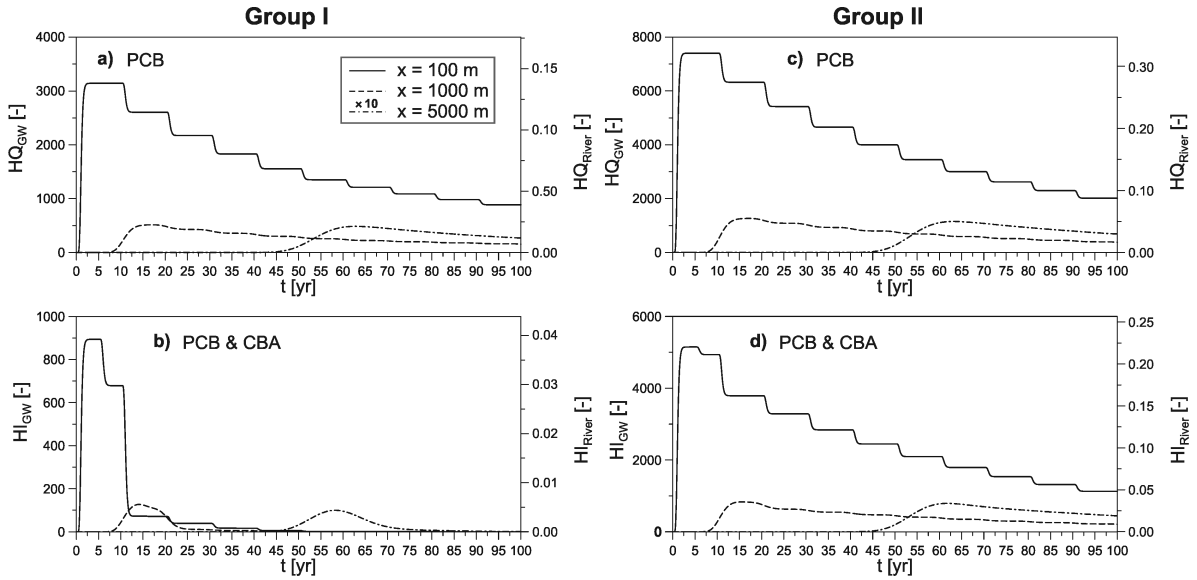


***Fig. 26**: Exposure of bluegill (*Lepomis *macrochirus) to contaminated groundwater and river water. For different groundwater wells (downstream distance* x *from the source), groundwater level at the source bottom (*z *= 0); neglecting retardation in the aquifer; a), b): Group I; c), d): Group II; a), c): hazard quotient (PCB, no biodegradation); b), d): hazard index (PCB and CBA, biodegradation). Curves for* x *= 5000 m are 10 fold exaggerated (x 10).*

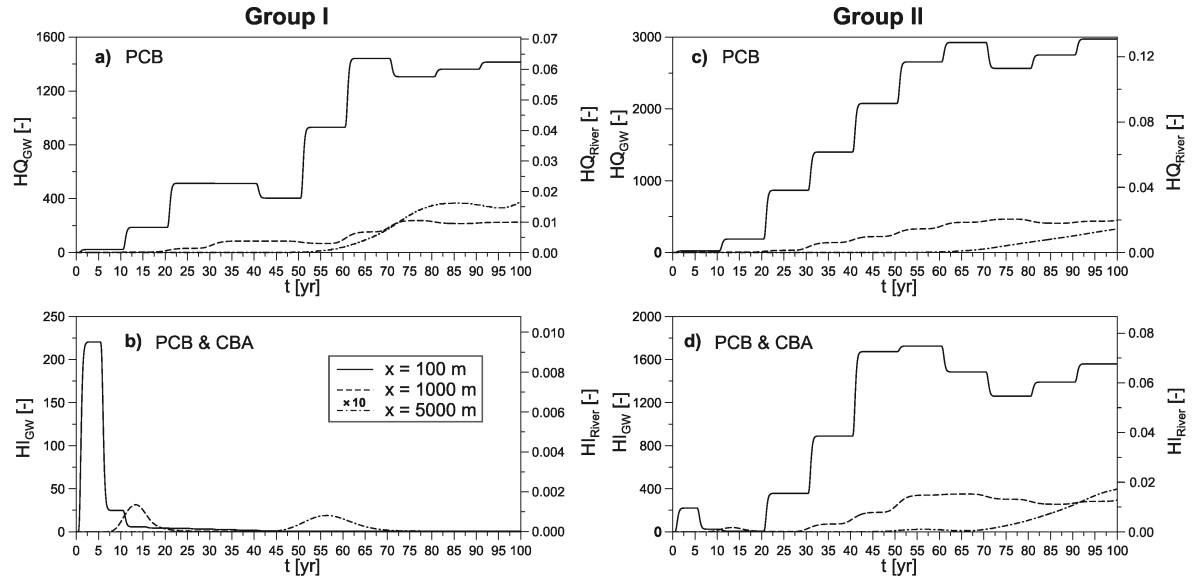


***Fig. 27**: Exposure of bluegill (*Lepomis *macrochirus) to contaminated groundwater and river water. For different groundwater wells (downstream distance* x *from the source), groundwater level at a depth* z *= 0.5 m beneath the source; neglecting retardation in the aquifer; a), b): Group I; c), d): Group II; a), c): hazard quotient (PCB, no biodegradation); b), d): hazard index (PCB and CBA, biodegradation). Curves for* x *= 5000 m are 10 fold exaggerated (x 10).*

4.2.4 Uncertainty and sensitivity analysis

Uncertainties associated to estimated risks are due to uncertain receptor point concentrations (section 4.1.2), and due to additional contributions.

4.2.4.1 Uncertainty of toxicity values and impacts on ecosystems

The utilised toxicity values for human health risk assessment were deduced from experiments with test animals. The considered oral reference dose RfD_o for Aroclor 1016 (7.0×10^{-5} mg $kg^{-1}d^{-1}$, Tab. 13) was derived by applying an uncertainty factor of 300 (10 for extrapolating from a low-adverse-effect-level LOAEL to a no-adverse-effect-level NOAEL, 3 for extrapolating from monkeys to humans, and 10 for human variability; IRIS, US HHS 2000). As described in section 3.2.5.1, reported inhalation and dermal reference doses (RfD_i, RfD_d) both are related to the RfD_o ($RfD_i = RfD_o$; $RfD_d = 0.9 \times RfD_o$; 0.9: gastrointestinal absorption factor). The reference dose used for CBA (0.01 mg $kg^{-1}d^{-1}$ for all CBA compounds and pathways) is assumed to account for an upper estimate (section 3.2.5.1).

Cancer slope factors recommended for PCBs are based upon rat liver tumour incidence data for Aroclor mixtures (US HHS 2000). The range of chronic oral slope factors (SF_o= 2, 0.4 and 0.07 per (mg kg^{-1} d^{-1}), section 3.2.5.1) reported for PCB represents an upper bound estimate. These approximations consider uncertainties due to changes in congener composition by environmental processes (partitioning, chemical transformation, bioaccumulation) and implement criteria of risk and persistence (US HHS 2000; section 3.2.5.1).

No-adverse-effect-concentrations (NOAECs) are only given for a small number of ecological receptors (section 3.2.5.1). Accordingly, there is considerable uncertainty concerning potential impacts on total ecosystems (i.e. organisms that might be more sensitive to PCB and CBA than the investigated fish species). Moreover, the number of CBA compounds is limited, for which data are available (Tab. 15). The NOAEC values from Tab. 15 were determined from subchronic LC50 data by applying an uncertainty factor of 1000 (10 for each extrapolation step: subchronic to chronic LC50, chronic LC50 to low-adverse-effect-concentrations LOAEC, LOAEC to NOAEC). Lowest values were considered for the modelling (upper estimate of potential impacts on the studied fish species).

4.2.4.2 Parameter sensitivity

Generally, all parameters (i.e. their uncertainty and/or variability) showing high contributions to the variance of receptor point concentrations were also found to be of relevance for the risk estimations (section 4.1.2). Exposure parameters that additionally revealed important influence were the inhalation rate *IH* and water ingestion rate *IR* (air inhalation and drinking water ingestion, respectively), body weight *BW* (especially for drinking water ingestion), and (to a lower extent) exposure time and frequency (*ET* and *EF*).

4.3 Impact analysis of GMOs

4.3.1 Bacterial dispersion – results of mesocosm experiments

Table 16 summarises results of bacterial counts in willow roots, willow leaves, roots and shoots of weeds, bulk soil and leachate (sampling after 224 days of experiment). Bacterial counts on TSA medium include all microbes, i.e. F113 derivatives and the natural background. Measurements on SA plus rifampicin medium were expected to be specific to the inoculated (rifampicin-resistant) strains. Surprisingly, bacterial counts with control samples (without inoculum) on SA plus rifampicin revealed positive result. These observations can be assigned to a background of rifampicin-resistant microbes and were treated as false positives. Accordingly, the detection limits of the experimental system (indicated in Tab. 16) were derived from no inoculum false positives and from the detection limit of the counting procedure, whatever was larger. The observed ranges in Tab. 16 were obtained from triplicate plate counts (expect for SA + rifampicin, no inoculum, soil: duplicate measurements).

As can be seen from Tab. 16, all inoculants (plate counts on SA + rifampicin) were below detection limit for willow leaves and weed shoots. Bacterial numbers in weed roots and leachate were below the background (false positives) in most cases. Slightly enhanced microbial numbers could be observed for F113rifpcb and weed roots, and for F113rif and F113rifL::1180 in leachate (observed maximum value). Nevertheless, a high measurement uncertainty is given as the level of bacterial counts is very low. Accordingly, after 224 days, bacteria are well established in root and soil (compare to Part III) but microbial dispersion into willow leaves, weed shoots and roots and leachate is supposed to be insignificant for the investigated strains.

***Tab. 16**: Bacterial plate counts in different media (mesocosm experiments), average values (observed ranges in parentheses).The sign < indicates below detection limit.*

	SA + rifampicin medium [cfu/mL or g fresh wt]		10%TSA medium [cfu/mL or g fresh wt]	
	Average	**Observed range**	**Average**	**Observed range**
No inoculum				
Leachate	62	45-83	4.0×10^4	$(1.1\text{-}8.9) \times 10^4$
Weed shoots	<100		6.0×10^5	
Weed roots	4500		4.9×10^6	
Soil	2900	1800-4000	3.2×10^6	$(2.2\text{-}4.8) \times 10^6$
F113rif				
Leachate	58	2-132	5.2×10^4	$(0.8\text{-}8.5) \times 10^4$
Alive willow leaves	<220		<220	
Dead willow leaves	<360		710	
Weed shoots	<100		8.0×10^6	
Weed roots	200		1.8×10^8	
Soil	1.4×10^4	$(1.3\text{-}2.7) \times 10^4$	4.6×10^6	$(3.1\text{-}7.0) \times 10^6$
Willow roots	5.1×10^4	$(2.5\text{-}6.6) \times 10^4$	7.8×10^7	$(4.5\text{-}9.5) \times 10^7$
F113rifpcb				
Leachate	2	1-5	9.8×10^4	$(4.2\text{-}21.0) \times 10^4$
Alive willow leaves	<390		380	
Dead willow leaves	<330		670	
Weed shoots	---		3.0×10^5	
Weed roots	4700		9.2×10^7	
Soil	9400	$(0.14\text{-}1.8) \times 10^4$	2.4×10^7	$(3.0\text{-}3.9) \times 10^7$
Willow roots	4.9×10^4	$(2.9\text{-}7.6) \times 10^4$	7.3×10^7	$(1.7\text{-}16.0) \times 10^7$
F113rifL::1180				
Leachate	40	1-101	1.6×10^5	$(1.1\text{-}2.5) \times 10^5$
Alive willow leaves	<310		<310	
Dead willow leaves	<1000		1.2×10^5	
Weed shoots	<100		2.7×10^6	
Weed roots	<100		4.7×10^7	
Soil	6200	4600-9091	7.5×10^6	$(4.6\text{-}13.0) \times 10^6$
Willow roots	1.2×10^5	$(0.54\text{-}3.0) \times 10^5$	7.7×10^7	$(5.6\text{-}9.9) \times 10^7$

4.3.2 Results of the field release experiment

4 ¼ years after the release, microbes were counted in samples of willow roots, root-free soil material, willow leaves and roots and shoots of fire weeds (*Epilobium* angustifolium), as illustrated in Fig. 28. Table 17 indicates the number and location of samples taken.

F113rif strains were only found in the rhizosphere of inoculated willows (plantation A, B and C, see Tab. 17 and Fig. 9). Numbers were very low, ranging between 20 cfu/g fresh weight fw (i.e. near the detection limit) and 140 cfu/g fw. At the time of sampling, there was no hint on microbial spreading from inoculated willow roots to other media within the plantation, nor could the microbes be detected in any of the samples taken outside (the samples points were located in 19, 45 and 59 m distance to the willow plantation, see Fig. 9).

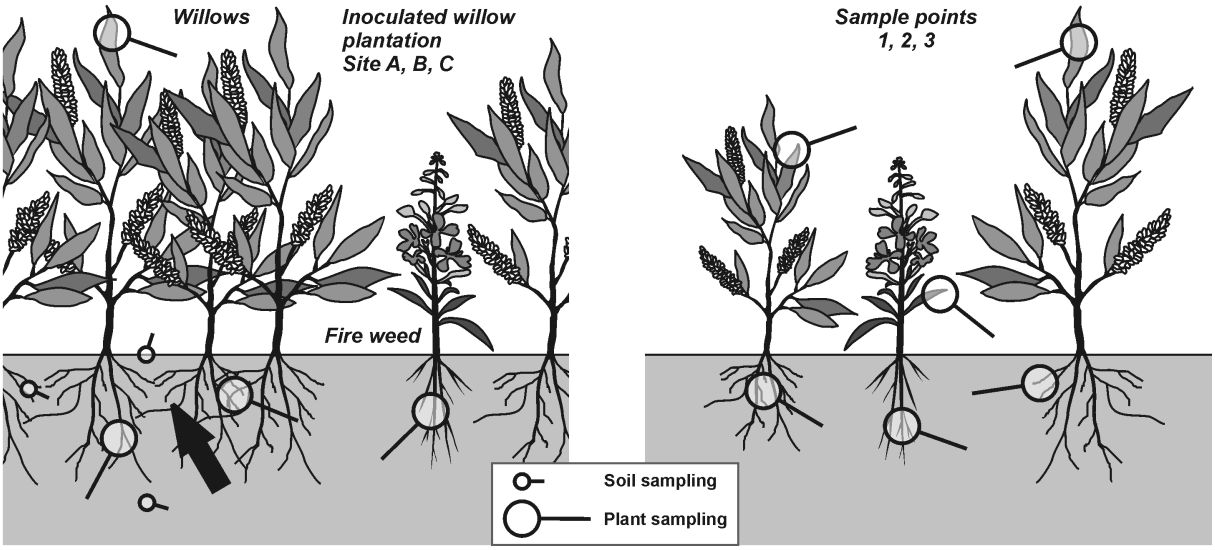


***Fig. 28**: Sampling campaign (field release experiment with F113rif).*

***Tab. 17**: Number of samples taken at the end of the field release experiment (after 4 ¼ years). In parentheses: number of positive results. (a): samples in the root system of one individual plant, (b): combined samples from several individuals, (c): beneath willow plant, (d): wild willow plants of different age (some were younger than those planted).*

	Depth	No. of samples			Depth	No. of samples
		Plantation A	Plantation B	Plantation C		Point 1, 2 and 3
Willow root	10-70 cm (a)	7 (1)	5 (1)	7 (3)	20-40 cm (d)	3
	20-60 cm (b)	2	2	1(1)		
Soil (root-free)	surface	1	1	1		
	20 cm	1	1	1		
	80-100 cm (c)	1	1	1		
Willow leaves		1	1	1		10
Fire weed roots			2	1		2
Fire weed shoots						2

4.3.3 Gene transfer

The studies performed *in vitro* and *in vivo* demonstrated that lateral transfer between homologue bacteria is possible, albeit at a very low frequency (10^{-9}). This accounts for lateral transfer of an introduced *bph* trait from strain F113pcb to a homologous recipient. Frequencies were low as the trait was stably inserted into the chromosome of the microbe (Brazil et al. 1995). Potential hazards resulting from gene transfer depend on the nature of the trait. The transfer of the investigated trait did not effect the fitness of the host strains.

4.3.4 Impacts of GMOs on microbial communities

The rhizospheric bacterial communitiy which evolved from the native soil community during the development of the root system was distinct from the soil community. This accounts for all studied groups except for *Actinobacteria*. *Proteobacteria* sequences, which were enriched in the rhizosphere were dominant. Respective results are based upon the analysis of 320 different clones, grouped into 105 Operational Taxonomic Units (OTUs) that were sequenced.

Generally, a good correlation was observed for the impact of GMOs on the function (BIOlog plates) and structure (PCR-TGGE analysis) of microbial communities. The findings can be summarised as follows:

a) Function of microbial communities:

- no statistical significant differences in soil samples of different treatments
- significant differences in rhizosphere samples of different treatments (for all communities)
- significant differences between rhizosphere and soil samples
- significant differences between planted and unplanted soil samples

b) Structure of bacterial communities:

- no differences in soil samples of different treatments
- differences between treatments in rhizosphere samples
- differences between soil and rhizosphere samples for most of the investigated bacterial groups
- no differences between planted and unplanted soil samples

Thus, effects due to the introduction of the considered GMOs can be expected for rhizosphere populations, but not for soil communities. The impact exerted by the GMOs (especially strain F113L::1180) on rhizosphere populations can be related to effects of the transgenes on the carbon sources present (Aguirre de Cárcer D, personal communication).

4.3.5 Uncertainty and sensitivity

There is lack of knowledge concerning long-term effects. This accounts for evaluated gene transfer (the experiments covered between one and two months) and the spreading and dispersion potential of F113 inoculants. Findings on the microbial fate refer to 4 ¼ years (field trial) and about 7 months (mesocosm experiments). The field trial was performed with non-GM F113 strains, but similar behaviour patterns between the wild type and the genetically modified strains can be assumed (Brazil 1995). Microbe leaching was not investigated in the field, but it is assumed to be irrelevant for the studied strains (based upon the mesocosm results). However, measurement uncertainty is considerably high, due to very low bacterial numbers being present in many of the analysed media (near the detection limit).

Potential impacts of GMOs on microbial communities were investigated, but information is lacking on interactions with other organisms. E.g., Schmidt et al. (1997) reported high numbers of *Pseudomonas* corrugata strains in earthworm casts. Tebbe et al. (1996) found bacterial enrichment in the guts of soil insects. Respective microbe uptake could have a negative influence on a host. Moreover, soil organisms might facilitate GMO transport, thus contributing to microbial spreading.

4.4 Summary – Chemical risk and GMO fate and impact

Low impacts were evaluated for the inhalation of contaminated air, considering a buried source at a mean depth of 30 cm. Risks were negligible for outdoor activities (e.g. at a sports facility), even directly adjacent to the site in main wind direction. Risk were found to be acceptable for housing scenarios, i.e. for receptors located 100 m or more downwind to the site (outdoor and indoor inhalation; conservative, preliminary assumption).
Despite the significant influence of CBA, risks were substantially reduced for the aquatic pathway, i.e. considering the bioprocess and the degradable fraction of Aroclor 1016 (Group I). Hypothetical risk associated to contaminated leachate beneath the source remained enhanced over long time periods, but risks for groundwater ingestion might be acceptable for drinking water wells located 5 km or more downstream of the site (conservative baseline estimate, maximum value among results obtained from different model codes). Potential impacts for all swimming scenarios (human health, exposure to contaminated river water) were negligibly low. Ecological hazard was indicated for exposure to leachate and groundwater (hypothetical risk), but decreased rapidly to an acceptable level for surface water (even for a small river, i.e. a low water flux and thus a low dilution factor).

Uncertainty is associated to the potential of F113L::1180 to metabolise Aroclor 1016 in total (Group II). Congener specific kinetics data were available for 39% of Aroclor 1016 only, and the modelling with Group II (assuming the remaining 61% to be recalcitrant as a worst case) yielded an insufficient risk reduction potential for the aquatic pathway. However, literature data indicate that this might be an overly conservative estimate (section 4.1.1.2). Furthermore, the calculated CBA concentrations in plant leaves might considerably be overestimated as CBA metabolisms was neglected (but which is likely to occur, section 4.1.1.2).
The estimation of PCB degradation performance and CBA production rates in soil is highly uncertain, as it refers to kinetics data determined from laboratory experiments with PCB in solution. Concerning the sensitivity of parameters, bacterial numbers in soil revealed highest contributions to the variance of results, often followed by uncertain kinetics parameters (maximal removal velocity). Furthermore, probability density functions (PDF) should be considered for soil properties (especially the content of soil organic carbon), hydraulic conductivity and effective porosity in an aquifer, initial PCB concentration in soil and source extension, physicochemical properties (Henry's law constant and log K_{OW}), and parameters related to meteorology (infiltration rate, air dispersion factor) resp. plant uptake (especially the transpiration stream). Concerning exposure parameters, PDF are required for inhalation and water ingestion rates, body weight and, for activity scenarios, exposure time and duration. For the modelling of groundwater transport, a high variability of results was also found due to different model codes and dispersivity estimations (more than a factor of 10 in total).

Bacterial counts at the mesocosm tests found no significant hint on microbial dispersion into leaves, root free soil and leachate. Observations 4¼ years after the field release identified non-GM derivates of the microbes in the rhizosphere of the inoculated willows only. The respective strains could not be detected in the sampled areas outside the plantations, and the results indicate that the microbes were restricted to the rhizosphere of the introduced plants. Therefore, the potential pathways of horizontal spreading, transport in leachate and plant uptake (Fig. 8) were not of concern for the considered GMOs. Concerning gene transfer, very low rates were observed, as the introduced bph-trait was stably inserted into the chromosome of the bacteria. Impacts of GMOs on the function and structure of microbial communities in soil are expected to be very low, but there were effects on rhizosphere communities. Uncertainty is given concerning long-term effects (gene transfer, impacts on microbial communities) and potential impacts on soil organisms other than bacteria, such as insects or earthworms. Furthermore, it is not known whether and to which extent soil fauna might facilitate GMO transport and spreading.

5 Conclusions

In Part IV, strategies and tools were developed to predict risks associated to the application of *in situ* bioremediation measures that are based upon the use of genetically modified soil bacteria. A baseline multimedia model was set up for this purpose, addressing the estimation of biodegradation (*Monod* kinetics) and metabolite formation in soil, contaminant partitioning (mass fluxes) and resulting concentrations in various environmental media, i.e. soil, air, leachate, groundwater, surface water and plant roots and leaves. A module for human health and ecological risk calculation was implemented, considering a large number of different exposure routes.

Results of preliminary modelling showed a clear potential for risk reduction. In generic scenarios, rhizoremediation of a fresh Aroclor 1016 soil contamination, utilising strain F113L::1180 in conjunction with willow plants was evaluated. CBAs as the degradation products of concern revealed significance for the aquatic pathway (leaching, groundwater transport and mixing with surface water) and for plant uptake. As a conservative estimate, groundwater wells should be located at least 5 km downstream of the source to exclude risks arising from enhanced CBA concentrations. Considerable uncertainty is associated to the degradation potential, as data for a large number of PCB congeners present in Aroclor 1016 were not available. Furthermore, considered kinetics parameter for biodegradation in soil were related from laboratory experiments in vials (solution), and respective estimation is highly uncertain (Part III).

No significant hint on bacterial dispersion into leaves, root free soil and leachate could be seen for F113 derivatives. Observed gene transfer rates were very low, as the introduced *bph* trait was stably inserted into the chromosome of the F113 strains. Potential impacts of GMOs on microbial soil communities also were very low, but there was a shift in rhizosphere populations. Uncertainty is given for long-term effects (especially for gene transfer and impacts on soil bacteria) and potential impacts on soil organisms other than microbes.

Probabilistic modelling is recommended to identify the magnitude of potential risk, as a high uncertainty and/or variability is given for many model input parameters. The developed multimedia risk model is a flexible tool suited to obtain baseline estimations and can be used to assist performance control and compliance monitoring. However, more sophisticated modelling is recommended for the aquatic pathway, utilising site specific data and applying numerical codes for groundwater transport modelling. Such modelling should consider heterogeneous hydraulic conductivity (K_f) fields based upon site specific data, as this parameter was highly sensitive for the estimation of groundwater concentrations and associated risks. Respective evaluations may consider uncertainty in two dimensions, i.e. spatial distribution and measurement uncertainty of K_f.

Further studies should be carried out to investigate the degradation performance in real contaminated soil or at a field test site. Such studies should especially concentrate on the heterogeneity (and survival and growth) of bacterial populations in soil and the distribution of soil organic carbon (f_{OC}). The author recommends representative f_{OC} sampling at a site, both in horizontal in vertical dimension (30 samples at least for the determination of statistically significant probability density functions). Microbial fate and impacts on the diversity of bacterial soil community should be monitored to obtain information for long time periods.

By the insertion of suitable gene cassettes into the chromosome of F113, the degradation capability of these strains can be extended to contaminants other than PCBs. The evaluated methodologies and tools, and the detailed data set of model input parameters (including most probable values, possible ranges and probability density functions) can be used for further impact analysis and risk estimation approaches.

Part V Monitoring guideline for the in situ remediation of contaminated soils by genetically modified microorganisms

Contents

1 Scope

An accepted implementation of biological *in situ* measures for the remediation of contaminated sites requires a detailed and reliable risk analysis. The scope of this paper is a guideline for preparing, controlling and monitoring field release applications of genetically modified (GM) bacterial strains. Guidance is given for determining the appropriateness of *in situ* soil bioremediation utilising genetically modified microorganisms (GMOs).
This guideline can be used by EU regulatory authorities, owners of contaminated sites and public authorities or end users of GMO-based remediation technologies. It may also be applied for planning and performing field release tests of bioremediation systems that have previously been investigated at a laboratory or lysimeter scale.

2 Objectives

Preliminary investigations and accompanying measures are advised for a safe application and implementation of *in situ* soil bioremediation utilising genetically modified microorganisms (GMOs). Respective tasks comprise:

- Prediction of potential impacts on possible receptors based on multi-media environmental modelling
- Performance control of the utilised bioprocess
- Compliance monitoring, addressing contaminants and metabolites of concern and GMOs

3 Strategies and concepts

3.1 Conceptual site model

An effective tool for the development of monitoring strategies is the use of conceptual site models (CSM, see Box 3.1). According to Rügner et al. (2006) a receptor-oriented, multi-compartimental approach is proposed that allows a model-based, comprehensive assessment of environmental impact caused by *in situ* remediation measures.
Figure 1 shows an example of a CSM at a generic level. Potential pathways are defined for compounds (contaminants and metabolites of concern, COC) and GMOs based on initial assumptions. Furthermore, possible receptors are indicated that might be affected by COC and GMOs. In an iterative process, the conceptual site model is refined taking into account results of multimedia environmental modelling and site specific data. That includes also the quantification of mass fluxes and concentrations in transfer pathways and the corresponding exposure rate for receptors. As a result of the CSM refinement, pathways not relevant for investigated substances (e.g. negligible low tendency to partition from soil into the air) or non-realistic exposure scenarios can be excluded for further investigation.

Box 3.1 Conceptual Site Model (CSM)

In the conceptual site model, specific features that are relevant for assessment objectives are defined, e.g.:

- contaminants and metabolites of concern and other entities of importance (GMOs)
- location and three-dimensional extent of sources (preliminary estimate)
- relevant release mechanisms
- pathways of concern and environmental matrices that potentially are affected
- potential receptors

For additional information on CSM, see e.g. US EPA 1999a, AFCEE 2004

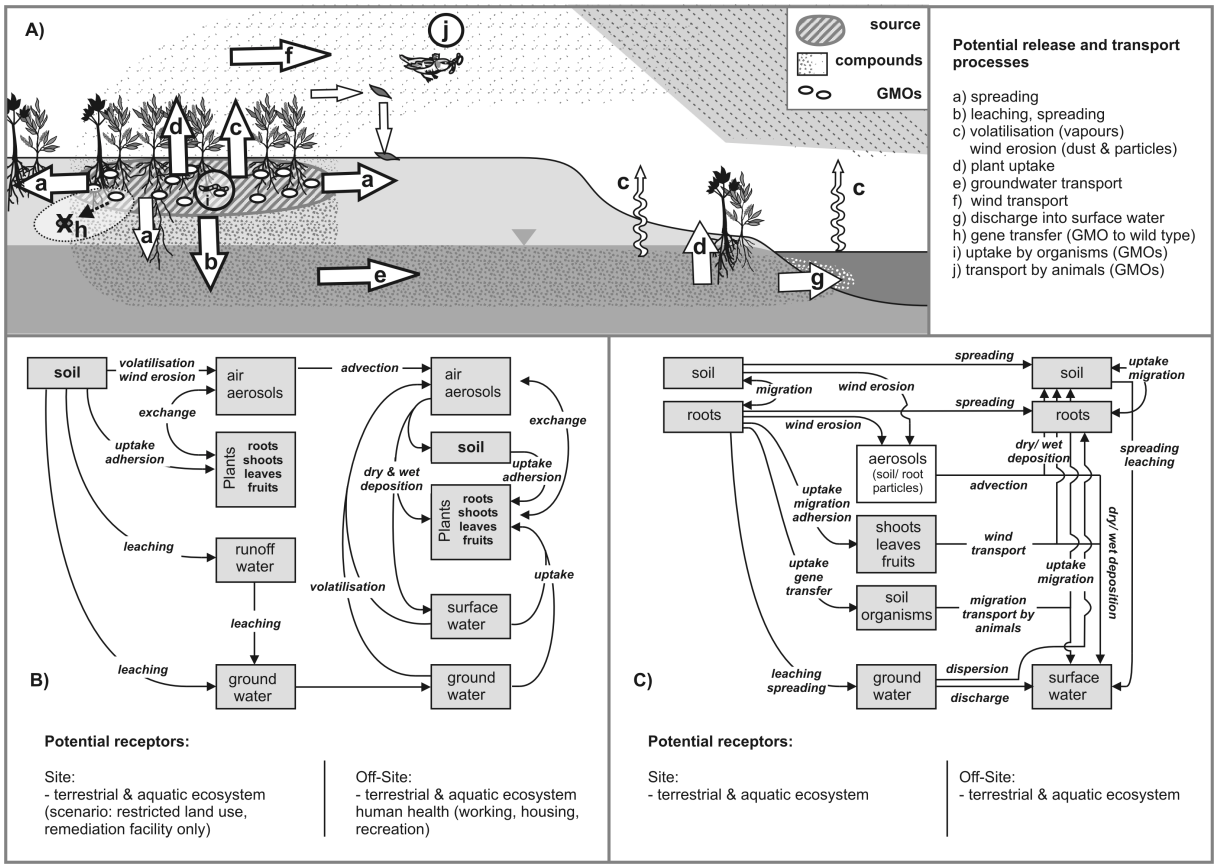


Fig. 1: *Conceptual site model at a generic level.*

3.2 Selection of monitoring areas

Based on the relevant pathways and receptors identified in the refined CSM, suitable compliance criteria have to be defined that comprise (i) appropriate points of compliance (POC) and (ii) corresponding trigger values to control the risk reduction and the performance of the remediation measure.

In an initial phase, usually environmental media directly adjacent to the contaminated area (leachate, air, plants) are selected as POC. As a result of further investigations, additional POCs may be selected that correspond to receptors locations. Monitoring areas then will be defined accordingly (see Fig. 2).

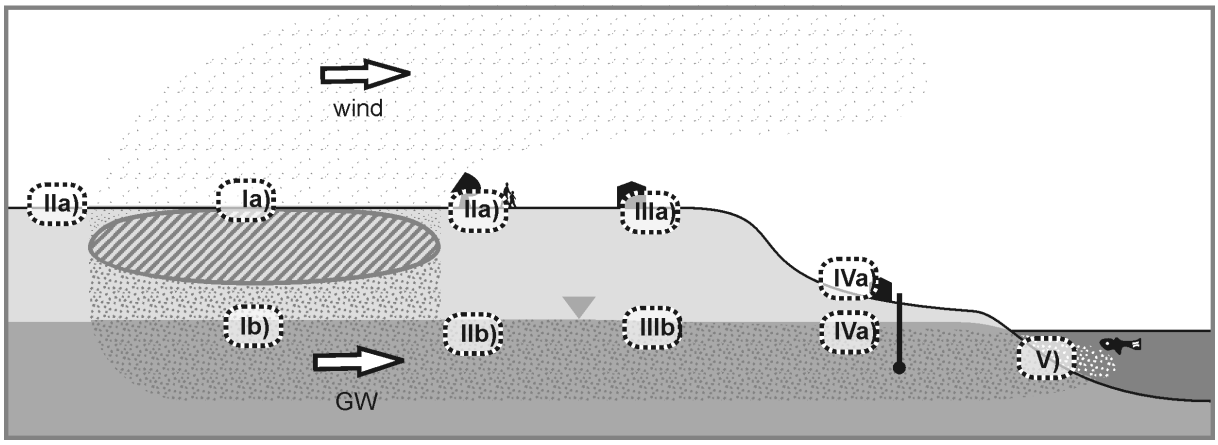


Fig. 2: *Location of possible monitoring areas; GW: groundwater.*

3.2.1 Area I

The function for a monitoring in Area I includes both performance control of the applied *in situ* measure and compliance monitoring (for methods and tools, see section 4). Area I is divided into Area Ia (site soil) and Ib (groundwater). Figure 3 gives an overview on COC and GMO sources, potential pathways and receptors. Furthermore, objectives of performance control are conveyed. Possible points of compliance (POC) are indicated with grey boxes.

- Performance control addresses contaminant and metabolite concentrations in site soil and the survival and growth of GMOs (see section 4).

- Compliance monitoring has to be performed for a) COC and b) GMOs. Affected environmental media potentially serve as secondary sources. Potential receptors in Area I are ecosystems (assuming that the land use of the contaminated site is restricted to remediation facilities).

a) Depending on the partitioning behaviour of the COC (see section 4.2), air, plant and groundwater concentrations have to be monitored in the site area.

b) GMOs have to be quantified in the source soil and root zone and in leachate and runoff water, and in aerial plant parts. When GMOs are detected in leachate samples or runoff water, also groundwater has to be analysed for the presence of GMOs. A tiered approach of subsequent sampling is recommended, details on the proposed procedure are given in section 4.

COC concentrations in Area I may exceed corresponding trigger values. Only locally increased concentrations and only small pollutant loads are accepted for biological measures (see Box 3.2 for additional information).

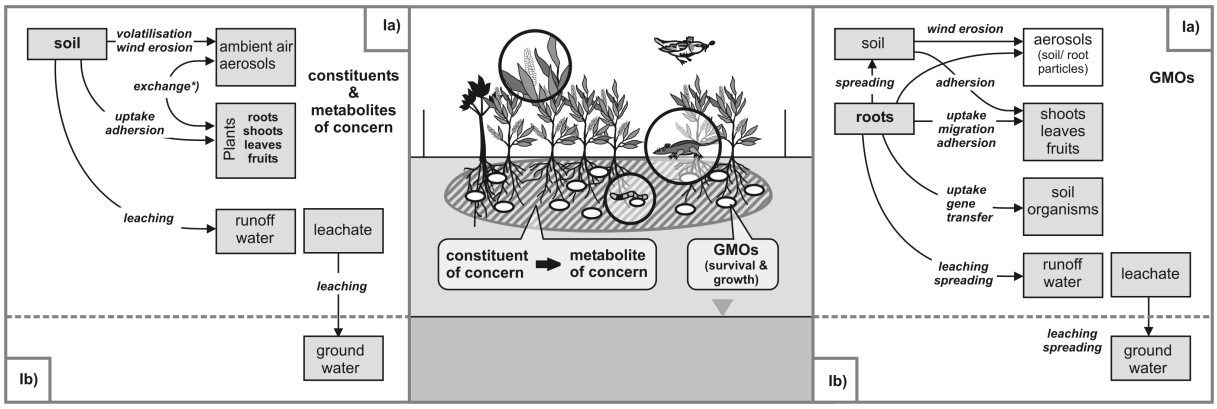


Fig. 3: *Overview, Area I (contaminated site).*

3.2.2 Areas II to IV

In Areas II to IV, compliance monitoring is being performed. Areas IIa and IIb are located directly adjacent to the contaminated site (see Fig. 2). Potential receptors are human health (recreational and workplace scenarios), ecosystems and groundwater at the local scale.
Areas IIIa/b and IVa/b are located at a distance to the site, e.g. in groundwater flow direction and/or main wind direction (depending on the relevant pathways). Possible receptors are human health (recreational, workplace, and housing scenarios), ecosystems, groundwater at the regional scale (Area IIIb) and drinking water supply (Area IVb).

- Possible POC that have to be monitored (depending on the fate and behaviour of the COC and GMOs and site characteristics):

a) For COC (monitoring of COC concentrations):
   - ambient air, surficial soils, plants (COC deposition from air, COC plant uptake) (Areas IIa to IVa)
   - groundwater directly downstream of the site (Area IIb)

- groundwater at a certain distance to a contaminant source or at the front or fringe of a contaminant plume (Area IIIb)
- drinking water wells or control wells at a certain distance from the drinking water supply (Area IVb)

b) For GMOs (monitoring of GMO numbers):
- soil and roots (potential spreading from the site zone)
- aerial plant parts and groundwater (according to the sampling strategy described in section 4).

COC concentrations in Area IIa/b may exceed corresponding trigger values. Only locally increased concentrations and only small pollutant loads are accepted for biological measures (see Box 3.2 for additional information).

Concentrations of COC may also be enhanced in Area IIIa/b. An excess of appropriate trigger values (see Box 3.2) is tolerated under certain conditions. I.e. the zone should not exceed a) a maximum tolerable steady-state plume length or b) a distance from the source beyond that trigger values have to be met again (e.g. a distance based on site- and landuse-specific risk considerations).
In Area IVa/b, trigger values have to be met (air quality and drinking water standards, see Box 3.2).

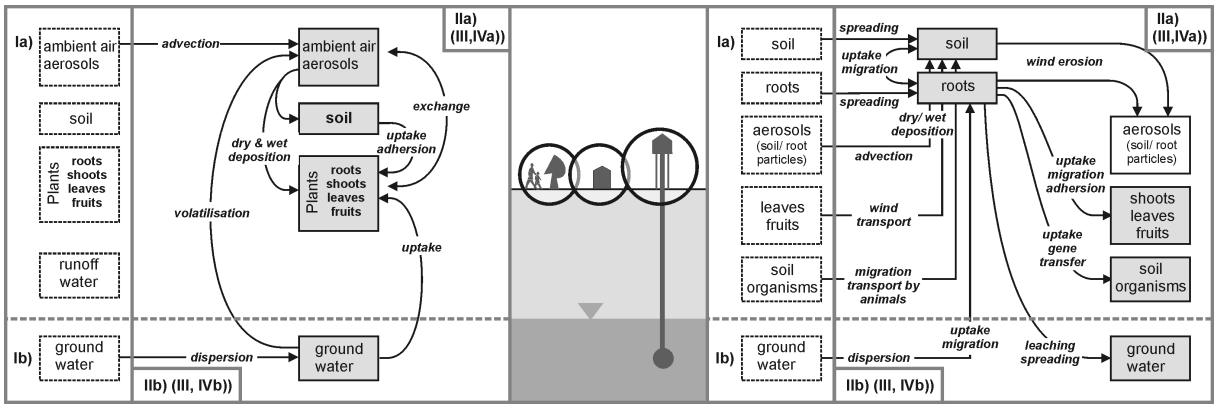


Fig. 4: *Overview, Areas II to IV.*

3.2.3 Area V

Compliance monitoring is also required in area V. The area is located at the surface water, where groundwater discharges to surface water.

Potential POC (depending on the fate and behaviour of the COC, GMOs and site characteristics) are:

a) For monitoring of COC concentrations:
- groundwater at the interface to surface water
- surface water
- soils in the flood area
- ambient air

b) For monitoring of GMO numbers
- soil and roots (potential spreading from the site zone)
- aerial plant parts and surface water (according to the sampling strategy described in section 4).

In Area V, trigger values have to be met according to air quality criteria for Area IV, groundwater (regional scale) quality criteria for Area III and surface water quality criteria (see section 3.2.2 and box 3.2).

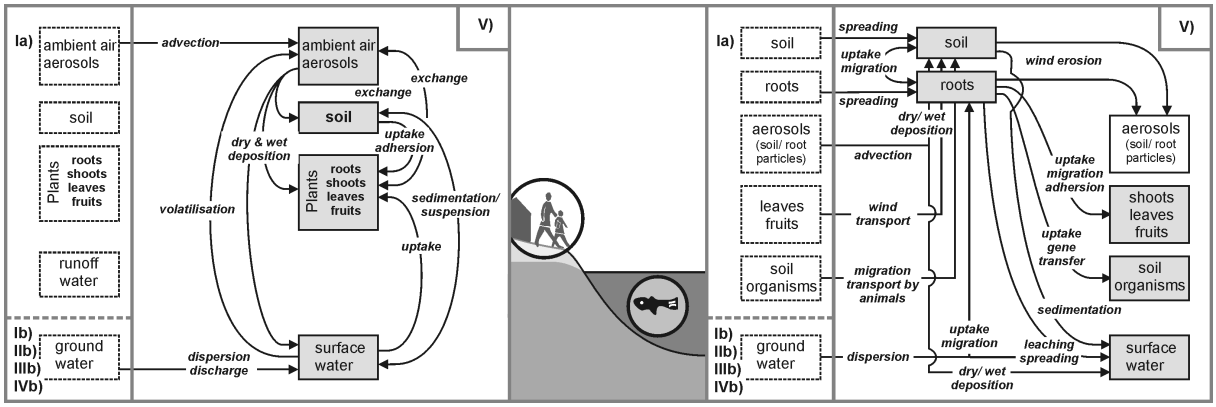


Fig. 5: *Overview, Area V.*

Box 3.2 Trigger Values

Areas I,II
Air trigger values (e.g. German Air Technical Guidance 2002)
Groundwater trigger values and corresponding maximal tolerable mass flow rates, for groundwater at the local scale (e.g. German Federal Soil Protection Ordinance 1999)
Area III
No-observed-effect-values, quality criteria "of a good chemical status", for groundwater at the regional scale (e.g. according to the EU-WFD 2000)
Area IV
Drinking water standards (e.g. German Drinking Water Ordinance 2001)
Air quality standards, scenario-specific (working/ housing, e.g. German Air Technical Guidance 2002)
Area V
No-observed-effect-values, surface water and groundwater quality criteria "of a good chemical status" (e.g. according to the EU-WFD 2000)
I to V, ecosystems as receptors
Trigger values for ecosystems: No/Lowest-Observed-Adverse-Effect-Levels (NOAEL, LOAEL), No/Lowest-Observed-Effect- Concentrations (NOEC, LOEC) (EU TGD 2003, US EPA 1998c, ECOTOX)

4 Methods and tools

Methods of performance control and compliance monitoring comprise direct measurements (e.g. concentrations and mass fluxes of contaminants and metabolites of concern) and prediction based on multimedia environmental partitioning modelling.

4.1 Evaluation of contaminants and metabolites of concern

- The evaluation of contaminants of concern is based on site specific criteria (compound concentrations) and chemical specific properties (mobility and toxicological potential or aesthetical characteristics like taste and odour). Pathways of concern are evaluated by multimedia environmental modelling. The potential of a given compound to distribute into certain environmental matrices is analysed (details on modelling approaches are discussed in the Monitoring Guideline Appendix). Results of the modelling may indicate that a specific pathway (e.g. soil to air pathway) is not of concern for investigated COC.
- Metabolites of concern are defined by analysing the process applied for the bioremediation approach. Beside the criteria already defined for the selection of contaminants of concern, the stability of the studied compound is of importance.

4.2 Definition of compliance criteria and monitoring areas

Compliance criteria (points of compliance POC and corresponding trigger values) are defined according to modelling-based environmental impact assessment (e.g. Rügner et al. 2006). Required steps are:

- Analysis and comparison of the most relevant impacts on receptors (e.g. risk assessment for groundwater and surface water, calculated potential exposure scenarios, etc.)
- Evaluation of maximum COC concentrations and/or mass fluxes (see Box 4.3) along relevant pathways (e.g. soil to groundwater) and at possible locations of compliance (in environmental media of concern, e.g. in groundwater, surface water, air, plants)
- Evaluation of appropriate monitoring areas, using modelling-based predictions (e.g. selection of groundwater wells that could deliver sufficient data to ensure reliable risk analyses for receptors of concern)
- Selection of POC and corresponding trigger values by the regulating authorities

Box 4.2 Maximum concentration levels and/or mass fluxes

Maximum concentration levels and/or mass fluxes are those values, for which no adverse effects at receptors inside the area of interest are expected (corresponding to maximum tolerable or acceptable concentrations and/or doses at receptors).
For receptors which are not part of directly monitored environmental matrices, the methodology of inverse quantification may be applied. Example: for a housing scenario (resident receptor) where groundwater is not used for any purpose (drinking water, irrigation water etc.), the pathway groundwater to indoor air may be of concern. Based on a tolerable daily dose, a corresponding maximum tolerable concentration in groundwater can be calculated (see Monitoring Guideline Appendix for further information and available modelling tools).

4.3 Performance control

If the considered bioremediation process is based on active aerobic microbes, the following aspects have to be analysed:

- Survival and growth of the GMOs over time and the functionality of the bioprocess (see section 4.3.1 and Tab. 1 for appropriate methods)
- Kinetics of contaminant degradation and subsequent formation of metabolites. Data on compound concentrations versus time are required to determine kinetics parameters (see section 4.3.2 and Tab. 1)
- Temporal development of contaminant and metabolite mass in the source and mass transfer rates from soil into other environmental compartments. This aspect is analysed by modelling based on the evaluated kinetics parameters (see Monitoring Guideline Appendix for modelling tools)

Table 1 gives an overview on available techniques and may be used as guidance for the set up of detailed monitoring plans.

4.3.1 Methods and tools for monitoring the functionality of the bioremediation system

- Sufficient supply of oxygen and nutrients/ root exudates (if plant-microorganism consortia are used): measurement of dissolved oxygen content and concentration of nutrients (see e.g. ASTM 1998), monitoring of plant health as an indirect hint on the sufficient production of root exudates (as root exudates may be difficult to analyse, see Tab. 1)
- Measurement of bacterial numbers, GMOs *in situ* activity and gene expression with molecular tools (if included in the chromosome of the GMOs, see Tab. 1).

4.3.2 Strategies and tools for monitoring degradation kinetics

- Chemical analysis of contaminant and metabolite concentrations (if continuous chemical analysis of metabolites is not possible with reasonable efforts, full (equimolar) conversion of contaminants into respective metabolites of concern may be assumed instead, to account for a worst case assumption)

***Tab. 1**: Objectives and methodologies for performance control. PCR: Polymerase Chain Reaction, FRET: Fluorescence resonance energy transfer, SYBR: Synergy Brands Inc.*

Objectives	Parameters of monitoring	Tools & methods
Survival & growth, functionality of GMOs	In situ activity (a)	(a,b,c) Biosensors included in the chromosome of GMOs (genes encoding autofluorescent proteins), measured by: - epi-fluorescent microscopy - laser confocal microscopy - fluorimetry *[adaptations to published protocols]* (c) Chemical analysis of contaminants *[standard methods]*
	Gene expression (b)	
	Contaminant degradation (c)	
	Bacterial numbers	Presence of GMOs and quantification: - molecular identification (primers, PCR based fingerprinting) - FRET real time PCR, SYBR real time PCR *[published protocols and adaptations]* Quantification: - Plate counts *[standard methods using selective plates]*
Health of inoculated plants	Plant health	Observation of health impact indicators (wilt leaves, reduced size of leaves) *[standard methods]*
Contaminant degradation	Contaminant concentration	Chemical analysis *[standard methods]* Kinetics modelling
Metabolite formation	Metabolite concentration	Chemical analysis *[standard methods]* Modelling

4.4 Compliance monitoring

Environmental matrices of concern have to be monitored at the selected POC by:

- Direct measurements, monitoring of COC concentrations, detection and quantification of GMOs (see section 4.4.1 and 4.4.2, respectively)
- Modelling of COC mass fluxes and respective concentrations for the POC, based on evaluated contaminant degradation kinetics and metabolite formation rates in the source area (see section 4.2 and Monitoring Guideline Appendix)
- Modelling of GMO dispersion (see section 4.4.3)

Monitored concentrations and modelled results are used for the assessment of potential impacts and risks as a function of time for possible receptors and current or future land-use options.

4.4.1 Methods and tools for compliance monitoring of COC

- Set up of appropriate monitoring strategies and plans (see box 4.4.1)
- Modelling-based prediction utilising adequate procedures (see Monitoring Guideline Appendix). In an iterative procedure, monitoring data are utilised and modelling parameters and procedures are adjusted.

Box 4.4.1 Monitoring strategies and data characterisation for COC

For information and guidance on the set up of appropriate monitoring strategies and plans, see e.g. US EPA 2005, ASTM 1998, AFCEE 2004. Links and short descriptions on further documents recommended by the US EPA are provided at (http://www.epa.gov/tio/pubichar.htm), related detailed information can be found at (http://www.cluin.org).

4.4.2 Sampling strategy of GMOs

A tiered sampling strategy is recommended, as shown in Tab. 2 (for detection methods, see Tab. 1).

- Within the contaminated area, environmental media according to Tab. 2 (grey boxes, indicated with I) have to be analysed for the presence of GMOs.
  - If GMOs are detected in runoff or leachate samples, also groundwater has to be analysed.

- Outside the contaminated area, soil and root samples have to be monitored to study potential uncontrolled horizontal spreading (see Tab. 2). This has to be done at different distances and in different directions from the source zone (to exclude e.g. wind transport of leaves containing microbes and subsequent deposition respectively plant uptake, or groundwater transport of GMOs).
  - If GMOs have been detected on-site in leaves or groundwater, the respective media have also to be analysed at off-site locations (in main wind direction and groundwater flow direction respectively).
  - If GMOs are found in groundwater, also surface water may be sampled, depending on the environmental setting (compare to the conceptual site models in section 3).

4.4.3 GMO quantification and study of survival and growth

- GMO quantification is required in on-site and off-site media in which GMOs have been detected (see Tab. 1 for methods)
- Survival and growth has to be analysed to identify secondary sources for GMOs (primary source is the site soil and rhizosphere) and to model GMO dispersion. E.g., if GMOs are found in groundwater, relevant transport distances are a function of the time period in that the microbes can survive and a function of growth rates. Depending on travel distances, potential secondary sources can be located, and it is possible to estimate the respective GMO spreading potential.

4.4.4 Gene transfer and potential impacts on microbial communities

An important decision criteria for the use of GMOs in remediation approaches (e.g. according to EU 2001) are gene transfer rates and potential impacts on indigenous microbial communities:

- Rates of lateral gene transfer between homologue bacteria (GMO and wild type) have to be evaluated in site soil and rhizosphere (if root-colonising microbes are used)
- Potential impacts on the function (e.g. enzymatic activities) and structure (genetic distribution) of indigenous soil and root-colonising microbial communities have to be investigated on-site

Tab. 2: *Sampling and analysis strategy for GMOs. Grey boxes: analysis has to be performed. Arrows: analysis is necessary if grey boxes are proved positive (see text). I: on-site, II: off-site, inoc.: inoculated plants, (a) and (lab): in view of potential analytical difficulties, results of preliminary laboratory studies may be used instead.*

	Soil		**Roots (inoc.)**		**Roots (other plants)**		**Leaves (inoc)**		**Leaves (other plants)**		**Soil organisms (a)**		**Leachate Runoff water**		**Ground water**		**Surface water**
Bacterial numbers (GMOs)	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II	
Survival & Growth	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
Gene transfer rates	(lab)		(lab)														
Analysis of microbial community	(lab)		(lab)														

Monitoring Guideline Appendix

This appendix presents information on the selection and use of detailed multimedia environmental models for fate and transport calculations, exposure analysis and subsequent risk evaluation. The discussed models are analysed for details on addressing:

a) Fate and transport processes and possible contaminant input into final sinks, e.g.:

- Volatilisation, air dispersion, dry and wet deposition
- Leaching and groundwater transport
- Discharge from groundwater into surface water and transport in surface water
- Sediment partitioning
- Uptake into plants and subsequent translocation
- Exchange between plant leaves and ambient air
- Uptake by aquatic and terrestrial organisms, bioconcentration and biomagnification within food nets

b) Exposure modelling and risk analysis:

- Human health, considering potential pathways for residential, working and recreational scenarios
- Ecological effects, for terrestrial and aquatic ecosystems

The reviewed models are only a subset of potentially appropriate models. Other models may also be applicable, depending on site- and compound-specific circumstances. A big variety of procedures is available for particular processes, like release rates from contaminant sources or transport in groundwater. Furthermore, there is a number of programs addressing multi-compartmental and multi-receptor concepts by delivering modules for distinct processes that can be selected by the user. Details are given in the following, with an emphasis on multi-compartmental models.

The appendix is organised as follows:

- MA1: Short overview on available models and tools addressing particular processes and objectives (examples) with additional information in box MA1
- MA2: comparison of multi-compartmental models, giving details on implemented modules
- MA3: considerations for the selection of appropriate models and procedures, discussing pros and cons specific to given circumstances and tasks

MA1 Models and tools addressing particular processes

Specific model objectives that are discussed in this chapter (i.e. release rates, volatilisation, atmospheric transport, etc.) are also addressed by modules included in multi-compartmental programs (see chapter MA2). Anyhow, additional models might be required (e.g. when plant uptake is not considered in the chosen multi-compartmental model) or other procedures are preferred (e.g. more sophisticated procedures). Examples for applicable models are given in the following in a brief overview. Additional information can be gathered from Box MA1.

- Release rates from contaminant sources and time frame of contaminant release
  - Analytical solutions for calculating release rates from source zones as well as time frames of NA (Grathwohl, 1998, Grathwohl, 2003, Huntley & Beckett, 2002).
  - Finite source volatilisation models, e.g. analytical solution based on the assumptions of Jury et al. (1990)

- Atmospheric transport and deposition processes
  - 1-D to 3-D analytical solutions for predicting reactive air transport and subsequent processes of dry and wet deposition, e.g.: *BLP*, *CALINE3*, *CALPUFF*, *CTDMPLUS*, and *OCD* (see Box MA1)
  - steady-state analytical model for calculating vapour intrusion into buildings (modified Johnson and Ettinger (1991) model, US EPA 2004a, see box MA1)
  - numerical models: e.g. *ISC3* (see Box MA1)

- Transport in groundwater
  - One-dimensional analytical solutions of equations describing reactive transport in groundwater including biodegradation rates and/or attenuation factors (Domenico 1987, Wiedemeier et al. 1998, Carey et al. 2000)
  - 1-D and 2-D numerical models for calculating reactive transport, e.g.: *BIONAPL* (Frind et al. 1999)*, SMART* (Finkel et al. 1999), *MIN3P* (Mayer 1999)*, PHT3D (MT3DMS+PhreeqC;* Prommer et al. 1999), *TBC* (Schäfer et al., 1998), *Geosys* (Kolditz and Bauer 2004), *Bioplume III* (US EPA 1997d)
  - 3-D finite-difference groundwater flow models: e.g. *MODFLOW-2000* (overview and links to guiding documents and detailed descriptions can be found at http://water.usgs.gov/nrp/gwsoftware/modflow2000/modflow2000.html)
  - Empirical equations for calculating plume length (e.g. Maier 2004, Cirpka et al. 2006, Ham et al. 2004, Liedl et al. 2005)

- Discharge from groundwater into surface water and surface water transport
  - Analytical models, e.g. *BASINS* for watershed management, *QUAL2K* for rivers and streams, *CORMIX* for mixing zones and *WASP* (see Box MA1)
  - 1-D analytical solute transport calculations considering advection, dispersion, first order decay and adsorption (retardation): *G3CTM* (NCDENR 1997)
  - Numerical models for solute transport in streams and rivers: e.g. *OTIS* (considering One-dimensional Transport with Inflow and Storage, Runkel 1998.

- Plant uptake
  - Numerical model considering dynamic uptake from soil, solution and atmosphere and metabolism and accumulation of neutral organic compounds in roots, stem, leaves and fruits (*PLANTX*, Trapp et al. 1994)
  - Analytical procedure for the uptake of ionisable organic compounds into plant roots and subsequent translocation in the plant (Trapp 2000, Trapp 2004).
  - Model review (theoretical basis of different models addressing neutral and ionic organic compounds, Trapp 2004)
  - Steady state and dynamic models for neutral organic compounds, e.g.: *Fruit Tree Model* (Trapp et al. 2003), *Carrot Model* (uptake into thick roots (carrots), Trapp 2002), *Potato Model* (Samsøe-Petersen et al. 2003) (see Box MA1)

- Guidelines and models for calculating exposure scenarios
  - *AQUATOX* (fate of pollutants, such as nutrients and organic toxicants, and their effects on the ecosystem)
  - Algorithms for calculating additional daily doses for relevant receptors and compilations of toxicological and eco-toxicological reference data (EU TGD 2003, *TPHCWG* 1999, Efroymson et al. 1997, *US EPA* 1998c, *ECOTOX* database).

- Screening tools
  - steady-state calculations based on volatilisation factors, leaching factors etc. and procedures to determine Risk Based Screening Levels (RBSLs): e.g. ASTM 2002

- Internally consistent chemical partitioning data
  - Algorithms to derive internally consistent physicochemical properties of organic compounds and to consider temperature dependence: Beyer et al. 2002 (see box MA1)

- Soil properties database and estimation of hydraulic soil parameters
  - e.g. ROSETTA (see box MA1)

Box MA1 Models for particular processes

- *BLP*, *CALINE3*, *CALPUFF*, *CTDMPLUS*, *ISC3* and *OCD, SCREEN*:

models for atmospheric transport and deposition processes, as recommended by the US EPA. Detailed descriptions of these and other models are presented by the US EPA Support Center for Regulatory Air Models SCRAM (http://www.epa.gov/scram001).

- *Modified Johnson and Ettinger (1991) model, US EPA 2004:*

spreadsheet-based models and a manual are provided by the EPA (http://www.epa.gov/oswer/riskassessment/airmodel/johnson_ettinger.htm)

- *BASINS*, *QUAL2K*, *CORMIX* and *WASP:*

models addressing discharge from groundwater into surface water, surface water transport and watershed management, as recommended by the US EPA. For further details, consult the Water Quality Model pages of the US EPA, where detailed descriptions and further links are given (http://www.epa.gov/OST/wqm).

- *AQUATOX*:

simulation model for aquatic systems, addressing fate of pollutants and their effects on the ecosystem, see (http://www.epa.gov/OST/wqm).

- *ECOTOX*:

Online-database source for locating single chemical toxicity data for aquatic life, terrestrial plants and wildlife. Created and maintained by the US EPA, peer-reviewed literature is the primary source of information encoded in the database (http://www.epa.gov/ecotox).

- *Plant models:*

A number of plant models can be downloaded at (http://www2.er.dtu.dk/homepages/stt).

- *Beyer at al. 2002:*

The spreadsheet-based procedure is provided for download at the ELPOS homepage (http://www.usf.uos.de/projects/elpos/download) .

- *ROSETTA*:
Soil database and program to estimate unsaturated hydraulic properties from basic soil data such as soil texture data and bulk density. The modelling approach is based on pedotransfer functions (PTFs) (http://www.ussl.ars.usda.gov/models/rosetta/rosetta.htm).

MA2 Multimedia models

A variety of multi-compartmental models is available consisting of different modules for particular processes and objectives. Examples are discussed in this chapter. Some programs concentrate on contaminant partitioning and spreading, others additionally consider exposure pathways and impacts on human health and ecosystems. There is also software available for a geospatial analysis of contaminated media and resulting risks. Except for the Program RISC, all models described in this chapter are non-commercial and available free of charge.

- Table MA1 to MA3 summarise characteristics and capabilities of the multi-compartmental models evaluated in this appendix
- Box MA2 indicates authors and sources for program downloads and background information
- In the following, some notes on the discussed programs are given

RISC 4.02

Program for fate and transport modelling, exposure prediction and risk estimation.

- Probabilistic calculations (Monte Carlo runs) are not possible for Risk Based Screening Level (RBSL) evaluation
- TIER1.xls: spreadsheet for the calculation of Risk-based Screening Levels (RBSLs) and site-specific target level (SSTLs) at a generic level. The calculations are consistent to the tiered Risk-Based Corrective Action approach (see e.g. US EPA 1999b, ASTM 2002).
  RBSL calculations are based on distribution factors according to ASTM 2002. These factors can also be applied to generic forward calculations (e.g. estimation of groundwater concentrations from soil concentrations and a leachate factor).

ARAMS 1.2.2/ FRAMES 1.5

Fate and transport modelling, exposure prediction and risk estimation

- ARAMS is a platform using the software-framework FRAMES to link disparate modules (open-architecture, object-oriented system). The user specifies objects (e.g. sources, multimedia pathways, risk scenarios) that are visualised at the screen and chose particular modules.
- A variety of modules is provided for respective calculations and for databases (software-immanent and web-based). Modules included in the current software version are given in the following. Each module contains links on background documents where detailed descriptions can be found.
  - Modules for fate and transport processes, exposure and risk evaluation:
    - *MEPAS* Multimedia Environmental Pollutant Assessment System
    - *RECOVERY* Evaluation of Contaminant Release from Bottom Sediment
    - *HELP* The Hydrologic Evaluation of Landfill
    - *HELPQ* Hydrologic Evaluation of Leachate Production and Quality
    - *Eco Receptor Intake* (exposure dose calculation, ecological receptors)
    - *WEAP* Wildlife Ecological Assessment Program (eco health effects)
    - *TBP* Theoretical Bioaccumulation Potential (sediment to organism partitioning)
  - Databases:
    - 2 Constituent databases
    - *ERED* Residue-Effects Database, *BSAF* Biota-Sediment Accumulation Factors, ITIS Taxonomic Information System web (linkage provided)
    - *TTD* Terrestrial Toxicity Database (terrestrial benchmarks, i.e. toxicity reference values and soil screening levels)
    - *TOS* Terrestrial Organism Selector (database for default ingestion rates and diets),
    - *AOS* Aquatic Organism Selector

- In addition to the provided modules, user defined input options are available (e.g. for the input of groundwater concentrations versus time, that can be further processed). New modules and databases can be added.
- Links to related web sites for human health and ecological risk information and tools are provided in ARAMS

Level I, II and III

Fugacity based partitioning models

- Level I and II calculations give the general impression of the likely media into which a chemical will tend to partition and an indication of relative concentrations in each medium. Equilibrium is assumed to prevail between all media.
- The Level III model accounts for partitioning kinetics, in addition to loss of the contaminant due to advection and degradation in the various phases. The considered compartments are not in equilibrium, therefore there are different fugacities specific to each phase.
- Mackay et al. (1992) recommend that the Level III model instead of Level I or II should be used as a minimum approach for chemical fate assessments, as the equilibrium assumption in Level I and II calculations is recognized as being excessively simplistic and even misleading.
- Model output:
  - partition coefficients (Type 1), Z values, fugacity of each medium
  - intermedia transport rates and D values, reaction and advection D values and loss rates
  - residence times or persistences (overall, reaction, and advection)
  - concentrations and amounts for each medium
- The following compartments are considered (phases in brackets):
  - Air (bulk air, air vapour, aerosol)
  - Water (bulk water, water, suspended particles, fish phase)
  - Soil (bulk soil, air, water, solid)
  - Sediment (bulk sediment, water, solid)

CemoS1

Software for fate and transport modelling and exposure prediction

- Beside the version 1, a beta version CemoS2 is available for download. This version is erroneous, the validation process is not finished yet.
- CemoS is implemented in a modular structure using object-oriented programming.
- Features specific to modules:
  - Air module: steady-state concentrations in air mixing layer after (continuous release from an area source required as input)
  - Buckets module: dynamic water balance (leaching process in soil),
  - Chain module: dynamic transport and accumulation in the food chain
  - Plant module: steady-state for root concentration, dynamic for uptake into leaves (both procedures restricted to neutral organic compounds)
  - Plume module: steady-state transport in air
  - Soil module: steady-state water balance in soil (transport into deeper soil layers, soil concentrations as a function of depth)
  - Water module: steady-state 1-D surface water model (continuous emission required as input)

SADA 4.1

Program for data visualisation, geospatial and statistical analysis, risk assessment, cost/benefit analysis, sampling design and decision analysis

- Preliminary risk-based goals PRGs can be calculated for contaminants (including radionuclides)
- The following landuse scenarios are considered:
  - Residential, Industrial, Agricultural, Recreational, Excavation

CalTOX 4.0

CalTOX is a spreadsheet based risk assessment model that relates the concentration of a chemical in soil to the risk of an adverse health effect for a person living or working on or near the contaminated soil. It consists of:

- a multimedia environmental fate model, which evaluates the distribution of a chemical among 7 different environmental compartments (air, ground-surface soil, plants, root-zone soil, vadose-zone soil below the root zone, surface water, sediments).
- a multiple pathway exposure model, which calculates how much of a chemical reaches the body by inhalation, ingestion, and dermal contact using environmental concentration and contact factors.
- a module (directly incorporated into the model operations) for sensitivity and uncertainty analyses. Parameter values suggested for use in CalTOX are described in terms of mean values and a coefficient of variation in place of plausible upper values.

MULTIMED 2.0

MULTIMED was developed as multimedia fate and transport model to simulate contaminant migration from waste disposal units. It includes:

- Simulation of waste infiltrated into the unsaturated zone by a landfill module or by direct infiltration to the unsaturated or saturated zones.
- Semianalytical simulation of contaminant flow in the unsaturated zone and for landfill module.
- Consideration of dispersion, sorption, volatilization, biodegradation, and first-order chemical decay in the unsaturated zone.
- One-dimensional simulation of contaminant transport in the saturated zone taking into account three-dimensional dispersion, linear adsorption, first-order decay, and dilution due to recharge.
- Saturated zone module simulates steady-state and transient groundwater flow.

EUSES

EUSES is designed to support decision-making in the evaluation of new and existing chemical substances. EUSES can be used to carry out tiered risk assessments of increasing complexity, requiring additional data. It consists of following modules:

- Input module including substance identification and physicochemical properties.
- Emission module including data of the substance, estimation of local emissions to waste water and air for various life-cycle stages, estimation of regional emissions to wastewater, air, and soil for various life-cycle stages.
- Distribution module including (i) local models (treatment model, air model, dilution and sorption in surface water, one-compartment soil model) and (ii) regional model (Mackay-type Level III multimedia model Simple Box).
- Exposure module including second poisoning, estimation of exposure levels for predating birds and mammals, exposure to humans through the environment (plus food products), human exposure through use of consumer products, human exposure in the workplace.
- Effects module including toxicological and ecotoxicological data, determination of predicted no effect concentrations, for the environmental end-points (water, soil, sediment, sewage treatment plants, predators) by applying assessment factors based on available data. For soil and sediment, equilibrium partitioning is used when data are lacking. Route-to-route extrapolation for human effects assessment.
- Risk characterization module including determination of risk characterization ratios for all end-points of risk assessment.

E4CHEM

E4CHEM offers a system of evaluative models for calculating characteristic exposure features of chemicals. It combines by formulation of mass balance, calculation of local equilibrium state and formulation of transfer kinetics a set of environmental related models. Following modules are provided:

- Estimation of physicochemical properties.
- Calculation of release rates from production, manufacturing and use.
- Simulation of the distribution tendency between different media.
- Estimation of contaminant accumulation, mobility and persistence in different environmental media (air, water, soil).

Box MA2 Multimedia models

- *Risc 4.02*
  Risk-Integrated Software For Clean-Ups *(RISC)*, developed by L.R. Spence and BP Oil, Ltd.
  Program purchase & background information: (http://www.bprisc.com)
  Detailed description of procedures: Spence and Walden 2001

- *ARAMS 1.2.2/ FRAMES 1.5*
  Army Risk Assessment Modeling System *(ARAMS)*, developed by the United States Army Engineer Research and Development Center, Environmental Laboratory, Vicksburg, MS, USA; Framework for Risk Analysis Multimedia Environmental Systems (*FRAMES)*, created by Pacific Northwest National Laboratory PNNL.
  Program download & background information: (http://el.erdc.usace.army.mil/arams)
  Information on FRAMES: (http://mepas.pnl.gov/FRAMESV1/index.html)

- *Level I, II and III*
  The programs are based on the following publications: Mackay 2001, Mackay et al. 1996a, b, c
  Program download & background information: (http://www.trentu.ca/cemc/models/models.html)

- *CemoS 1*
  CemoS Chemical exposure model System, developed and programmed at the University of Osnabrück, Germany by G Baumgarten, B Reiter, S Scheil, S Schwartz, J-O Wagner, supervised by M Matthies and S Trapp.
  The program is based on the following publications: Scheil et al. 1995, Trapp and Matthies 1998
  Program download & background information: (http://www.trentu.ca/cemc/models/models.html)

- *SADA 4.1*
  SADA Spatial Analysis and Decision Assistance, developed at the Institute for Environmental Modeling at the University of Tennessee, Knoxville. It is funded by the United States Environmental Protection Agency and the United States Nuclear Regulatory Commission (http://www.epa.gov/region5fields), (http://www.nrc.gov)
  Program download & background information: (http://www.tiem.utk.edu/~sada/)

- *CalTOX 4.0*
  CalTOX, the multimedia total exposure model for hazardous waste site was developed by the Department of Toxic Substances Control, California Environmental Protection Agency (http://www.dtsc.ca.gov/index.html). Program files and background information can be downloaded from: (http://eetd.lbl.gov/ied/ERA/caltox/)

- *MULTIMED 2.0*
  MULTIMED was developed by: National Exposure Research Laboratory - Ecosystems Research Division. Office of Research and Development (ORD). U.S. Environmental Protection Agency.
  The model and a detailed description can be obtained from:
  (http://www.epa.gov/ceampubl/mmedia/multim2/index.htm).

- *EUSES*
  EUSES is based on the EU Technical Guidance Documents (TGD) for risk assessment of new and existing substances (http://ecb.jrc.it/Technical-Guidance-Document/). The documentation and the program can be obtained from the European Chemicals Bureau, Ispra, Italy.

- *E4CHEM*
  E4Chem is a simulation program for the fate of chemicals in the environment. It was developed from the GSF-National Research Center for Environment and Health.

Tab. MA1: *Characteristics of evaluated multi-compartmental models: overview on program and model type, available features and tools.*

Program		**RISC 4.02**	**TIER1.xls (in RISC 4.02)**	**ARAMS 1.2.2/ FRAMES 1.5**	**MULTIMED**	**Level III**	**CalTOX**	**EUSES**	**CemoS1**	**E4CHEM**	**SADA 4.1**
Program Type	Stand-alone program	X			X	X		X	X	X	
	Spreadsheet tool		X				X				
	Platform/ framework			X							
Model type	Dynamic	X		X	X				X (e)	X (e)	
	Steady state		X			X	X	X	X (e)	X (e)	X
Model procedures	Analytical	X		X	X	X	X	X	X	X	X
	Numerical				X				X	X	
	Semi-analytical	X		X	X						
Features & tools	Optional multiple comp. analysis (a)	X (20)	X (-)	X (-)							X
	Simulation resolution (time steps, [years])	1		1 (b)	(-)		(-)	(-)	(-)		
	Max. simulation time [years]	100		7000	(-)		(-)	(-)	(-)		
	Optional Monte Carlo analysis (c)	X (-)		X (500)	X (5000		X (-)				
	Optional back calcula-tion: RBSL,SSTL, PRG	X	X				X				X
	TPH-mixture modelling	X	X					X			
	CSM construction			X							
	GIS-based tools			(d)							X
	Geo statistics										X
	Sampling design										X
	Cost-benefit analysis										X

RBSL: Risk-Based Screening Level, SSTL: site-specific target level, PRG: preliminary risk-based goal, TPH: total petroleum hydrocarbon (see e.g. TPHCWG 1997), CSM: Conceptual Site Model, GIS: Geographical Information System, (-): not limited, comp.: compound, (a): maximum number of Monte Carlo runs in brackets, (b): time step of the MEPAS source module algorithms is fixed to 1 year (optional selection of shorter time steps is planned for future versions), (c) in brackets: maximal number of runs that can be selected, (d): planned for future software versions, (e): module-specific (see text)

Tab. MA2: *Characteristics of evaluated multi-compartmental models: overview on considered fate and transport processes.*

Program		**RISC 4.02**	**TIER1.xls (in RISC 4.02)**	**ARAMS 1.2.2/ FRAMES 1.5**	**MULTIMED**	**Level III**	**CalTOX**	**EUSES**	**CemoS1**	**E4CHEM**	**SADA 4.1**
Fate & transport processes considered	Volatilisation from soil	X	X	X	X	(a)	X	X	X	X	X
	Volatilisation from GW	X	X			(a)					
	Dry/ wet deposition	X		X			X	X	X	X	
	Leaching	X	X	X	X	(a)	X	X	X (c)	X	X
	Overland flow			X				X			
	Transport in air			X	X			X	X (b)	X	
	GW transport	X		X	X		X				
	SW mixing	X		X	X		X	X		X	
	SW transport	X		X	X			X	X	X	
	Sediment partitioning	X		X		(a)	X	X		X	
	Plant uptake						X	X	X	X	X
	Food chain accumul.			X	X		X	X	X		X

GW: groundwater, SW: surface water, accumul.: accumulation, (a): concentration and mass can be calculated for different phases in the air, water, soil and sediment compartment (see text), (b): input of constant emission rate into air required, (c): soil concentrations as a function of depth can be calculated.

Tab. MA3: *Characteristics of evaluated multi-compartmental models: overview on considered exposure pathways and risk analysis options.*

Program		RISC 4.02	TIER1.XLS (in RISC 4.02)	ARAMS 1.2.2/ FRAMES 1.5	MULTIMED	Level III	CalTOX	EUSES	CemoS1	E4CHEM	SADA 4.1
Exposure & risk analysis	Human health	X	X	X	X		X	X			X
	Ecological receptors	X		X	X			X			X
Exposure pathways human health	DC (soil)	X	X	X (a)			X				X (a)
	IG (soil)	X	X	X			X				X
	IH (soil particles)		X	X			X				
	IG (GW)	X	X	X	X		X	X			X
	DC sh (GW)	X		X			X				
	IH sh (air)	X		X (b)			X				X (b)
	IG sh (GW)			X			X				
	IH (outdoor air)	X	X	X	X		X		X		X
	IH (indoor air)	X	X	X			X	X			
	IG (SW; swim.)	X	X	X			X				
	DC (SW, swim.)	X	X	X (a)			X				X
	DC (sed., swim.)			X (a)			X				
	IG (vegetable)	X		X			X	X			X
	IG (veg., GW SM)	X		X			X				X
	IG (veg., SW SM)			X			X				X
	IG (veg., air SM)			X			X				
	IG (irrig. water)	X					X				
	IG (meat)			X			X	X			X
	IG (milk)			X			X	X			X
	IG (fish)			X			X	X			X
	IG (shellfish)			X			X				
	DC (irrig. water)	X					X				
	IH (irrig. water spray)	X					X				
Exposure pathways ecosystem	Exposure to soil			X (c)							X
	Exposure to SW	X		X (c)	X						X
	Exposure to Sediment	X		X (c)							X

GW: groundwater, SW: surface water, IG: ingestion, IH: inhalation, DC: dermal contact, irrig.: irrigation, veg.: vegetable, sh: showering (e.g. inadvertent water ingestion while showering), SM: source medium, swim.: swimming (e.g. inadvertent water ingestion while swimming), sed.: sediment, (-): not limited (a): direct (external) exposure to radionuclides can be calulated (additional exposure route in ARAMS/FRAMES: external exposure to radionuclides while boating), (b): volatiles from showering and other domestic water use, (c): module Eco Receptor Intake (see text) is not time-varying; a time-varying version is under development.

MA3 Considerations for model selection

In this appendix, base-line models are discussed giving advice on real behaviour but providing no exact values. It should be aware, that great simplifications are made. Results may considerably deviate from real case studies so that more sophisticated modelling may be necessary. Some general remarks:

- Models should be selected carefully, depending on the question involved, the media in which the contaminant is released, available input data (chemical-specific, site-specific, meteorological data) and the type of contaminants considered
- Model assumptions are specific to contaminant classes (e.g. some models are restricted to neutral organics)
- For dynamic models, care should be taken considering the temporal resolution. E.g., time steps of a chosen simulation procedure might be too small to resolve significant peaks.
- When Monte Carlo runs are performed it has to be ensured that a appropriate number of runs is chosen, depending on the achieved precision of results (e.g. Cullen and Frey 1999, US EPA 1997c)

In the following, multimedia models are suggested specific to objectives:

- Evaluation of partitioning tendency of contaminants, affected environmental media, final sinks, partitioning for diffuse emissions (initial estimates): *Level III*, *EUSES, E4CHEM*
  - Recommended for screening calculations on a generic level
  - Identification of key parameters for further detailed modelling
  - Allows simulation of fate and transport processes on a large scale
  - Not appropriate for complex environmental matrices (e.g. heterogeneous soils)

- Initial site assessment and back-calculation (evaluation of environmental media concentrations for an input value of acceptable risk) : *TIER1.XLS in RISC*, *SADA*
  - *TIER1.XLS* : distribution factors (e.g. volatilisation, leaching), site classification based on conservative risk-based screening levels (RBSLs)
  - *SADA*: all descriptors relevant to exposure can be edited

- Multiphase contaminant fate and transport modelling, exposure and risk estimation: *RISC, ARAMS/FRAMES*
  - *RISC* : recommended for initial phase calculations; enables the modelling of total petroleum hydrocarbon (TPH) mixtures
  - *ARAMS/FRAMES:* large number of transport and exposure pathways, detailed database information; disadvantages: low temporal resolution (time step fixed to 1 year for most source term algorithms), low number of Monte Carlo steps (500 in maximum), advantages: flexibility, various data import and export options (e.g. the input of concentrations vs. time)

- Multiphase contaminant fate and transport modelling: *ARAMS/FRAMES, CemoS*
  - *ARAMS/FRAMES* (see above)
  - *CemoS:* dynamic uptake into plant leaves, soil concentrations as a function of depth is considered (not included in *ARAMS/FRAMES, RISC*)

- Data visualisation and geospatial analysis
  - SADA: e.g. mapping of concentrations and risk values, geostatistical evaluations; tools are provided for cost/benefit analysis, sampling design and decision analysis

Part VI General conclusions and outlook

In this thesis, strategies and tools for a quantitative multimedia risk assessment of *in situ* soil bioremediation were developed, addressing complex contaminations. One focus was aimed on the use of degrader bacteria in conjunction with plant roots (rhizoremediation), and in particular the application of genetically modified microorganisms (GMOs). Based upon elaborated procedures and experimental data, impacts that potentially arise from a field application of GMO-based rhizoremediation of PCB contaminated soils were estimated.

When contaminant mixtures are present at a site, compounds of environmental relevance should be determined with respect to their toxicity and environmental frequency, and the mobility potential. Part II revealed 56 PCB congeners of concern, and multimedia risk analyses of PCB contaminated soils should consider this group as target compounds. For the modelling of contaminant partitioning in environmental compartments, it is recommended to compile an internally consistent data set of physicochemical properties, including information on the temperature dependency of Henry's law constant and log K_{OW}. The procedure presented in Part II can be adapted to other groups of contaminants, such as polycyclic aromatic hydrocarbons (PAHs) or volatile chlorinated hydrocarbons (VCHs).

A procedure to quantify contaminant breakdown, and to estimate the time scale of microbial biodegradation was developed in Part III. In laboratory experiments, low and moderately chlorinated PCB congeners were readily metabolised by the investigated strains. F113-like inoculants showed a good survival ability in willow rhizosphere, i.e. in mesocosm experiments with PCB contaminated soil material. Rhizoremediation with the GM strain F113L::1180 and willow plants might efficiently degrade PCB mixtures in soil. This was found from preliminary degradation modelling. However, high uncertainties are associated to these results, as degradation kinetics in soil was estimated from laboratory experiments with individual PCB congeners in solution. Considerable uncertainty is further associated to the bacterial numbers in soil. The maintenance and frequency of microbial degraders in soil can be seen as a crucial aspect for the assessment of the biodegradation potential.

In Part IV, a baseline multimedia model was set up to estimate biodegradation and metabolite formation, fate and transport of contaminants and risks arising from the exposure to contaminated media. Results of generic modelling revealed a clear potential for risk reduction associated to the use of rhizoremediation with F113L::1180 and willow plants in PCB contaminated soil. Nevertheless, CBAs as degradation products of concern are mobile compounds showing significance for the aquatic pathway and plant uptake. Groundwater water wells for drinking water supply should be located at a sufficient distance downstream to the source. Considerable uncertainty is associated to the degradation potential for Aroclor 1016 (modelled exemplarily), as kinetics data for a large number of PCB congeners present in this mixture were not available.

Probabilistic modelling is recommended to comply with the uncertainty and/or variability of the required model input. Relevant parameters were identified specifically to the considered pathways and models, and a detailed data set of best estimates, value ranges and statistical information is provided in this thesis. The given instructions to obtain these data along with the information on probability density functions can be utilised for further modelling approaches.

From laboratory experiments and a field release test (non-GM derivatives), no significant hint on bacterial spreading into leaves, root free soil and leachate was given. Very low gene transfer rates were observed as the introduced *bph* trait was stably inserted into the chromosome of the F113 strains. Uncertainty is given for long-term effects (especially for gene transfer and impacts on soil bacteria) and potential impacts on soil organisms other than microbes.

Further studies should be carried out to elucidate the degradation performance in real contaminated soil and at the field scale. Such investigations should especially concentrate on bacterial survival and growth, the heterogeneity of population density, as well as the distribution of soil organic carbon. Microbial fate and impacts on the diversity of bacterial soil communities should be monitored to obtain information for long time periods.

Part V gives instructions for preparing, controlling and monitoring field release applications of *in situ* biodegradation based upon the use of GMOs. A review on required methodologies and tools available to date is provided here. The methodologies and tools evaluated in this thesis can be used not only for preliminary site investigations, i.e. for impact analyses of polluted soils but also to assist performance control and compliance monitoring accompanying *in situ* measures, and in order to evaluate the success of remedial actions.

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A

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Appendix A

Physicochemical properties of PCBs and CBAs

Tab. A1: *Selected physicochemical properties of PCBs at 25 °C (literature values and estimations). P_L: liquid vapour pressure, S_L: water solubility, S_{OL}: octanol solubility, H: Henry's law constant, log K_{OW}: log octanol-water partition coefficient, log K_{OA}: log octanol-air partition coefficient, T_M: melting point, T_B: boiling point, ΔS_{fus}: entropy of fusion. ΔU: Internal energy change applying to the supercooled liquid state, for air (A) and water (W) solubility and air-water (AW), octanol-water (OW) and octanol-air (OA) partition coefficient.*

PCB (a)	P_L (Pa)	S_{WL} (mg/L)	S_{OL} (mg/L)	H (Pa m^3/mol)	log K_{OW} (-)	log K_{OA} (b) (-)	T_M (°C)	T_B (°C)	ΔS_{fus} (J/mol/K)	ΔU_A (c) (kJ/mol)	ΔU_W (d) (kJ/mol)	ΔU_{AW} (kJ/mol)	ΔU_{OW} (kJ/mol)	ΔU_{OA} (e) (kJ/mol)
1	1.91E+00 [4]	6.60E+00 [1,2,3]		28.90 {div}	4.30 [2,3]		34 [2,3,17,26]	274 [2,3,26]	50.21 [2,3]	62.050 [4]				
2	9.80E-01 [4]	3.64E+00 [5]		28.95 [14] #	4.66 [16]		25.1 [2,3]	284 [2,3]		64.156 [4]				
3	9.36E-01 [4]	3.38E+00 [1]		27.78 [14] #	4.63 [16]	6.80 (24,25)	77.9 [2,3]	291 [2,3]	38.095 [1]	64.386 [4]	12.127 (27,28)			-75.9 [24]
4	3.27E-01 [4]	2.26E+00 [2,3]		27.81 {div}	4.72 [16]	7.20 [23]	61 [2,3,17]	320.3 #		67.334 [4]				-70 [23]
5	1.47E-01 [4]	1.07E+00 [7]		23.75 (13,14)	4.99 [16]	7.40 [23]	28 [2,17]	320.3 #		69.766 [4]				-75 [23]
6	1.73E-01 [4]	1.62E+00 [10] #		29.21 {div}	4.84 [16]		81.5 #	320.3 #		69.766 [4]				
7	1.85E-01 [4]	1.25E+00 [2,3]		35.26 {div}	5.15 [16]		24.4 [2,3]	320.3 #		71.144 [4]				
8	1.58E-01 [4]	1.50E+00 [2,3]		24.89 {div}	5.09 [16,21]	7.40 [23]	43 [2,3,17]	320.3 #		69.766 [4]				-75 [23]
9	1.85E-01 [4]	1.12E+00 [5]		32.79 {div}	5.10 [2,3,21]		25.1 [2,3]	320.3 #		71.546 [4]				
10	3.35E-01 [4]	2.84E+00 [5]		23.30 {div}	5.00 [2,3]	7.20 [23]	34.9 [2,3]	320.3 #	41 [2,3]	67.334 [4]				-70 [23]
11	8.68E-02 [4]	3.83E-01 [2]		24.42 {div}	5.27 [16,21]		29 [2,3,17,26]	322 [2]		72.963 [4]				
12	7.76E-02 [4]	1.56E-01 [6]		19.86 {div}	5.23 [16]		49 [2,17]	197 [2]		71.986 [4]				
13	8.31E-02 [4]	3.18E-01 [5]		25.74 [14] #	5.15 [16,21]		81.5 #	320.3 #		71.986 [4]				
14	1.26E-01 [4]	3.52E-01 [10] #		32.46 (15,14)	5.40 [3]		31 [2,3,17]	320.3 #		71.986 [4]				
15	7.26E-02 [4]	9.47E-01 (1,2)		20.16 {div}	5.23 [16,21]	7.64 (24,25)	149 [2,3,17]	315 [2,3]		73.633 [4]	17.066 [27]		-20.9 [32]	-72.6 [24]
16	5.39E-02 [4]	3.14E-01 [5]		25.45 {div}	5.12 [16]	7.72 [23]	28 [2,3,17]	341 #		72.944 [4]				-83 [23]
17	7.11E-02 [4]	4.62E-01 [6]		37.82 [14] #	5.39 [16]		100.9 #	341 #		72.944 [4]				
18	7.80E-02 [4]	6.14E-01 [1,2,3]		35.25 {div}	5.33 [16]	7.62 [23]	44 [2,3,17]	341 #		72.944 [4]				-79 [23]
19	1.16E-01 [4]	1.80E+00 [7]		34.02 (13,14)	5.04 [16]		100.9 #	341 #		71.048 [4]				
20	2.83E-02 [4]	7.78E-01 [10] #		22.01 {div}	5.60 [16,3]		100.9 #	341 #		75.624 [4]				
21	2.77E-02 [4]	9.68E-01 [6]		23.00 [14] #	5.68 [16]		102 [2]	341 #		75.624 [4]				
22	2.58E-02 [4]	4.84E-01 [10] #		19.35 {div}	5.29 [16]		73 [2,3,17]	341 #		75.624 [4]				
23	4.92E-02 [4]	1.20E-01 [10] #		32.26 [14] #	5.67 [16] #		41 [2,3]	341 #		75.624 [4]				
24	6.64E-02 [4]	4.62E-01 [7]		26.91 (13,14)	5.44 [16]		100.9 #	341 #		72.944 [4]				
25	3.74E-02 [4]	4.62E-01 [10] #		33.75 [14]	5.54 [16]		100.9 #	341 #		75.624 [4]				
26	4.10E-02 [4]	3.55E-01 [2]		30.18 {div}	5.65 [16]		40.5 [2]	341 #		75.624 [4]				
27	5.91E-02 [4]	6.49E-01 [10] #		38.78 [14]	5.24 [16] #		100.9 #	341 #		72.944 [4]				
28	3.41E-02 [4]	3.30E-01 [2,3]		30.48 {div}	5.71 [16]	7.93 [23]	57 [2,3,17]	207 [2]		75.624 [4]		47.230 [31]		-82 [23]
29	4.47E-02 [4]	5.68E-01 [1,2,3]		27.63 {div}	5.60 [2,3]	7.93 (24,25)	78 [2,3,17]	341 #	65.52 [2,3]	74.322 [4]	13.893 [27]			-72.6 [24]
30	9.69E-02 [4]	5.32E-01 [5]		62.60 [14]	5.50 [2,3]		62.5 [2,3]	341 #	49.37 [2,3]	72.006 [4]	16.729 [29]		-20.4 [32]	
31	3.46E-02 [4]	3.69E-01 [5]		24.02 {div}	5.68 [16]	7.93 [23]	67 [2,3,17]	341 #		75.298 [4]				-82 [23]
32	5.39E-02 [4]	8.82E-01 [7]		29.98 (13,14)	5.24 [16]	7.72 [23]	100.9 #	341 #		72.944 [4]				-83 [23]
33	2.64E-02 [4]	1.76E-01 [2,3]		20.26 {div}	5.71 [16]		60 [2,3,17]	341 #		75.624 [4]				
34	5.04E-02 [4]	2.72E-01 [6]		31.49 (13,14)	5.71 [16]		58 [17]	341 #		75.624 [4]				
35	1.39E-02 [4]	5.04E-01 [10] #		18.23 [14] #	5.72 [16] #		87 [2]	341 #		78.821 [4]				
36	1.79E-02 [4]	4.39E-01 [10] #		25.66 (13,14)	5.70 [3],		100.9 #	341 #		78.821 [4]				
37	1.27E-02 [4]	2.92E-01 [5]		18.09 {div}	5.90 [2,3,19]		87 [2,3]	341 #		78.821 [4]				
38	2.96E-02 #	5.83E-01 [10] #		23.53 [14] #	5.73 [16] #		100.9 #	341 #		78.821 [4]				
39	2.01E-02 [4]	4.11E-01 [10] #		30.32 [14] #	5.82 [16] #		100.9 #	341 #		78.821 [4]				
40	9.89E-03 [4]	1.36E-01 [5]		18.52 {div}	5.67 [16]		121 [2,3,17]	359.5 #		79.376 [4]				
41	1.09E-02 [4]	2.63E-01 [6]		22.70 {div}	5.79 [16]		122.3 #	359.5 #		78.572 [4]				
42	1.16E-02 [4]	1.09E-01 [10] #		20.05 (13,14)	5.72 [16]		69 [17]	359.5 #		78.572 [4]				

***Tab. A1** (continued)*

PCB (a)	P_L (Pa)	S_{WL} (mg/L)	S_{OL} (mg/L)	H (Pa m^3/mol)	log K_{OW} (-)	log K_{OA} (b) (-)	T_M (°C)	T_B (°C)	ΔS_{fus} (J/mol/K)	ΔU_A (c) (kJ/mol)	ΔU_W (d) (kJ/mol)	ΔU_{AW} (kJ/mol)	ΔU_{OW} (kJ/mol)	ΔU_{OA} (e) (kJ/mol)
43	1.64E-02 [4]	1.55E+00 [8]		33.94 [14] #	5.86 [16] #		122.3 #	359.5 #		78.572 [4]				
44	1.28E-02 [4]	1.64E-01 [2,3]		24.30 {div}	5.73 [16]	8.36 [23]	47 [2,3,17]	359.5 #		78.572 [4]				-85 [23]
45	2.25E-02 [4]	1.32E+00 [6]		35.25 [14]	4.84 [16]		122.3 #	359.5 #		76.428 [4]				
46	1.87E-02 [4]	1.32E+00 [6]		34.33 [14] #	4.84 [16]		122.3 #	359.5 #		76.428 [4]				
47	1.53E-02 [4]	2.01E-01 [5]		28.27 (13,14)	5.94 [16]		83 [2,3]	359.5 #		78.572 [4]	13 [30]			
48	1.53E-02 [4]	5.18E-02 [3]		30.67 [14] #	5.69 [16]		66.1 [2,3]	359.5 #	69.4 [2,3]	78.572 [4]				
49	1.68E-02 [4]	1.88E-01 [5]		21.28 {div}	5.87 [16]	8.39 [25]	64 [2,3]	359.5 #		78.572 [4]				-76 [23]
50	1.77E-03 #	5.27E-02 [6]		70.55 {div}	5.75 [16]		45 [2]	359.5 #		76.428 [4]				
51	2.46E-02 [4]	1.03E-01 [6]		22.30 {div}	5.51 [16]		45 [2]	359.5 #		76.428 [4]				
52	1.61E-02 [4]	1.22E-01 [1,2,3]	8.80E+07 [11]	32.63 {div}	5.79 [16]	8.22 [23]	87 [2,3,17]	359.5 #		78.400 [4]		48.437 [31]		-85 [23]
53	2.76E-02 [4]	2.84E-01 [5]		41.14 {div}	5.55 [16]	8.04 [25]	104 [2]	359.5 #		76.371 [4]				-76 [23]
54	3.88E-02 [4]	5.93E-01 [5]		53.29 {div}	5.24 [16]		198 [2,17]	359.5 #		69.421 [4]				
55	5.79E-03 [4]	4.47E-01 [6]		18.48 [14] #	6.10 [16]		122.3 #	359.5 #		81.501 [4]				
56	4.29E-03 [4]	4.07E-01 [10] #		15.34 [14] #	5.98 [16] #		122.3 #	359.5 #		81.501 [4]				
57	1.02E-02 #	1.79E-01 [10] #		27.40 [14] #	6.14 [16] #		122.3 #	359.5 #		81.501 [4]				
58	1.02E-02 #	2.38E-01 [10] #		25.33 [14] #	6.17 [18]		122.3 #	359.5 #		81.501 [4]				
59	1.02E-02 #	2.38E-01 [10] #		30.81 [14] #	5.85 [16] #		122.3 #	359.5 #		78.572 [4]				
60	5.28E-03 [4]	5.15E-01 [10] #		15.48 [14] #	6.24 [16]		142 [2,3,17]	359.5 #		81.501 [4]				
61	1.21E-02 [4]	1.31E-01 [1,2,3]	1.74E+08 [11]	25.44 [14]	5.90 [2,3]	8.72 (24,25)	92 [2,3,17]	359.5 #	69.45 [2,3]	81.501 [4]	15.94 [27]		-24 [32]	-66.3 [24]
62	1.02E-02 #	1.29E-01 [10] #		29.37 (13,14)	6.03 [16] #		122.3 #	359.5 #		78.572 [4]				
63	6.80E-03 [4]	4.47E-01 [6]		24.59 [14] #	6.10 [16]		122.3 #	359.5 #		81.501 [4]				
64	1.31E-02 [4]	2.65E-01 [10] #		20.89 (13,14)	5.76 [16]	8.39 [23]	122.3 #	359.5 #		78.572 [4]				-86 [23]
65	1.40E-02 [4]	5.55E-02 [6]		28.45 (15,14)	5.96 [16]		79 [2,17]	359.5 #		78.572 [4]				
66	6.21E-03 [4]	3.74E-01 [2,3]		20.54 {div}	5.98 [16]	9.02 [25]	124 [2,3]	359.5 #		80.870 [4]				-73 [23]
67	6.65E-03 [4]	1.96E-01 [6]		16.91 (13,14)	6.32 [16]		122.3 #	359.5 #		81.501 [4]				
68	2.94E-02 #	1.59E-01 [10] #		22.83 (13,14)	6.26 [16] #		122.3 #	340 [26]		81.501 [4]				
69	1.76E-02 [4]	1.28E-01 [10] #		36.26 (13,14)	6.03 [16]		122.3 #	359.5 #		78.572 [4]				
70	5.47E-03 [4]	2.44E-01 [3,3]		20.26 {div}	6.22 [16]		104 [2,3]	359.5 #		82.440 [4]				
71	9.03E-03 [4]	2.51E-01 [6]		31.82 [14] #	5.76 [16]		122.3 #	359.5 #		78.572 [4]				
72	1.01E-02 [4]	1.63E-01 [10] #		36.70 [14] #	6.21 [16] #		122.3 #	359.5 #		81.501 [4]				
73	1.02E-02 #	2.19E-01 [10] #		52.69 [14] #	5.80 [16] #		122.3 #	359.5 #		78.572 [4]				
74	7.29E-03 [4]	4.75E-02 [5]		21.76 {div}	6.10 [16,3]		125 [2,3,17]	359.5 #		81.501 [4]				
75	1.80E-02 [4]	4.18E-01 [2]		47.06 [14] #	6.03 [16]		93 [2]	359.5 #		78.572 [4]				
76	6.06E-03 [4]	1.67E-01 [10] #		24.19 [14] #	5.98 [16]		106 [26]	359.5 #		81.501 [4]				
77	2.20E-03 [4]	1.18E-01 [5]		9.52 {div}	6.50 [2]	9.70 [25]	180 [2,3,17]	359.5 #	85.35 [2,3]	84.756 [4]	11.924 [28]			-73 [23]
78	3.15E-03 [4]	2.17E-01 [10] #		16.55 [14] #	6.23 [16] #		122.3 #	359.5 #		85.637 [4]				
79	3.37E-03 [4]	2.31E-01 [10] #		14.55 (13,14)	6.30 [16] #		122.3 #	359.5 #		85.637 [4]				
80	5.47E-03 [4]	2.84E-02 [5]		31.71 [14]	6.10 [3]		164 [2,3,17]	359.5 #		85.637 [4]				
81	2.87E-03 [4]	2.37E-01 [10] #		14.51 [14] #	6.24 [16] #		122.3 #	359.5 #		85.637 [4]				
82	2.90E-03 [4]	1.69E-01 [10] #		17.54 (div)	6.05 [16] #		134.6 #	378.2 #		84.182 [4]				
83	2.71E-03 [4]	1.20E-01 [10] #		21.46 [14] #	6.19 [16] #		134.6 #	378.2 #		84.182 [4]				
84	3.68E-03 [4]	6.45E-01 [7]		25.45 [14] #	5.60 [16]	8.78 [23]	134.6 #	378.2 #		81.827 [4]				-85 [23]

***Tab. A1** (continued)*

PCB (a)	P_L (Pa)	S_{WL} (mg/L)	S_{OL} (mg/L)	H (Pa m^3/mol)	log K_{OW} (-)	log K_{OA} (b) (-)	T_M (°C)	T_B (°C)	ΔS_{fus} (J/mol/K)	ΔU_A (c) (kJ/mol)	ΔU_W (d) (kJ/mol)	ΔU_{AW} (kJ/mol)	ΔU_{OW} (kJ/mol)	ΔU_{OA} (e) (kJ/mol)
85	2.36E-03 [4]	9.31E-02 [7]		13.09 (13,14)	6.18 [16]		134.6 #	378.2 #		84.182 [4]				
86	2.77E-03 [4]	5.33E-02 [5]		24.14 [14] #	6.38 [16]		100 [2,3,17]	378.2 #		84.182 [4]				
87	2.29E-03 [4]	2.99E-02 [2,3]		19.90 {div}	6.23 [16]		114 [2,3]	378.2 #		84.948 [4]				
88	5.97E-03 [4]	6.53E-02 [2,3,5]		38.97 [14] #	6.50 [16,3]		100 [2,3]	378.2 #		81.827 [4]				
89	3.52E-03 #	6.45E-01 [6]		30.18 [14] #	5.60 [16]		134.6 #	378.2 #		81.827 [4]				
90	3.34E-03 [4]	5.87E-02 [6]		29.83 [14] #	6.32 [16]		134.6 #	378.2 #		84.182 [4]				
91	4.85E-03 [4]	2.63E-01 [6]		23.60 (13,14)	5.87 [16]		134.6 #	378.2 #		81.827 [4]				
92	3.92E-03 [4]	5.87E-02 [7]		26.34 [14] #	6.32 [16]		134.6 #	378.2 #		84.182 [4]				
93	6.54E-03 [4]	1.55E-01 [6]		34.49 [14] #	6.06 [16]		134.6 #	378.2 #		81.827 [4]				
94	3.52E-03 #	1.64E-01 [10] #		39.69 [14] #	6.04 [16] #		134.6 #	378.2 #		81.827 [4]				
95	5.32E-03 [4]	8.79E-02 [10] #		21.27 (13,14)	5.92 [16]	8.74 (23], [25)	100 [2]	378.2 #		81.827 [4]				-85 [23]
96	3.52E-03 #	4.77E-01 [10] #		41.56 [14] #	5.54 [16] #	8.52 [25]	134.6 #	378.2 #		74.705 [4]				-75 [23]
97	2.47E-03 [4]	2.94E-02 [10] #		18.23 [14] #	6.30 [16]		81 [2,3]	378.2 #	53.77 [2,3]	84.182 [4]				
98	6.10E-03 [4]	1.55E-01 [6]		39.69 [14] #	6.04 [16]		134.6 #	378.2 #		81.827 [4]				
99	2.99E-03 [4]	1.30E-02 [6]		16.59 (13,14)	6.41 [16]		81 [2]	378.2 #		84.392 [4]				
100	3.52E-03 #	8.49E-02 [6]		56.98 [14] #	6.23 [16]		134.6 #	378.2 #		81.827 [4]				
101	3.39E-03 [4]	3.81E-02 (1,2)		26.38 {div}	6.40 [2,3]	8.92 (23], [25)	76.5 [2,3]	378.2 #	53.6 [2,3]	84.029 [4]	13.129 [28]			-82 [23]
102	5.32E-03 [4]	1.42E-01 [10] #		23.34 (13,14)	6.10 [16] #		134.6 #	378.2 #		81.827 [4]				
103	8.82E-03 [4]	1.32E-01 [6]		51.01 [14] #	6.11 [16]		134.6 #	378.2 #		81.827 [4]				
104	4.41E-03 #	6.93E-02 [2]		88.96 {div}	5.76 [16] #		91 [2]	378.2 #		74.705 [4]				
105	8.74E-04 [4]	2.07E-02 [9]		10.06 {div}	6.79 [16,22]	10.01 [25]	105 [2]	378.2 #		88.700 [4]				-90 [23]
106	1.37E-03 [4]	5.72E-02 [10] #		16.70 [14] #	6.92 [16]		134.6 #	378.2 #		87.360 [4]				
107	1.25E-03 [4]	7.83E-02 [10] #		16.13 [14] #	6.60 [16] #		134.6 #	378.2 #		87.360 [4]				
108	1.40E-03 [4]	7.01E-02 [10] #		17.81 [14] #	6.59 [16] #		134.6 #	378.2 #		87.360 [4]				
109	3.52E-03 #	4.65E-02 [10] #		28.56 [14] #	6.51 [16] #		134.6 #	378.2 #		84.182 [4]				
110	1.83E-03 [4]	2.48E-02 [7]		19.89 [14] #	6.20 [16]	9.07 [23]	79 [2]	378.2 #		84.182 [4]				-88 [23]
111	2.06E-04 #	4.53E-02 [10] #		27.02 [14] #	6.72 [16] #		134.6 #	378.2 #		87.360 [4]				
112	3.04E-03 [4]	6.74E-02 [6]		27.02 [14] #	6.41 [16]		134.6 #	378.2 #		84.182 [4]				
113	2.90E-03 [4]	4.35E-02 [6]		33.01 [14] #	6.45 [16]		134.6 #	378.2 #		84.182 [4]				
114	1.25E-03 [4]	3.09E-02 [10] #		14.48 [14] #	6.71 [16]		99 [17]	378.2 #		87.360 [4]				
115	2.15E-03 [4]	4.35E-02 [6]		24.87 [14] #	6.44 [16]		134.6 #	378.2 #		84.182 [4]				
116	2.31E-03 [4]	3.44E-02 [5]		30.59 [14]	6.30 [2,3]		124 [2,3,17]	378.2 #	53.81 [2,3]	84.182 [4]				
117	2.47E-03 [4]	5.11E-02 [6]		24.42 [14] #	6.39 [16]		134.6 #	378.2 #		84.182 [4]				
118	1.19E-03 [4]	4.15E-02 [10] #		24.46 {div}	6.57 [16]	9.82 [25]	107 [2]	378.2 #		86.900 [4]				-90 [23]
119	2.77E-03 [4]	4.78E-02 [6]		19.48 (13,14)	6.40 [16]		134.6 #	378.2 #		84.182 [4]				
120	1.98E-03 [4]	3.59E-02 [6]		15.27 (13,14)	6.30 [16,3]		77 [2,3]	378.2 #		87.360 [4]				
121	4.82E-03 [4]	4.66E-02 [6]		56.58 [14] #	6.42 [16]		134.6 #	378.2 #		84.182 [4]				
122	9.92E-04 [4]	9.69E-02 [10] #		12.73 [14] #	6.50 [16] #		134.6 #	378.2 #		87.360 [4]				
123	1.31E-03 [4]	1.32E-01 [10] #		17.65 [14] #	6.64 [16]		134.6 #	378.2 #		87.360 [4]				
124	7.88E-04 [4]	3.68E-02 [10] #		17.29 [14] #	6.62 [16] #		105 [26]	378.2 #		87.360 [4]				
125	1.92E-03 [4]	7.82E-02 [10] #		29.15 [14] #	6.29 [16] #		135 #	378.2 #		84.182 [4]				
126	4.87E-04 [4]	9.08E-02 [10] #		8.29 {div}	6.67 [16] #	10.35 [25]	135 #	378.2 #		92.491 [4]				-93 [23]

***Tab. A1** (continued)*

PCB (a)	P_L (Pa)	S_{WL} (mg/L)	S_{OL} (mg/L)	H (Pa m^3/mol)	log K_{OW} (-)	log K_{OA} (b) (-)	T_M (°C)	T_B (°C)	ΔS_{fus} (J/mol/K)	ΔU_A (c) (kJ/mol)	ΔU_W (d) (kJ/mol)	ΔU_{AW} (kJ/mol)	ΔU_{OW} (kJ/mol)	ΔU_{OA} (e) (kJ/mol)
127	7.72E-04 [4]	5.49E-02 [10] #		15.80 [14] #	6.80 [16] #		134.6 #	378.2 #		92.491 [4]				
128	3.46E-04 [4]	1.91E-02 [2,3]		6.85 {div}	7.00 [2,3]		150 [2,3,17]	396.9 #	68.62 [2,3]	91.055 [4]				
129	4.44E-04 [4]	5.31E-03 [5]		8.56 (13,14)	6.76 [16]		85 [2,3,17]	396.9 #		89.810 [4]				
130	5.46E-04 [4]	4.37E-02 [10] #		9.60 (13,14)	7.30 [16,3]		146.3 #	396.9 #		89.810 [4]				
131	1.26E-03 [4]	1.86E-02 [6]		14.24 (13,14)	6.78 [16]		146.3 #	396.9 #		87.226 [4]				
132	7.58E-04 [4]	1.25E-01 [6]		12.50 (13,14)	6.20 [16]		146.3 #	396.9 #		87.226 [4]				
133	8.45E-04 [4]	2.81E-02 [10] #		20.64 [14] #	7.07 [18],		146.3 #	396.9 #		89.810 [4]				
134	1.23E-03 [4]	2.18E-03 [2,3]		23.26 {div}	6.20 [16]		100 [2,3]	396.9 #		87.226 [4]				
135	1.15E-03 [4]	8.43E-02 [7]		16.44 (13,14)	6.32 [16]		146.3 #	396.9 #		87.226 [4]				
136	1.58E-03 [4]	3.10E-02 [5]		20.78 (13,14)	6.70 [2,3]		112 [2,3]	396.9 #	54.847 [2]	79.989 [4]	24.465 [28]			
137	2.86E-04 [4]	4.58E-03 [10] #		18.82 [14] #	6.82 [16]		77 [2,3,17]	396.9 #		89.810 [4]				
138	5.14E-04 [4]	8.40E-03 [10] #		13.17 {div}	6.73 [16]	9.66 (23], [25)	80 [2]	396.9 #		89.504 [4]				-86 [23]
139	1.20E-03 [4]	6.68E-03 [10] #		33.32 [14] #	6.64 [16] #		73 [26]	396.9 #		87.226 [4]				
140	1.20E-03 #	3.22E-02 [6]		31.17 [14] #	6.58 [16]		146.3 #	396.9 #		87.226 [4]				
141	6.12E-04 [4]	2.50E-02 [10] #		17.61 {div}	6.75 [16]		146.3 #	396.9 #		89.810 [4]				
142	1.20E-03 #	3.89E-02 [10] #		31.89 [14] #	6.57 [16] #		146.3 #	396.9 #		87.226 [4]				
143	8.91E-04 [4]	4.14E-02 [6]		16.89 (13,14)	6.56 [16]		146.3 #	396.9 #		87.226 [4]				
144	1.00E-03 [4]	5.47E-02 [6]		45.38 (div)	6.45 [16]		146.3 #	396.9 #		87.226 [4]				
145	2.94E-03 [4]	9.95E-02 [10] #		47.61 [14] #	6.26 [16] #		146.3 #	396.9 #		79.989 [4]				
146	7.71E-04 [4]	1.47E-02 [6]		10.77 (13,14)	6.85 [16]		146.3 #	396.9 #		89.810 [4]				
147	1.20E-03 #	4.29E-02 [10] #		18.57 (13,14)	6.61 [16] #		146.3 #	396.9 #		87.226 [4]				
148	1.90E-03 [4]	3.77E-02 [10] #		43.52 [14] #	6.63 [16] #		146.3 #	396.9 #		87.226 [4]				
149	1.13E-03 [4]	6.57E-02 [7]		27.21 (div)	6.41 [16]	9.26 [23]	146.3 #	396.9 #		87.379 [4]				-91 [23]
150	1.20E-03 #	1.08E-01 [10] #		51.25 [14] #	6.16 [16] #		146.3 #	396.9 #		79.989 [4]				
151	1.78E-03 [4]	1.48E-02 [10] #		28.69 {div}	6.42 [16]		100 [17]	396.9 #		87.226 [4]				
152	1.20E-03 #	1.16E-01 [10] #		43.32 [14] #	6.23 [16] #		146.3 #	396.9 #		79.989 [4]				
153	6.83E-04 [4]	5.39E-03 (1,2)		16.70 {div}	6.80 [16]	9.55 (23], [25)	103 [2,3,17]	396.9 #		89.025 [4]	4.962 [28]			-87 [23]
154	1.74E-03 [4]	4.25E-02 [6]		58.50 {div}	6.65 [16]		146.3 #	396.9 #		87.226 [4]				
155	3.87E-03 [4]	1.09E-02 {1,2,3}		80.87 [14]	6.54 [16]	10.02 (24,25)	114 [2,3,17]	396.9 #	45.19 [2,3]	79.989 [4]	16.705 [27]			-63.9 [24]
156	2.19E-04 [4]	2.56E-02 [10] #		48.56 (div)	7.44 [16]		146.3 #	396.9 #		92.357 [4]				
157	2.00E-04 [4]	3.13E-02 [10] #		33.67 (div)	6.97 [16] #		146.3 #	396.9 #		93.218 [4]				
158	6.12E-04 [4]	8.92E-03 [10] #		40.79 (div)	6.78 [16]	9.52 [23]	107 [26]	396.9 #		89.810 [4]				-85 [23]
159	1.20E-03 #	1.39E-02 [10] #		8.90 (13,14)	7.43 [18]		146.3 #	396.9 #		92.357 [4]				
160	1.20E-03 #	1.42E-02 [10] #		11.84 (13,14)	7.30 [18]		146.3 #	396.9 #		89.025 [4]				
161	1.20E-03 #	1.35E-02 [10] #		28.89 [14] #	7.10 [18]		146.3 #	396.9 #		89.025 [4]				
162	1.20E-03 #	1.98E-02 [10] #		13.33 [14] #	7.47 [18]		146.3 #	396.9 #		92.357 [4]				
163	5.98E-04 [4]	2.21E-02 [3]		9.15 (13,14)	6.78 [16]		88.2 [2,3]	396.9 #		89.810 [4]				
164	1.20E-03 #	3.01E-02 [6]		17.85 [14] #	6.63 [16]		146.3 #	396.9 #		89.025 [4]				
165	1.20E-03 #	3.01E-02 [6]		15.42 (13,14)	7.00 [16,3]		146.3 #	396.9 #		89.025 [4]				
166	1.20E-03 #	1.55E-02 [10] #		15.30 (15,14)	7.31 [18]		146.3 #	396.9 #		92.357 [4]				
167	2.82E-04 [4]	3.46E-02 [6]		11.13 [14] #	7.29 [16]		146.3 #	396.9 #		93.218 [4]				
168	6.87E-04 [4]	1.61E-02 [10] #		27.97 [14] #	7.25 [18]		146.3 #	396.9 #		89.810 [4]				

***Tab. A1** (continued)*

PCB (a)	P_L (Pa)	S_{WL} (mg/L)	S_{OL} (mg/L)	H (Pa m^3/mol)	log K_{OW} (-)	log K_{OA} (b) (-)	T_M (°C)	T_B (°C)	ΔS_{fus} (J/mol/K)	ΔU_A (c) (kJ/mol)	ΔU_W (d) (kJ/mol)	ΔU_{AW} (kJ/mol)	ΔU_{OW} (kJ/mol)	ΔU_{OA} (e) (kJ/mol)
169	6.61E-05 [4]	2.78E-02 [6]		6.60 [14] #	7.55 [16]		202 [2]	396.9 #		99.325 [4]				
170	8.58E-05 [4]	6.64E-03 [10] #		14.07 {div}	7.08 [16]		134 [2]	415.6 #		95.994 [4]				
171	1.88E-04 [4]	1.49E-02 [2,3]		17.49 [14] #	6.70 [2,3]	10.25 [25]	122 [2,3]	415.6 #	51.05 [2,3]	93.486 [4]				-91 [23]
172	1.39E-04 [4]	7.18E-03 [6]		6.69 (13,14)	7.21 [16]		163.6 #	415.6 #		95.420 [4]				
173	3.96E-04 #	1.98E-02 [10] #		9.95 (13,14)	6.96 [16] #		163.6 #	415.6 #		92.605 [4]				
174	1.81E-04 [4]	1.12E-02 [6]		9.27 (13,14)	6.85 [16]		131 [17]	415.6 #		92.605 [4]				
175	3.78E-04 [4]	1.89E-02 [6]		22.63 [14] #	6.92 [16]		163.6 #	415.6 #		92.605 [4]				
176	5.15E-04 [4]	6.41E-02 [6]		30.11 [14] #	6.55 [16]		163.6 #	415.6 #		85.273 [4]				
177	2.50E-04 [4]	3.43E-02 [6]		16.55 [14] #	6.73 [16]		163.6 #	415.6 #		92.605 [4]				
178	4.34E-04 [4]	2.33E-02 [6]		11.97 (13,14)	6.85 [16]		163.6 #	415.6 #		92.605 [4]				
179	5.15E-04 [4]	1.04E-01 [6]		15.17 (13,14)	6.41 [16]		163.6 #	415.6 #		85.273 [4]				
180	1.32E-04 [4]	2.74E-03 [10] #		20.64 {div}	7.21 [16]	10.19 (23], [25)	110 [2]	415.6 #		94.137 [4]				-80 [23]
181	2.93E-04 [4]	9.68E-03 [6]		23.32 [14] #	7.13 [16]		163.6 #	415.6 #		92.605 [4]				
182	2.93E-04 [4]	1.46E-02 [6]		26.04 [14] #	6.92 [16]		152 [17]	415.6 #		92.605 [4]				
183	3.53E-04 [4]	2.30E-03 [10] #		42.12 (div)	7.04 [16]		83 [26]	415.6 #		92.605 [4]				
184	2.20E-03 #	2.38E-02 [10] #		46.42 [14] #	6.82 [16] #		163.6 #	415.6 #		85.273 [4]				
185	3.22E-04 [4]	7.41E-03 [2]		11.67 (13,14)	6.99 [16]		149 [2,3,17]	415.6 #		92.605 [4]				
186	4.70E-04 [4]	3.47E-02 [10] #		37.30 [14] #	6.71 [16] #		163.6 #	415.6 #		85.273 [4]				
187	3.08E-04 [4]	6.63E-02 [5]		42.20 {div}	7.05 [16] #	9.86 [23]	144 [2]	415.6 #		91.629 [4]				-87 [23]
188	8.55E-04 [4]	2.93E-02 [6]		112.99 {div}	6.78 [16]		163.6 #	415.6 #		85.273 [4]				
189	4.83E-05 [4]	1.66E-02 [6]		6.74 [14] #	7.72 [16]		162 [17]	415.6 #		99.076 [4]				
190	1.08E-04 [4]	2.55E-03 [10] #		11.37 [14] #	7.08 [16]		116 [17]	415.6 #		95.420 [4]				
191	1.03E-04 [4]	7.18E-03 [6]		13.48 [14] #	7.21 [16]		163.6 #	415.6 #		95.420 [4]				
192	1.76E-04 [4]	7.18E-03 [6]		19.40 [14] #	7.21 [16]		163.6 #	415.6 #		95.420 [4]				
193	1.36E-04 [4]	7.18E-03 [6]		13.60 [14] #	7.21 [16]		163.6 #	415.6 #		95.420 [4]				
194	2.05E-05 [4]	4.13E-03 [2,3]		3.90 (13,14)	7.62 [16]		159 [2,3,17]	434.3 #		101.029 [4]				
195	4.48E-05 [4]	7.43E-03 [6]		12.41 {div}	7.35 [16]		180.8 #	434.3 #		98.004 [4]				
196	6.05E-05 [4]	5.50E-03 [6]		7.12 (13,14)	7.43 [16]		180.8 #	434.3 #		98.004 [4]				
197	1.78E-04 [4]	3.82E-03 [6]		25.69 [14] #	8.91 #		132 [17]	434.3 #		90.480 [4]				
198	6.78E-05 [4]	5.50E-03 [6]		8.52 (13,14)	8.91 #		180.8 #	434.3 #		98.004 [4]				
199	5.91E-05 [4]	7.43E-03 [6]		12.01 (13,14)	8.91 #		180.8 #	434.3 #		98.004 [4]				
200	9.33E-05 [4]	1.15E-02 [6]		24.36 [14] #	8.91 #		180.8 #	434.3 #		90.480 [4]				
201	1.74E-04 [4]	9.15E-03 [6]		38.87 {div}	8.91 #		180.8 #	434.3 #		90.480 [4]				
202	5.24E-04 [4]	1.66E-02 (1,2)		12.23 (13,14)	7.10 [2,3]		162 [2,3,17]	434.3 #	52.74 [2,3]	90.480 [4]	27.750 [28]			
203	6.33E-05 [4]	4.59E-03 [6]		14.21 [14] #	7.49 [16]		180.8 #	434.3 #		98.004 [4]				
204	1.55E-04 [4]	4.79E-03 [6]		34.89 [14] #	7.48 [16]		180.8 #	434.3 #		90.480 [4]				
205	2.46E-05 [4]	2.90E-03 [6]		8.84 [14] #	7.62 [16]		180.8 #	434.3 #		101.029 [4]				
206	1.09E-05 [4]	1.16E-02 [5]		8.84 [14] #	7.94 [16]		206 [2,3,17]	453 #	84.09 [2,3]	103.403 [4]	9.508 [28]			
207	3.19E-05 [4]	7.90E-04 [6]		17.13 [14] #	7.88 [16]		161 [2]	453 #		95.764 [4]				
208	3.05E-05 [4]	4.27E-04 [2,3,5]		16.93 [14] #	8.16 [2,3,20]		183 [2,3]	453 #	49.74 [2,3]	95.764 [4]				
209	1.42E-05 [4]	2.96E-04 (1,2)		11.42 [14] #	8.26 [2,3]		306 [2,3]	471.7 #	49.37 [2,3]	101.029 [4]	38.212 [28]			

(a) IUPAC-number, (b) [24], [25]: extrapolated to 25 °C (not measured above 20°C), (c) obtained by substracting 2.391 kJ/mol from the enthalpy reported for vapor pressure ΔHVP (Part II, section 2.3.2), (d) literature values changed to apply to the supercooled liquid state (Part II, section 2.3.1), (e) parameter measured by [23] with coeluting congener (PCBs IUPAC-no. 4+10, 8+5, 16+32, 31+28, 84+101, 138+158). [1,2,3]: value quoted by [1], [2] and [3]. (1,2): mean calculated from values quoted by [1] and [2]. {1,2,3}: median calculated from values quoted by [1], [2] and [3]. (div), {div}: mean, median of values quoted by [1], [3], [12], [13], [14] or [26]. #: estimated value (# without citation: estimation using EPI Suite 3.10 [26]). References [3], [6], [7], [13], [15], [17], [18], [19], [20], [21], [22], [24]: cited by the database included in EPI Suite 3.10 [26].

Tab. A2: *Adjustments and value ranges for physicochemical properties of PCBs. Min., max.: minimum, maximum value determined from the selected literature data (Tab. A1), lik.: likeliest value, i.e. adjustment of the selected data to conform to thermodynamic constraints (Part II, section 2.3.1). Dev.: deviation of the adjusted property from the selected value in Tab. A1.* ΔU_O*: internal energy change for octanol solubility, other abbreviations according to Tab. A1.*

PCB	P_L (Pa)			Dev.	S_L (mg/L)			Dev.	H (Pa m^3/mol)			Dev.	log K_{OW} (-)			Dev.	S_{OL} (mg/L)	log K_{OA}	Dev.	ΔU_A	ΔU_W	ΔU_O	ΔU_{AW}	ΔU_{OW}	ΔU_{OA}
	Min.	Max.	Lik.	(%)	Min.	Max.	Lik.	(%)	Min.	Max.	Lik.	(%)	Min.	Max.	Lik.	(%)		Lik. (-)	(%)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)
1	1.01E+00	1.91E+00	1.54E+00	-19	6.60E+00	1.24E+01	8.15E+00	24	28.90	54.51	35.71	24	4.24	4.55	4.30		1.44E+05	6.09		62.05	20.00	0.00	42.05	-20.00	-62.05
2	5.58E-01	9.80E-01	8.13E-01	-17	3.64E+00	6.39E+00	4.39E+00	21	28.95	50.84	34.93	21	4.60	4.91	4.66		2.40E+05	6.59		64.16	20.00	0.00	44.16	-20.00	-64.16
3	3.48E-01	9.36E-01	6.98E-01	-25	3.38E+00	9.11E+00	4.53E+00	34	19.39	52.20	29.06	5	4.63	4.95	4.69	16	2.76E+05	6.72	-18	64.39	12.13	-6.76	52.26	-18.88	-71.14
4	1.04E-01	3.27E-01	2.83E-01	-14	2.26E+00	7.09E+00	2.61E+00	16	10.29	32.36	24.17	-13	4.72	5.09	4.86	37	2.64E+05	7.02	-35	67.33	20.00	-2.53	47.33	-22.53	-69.87
5	7.21E-02	1.47E-01	1.27E-01	-14	1.07E+00	2.18E+00	1.24E+00	16	15.08	30.84	23.00	-3	4.99	5.22	5.06	17	2.34E+05	7.31	-19	69.77	20.00	-4.80	49.77	-24.80	-74.57
6	1.73E-01	2.12E-01	1.85E-01	7	1.32E+00	1.62E+00	1.51E+00	-6	23.90	29.21	27.32	-6	4.80	4.94	4.84		1.45E+05	6.94		69.77	20.00	0.00	49.77	-20.00	-69.77
7	1.85E-01	1.98E-01	1.89E-01	2	1.17E+00	1.25E+00	1.22E+00	-2	33.02	35.26	34.50	-2	5.11	5.25	5.15		3.10E+05	7.26		71.14	20.00	0.00	51.14	-20.00	-71.14
8	1.39E-01	1.68E-01	1.59E-01	1	1.42E+00	1.71E+00	1.49E+00	-1	20.62	24.89	23.89	-4	5.09	5.15	5.11	6	3.37E+05	7.37	-7	69.77	20.00	-4.80	49.77	-24.80	-74.57
9	1.65E-01	1.85E-01	1.78E-01	-4	1.12E+00	1.26E+00	1.17E+00	4	32.79	36.73	34.05	4	5.06	5.20	5.10		2.53E+05	7.20		71.55	20.00	0.00	51.55	-20.00	-71.55
10	2.97E-01	3.35E-01	3.20E-01	-4	2.84E+00	3.20E+00	2.97E+00	5	23.30	26.30	24.02	3	4.98	5.02	5.00	-1	4.64E+05	7.21	1	67.33	20.00	-2.53	47.33	-22.53	-69.87
11	4.19E-02	8.68E-02	6.81E-02	-22	3.83E-01	7.93E-01	4.88E-01	27	24.42	50.55	31.12	27	5.24	5.29	5.27		1.80E+05	7.47		72.96	20.00	0.00	52.96	-20.00	-72.96
12	1.39E-02	7.76E-02	4.37E-02	-44	1.56E-01	8.71E-01	2.77E-01	77	19.86	110.69	35.21	77	5.20	5.25	5.23		9.03E+04	7.36		71.99	20.00	0.00	51.99	-20.00	-71.99
13	3.67E-02	8.31E-02	6.33E-02	-24	3.18E-01	7.20E-01	4.18E-01	31	25.74	58.30	33.81	31	5.12	5.17	5.15		1.06E+05	7.27		71.99	20.00	0.00	51.99	-20.00	-71.99
14	5.13E-02	1.26E-01	9.33E-02	-26	3.52E-01	8.65E-01	4.75E-01	35	32.46	79.66	43.78	35	5.37	5.42	5.40		2.64E+05	7.50		71.99	20.00	0.00	51.99	-20.00	-71.99
15	7.26E-02	8.56E-02	7.72E-02	6	8.04E-01	9.47E-01	8.90E-01	-6	17.12	20.16	19.35	-4	5.20	5.26	5.24	2	2.96E+05	7.63	-2	72.42 (c)	18.28 (d)	-1.40	54.13	-19.68 (e)	-73.81 (f)
16	1.32E-02	5.39E-02	3.99E-02	-26	3.14E-01	1.28E+00	4.24E-01	35	10.87	44.31	24.23	-5	5.12	5.57	5.25	34	1.46E+05	7.55	-33	72.94	20.00	-9.64	52.94	-29.64	-82.59
17	6.79E-02	7.11E-02	7.00E-02	-2	4.62E-01	4.84E-01	4.69E-01	2	37.82	39.63	38.41	2	5.31	5.57	5.39		2.52E+05	7.54		72.94	20.00	0.00	52.94	-20.00	-72.94
18	6.36E-02	8.41E-02	7.86E-02	1	5.70E-01	7.53E-01	6.09E-01	-1	26.65	35.25	33.23	-6	5.33	5.42	5.37	8	3.03E+05	7.57	-10	72.94	20.00	-5.92	52.94	-25.92	-78.86
19	1.16E-01	2.37E-01	1.47E-01	27	8.77E-01	1.80E+00	1.42E+00	-21	16.60	34.02	26.78	-21	4.96	5.22	5.04		2.54E+05	7.22		71.05	20.00	0.00	51.05	-20.00	-71.05
20	2.83E-02	6.65E-02	3.77E-02	33	3.32E-01	7.78E-01	5.85E-01	-25	9.39	22.01	16.57	-25	5.50	5.64	5.60		6.07E+05	8.19		75.62	20.00	0.00	55.62	-20.00	-75.62
21	2.77E-02	8.64E-02	4.05E-02	46	3.10E-01	9.68E-01	6.62E-01	-32	7.37	23.00	15.74	-32	5.58	5.72	5.68		8.83E+05	8.32		75.62	20.00	0.00	55.62	-20.00	-75.62
22	2.58E-02	3.64E-02	2.90E-02	12	3.44E-01	4.84E-01	4.32E-01	-11	13.75	19.35	17.27	-11	5.19	5.33	5.29		1.70E+05	7.75		75.62	20.00	0.00	55.62	-20.00	-75.62
23	1.50E-02	4.92E-02	3.31E-02	-33	1.20E-01	3.93E-01	1.78E-01	49	32.26	105.90	47.95	49	5.57	5.72	5.67		2.32E+05	7.83		75.62	20.00	0.00	55.62	-20.00	-75.62
24	4.83E-02	6.64E-02	5.97E-02	-10	4.62E-01	6.35E-01	5.14E-01	11	26.91	36.98	29.92	11	5.36	5.62	5.44		3.23E+05	7.72		72.94	20.00	0.00	52.94	-20.00	-72.94
25	3.74E-02	6.06E-02	4.39E-02	17	2.85E-01	4.62E-01	3.94E-01	-15	20.81	33.75	28.72	-15	5.44	5.58	5.54		3.38E+05	7.87		75.62	20.00	0.00	55.62	-20.00	-75.62
26	4.10E-02	4.16E-02	4.12E-02	0	3.50E-01	3.55E-01	3.53E-01	0	29.73	30.18	30.03	0	5.55	5.69	5.65		4.28E+05	8.00		75.62	20.00	0.00	55.62	-20.00	-75.62
27	5.91E-02	9.78E-02	6.99E-02	18	3.93E-01	6.49E-01	5.49E-01	-15	23.47	38.78	32.80	-15	5.17	5.43	5.24		1.85E+05	7.41		72.94	20.00	0.00	52.94	-20.00	-72.94
28	3.41E-02	5.42E-02	3.70E-02	9	2.07E-01	3.30E-01	3.03E-01	-8	26.62	42.32	31.47	3	5.56	5.71	5.66	-10	3.83E+05	8.00	16	75.62	28.39	-5.98	47.23	-34.38	-81.61
29	4.47E-02	6.61E-02	5.12E-02	15	3.84E-01	5.68E-01	4.96E-01	-13	20.27	29.98	26.60	-4	5.47	5.60	5.58	-4	4.85E+05	7.96	6	74.32	13.89	1.72	60.43	-12.17	-72.60
30	9.69E-02	1.29E-01	1.07E-01	10	3.99E-01	5.32E-01	4.83E-01	-9	46.92	62.60	56.87	-9	5.42	5.68	5.50		3.66E+05	7.52		72.01	16.73	-3.67	55.28	-20.40	-75.68
31	3.44E-02	5.52E-02	3.59E-02	4	2.31E-01	3.71E-01	3.56E-01	-4	24.02	38.52	26.01	8	5.53	5.68	5.62	-13	3.90E+05	8.02	22	75.30	20.00	-6.31	55.30	-26.31	-81.61
32	5.39E-02	1.03E-01	6.69E-02	24	4.63E-01	8.82E-01	7.11E-01	-19	15.75	29.98	24.21	-19	5.24	5.44	5.31	17	2.96E+05	7.63	-19	72.94	20.00	-9.64	52.94	-29.64	-82.59
33	1.39E-02	2.64E-02	2.13E-02	-19	1.76E-01	3.36E-01	2.19E-01	24	20.26	38.61	25.12	24	5.61	5.75	5.71		3.20E+05	8.16		75.62	20.00	0.00	55.62	-20.00	-75.62
34	3.32E-02	5.04E-02	4.39E-02	-13	2.72E-01	4.12E-01	3.12E-01	15	31.49	47.74	36.18	15	5.61	5.75	5.71		4.57E+05	8.00		75.62	20.00	0.00	55.62	-20.00	-75.62
35	1.39E-02	3.57E-02	1.90E-02	37	1.96E-01	5.04E-01	3.68E-01	-27	7.08	18.23	13.30	-27	5.62	5.76	5.72		5.48E+05	8.44		78.82	20.00	0.00	58.82	-20.00	-78.82
36	1.79E-02	4.38E-02	2.41E-02	35	1.79E-01	4.39E-01	3.26E-01	-26	10.48	25.66	19.04	-26	5.60	5.74	5.70		4.63E+05	8.27		78.82	20.00	0.00	58.82	-20.00	-78.82
37	1.27E-02	2.05E-02	1.49E-02	17	1.80E-01	2.92E-01	2.48E-01	-15	11.17	18.09	15.40	-15	5.80	5.94	5.90		6.60E+05	8.63		78.82	20.00	0.00	58.82	-20.00	-78.82
38	2.96E-02	5.32E-02	3.60E-02	22	3.24E-01	5.83E-01	4.79E-01	-18	13.08	23.53	19.35	-18	5.63	5.77	5.73		7.46E+05	8.30		78.82	20.00	0.00	58.82	-20.00	-78.82
39	2.01E-02	4.84E-02	2.69E-02	34	1.70E-01	4.11E-01	3.07E-01	-25	12.56	30.32	22.60	-25	5.72	5.86	5.82		6.28E+05	8.35		78.82	20.00	0.00	58.82	-20.00	-78.82
40	8.66E-03	9.89E-03	9.46E-03	-4	1.36E-01	1.56E-01	1.43E-01	5	18.52	21.15	19.36	5	5.58	5.77	5.67		1.84E+05	8.22		79.38	20.00	0.00	59.38	-20.00	-79.38
41	1.09E-02	2.05E-02	1.34E-02	23	1.40E-01	2.63E-01	2.13E-01	-19	12.05	22.70	18.38	-19	5.70	5.89	5.79		4.01E+05	8.40		78.57	20.00	0.00	58.57	-20.00	-78.57
42	7.47E-03	1.16E-02	1.00E-02	-14	1.09E-01	1.69E-01	1.26E-01	16	20.05	31.24	23.25	16	5.63	5.82	5.72		1.90E+05	8.21		78.57	20.00	0.00	58.57	-20.00	-78.57

***Tab. A2** (continued)*

PCB	P_L (Pa)			Dev.	S_L (mg/L)			Dev.	H ($Pa\ m^3/mol$)			Dev.	log K_{OW} (-)			Dev.	S_{OL} (mg/L)	log K_{OA}	Dev.	ΔU_A	ΔU_W	ΔU_O	ΔU_{AW}	ΔU_{OW}	ΔU_{OA}
	Min.	Max.	Lik.	(%)	Min.	Max.	Lik.	(%)	Min.	Max.	Lik.	(%)	Min.	Max.	Lik.	(%)		Lik. (-)	(%)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)
43	1.64E-02	1.80E-01	3.65E-02	122	1.41E-01	1.55E+00	6.98E-01	-55	3.10	33.94	15.28	-55	5.78	5.96	5.86		1.65E+06	8.58		78.57	20.00	0.00	58.57	-20.00	-78.57
44	9.57E-03	1.37E-02	1.28E-02	0	1.53E-01	2.19E-01	1.64E-01	0	17.01	24.30	22.63	-7	5.73	5.84	5.78	11	2.96E+05	8.29	-13	78.57	20.00	-5.97	58.57	-25.97	-84.54
45	2.25E-02	1.59E-01	4.31E-02	92	1.86E-01	1.32E+00	6.85E-01	-48	4.99	35.25	18.37	-48	4.75	4.98	4.84		6.58E+04	7.11		76.43	20.00	0.00	56.43	-20.00	-76.43
46	1.87E-02	1.55E-01	3.78E-02	102	1.59E-01	1.32E+00	6.50E-01	-51	4.15	34.33	16.97	-51	4.75	4.98	4.84		6.25E+04	7.15		76.43	20.00	0.00	56.43	-20.00	-76.43
47	1.53E-02	1.94E-02	1.66E-02	8	1.58E-01	2.01E-01	1.85E-01	-8	22.34	28.27	26.14	-8	5.85	6.04	5.94		5.58E+05	8.46		78.57	13.00	0.00	65.57	-13.00	-78.57
48	5.44E-03	1.53E-02	1.09E-02	-29	5.18E-02	1.46E-01	7.32E-02	41	30.67	86.43	43.32	41	5.60	5.79	5.69		1.01E+05	7.90		78.57	20.00	0.00	58.57	-20.00	-78.57
49	1.37E-02	1.68E-02	1.56E-02	-7	1.88E-01	2.31E-01	2.03E-01	8	21.28	26.06	22.50	6	5.83	5.89	5.86	-3	4.72E+05	8.41	4	78.57	20.00	2.36	58.57	-17.64	-76.22
50	1.77E-03	1.27E-02	3.42E-03	93	7.33E-03	5.27E-02	2.73E-02	-48	9.81	70.55	36.55	-48	5.66	5.89	5.75		4.53E+04	8.05		76.43	20.00	0.00	56.43	-20.00	-76.43
51	7.85E-03	2.46E-02	1.68E-02	-32	1.03E-01	3.23E-01	1.50E-01	46	22.30	69.99	32.65	46	5.42	5.65	5.51		1.18E+05	7.77		76.43	20.00	0.00	56.43	-20.00	-76.43
52	1.18E-02	5.23E-02	1.31E-02	-18	1.22E-01	4.68E-01	1.57E-01	29	10.03	108.91	24.50	-25	5.79	6.22	6.01	67	5.92E+05 (a)	8.58	132	78.40	29.96	-6.14	48.44	-36.11	-84.54
53	1.95E-02	4.00E-02	3.04E-02	10	1.96E-01	4.01E-01	2.58E-01	-9	20.12	41.14	34.34	-17	5.55	5.78	5.64	22	2.99E+05	7.92	-23	76.37	20.00	0.46	56.37	-19.54	-75.91
54	3.88E-02	1.08E-01	5.46E-02	41	2.13E-01	5.93E-01	4.21E-01	-29	19.13	53.29	37.87	-29	5.15	5.38	5.24		1.42E+05	7.34		69.42	20.00	0.00	49.42	-20.00	-69.42
55	5.79E-03	2.83E-02	9.83E-03	70	9.15E-02	4.47E-01	2.63E-01	-41	3.78	18.48	10.89	-41	5.83	6.32	6.10		1.31E+06	9.05		81.50	20.00	0.00	61.50	-20.00	-81.50
56	4.29E-03	2.14E-02	7.33E-03	71	8.17E-02	4.07E-01	2.38E-01	-41	3.08	15.34	8.98	-41	5.71	6.20	5.98		8.17E+05	8.98		81.50	20.00	0.00	61.50	-20.00	-81.50
57	1.02E-02	1.68E-02	1.20E-02	18	1.08E-01	1.79E-01	1.51E-01	-15	16.56	27.40	23.17	-15	5.87	6.35	6.14		8.45E+05	8.78		81.50	20.00	0.00	61.50	-20.00	-81.50
58	1.02E-02	2.07E-02	1.29E-02	27	1.17E-01	2.38E-01	1.88E-01	-21	12.45	25.33	19.99	-21	5.90	6.39	6.17		1.16E+06	8.88		81.50	20.00	0.00	61.50	-20.00	-81.50
59	1.02E-02	2.51E-02	1.37E-02	35	9.62E-02	2.38E-01	1.76E-01	-26	12.47	30.81	22.79	-26	5.76	5.94	5.85		3.96E+05	8.39		78.57	20.00	0.00	58.57	-20.00	-78.57
60	5.28E-03	2.73E-02	9.13E-03	73	9.96E-02	5.15E-01	2.98E-01	-42	3.00	15.48	8.95	-42	5.97	6.46	6.24		2.29E+06	9.33		81.50	20.00	0.00	61.50	-20.00	-81.50
61	5.57E-03	5.71E-02	1.04E-02	-14	1.31E-01	6.55E-01	1.73E-01	32	5.39	62.41	17.61	-31	5.90	6.41	6.20	97	1.16E+06 (b)	8.97	78	75.69 (g)	21.75 (h)	3.56	53.94	-18.19 (i)	-72.13 (j)
62	1.02E-02	1.30E-02	1.10E-02	9	1.01E-01	1.29E-01	1.19E-01	-8	22.93	29.37	27.05	-8	5.95	6.13	6.03		4.78E+05	8.57		78.57	20.00	0.00	58.57	-20.00	-78.57
63	6.80E-03	3.76E-02	1.20E-02	77	8.08E-02	4.47E-01	2.53E-01	-43	4.44	24.59	13.90	-43	5.83	6.32	6.10		1.25E+06	8.95		81.50	20.00	0.00	61.50	-20.00	-81.50
64	1.31E-02	1.90E-02	1.50E-02	15	1.83E-01	2.65E-01	2.31E-01	-13	14.37	20.89	18.98	-9	5.70	5.82	5.78	4	4.16E+05	8.37	-5	78.57	20.00	-7.24	58.57	-27.24	-85.81
65	5.41E-03	1.40E-02	1.02E-02	-27	5.55E-02	1.44E-01	7.62E-02	37	28.45	73.55	39.04	37	5.87	6.06	5.96		2.44E+05	8.31		78.57	20.00	0.00	58.57	-20.00	-78.57
66	6.21E-03	2.63E-02	1.05E-02	69	8.83E-02	3.74E-01	2.22E-01	-41	4.85	20.54	13.84	-33	5.81	6.28	6.06	21	9.84E+05	8.90	-23	80.87	20.00	7.60	60.87	-12.40	-73.27
67	6.65E-03	1.13E-02	7.94E-03	19	1.15E-01	1.96E-01	1.64E-01	-16	9.93	16.91	14.16	-16	6.05	6.54	6.32		1.62E+06	9.24		81.50	20.00	0.00	61.50	-20.00	-81.50
68	1.25E-02	2.94E-02	2.21E-02	-25	1.59E-01	3.76E-01	2.12E-01	33	22.83	53.91	30.40	33	5.99	6.48	6.26		1.75E+06	8.83		81.50	20.00	0.00	61.50	-20.00	-81.50
69	1.59E-02	1.76E-02	1.70E-02	-3	1.28E-01	1.42E-01	1.32E-01	4	36.26	40.25	37.55	4	5.94	6.13	6.03		5.28E+05	8.42		78.57	20.00	0.00	58.57	-20.00	-78.57
70	5.47E-03	1.69E-02	7.98E-03	46	7.89E-02	2.44E-01	1.68E-01	-31	6.54	20.26	13.90	-31	5.95	6.44	6.22		1.21E+06	9.11		82.44	20.00	0.00	62.44	-20.00	-82.44
71	9.03E-03	2.74E-02	1.31E-02	45	8.29E-02	2.51E-01	1.74E-01	-31	10.49	31.82	21.98	-31	5.67	5.86	5.76		2.97E+05	8.29		78.57	20.00	0.00	58.57	-20.00	-78.57
72	1.01E-02	2.05E-02	1.28E-02	27	8.00E-02	1.63E-01	1.29E-01	-21	18.01	36.70	28.95	-21	5.94	6.43	6.21		9.02E+05	8.78		81.50	20.00	0.00	61.50	-20.00	-81.50
73	1.02E-02	3.96E-02	1.60E-02	57	5.63E-02	2.19E-01	1.39E-01	-36	13.51	52.69	33.47	-36	5.72	5.90	5.80		2.73E+05	8.16		78.57	20.00	0.00	58.57	-20.00	-78.57
74	3.54E-03	7.29E-03	5.73E-03	-21	4.75E-02	9.78E-02	6.04E-02	27	21.76	44.82	27.69	27	5.83	6.32	6.10		3.00E+05	8.65		81.50	20.00	0.00	61.50	-20.00	-81.50
75	1.80E-02	6.74E-02	2.80E-02	55	1.12E-01	4.18E-01	2.69E-01	-36	12.58	47.06	30.32	-36	5.94	6.13	6.03		1.07E+06	8.51		78.57	20.00	0.00	58.57	-20.00	-78.57
76	6.06E-03	1.39E-02	7.99E-03	32	7.32E-02	1.67E-01	1.27E-01	-24	10.58	24.19	18.36	-24	5.71	6.20	5.98		4.33E+05	8.66		81.50	20.00	0.00	61.50	-20.00	-81.50
77	2.20E-03	3.86E-03	2.76E-03	25	6.75E-02	1.18E-01	9.44E-02	-20	5.43	9.52	8.53	-10	6.35	6.53	6.50	0	1.63E+06	9.70	0	84.76	11.92	11.47	72.83	-0.45	-73.29
78	3.15E-03	1.23E-02	4.96E-03	58	5.56E-02	2.17E-01	1.38E-01	-37	4.23	16.55	10.50	-37	6.08	6.26	6.23		1.02E+06	9.24		85.64	20.00	0.00	65.64	-20.00	-85.64
79	3.37E-03	1.15E-02	5.08E-03	50	6.77E-02	2.31E-01	1.53E-01	-34	4.27	14.55	9.67	-34	6.16	6.34	6.30		1.44E+06	9.38		85.64	20.00	0.00	65.64	-20.00	-85.64
80	3.09E-03	5.47E-03	4.52E-03	-17	2.84E-02	5.04E-02	3.44E-02	21	31.71	56.23	38.38	21	5.95	6.13	6.10		1.71E+05	8.51		85.64	20.00	0.00	65.64	-20.00	-85.64
81	2.87E-03	1.18E-02	4.60E-03	60	5.78E-02	2.37E-01	1.48E-01	-38	3.53	14.51	9.06	-38	6.09	6.27	6.24		1.12E+06	9.32		85.64	20.00	0.00	65.64	-20.00	-85.64
82	2.90E-03	9.10E-03	4.25E-03	46	5.41E-02	1.69E-01	1.16E-01	-32	5.60	17.54	11.99	-32	5.99	6.13	6.05		4.85E+05	8.94		84.18	20.00	0.00	64.18	-20.00	-84.18
83	2.71E-03	7.91E-03	3.87E-03	43	4.12E-02	1.20E-01	8.42E-02	-30	7.35	21.46	15.02	-30	6.14	6.28	6.19		5.63E+05	9.04		84.18	20.00	0.00	64.18	-20.00	-84.18
84	3.68E-03	5.03E-02	9.42E-03	156	4.72E-02	6.45E-01	2.52E-01	-61	1.86	25.45	12.21	-52	5.34	6.17	5.77	48	4.44E+05	8.55	-41	81.83	20.00	-2.91	61.83	-22.91	-84.74

***Tab. A2** (continued)*

PCB	P_L (Pa)			Dev.	S_L (mg/L)			Dev.	H (Pa m^3/mol)			Dev.	log K_{OW} (-)			Dev.	S_{OL} (mg/L)	log K_{OA}	Dev.	ΔU_A	ΔU_W	ΔU_O	ΔU_{AW}	ΔU_{OW}	ΔU_{OA}
	Min.	Max.	Lik.	(%)	Min.	Max.	Lik.	(%)	Min.	Max.	Lik.	(%)	Min.	Max.	Lik.	(%)		Lik. (-)	(%)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)
85	2.36E-03	3.73E-03	2.75E-03	16	5.89E-02	9.31E-02	7.99E-02	-14	8.28	13.09	11.23	-14	6.12	6.26	6.18		5.10E+05	9.15		84.18	20.00	0.00	64.18	-20.00	-84.18
86	2.77E-03	3.94E-03	3.12E-03	12	3.75E-02	5.33E-02	4.74E-02	-11	16.98	24.14	21.47	-11	6.32	6.46	6.38		5.66E+05	9.14		84.18	20.00	0.00	64.18	-20.00	-84.18
87	1.82E-03	2.29E-03	2.12E-03	-7	2.99E-02	3.75E-02	3.22E-02	8	19.90	24.98	21.46	8	6.17	6.31	6.23		2.40E+05	8.94		84.95	20.00	0.00	64.95	-20.00	-84.95
88	5.97E-03	7.80E-03	6.52E-03	9	5.00E-02	6.53E-02	5.97E-02	-9	29.82	38.97	35.64	-9	6.29	6.78	6.50		1.04E+06	9.08		81.83	20.00	0.00	61.83	-20.00	-81.83
89	3.52E-03	5.96E-02	9.04E-03	157	3.81E-02	6.45E-01	2.51E-01	-61	1.78	30.18	11.75	-61	5.39	5.88	5.60		2.60E+05	8.34		81.83	20.00	0.00	61.83	-20.00	-81.83
90	3.34E-03	5.37E-03	3.91E-03	17	3.65E-02	5.87E-02	5.01E-02	-15	18.53	29.83	25.45	-15	6.26	6.40	6.32		4.96E+05	8.98		84.18	20.00	0.00	64.18	-20.00	-84.18
91	4.85E-03	1.90E-02	7.65E-03	58	6.71E-02	2.63E-01	1.67E-01	-37	6.02	23.60	14.97	-37	5.66	6.15	5.87		4.03E+05	8.60		81.83	20.00	0.00	61.83	-20.00	-81.83
92	3.92E-03	4.74E-03	4.18E-03	7	4.86E-02	5.87E-02	5.51E-02	-6	21.77	26.34	24.72	-6	6.26	6.40	6.32		5.45E+05	9.00		84.18	20.00	0.00	64.18	-20.00	-84.18
93	6.54E-03	1.63E-02	8.87E-03	36	6.19E-02	1.55E-01	1.14E-01	-26	13.81	34.49	25.42	-26	5.85	6.34	6.06		4.99E+05	8.63		81.83	20.00	0.00	61.83	-20.00	-81.83
94	3.52E-03	1.99E-02	6.27E-03	78	2.89E-02	1.64E-01	9.19E-02	-44	7.02	39.69	22.28	-44	5.83	6.31	6.04		3.75E+05	8.66		81.83	20.00	0.00	61.83	-20.00	-81.83
95	3.41E-03	5.73E-03	5.25E-03	-1	8.16E-02	1.37E-01	8.90E-02	1	12.68	21.27	19.27	-9	5.92	6.09	5.99	17	3.10E+05	8.65	-19	81.83	20.00	-3.64	61.83	-23.64	-85.46
96	3.52E-03	6.07E-02	9.85E-03	180	2.76E-02	4.77E-01	1.70E-01	-64	2.41	41.56	18.88	-55	5.23	6.14	5.71	50	2.51E+05	8.29	-42	74.70	20.00	-0.21	54.70	-20.21	-74.91
97	1.64E-03	2.47E-03	2.16E-03	-13	2.94E-02	4.43E-02	3.37E-02	15	18.23	27.48	20.90	15	6.24	6.38	6.30		3.13E+05	9.04		84.18	20.00	0.00	64.18	-20.00	-84.18
98	6.10E-03	1.88E-02	8.88E-03	45	5.02E-02	1.55E-01	1.06E-01	-31	12.89	39.69	27.28	-31	5.83	6.32	6.04		4.37E+05	8.57		81.83	20.00	0.00	61.83	-20.00	-81.83
99	6.59E-04	2.99E-03	1.81E-03	-40	1.30E-02	5.89E-02	2.15E-02	66	16.59	75.36	27.47	66	6.35	6.49	6.41		2.82E+05	9.07		84.39	20.00	0.00	64.39	-20.00	-84.39
100	3.52E-03	1.48E-02	5.68E-03	61	2.02E-02	8.49E-02	5.26E-02	-38	13.53	56.98	35.28	-38	6.02	6.51	6.23		3.92E+05	8.72		81.83	20.00	0.00	61.83	-20.00	-81.83
101	3.08E-03	4.38E-03	3.35E-03	-1	2.94E-02	4.19E-02	3.85E-02	1	26.38	37.59	28.44	8	6.29	6.40	6.36	-10	4.25E+05	8.98	15	84.03	13.13	1.78	70.90	-11.35	-82.25
102	5.32E-03	1.02E-02	6.60E-03	24	7.44E-02	1.42E-01	1.15E-01	-19	12.19	23.34	18.79	-19	5.88	6.37	6.10		5.62E+05	8.81		81.83	20.00	0.00	61.83	-20.00	-81.83
103	8.82E-03	2.06E-02	1.17E-02	33	5.65E-02	1.32E-01	9.95E-02	-25	21.82	51.01	38.44	-25	5.90	6.39	6.11		5.10E+05	8.52		81.83	20.00	0.00	61.83	-20.00	-81.83
104	4.41E-03	1.89E-02	7.16E-03	62	1.62E-02	6.93E-02	4.27E-02	-38	20.76	88.96	54.76	-38	5.28	6.19	5.76		7.39E+04	7.89		74.70	20.00	0.00	54.70	-20.00	-74.70
105	6.39E-04	8.74E-04	7.69E-04	-12	2.07E-02	2.84E-02	2.35E-02	14	10.06	13.77	10.67	6	6.78	6.88	6.79	1	1.03E+06	10.01	-1	88.70	20.00	-0.86	68.70	-20.86	-89.56
106	1.37E-03	2.93E-03	1.76E-03	29	2.68E-02	5.72E-02	4.44E-02	-22	7.81	16.70	12.96	-22	6.85	7.08	6.92		2.87E+06	10.09		87.36	20.00	0.00	67.36	-20.00	-87.36
107	1.25E-03	3.87E-03	1.82E-03	46	2.53E-02	7.83E-02	5.37E-02	-31	5.20	16.13	11.06	-31	6.53	6.76	6.60		1.26E+06	9.72		87.36	20.00	0.00	67.36	-20.00	-87.36
108	1.40E-03	3.82E-03	1.96E-03	40	2.57E-02	7.01E-02	5.01E-02	-28	6.53	17.81	12.74	-28	6.53	6.76	6.59		1.16E+06	9.65		87.36	20.00	0.00	67.36	-20.00	-87.36
109	3.52E-03	4.07E-03	3.69E-03	5	4.02E-02	4.65E-02	4.43E-02	-5	24.69	28.56	27.20	-5	6.45	6.59	6.51		7.86E+05	9.21		84.18	20.00	0.00	64.18	-20.00	-84.18
110	1.09E-03	1.83E-03	1.65E-03	-10	2.48E-02	4.15E-02	2.76E-02	11	14.42	24.17	19.48	-2	6.20	6.36	6.25	12	2.18E+05	9.00	-14	84.18	20.00	-3.78	64.18	-23.78	-87.96
111	2.06E-04	3.75E-03	5.42E-04	163	2.49E-03	4.53E-02	1.72E-02	-62	1.48	27.02	10.27	-62	6.66	6.89	6.72		6.01E+05	9.93		87.36	20.00	0.00	67.36	-20.00	-87.36
112	3.04E-03	5.58E-03	3.72E-03	22	3.67E-02	6.74E-02	5.51E-02	-18	14.73	27.02	22.07	-18	6.35	6.49	6.41		7.22E+05	9.17		84.18	20.00	0.00	64.18	-20.00	-84.18
113	2.90E-03	4.40E-03	3.34E-03	15	2.87E-02	4.35E-02	3.79E-02	-13	21.79	33.01	28.74	-13	6.39	6.53	6.45		5.63E+05	9.11		84.18	20.00	0.00	64.18	-20.00	-84.18
114	1.25E-03	1.37E-03	1.29E-03	3	2.81E-02	3.09E-02	2.99E-02	-3	13.19	14.48	14.04	-3	6.64	6.87	6.71		1.00E+06	9.77		87.36	20.00	0.00	67.36	-20.00	-87.36
115	2.15E-03	3.32E-03	2.49E-03	15	2.83E-02	4.35E-02	3.77E-02	-13	16.15	24.87	21.54	-13	6.38	6.52	6.44		5.43E+05	9.22		84.18	20.00	0.00	64.18	-20.00	-84.18
116	2.31E-03	3.22E-03	2.58E-03	12	2.46E-02	3.44E-02	3.08E-02	-11	21.90	30.59	27.37	-11	6.24	6.38	6.30		2.86E+05	8.93		84.18	20.00	0.00	64.18	-20.00	-84.18
117	2.47E-03	3.83E-03	2.86E-03	16	3.31E-02	5.11E-02	4.42E-02	-14	15.78	24.42	21.11	-14	6.33	6.47	6.39		5.44E+05	9.16		84.18	20.00	0.00	64.18	-20.00	-84.18
118	1.03E-03	3.11E-03	1.62E-03	36	1.59E-02	4.80E-02	3.05E-02	-26	8.11	24.46	17.35	-29	6.57	6.92	6.69	32	9.66E+05	9.66	-32	86.90	20.00	-2.95	66.90	-22.95	-89.85
119	2.77E-03	2.85E-03	2.80E-03	1	4.65E-02	4.78E-02	4.74E-02	-1	18.94	19.48	19.30	-1	6.34	6.48	6.40		6.02E+05	9.21		84.18	20.00	0.00	64.18	-20.00	-84.18
120	1.68E-03	1.98E-03	1.87E-03	-5	3.59E-02	4.23E-02	3.79E-02	6	15.27	17.97	16.12	6	6.23	6.46	6.30		3.52E+05	9.15		87.36	20.00	0.00	67.36	-20.00	-87.36
121	4.82E-03	8.08E-03	5.73E-03	19	2.78E-02	4.66E-02	3.92E-02	-16	33.76	56.58	47.63	-16	6.36	6.50	6.42		5.31E+05	8.85		84.18	20.00	0.00	64.18	-20.00	-84.18
122	9.92E-04	3.78E-03	1.55E-03	56	2.54E-02	9.69E-02	6.20E-02	-36	3.34	12.73	8.15	-36	6.43	6.66	6.50		1.07E+06	9.72		87.36	20.00	0.00	67.36	-20.00	-87.36
123	1.31E-03	7.13E-03	2.30E-03	76	2.42E-02	1.32E-01	7.49E-02	-43	3.24	17.65	10.03	-43	6.57	6.80	6.64		2.02E+06	9.82		87.36	20.00	0.00	67.36	-20.00	-87.36
124	7.88E-04	1.95E-03	1.07E-03	35	1.49E-02	3.68E-02	2.72E-02	-26	6.99	17.29	12.78	-26	6.55	6.78	6.62		6.84E+05	9.69		87.36	20.00	0.00	67.36	-20.00	-87.36
125	1.92E-03	6.98E-03	2.95E-03	54	2.15E-02	7.82E-02	5.08E-02	-35	8.01	29.15	18.95	-35	6.23	6.38	6.29		4.62E+05	9.08		84.18	20.00	0.00	64.18	-20.00	-84.18
126	4.87E-04	2.31E-03	8.62E-04	77	1.92E-02	9.08E-02	5.13E-02	-43	1.75	8.29	5.48	-34	6.47	6.97	6.76	21	1.98E+06	10.24	-23	92.49	20.00	-0.74	72.49	-20.74	-93.24

***Tab. A2** (continued)*

PCB	P_L (Pa)			Dev.	S_L (mg/L)			Dev.	H ($Pa\ m^3/mol$)			Dev.	log K_{OW} (-)			Dev.	S_{OL} (mg/L)	log K_{OA}	Dev.	ΔU_A	ΔU_W	ΔU_O	ΔU_{AW}	ΔU_{OW}	ΔU_{OA}
	Min.	Max.	Lik.	(%)	Min.	Max.	Lik.	(%)	Min.	Max.	Lik.	(%)	Min.	Max.	Lik.	(%)		Lik. (-)	(%)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)
127	7.72E-04	2.66E-03	1.17E-03	51	1.59E-02	5.49E-02	3.63E-02	-34	4.59	15.80	10.47	-34	6.52	7.02	6.80		1.63E+06	10.03		92.49	20.00	0.00	72.49	-20.00	-92.49
128	3.46E-04	3.62E-04	3.51E-04	2	1.82E-02	1.91E-02	1.88E-02	-2	6.54	6.85	6.74	-2	6.89	7.11	7.00		1.56E+06	10.49		91.05	20.00	0.00	71.05	-20.00	-91.05
129	1.26E-04	4.44E-04	2.92E-04	-34	5.31E-03	1.87E-02	8.08E-03	52	8.56	30.13	13.02	52	6.65	6.87	6.76		3.17E+05	9.87		89.81	20.00	0.00	69.81	-20.00	-89.81
130	5.46E-04	1.16E-03	7.02E-04	29	2.05E-02	4.37E-02	3.40E-02	-22	4.51	9.60	7.46	-22	7.19	7.41	7.30		7.23E+06	10.85		89.81	20.00	0.00	69.81	-20.00	-89.81
131	7.34E-04	1.26E-03	1.05E-03	-16	1.86E-02	3.19E-02	2.23E-02	20	14.24	24.41	17.04	20	6.43	6.90	6.78		9.30E+05	9.78		87.23	20.00	0.00	67.23	-20.00	-87.23
132	7.58E-04	4.34E-03	1.36E-03	79	2.19E-02	1.25E-01	7.00E-02	-44	2.18	12.50	6.99	-44	5.85	6.32	6.20		4.76E+05	9.38		87.23	20.00	0.00	67.23	-20.00	-87.23
133	8.45E-04	1.61E-03	1.05E-03	24	1.48E-02	2.81E-02	2.27E-02	-19	10.84	20.64	16.65	-19	6.96	7.18	7.07		2.35E+06	10.19		89.81	20.00	0.00	69.81	-20.00	-89.81
134	1.40E-04	1.23E-03	5.97E-04	-51	2.18E-03	1.91E-02	4.49E-03	106	23.26	203.85	47.96	106	5.85	6.32	6.20		3.05E+04	8.55		87.23	20.00	0.00	67.23	-20.00	-87.23
135	1.15E-03	3.84E-03	1.72E-03	50	2.52E-02	8.43E-02	5.64E-02	-33	4.91	16.44	10.99	-33	5.97	6.44	6.32		5.58E+05	9.35		87.23	20.00	0.00	67.23	-20.00	-87.23
136	1.58E-03	1.79E-03	1.64E-03	4	2.74E-02	3.10E-02	2.98E-02	-4	18.32	20.78	19.92	-4	6.31	7.37	6.70		9.68E+05	9.61		79.99	24.46	0.00	55.52	-24.46	-79.99
137	2.39E-04	2.86E-04	2.70E-04	-6	4.58E-03	5.49E-03	4.87E-03	6	18.82	22.55	19.99	6	6.71	6.93	6.82		2.30E+05	9.77		89.81	20.00	0.00	69.81	-20.00	-89.81
138	3.07E-04	5.14E-04	4.28E-04	-17	8.40E-03	1.41E-02	1.01E-02	20	13.17	22.08	15.29	16	6.61	6.77	6.69	-8	3.21E+05	9.71	12	89.50	20.00	3.60	69.50	-16.40	-85.90
139	6.16E-04	1.20E-03	9.62E-04	-20	6.68E-03	1.30E-02	8.34E-03	25	33.32	64.95	41.62	25	6.29	6.76	6.64		2.26E+05	9.21		87.23	20.00	0.00	67.23	-20.00	-87.23
140	1.20E-03	2.79E-03	1.59E-03	32	1.39E-02	3.22E-02	2.44E-02	-24	13.44	31.17	23.55	-24	6.23	6.70	6.58		5.44E+05	9.37		87.23	20.00	0.00	67.23	-20.00	-87.23
141	6.12E-04	1.22E-03	7.71E-04	26	1.26E-02	2.50E-02	1.99E-02	-21	8.84	17.61	13.99	-21	6.64	6.86	6.75		7.55E+05	9.83		89.81	20.00	0.00	69.81	-20.00	-89.81
142	1.20E-03	3.44E-03	1.71E-03	42	1.36E-02	3.89E-02	2.74E-02	-30	11.14	31.89	22.46	-30	6.22	6.69	6.57		5.98E+05	9.38		87.23	20.00	0.00	67.23	-20.00	-87.23
143	8.91E-04	1.94E-03	1.15E-03	30	1.90E-02	4.14E-02	3.19E-02	-23	7.77	16.89	13.04	-23	6.21	6.68	6.56		6.70E+05	9.60		87.23	20.00	0.00	67.23	-20.00	-87.23
144	1.00E-03	6.88E-03	1.90E-03	90	7.95E-03	5.47E-02	2.88E-02	-47	6.59	45.38	23.86	-47	6.10	6.57	6.45		4.27E+05	9.19		87.23	20.00	0.00	67.23	-20.00	-87.23
145	2.94E-03	1.31E-02	4.84E-03	65	2.22E-02	9.95E-02	6.04E-02	-39	10.64	47.61	28.89	-39	5.87	6.93	6.26		4.96E+05	8.85		79.99	20.00	0.00	59.99	-20.00	-79.99
146	4.39E-04	7.71E-04	6.39E-04	-17	1.47E-02	2.58E-02	1.78E-02	21	10.77	18.91	12.99	21	6.74	6.96	6.85		9.23E+05	10.00		89.81	20.00	0.00	69.81	-20.00	-89.81
147	1.20E-03	2.20E-03	1.47E-03	22	2.33E-02	4.29E-02	3.50E-02	-18	10.11	18.57	15.16	-18	6.25	6.73	6.61		8.50E+05	9.60		87.23	20.00	0.00	67.23	-20.00	-87.23
148	1.90E-03	4.55E-03	2.55E-03	34	1.58E-02	3.77E-02	2.82E-02	-25	18.21	43.52	32.55	-25	6.28	6.75	6.63		7.35E+05	9.30		87.23	20.00	0.00	67.23	-20.00	-87.23
149	1.13E-03	4.96E-03	2.02E-03	79	1.50E-02	6.57E-02	3.68E-02	-44	6.20	27.21	19.80	-27	6.08	6.55	6.43	4	5.10E+05	9.24	-5	87.38	20.00	-4.11	67.38	-24.11	-91.49
150	1.20E-03	1.54E-02	2.81E-03	134	8.46E-03	1.08E-01	4.63E-02	-57	4.00	51.25	21.89	-57	5.77	6.83	6.16		2.81E+05	8.84		79.99	20.00	0.00	59.99	-20.00	-79.99
151	1.18E-03	1.78E-03	1.55E-03	-13	1.48E-02	2.24E-02	1.70E-02	15	28.69	43.34	32.92	15	6.07	6.54	6.42		2.30E+05	9.01		87.23	20.00	0.00	67.23	-20.00	-87.23
152	1.20E-03	1.39E-02	2.71E-03	126	1.00E-02	1.16E-01	5.11E-02	-56	3.75	43.32	19.16	-56	5.84	6.90	6.23		3.81E+05	8.98		79.99	20.00	0.00	59.99	-20.00	-79.99
153	2.49E-04	6.83E-04	4.73E-04	-31	5.39E-03	1.48E-02	7.78E-03	44	16.70	45.76	21.93	31	6.60	6.92	6.74	-12	2.90E+05	9.62	19	89.03	4.96	1.85	84.06	-3.11	-87.17
154	1.74E-03	6.89E-03	2.75E-03	58	1.07E-02	4.25E-02	2.68E-02	-37	14.76	58.50	36.96	-37	6.30	6.77	6.65		7.46E+05	9.27		87.23	20.00	0.00	67.23	-20.00	-87.23
155	1.41E-04	3.87E-03	2.52E-03	-35	1.09E-02	3.01E-01	1.68E-02	53	4.64	127.63	54.19	-33	6.54	7.60	6.93	147	1.13E+06	9.49	-71	79.99	16.70	10.20	63.28	-6.51	-69.79
156	2.19E-04	3.45E-03	5.49E-04	150	1.63E-03	2.56E-02	1.02E-02	-60	3.09	48.56	19.39	-60	7.33	7.55	7.44		3.37E+06	10.63		92.36	20.00	0.00	72.36	-20.00	-92.36
157	2.00E-04	2.92E-03	4.88E-04	145	2.14E-03	3.13E-02	1.28E-02	-59	2.30	33.67	13.76	-59	6.86	7.08	6.97		9.58E+05	10.13		93.22	20.00	0.00	73.22	-20.00	-93.22
158	6.12E-04	1.01E-03	7.37E-04	20	5.42E-03	8.92E-03	7.41E-03	-17	24.77	40.79	35.90	-12	6.71	6.87	6.80	5	3.32E+05	9.49	-7	89.81	20.00	4.88	69.81	-15.12	-84.93
159	3.43E-04	1.20E-03	7.91E-04	-34	1.39E-02	4.87E-02	2.11E-02	52	8.90	31.19	13.51	52	7.32	7.54	7.43		6.75E+06	10.77		92.36	20.00	0.00	72.36	-20.00	-92.36
160	4.65E-04	1.20E-03	8.75E-04	-27	1.42E-02	3.66E-02	1.94E-02	37	11.84	30.62	16.25	37	7.19	7.41	7.30		4.13E+06	10.51		89.03	20.00	0.00	69.03	-20.00	-89.03
161	1.08E-03	1.20E-03	1.16E-03	-4	1.35E-02	1.50E-02	1.40E-02	4	28.89	32.17	29.94	4	6.99	7.21	7.10		1.59E+06	9.97		89.03	20.00	0.00	69.03	-20.00	-89.03
162	7.31E-04	1.20E-03	1.02E-03	-15	1.98E-02	3.25E-02	2.34E-02	18	13.33	21.89	15.72	18	7.36	7.58	7.47		8.47E+06	10.76		92.36	20.00	0.00	72.36	-20.00	-92.36
163	5.61E-04	5.98E-04	5.86E-04	-2	2.21E-02	2.36E-02	2.26E-02	2	9.15	9.76	9.35	2	6.67	6.89	6.78		9.45E+05	10.04		89.81	20.00	0.00	69.81	-20.00	-89.81
164	1.20E-03	1.49E-03	1.29E-03	7	2.43E-02	3.01E-02	2.80E-02	-7	14.41	17.85	16.62	-7	6.52	6.74	6.63		7.31E+05	9.59		89.03	20.00	0.00	69.03	-20.00	-89.03
165	1.20E-03	1.29E-03	1.23E-03	2	2.81E-02	3.01E-02	2.94E-02	-2	14.41	15.42	15.08	-2	6.89	7.11	7.00		2.45E+06	10.14		89.03	20.00	0.00	69.03	-20.00	-89.03
166	6.59E-04	1.20E-03	9.83E-04	-18	1.55E-02	2.83E-02	1.90E-02	22	15.30	27.88	18.69	22	7.20	7.42	7.31		4.17E+06	10.46		92.36	20.00	0.00	72.36	-20.00	-92.36
167	2.82E-04	1.07E-03	4.39E-04	56	9.13E-03	3.46E-02	2.22E-02	-36	2.94	11.13	7.15	-36	7.18	7.40	7.29		4.58E+06	10.85		93.22	20.00	0.00	73.22	-20.00	-93.22
168	6.87E-04	1.25E-03	8.38E-04	22	8.87E-03	1.61E-02	1.32E-02	-18	15.41	27.97	22.93	-18	7.14	7.36	7.25		2.40E+06	10.29		89.81	20.00	0.00	69.81	-20.00	-89.81

***Tab. A2** (continued)*

PCB	P_L (Pa)			Dev.	S_L (mg/L)			Dev.	H (Pa m^3/mol)			Dev.	log K_{OW} (-)			Dev.	S_{OL} (mg/L)	log K_{OA}	Dev.	ΔU_A	ΔU_W	ΔU_O	ΔU_{AW}	ΔU_{OW}	ΔU_{OA}
	Min.	Max.	Lik.	(%)	Min.	Max.	Lik.	(%)	Min.	Max.	Lik.	(%)	Min.	Max.	Lik.	(%)		Lik. (-)	(%)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)
169	6.61E-05	5.09E-04	1.30E-04	97	3.61E-03	2.78E-02	1.41E-02	-49	0.86	6.60	3.34	-49	7.44	7.66	7.55		6.56E+06	11.54		99.33	20.00	0.00	79.33	-20.00	-99.33
170	8.58E-05	2.37E-04	1.20E-04	40	2.41E-03	6.64E-03	4.74E-03	-29	5.11	14.07	10.04	-29	7.02	7.11	7.08		5.06E+05	10.42		95.99	20.00	0.00	75.99	-20.00	-95.99
171	1.72E-04	6.57E-04	2.83E-04	51	4.24E-03	1.62E-02	9.85E-03	-34	4.58	17.49	11.35	-35	6.70	7.13	6.84	40	5.04E+05	10.05	-36	93.49	20.00	2.41	73.49	-17.59	-91.07
172	1.22E-04	1.39E-04	1.33E-04	-4	7.18E-03	8.23E-03	7.52E-03	5	6.69	7.67	7.01	5	7.15	7.24	7.21		1.21E+06	10.75		95.42	20.00	0.00	75.42	-20.00	-95.42
173	3.96E-04	4.99E-04	4.28E-04	8	1.58E-02	1.98E-02	1.84E-02	-7	7.90	9.95	9.21	-7	6.58	7.17	6.96		1.33E+06	10.29		92.61	20.00	0.00	72.61	-20.00	-92.61
174	1.81E-04	2.62E-04	2.05E-04	13	7.71E-03	1.12E-02	9.88E-03	-12	6.39	9.27	8.19	-12	6.48	7.06	6.85		5.14E+05	10.20		92.61	20.00	0.00	72.61	-20.00	-92.61
175	3.78E-04	1.08E-03	5.37E-04	42	6.60E-03	1.89E-02	1.33E-02	-30	7.91	22.63	15.94	-30	6.55	7.13	6.92		8.62E+05	10.00		92.61	20.00	0.00	72.61	-20.00	-92.61
176	5.15E-04	4.88E-03	1.09E-03	112	6.76E-03	6.41E-02	3.03E-02	-53	3.18	30.11	14.23	-53	6.18	6.76	6.55		6.15E+05	9.55		85.27	20.00	0.00	65.27	-20.00	-85.27
177	2.50E-04	1.44E-03	4.47E-04	79	5.97E-03	3.43E-02	1.92E-02	-44	2.88	16.55	9.23	-44	6.36	6.94	6.73		6.84E+05	9.98		92.61	20.00	0.00	72.61	-20.00	-92.61
178	4.34E-04	7.07E-04	5.10E-04	18	1.43E-02	2.33E-02	1.98E-02	-15	7.35	11.97	10.17	-15	6.48	7.06	6.85		1.03E+06	10.10		92.61	20.00	0.00	72.61	-20.00	-92.61
179	5.15E-04	3.99E-03	1.02E-03	98	1.34E-02	1.04E-01	5.25E-02	-49	1.96	15.17	7.67	-49	6.04	6.62	6.41		6.88E+05	9.63		85.27	20.00	0.00	65.27	-20.00	-85.27
180	1.32E-04	1.78E-04	1.39E-04	5	2.03E-03	2.74E-03	2.60E-03	-5	18.99	25.64	21.10	2	7.11	7.21	7.18	-7	3.78E+05	10.23	10	94.14	20.00	14.62	74.14	-5.38	-79.52
181	2.93E-04	5.71E-04	3.66E-04	25	4.97E-03	9.68E-03	7.75E-03	-20	11.98	23.32	18.68	-20	6.76	7.34	7.13		9.69E+05	10.22		92.61	20.00	0.00	72.61	-20.00	-92.61
182	2.93E-04	9.59E-04	4.35E-04	48	4.45E-03	1.46E-02	9.81E-03	-33	7.97	26.04	17.55	-33	6.55	7.13	6.92		6.35E+05	9.96		92.61	20.00	0.00	72.61	-20.00	-92.61
183	2.45E-04	3.53E-04	3.12E-04	-11	2.30E-03	3.31E-03	2.59E-03	13	42.12	60.72	47.58	13	6.67	7.25	7.04		2.45E+05	9.69		92.61	20.00	0.00	72.61	-20.00	-92.61
184	2.20E-03	2.80E-03	2.38E-03	8	1.88E-02	2.38E-02	2.20E-02	-8	36.54	46.42	42.86	-8	6.45	7.03	6.82		1.04E+06	9.44		85.27	20.00	0.00	65.27	-20.00	-85.27
185	2.19E-04	3.22E-04	2.83E-04	-12	7.41E-03	1.09E-02	8.43E-03	14	11.67	17.16	13.27	14	6.62	7.20	6.99		6.79E+05	10.18		92.61	20.00	0.00	72.61	-20.00	-92.61
186	4.70E-04	3.27E-03	8.97E-04	91	4.98E-03	3.47E-02	1.82E-02	-48	5.36	37.30	19.53	-48	6.34	6.92	6.71		6.08E+05	9.63		85.27	20.00	0.00	65.27	-20.00	-85.27
187	3.08E-04	7.08E-03	1.11E-03	262	2.88E-03	6.63E-02	1.83E-02	-72	1.84	42.20	24.01	-43	6.12	7.13	7.00	-11	1.51E+06	9.93	17	91.63	20.00	4.15	71.63	-15.85	-87.48
188	8.55E-04	8.37E-03	1.83E-03	114	2.99E-03	2.93E-02	1.37E-02	-53	11.54	112.99	52.82	-53	6.41	6.99	6.78		5.72E+05	9.29		85.27	20.00	0.00	65.27	-20.00	-85.27
189	4.83E-05	2.84E-04	8.71E-05	80	2.83E-03	1.66E-02	9.22E-03	-45	1.15	6.74	3.74	-45	7.66	7.75	7.72		7.31E+06	11.72		99.08	20.00	0.00	79.08	-20.00	-99.08
190	7.34E-05	1.08E-04	9.51E-05	-12	2.55E-03	3.76E-03	2.90E-03	14	11.37	16.77	12.94	14	7.02	7.11	7.08		3.10E+05	10.31		95.42	20.00	0.00	75.42	-20.00	-95.42
191	1.03E-04	2.45E-04	1.38E-04	33	3.03E-03	7.18E-03	5.39E-03	-25	5.69	13.48	10.11	-25	7.15	7.24	7.21		8.65E+05	10.60		95.42	20.00	0.00	75.42	-20.00	-95.42
192	1.76E-04	3.52E-04	2.21E-04	26	3.58E-03	7.18E-03	5.69E-03	-21	9.66	19.40	15.37	-21	7.15	7.24	7.21		9.14E+05	10.41		95.42	20.00	0.00	75.42	-20.00	-95.42
193	1.36E-04	2.47E-04	1.66E-04	22	3.96E-03	7.18E-03	5.89E-03	-18	7.50	13.60	11.15	-18	7.15	7.24	7.21		9.45E+05	10.55		95.42	20.00	0.00	75.42	-20.00	-95.42
194	2.05E-05	3.75E-05	2.51E-05	22	2.26E-03	4.13E-03	3.38E-03	-18	2.13	3.90	3.19	-18	7.25	7.83	7.62		1.96E+06	11.65		101.03	20.00	0.00	81.03	-20.00	-101.03
195	4.48E-05	2.14E-04	7.55E-05	68	1.55E-03	7.43E-03	4.41E-03	-41	2.59	12.41	7.36	-41	6.98	7.56	7.35		1.10E+06	10.92		98.00	20.00	0.00	78.00	-20.00	-98.00
196	6.05E-05	9.12E-05	6.93E-05	15	3.65E-03	5.50E-03	4.80E-03	-13	4.72	7.12	6.21	-13	7.06	7.64	7.43		1.53E+06	11.11		98.00	20.00	0.00	78.00	-20.00	-98.00
197	1.78E-04	2.29E-04	1.93E-04	9	2.97E-03	3.82E-03	3.52E-03	-8	19.97	25.69	23.62	-8	8.54	9.12	8.91		1.16E+08	12.54		90.48	20.00	0.00	70.48	-20.00	-90.48
198	6.78E-05	1.09E-04	7.95E-05	17	3.42E-03	5.50E-03	4.70E-03	-15	5.30	8.52	7.27	-15	8.54	9.12	8.91		1.55E+08	13.05		98.00	20.00	0.00	78.00	-20.00	-98.00
199	5.91E-05	2.07E-04	8.98E-05	52	2.12E-03	7.43E-03	4.89E-03	-34	3.42	12.01	7.90	-34	8.54	9.12	8.91		1.61E+08	13.01		98.00	20.00	0.00	78.00	-20.00	-98.00
200	9.33E-05	6.52E-04	1.78E-04	91	1.65E-03	1.15E-02	6.02E-03	-48	3.48	24.36	12.74	-48	8.54	9.12	8.91		1.98E+08	12.81		90.48	20.00	0.00	70.48	-20.00	-90.48
201	1.74E-04	8.27E-04	2.92E-04	68	1.92E-03	9.15E-03	5.44E-03	-41	8.16	38.87	23.10	-41	8.54	9.12	8.91		1.79E+08	12.55		90.48	20.00	0.00	70.48	-20.00	-90.48
202	4.72E-04	5.24E-04	5.06E-04	-3	1.66E-02	1.84E-02	1.72E-02	4	12.23	13.58	12.66	4	6.73	7.31	7.10		1.96E+06	10.35		90.48	27.75	0.00	62.73	-27.75	-90.48
203	6.33E-05	1.52E-04	8.47E-05	34	1.91E-03	4.59E-03	3.43E-03	-25	5.93	14.21	10.62	-25	7.12	7.70	7.49		1.32E+06	10.95		98.00	20.00	0.00	78.00	-20.00	-98.00
204	1.55E-04	3.89E-04	2.10E-04	36	1.91E-03	4.79E-03	3.52E-03	-26	13.88	34.89	25.66	-26	7.11	7.69	7.48		1.32E+06	10.56		90.48	20.00	0.00	70.48	-20.00	-90.48
205	2.46E-05	5.96E-05	3.31E-05	34	1.20E-03	2.90E-03	2.16E-03	-26	3.66	8.84	6.59	-26	7.25	7.83	7.62		1.25E+06	11.34		101.03	20.00	0.00	81.03	-20.00	-101.03
206	1.09E-05	2.21E-04	2.96E-05	173	5.70E-04	1.16E-02	4.25E-03	-63	0.43	8.84	3.24	-63	7.57	8.15	7.94		6.71E+06	12.08		103.40	9.51	0.00	93.89	-9.51	-103.40
207	2.92E-05	3.19E-05	3.10E-05	-3	7.90E-04	8.65E-04	8.14E-04	3	17.13	18.75	17.65	3	7.51	8.09	7.88		1.07E+06	11.26		95.76	20.00	0.00	75.76	-20.00	-95.76
208	1.56E-05	3.05E-05	2.44E-05	-20	4.27E-04	8.36E-04	5.34E-04	25	16.93	33.14	21.18	25	7.79	8.37	8.16		1.68E+06	11.57		95.76	20.00	0.00	75.76	-20.00	-95.76
209	6.77E-06	1.42E-05	1.11E-05	-22	2.96E-04	6.19E-04	3.78E-04	28	11.42	23.90	14.61	28	7.89	8.47	8.26		1.63E+06	11.86		101.03	38.21	0.00	62.82	-38.21	-101.03

Tab. A3: *Selected physicochemical properties of CBAs at 25 °C (literature values and estimations, adjustments and value ranges). Pos. Cl: position of chlorines, P_L: liquid vapour pressure, S_L: water solubility, S_{OL}: octanol solubility, H: Henry's law constant, log K_{OW}: log octanol-water partition coefficient, log K_{OA}: log octanol-air partition coefficient, T_M: melting point, T_B: boiling point. Lit.: selected literature data and estimations, Min., max.: minimum, maximum value determined from the selected literature data, Lik.: likeliest value, i.e. adjustment of the selected data to conform to thermodynamic constraints (Part II, section 2.3.1). Dev.: deviation of the adjusted property (Lik.) from the selected value (Lit.).*

CBA		M	P_L (Pa)				Dev.	S_L [mg/L]				Dev.	H (Pa m^3/mol)				Dev.	log K_{OW} [-]				Dev.	log K_{OA}	pKA	T_M	T_B
Pos. Cl	CAS-No.	[g/mol]	Lit.	Min.	Max.	Lik.	[%]	Lit.	Min.	Max.	Lik.	[%]	Lit.	Min.	Max.	Lik.	[%]	Lit.	Min.	Max.	Lik.	[%]	Lik. [-]	[-]	(°C)	(°C)
2	118-91-2	156.57	8.80E-02 [33]	8.59E-02	1.47E+00	2.21E-01	157	1.80E+02 [35]	1.65E+03	2.82E+04	1.10E+04	-61	3.28E-06 #	4.77E-04	8.14E-03	3.16E-03	-61	2.05 [39]	1.95	2.13	2.05	0	7.08	2.89 [42]	140.2 [7]	287 [7]
3	535-80-8	156.57	3.89E-02 #	3.79E-02	4.72E-01	8.78E-02	132	5.80E+01 [35]	7.29E+02	9.08E+03	3.92E+03	-57	3.28E-06 #	6.53E-04	8.14E-03	3.51E-03	-57	2.68 [40]	2.58	2.76	2.68	0	7.89	3.81 [42]	158 [7]	276.6 #
4	74-11-3	156.57	3.89E-03 #	3.72E-03	5.15E-01	1.92E-02	417	6.33E+01 [36]	7.16E+01	9.91E+03	1.92E+03	-81	3.28E-06 #	5.88E-05	8.14E-03	1.57E-03	-81	2.65 [40]	2.55	2.73	2.65	0	8.20	3.98 [43]	243 [7]	276.6 #
2,3	50-45-3	191.01	5.96E-02 #	2.51E-02	5.88E-02	4.43E-02	-25	4.16E+00 #	7.96E+02	1.86E+03	1.06E+03	33	2.43E-06 #	6.03E-03	1.41E-02	8.01E-03	33	2.82 #	2.72	2.90	2.82	0	7.73	2.55 [44]	88.5 #	301.3 #
2,4	50-84-0	191.01	9.00E-03 #	8.74E-03	3.52E-01	2.99E-02	243	5.83E+01 [36]	2.77E+02	1.11E+04	3.25E+03	-71	2.43E-06 #	1.50E-04	6.03E-03	1.76E-03	-71	2.82 [38]	2.72	2.90	2.82	0	8.38	2.68 [44]	164.2 [7]	301.3 #
2,5	50-79-3	191.01	1.18E-02 #	1.15E-02	1.11E-01	2.45E-02	113	1.85E+01 #	3.63E+02	3.53E+03	1.65E+03	-53	2.43E-06 #	6.20E-04	6.03E-03	2.82E-03	-53	2.82 [41]	2.72	2.90	2.82	0	8.18	2.47 [44]	154.4 [7]	301 [7]
2,6	50-30-6	191.01	1.52E-02 #	1.48E-02	2.81E-01	3.95E-02	167	4.66E+01 #	4.70E+02	8.90E+03	3.34E+03	-62	2.43E-06 #	3.18E-04	6.03E-03	2.26E-03	-62	2.23 [40]	2.13	2.31	2.23	0	7.47	1.59 [44]	144 [7]	301.3 #
3,4	51-44-5	191.01	4.72E-03 #	8.57E-03	5.79E-02	1.62E-02	89	4.94E+02 [36]	1.40E+00	9.43E+04	2.32E+03	-98	2.43E-06 #	8.93E-08	6.03E-03	1.48E-04	-98	3.25 [41]	3.15	3.33	3.25	0	10.04	3.64 [44]	350 [7]	301.3 #
3,5	51-36-5	191.01	4.79E-03 #	4.63E-03	1.84E-01	1.58E-02	242	3.06E+01 [36]	1.47E+02	5.84E+03	1.71E+03	-71	2.43E-06 [38]	1.51E-04	6.03E-03	1.76E-03	-71	3 [40]	2.90	3.08	3.00	0	8.63	3.54 [44]	188 [7]	302.3 #
2,3,4	50-75-9	225.46	1.10E-02 #	4.67E-03	1.08E-02	8.18E-03	-24	1.04E+00 #	2.35E+02	5.47E+02	3.12E+02	32	1.80E-06 #	4.47E-03	1.04E-02	5.92E-03	32	3.47 #	3.37	3.55	3.47	0	8.74	2.32 ##	108.9 #	323.6 #
2,3,5	50-73-7	225.46	1.10E-02 #	4.67E-03	1.08E-02	8.18E-03	-24	1.04E+00 #	2.35E+02	5.47E+02	3.12E+02	32	1.80E-06 #	4.47E-03	1.04E-02	5.92E-03	32	3.47 #	3.37	3.55	3.47	0	8.74	2.17 ##	108.9 #	323.6 #
2,3,6	50-31-7	225.46	7.33E-02 [34]	2.94E-02	7.18E-02	5.33E-02	-26	6.58E+00 #	1.48E+03	3.62E+03	2.00E+03	35	1.80E-06 #	4.47E-03	1.09E-02	6.02E-03	35	2.71 #	2.61	2.79	2.71	0	7.70	1.50 [45]	124.5 [7]	323.6 #
2,4,5	50-82-8	225.46	2.56E-03 #	2.48E-03	3.92E-01	1.34E-02	441	8.78E+01 [37]	1.25E+02	1.98E+04	3.66E+03	-81	1.80E-06 #	2.83E-05	4.47E-03	8.27E-04	-81	3.47 #	3.37	3.55	3.47	0	9.60	2.32 ##	166.5 [7]	323.6 #
2,4,6	50-43-1	225.46	1.10E-02 #	1.08E-02	2.07E-02	1.34E-02	24	4.63E+00 #	5.47E+02	1.04E+03	8.41E+02	-19	1.80E-06 #	2.34E-03	4.47E-03	3.60E-03	-19	2.71 #	2.61	2.79	2.71	0	7.92	1.40 [45]	108.9 #	323.6 #
3,4,5	51-39-8	225.46	1.10E-02 #	2.38E-03	1.08E-02	6.54E-03	-40	5.32E-01 #	1.20E+02	5.47E+02	1.99E+02	66	1.80E-06 #	4.47E-03	2.03E-02	7.41E-03	66	3.81 #	3.67	3.92	3.81	0	9.11	3.23 ##	108.9 #	323.6 #
2,3,4,5	50-74-8	259.9	2.84E-03 #	7.03E-04	2.78E-03	1.76E-03	-37	2.12E-01 #	5.51E+01	2.18E+02	8.72E+01	58	1.34E-06 #	3.31E-03	1.31E-02	5.24E-03	58	4.11 #	3.96	4.23	4.11	0	9.66	1.95 ##	120.1 #	343.6 #
2,3,4,6	50-40-8	259.9	2.84E-03 #	2.78E-03	3.12E-03	2.89E-03	4	9.41E-01 #	2.18E+02	2.44E+02	2.35E+02	-4	1.34E-06 #	2.96E-03	3.31E-03	3.19E-03	-4	3.35 #	3.23	3.45	3.35	0	8.85	1.04 ##	120.1 #	343.6 #
2,3,5,6	50-38-4	259.9	2.84E-03 #	2.78E-03	3.12E-03	2.89E-03	4	9.41E-01 #	2.18E+02	2.44E+02	2.35E+02	-4	1.34E-06 #	2.96E-03	3.31E-03	3.19E-03	-4	3.35 #	3.23	3.45	3.35	0	8.85	0.89 ##	120.1 #	343.6 #
2,3,4,5,6	1012-84-6	294.35	9.87E-05 #	9.49E-05	2.74E-03	2.91E-04	207	1.12E+00 #	1.14E+01	3.29E+02	1.07E+02	-67	9.89E-07 #	8.50E-05	2.45E-03	7.99E-04	-67	4 #	3.86	4.12	4.00	0	10.33	0.67 ##	209.3 [7]	362.4 #

log Koa: calculated from adjusted properties (Part II, section 2.3.1), #: estimated value using EPI Suite 3.10 [26], ##: estimated according to section 3.1.3.3.

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Appendix B

Composition of Aroclor mixtures

Tab. B: *Weight % of PCB congeners in Aroclor mixtures. Aroclors A1016, A1232, A1242, A1248, A1254, A1260, A1262: minimum and maximum values reported in literature, A1221: single values. a: Albro & Parker 1979, Albro et el. 1981), b: Frame et al. 1996, c: Frame 1999, d: Kodavanti et al. 2001.*

PCB	A 1016			1221	A 1232 b		A 1242			A 1248			A 1254			A 1260			A 1262 b	
	min	max		b	min	max	min	max		min	max		min	max		min	max		min	min
1	0.52	0.59	a,b	35.80	15.21	15.84	0.34	0.78	b	0.00	0.05	a,b	0.00	0.02	a,b,c,d	0.00	0.03	a,b	0.02	0.03
2	0.02	0.07	a,b	3.81	1.94	1.98	0.02	0.05	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
3	0.15	0.74	a,b	20.44	10.20	10.36	0.11	0.27	b	0.00	0.01	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.01
4	3.62	3.81	a,b	6.19	5.32	5.38	2.71	3.41	b	0.04	0.32	b	0.00	0.06	a,c,d	0.00	0.03	a,b	0.04	0.07
5	0.15	0.17	b	0.74	0.49	0.50	0.11	0.19	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
6	1.20	1.69	a,b	3.82	3.00	3.02	1.05	1.63	a,b	0.00	0.54	a	0.00	0.05	c,d	0.00	0.01	a,b	0.02	0.03
7	0.29	1.01	a,b	1.70	1.09	1.12	0.18	0.88	a,b	0.00	0.02	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
8	8.29	9.00	a,b	12.34	10.71	10.72	6.48	7.68	b	0.14	0.81	a,b	0.00	0.13	a,c,d	0.00	0.06	a,b	0.08	0.15
9	0.30	0.59	a,b	1.74	1.25	1.29	0.26	0.60	a,b	0.00	0.04	b	0.00	0.00	a,b,c,d	0.00	0.00	a,b	0.00	0.00
10	0.17	0.23	a,b	0.80	0.58	0.60	0.11	0.25	a,b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
11	0.00	0.00	b	0.16	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
12	0.07	0.10	a,b	0.59	0.35	0.35	0.04	0.09	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
13	0.10	0.25	a,b	1.12	0.72	0.73	0.10	0.27	a,b	0.00	0.02	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
14	0.00	0.32	a,b	0.00	0.00	0.02	0.00	0.30	a,b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
15	0.93	2.49	a,b	4.18	3.19	3.24	0.84	2.39	a,b	0.06	0.22	b	0.00	0.03	a,c,d	0.00	0.02	b	0.02	0.03
16	3.53	3.88	a,b	0.31	1.79	1.79	2.94	3.44	b	0.71	1.04	b	0.00	0.13	c	0.00	0.02	a,b	0.03	0.07
17	3.17	3.98	a,b	0.34	1.82	1.83	2.86	3.29	a,b	0.17	1.05	a,b	0.00	0.13	c	0.00	0.02	a,b	0.03	0.07
18	10.75	10.96	a,b	0.78	4.83	4.89	7.93	9.17	a,b	3.29	8.94	a	0.00	0.36	c	0.00	0.07	a,b	0.10	0.19
19	0.99	1.09	a,b	0.08	0.46	0.47	0.75	0.95	a,b	0.14	0.22	b	0.00	0.03	a,b,c,d	0.00	0.00	b	0.00	0.02
20	0.88	4.02	a,b	0.07	0.42	0.42	0.68	3.56	a,b	0.08	0.14	b	0.00	0.30	c	0.00	0.00	b	0.00	0.00
21	0.00	0.00	b		0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
22	2.82	3.51	a,b	0.26	1.62	1.62	2.59	3.08	a,b	1.11	1.38	a	0.00	0.14	c	0.00	0.02	a,b	0.03	0.06
23	0.01	0.02	b	0.00	0.01	0.01	0.01	0.01	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
24	0.16	0.17	b	0.02	0.08	0.08	0.13	0.14	b	0.00	0.01	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
25	0.72	1.80	a,b	0.09	0.37	0.37	0.57	1.65	a,b	0.04	0.11	b	0.00	0.02	a,b,c,d	0.00	0.00	b	0.00	0.01
26	0.63	1.59	a,b	0.13	0.74	0.75	0.54	1.38	a,b	0.23	0.67	a	0.00	0.05	c	0.00	0.01	a,b	0.01	0.03
27	0.50	0.58	a,b	0.05	0.12	0.12	0.39	0.53	a,b	0.07	0.12	b	0.00	0.02	a,b,c,d	0.00	0.00	b	0.00	0.01
28	8.50	14.60	a,b	0.62	3.89	3.92	6.60	13.03	a,b	0.00	5.57	a	0.00	0.35	c	0.00	0.05	a,b	0.08	0.15
29	0.10	0.10	b	0.01	0.05	0.05	0.08	0.09	b	0.00	0.01	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
30	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
31	4.76	9.32	a,b	0.60	4.11	4.17	4.44	7.82	a,b	5.07	8.36	a,b	0.00	0.54	c	0.00	0.06	a,b	0.08	0.16
32	2.33	2.37	a,b	0.17	1.07	1.08	1.79	2.11	a,b	0.88	1.31	a,b	0.00	0.08	c	0.00	0.01	a,b	0.02	0.05
33	3.11	6.21	a,b	0.48	2.84	2.88	2.77	5.35	a,b	2.21	2.23	b	0.00	0.30	c	0.00	0.04	b	0.07	0.13
34	0.03	0.03	b	0.00	0.01	0.01	0.02	0.03	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
35	0.05	0.38	a,b	0.01	0.05	0.06	0.07	0.65	a,b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
36	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
37	1.01	1.91	a,b	0.19	1.12	1.15	1.59	2.19	a,b	0.79	1.15	a,b	0.00	0.39	c	0.00	0.07	a,b	0.02	0.04
38	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
39	0.00	1.09	a,b	0.00	0.00	0.00	0.00	1.01	a,b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
40	0.21	0.58	a,b	0.04	0.36	0.40	0.17	0.79	a,b	0.92	1.14	a	0.00	0.30	c	0.00	0.03	a,b	0.00	0.01
41	0.76	2.29	a,b	0.03	0.35	0.36	0.65	1.85	a,b	0.75	0.77	b	0.00	0.99	c	0.00	0.00	b	0.00	0.01
42	1.59	1.59	b	0.09	0.66	0.69	1.13	1.25	b	1.67	7.18	a,b	0.00	1.85	c	0.00	0.55	a,b	0.01	0.03
43	0.25	0.54	a,b	0.00	0.09	0.12	0.16	0.49	a,b	0.19	0.30	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
44	1.30	4.48	a,b	0.21	1.81	1.81	1.18	3.63	a,b	5.09	6.31	b	0.67	2.56	c	0.03	0.04	b	0.05	0.10
45	1.14	1.23	a,b	0.04	0.45	0.47	0.84	1.00	a,b	0.91	5.83	a	0.00	0.13	c	0.00	0.00	a,b	0.01	0.01
46	0.38	0.49	a,b	0.02	0.19	0.19	0.33	0.38	b	0.39	0.47	b	0.00	0.03	a,b,c,d	0.00	0.00	b	0.00	0.00
47	1.24	2.06	a,b	0.05	0.49	0.49	0.91	1.83	a,b	1.49	3.24	a,b	0.00	0.54	c	0.00	0.73	a,b	0.01	0.01
48	1.59	1.61	a,b	0.06	0.61	0.62	1.17	1.48	a,b	1.54	1.66	b	0.00	1.46	c	0.00	0.01	b	0.01	0.01
49	3.35	3.98	a,b	0.15	1.36	1.37	2.38	3.64	a,b	4.12	4.17	b	0.26	2.17	c	0.01	0.02	b	0.04	0.07
50	0.01	0.01	b	0.00	0.00	0.00	0.00	0.01	b	0.00	3.88	a,b	0.00	1.39	b,c,d	0.00	0.37	a,b	0.00	0.00
51	0.32	0.32	b	0.01	0.12	0.13	0.22	0.25	b	0.30	0.31	b	0.00	0.31	c	0.00	0.00	b	0.00	0.00
52	4.61	4.97	a,b	0.22	1.83	1.86	3.47	4.53	a,b	5.58	8.51	a	0.70	5.38	c	0.21	1.59	a,b	0.11	0.17
53	0.94	1.22	a,b	0.04	0.37	0.37	0.68	1.08	a,b	0.88	6.42	a	0.00	0.14	c	0.00	0.00	a,b	0.01	0.01
54	0.01	0.22	a,b	0.00	0.00	0.00	0.01	0.19	a,b	0.00	0.01	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
55	0.00	0.00	b	0.00	0.05	0.05	0.09	0.11	b	0.05	0.11	a	0.00	0.37	b,c,d	0.00	0.10	a,b	0.00	0.00
56	0.00	0.07	a,b	0.12	0.92	0.93	0.67	1.85	a,b	0.18	3.19	a	0.00	2.07	c	0.00	0.02	a,b	0.02	0.04
57	0.01	0.01	b	0.00	0.01	0.01	0.01	0.03	b	0.02	0.02	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
58	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
59	0.38	0.41	b	0.01	0.15	0.20	0.27	0.37	b	0.23	0.37	b	0.00	0.22	c	0.00	0.00	b	0.00	0.00
60	0.00	0.04	a,b	0.07	0.60	0.61	0.23	1.19	a,b	1.85	2.67	b	0.00	1.34	c	0.03	0.04	b	0.02	0.02
61	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
62	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
63	0.05	0.06	b	0.01	0.10	0.10	0.11	0.13	b	0.17	0.19	b	0.00	0.13	c	0.00	0.00	b	0.00	0.00
64	1.84	1.87	b	0.10	0.87	0.87	1.67	1.76	b	3.01	3.32	b	0.00	0.76	c	0.01	0.01	b	0.02	0.04
65	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
66	0.16	0.39	a,b	0.21	1.71	1.74	0.90	3.40	a,b	5.04	7.22	a	1.01	9.22	c	0.01	0.18	a,b	0.05	0.08
67	0.06	0.06	b	0.01	0.08	0.09	0.15	0.17	b	0.10	0.13	b	0.00	0.01	a,b,c,d	0.00	0.00	b	0.00	0.00
68	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
69	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
70	0.00	0.59	a,b	0.24	1.90	1.90	1.23	3.76	a,b	6.50	7.39	a	2.56	6.83	c	0.04	0.71	a,b	0.07	0.12
71	1.16	1.17	b	0.06	0.54	0.54	1.00	1.06	b	0.66	1.86	a	0.00	0.19	c	0.00	0.01	a,b	0.01	0.02
72	0.00	0.01	a,b	0.00	0.00	0.00	0.01	0.37	a,b	0.01	2.14	a	0.00	0.86	b,c,d	0.00	0.23	a,b	0.00	0.00
73	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
74	0.33	1.54	a,b	0.12	0.92	0.92	1.76	2.24	a,b	0.25	4.67	a	0.26	2.52	c	0.04	0.07	a,b	0.04	0.06
75	0.06	2.74	a,b	0.00	0.02	0.02	0.03	2.42	a,b	0.08	0.08	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
76	0.00	0.00	a,b	0.01	0.00	0.00	0.00	0.09	a,b	0.00	0.13	a,b	0.00	0.15	c	0.00	0.01	a,b	0.00	0.00
77	0.00	0.00	a,b	0.01	0.16	0.17	0.27	0.38	a,b	0.41	0.52	b	0.00	2.45	c	0.00	0.03	a,b	0.00	0.00
78	0.00	0.00	a,b	0.00	0.00	0.00	0.00	0.58	a,b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
79	0.00	0.00	a,b	0.00	0.00	0.00	0.00	0.27	a,b	0.00	0.00	a,b	0.00	0.20	b,c,d	0.00	0.03	a,b	0.00	0.00
80	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.00	b,c,d	0.00	0.00	a,b	0.00	0.00

***Tab. B** (continued)*

PCB	A 1016			1221	A 1232 b		A 1242			A 1248			A 1254			A 1260			A 1262 b	
	min	max		b	min	max	min	max		min	max		min	max		min	max		min	min
81	0.00	0.00	a,b	0.00	0.00	0.00	0.01	0.31	a,b	0.01	0.02	b	0.00	0.03	a,b,c	0.00	0.00	b	0.00	0.00
82	0.00	0.00	b	0.00	0.12	0.12	0.22	0.29	b	0.00	0.81	a,b	0.30	2.24	c	0.00	0.08	a,b	0.00	0.00
83	0.00	0.01	a,b	0.00	0.04	0.05	0.09	0.47	a,b	0.20	0.81	a	0.39	1.64	cb,c	0.00	0.64	a,b	0.00	0.00
84	0.05	0.05	b	0.02	0.18	0.20	0.35	0.46	b	0.91	1.26	b	0.00	2.55	c	0.10	0.12	b	0.03	0.05
85	0.00	0.00	a,b	0.03	0.17	0.17	0.24	0.50	a,b	0.63	1.14	a	0.00	3.26	c	0.00	0.29	a,b	0.01	0.03
86	0.00	0.00	b	0.00	0.01	0.01	0.00	0.04	b	0.02	0.11	a,b	0.00	0.52	c,d	0.00	0.13	a,b	0.00	0.00
87	0.00	0.00	a,b	0.04	0.22	0.22	0.11	0.52	a,b	1.11	1.45	b	3.41	4.29	c	0.36	1.02	a,b	0.11	0.11
88	0.00	0.00	b	0.00	0.00	0.00	0.00	0.01	b	0.02	0.02	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
89	0.00	0.00	b		0.05	0.05	0.07	0.10	b	0.17	0.20	b	0.00	2.55	c	0.00	0.00	b	0.00	0.00
90	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	5.44	8.57	c	0.00	0.00	b	0.00	0.00
91	0.00	0.06	a,b	0.00	0.10	0.10	0.00	0.24	a,b	0.56	2.03	a	0.53	4.75	c	0.00	2.99	a,b	0.00	0.01
92	0.00	0.00	a,b	0.02	0.05	0.05	0.06	0.15	a,b	0.23	0.38	a,b	0.57	3.24	c	0.20	0.34	a,b	0.07	0.09
93	0.00	0.00	b	0.00	0.00	0.00	0.00	0.01	b	0.03	0.04	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
94	0.00	0.00	b	0.00	0.00	0.00	0.00	0.01	b	0.02	0.03	b	0.00	0.02	a,c,d	0.00	0.00	b	0.00	0.00
95	0.23	0.31	a,b	0.05	0.30	0.30	0.51	0.68	b	1.43	1.96	b	0.00	6.29	c	2.27	2.56	b	0.87	0.99
96	0.04	0.04	b	0.00	0.01	0.01	0.02	0.03	b	0.06	0.08	b	0.00	0.04	a,c,d	0.00	0.00	b	0.00	0.00
97	0.00	0.04	b	0.03	0.17	0.18	0.31	0.43	b	0.89	1.22	a,b	0.00	2.96	c	0.08	0.59	a,b	0.03	0.06
98	0.00	0.05	a,b	0.00	0.00	0.00	0.00	0.16	a,b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
99	0.00	0.01	a,b	0.04	0.21	0.21	0.36	0.68	a,b	1.47	2.87	a,b	2.26	5.80	c	0.03	0.76	a,b	0.03	0.06
100	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.01	a,b,c,d	0.00	0.00	b	0.00	0.00
101	0.00	0.04	a,b	0.07	0.32	0.33	0.34	0.78	a,b	1.71	2.22	a,b	0.00	8.57	c	2.99	4.68	a,b	1.03	1.23
102	0.04	0.04	b	0.00	0.03	0.03	0.05	0.08	b	0.00	0.19	a,b	0.00	0.17	c	0.00	0.00	a,b	0.00	0.00
103	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.01	0.02	b	0.00	0.04	c	0.00	0.00	b	0.00	0.00
104	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
105	0.00	0.00	a,b	0.05	0.21	0.22	0.31	0.52	a,b	1.45	1.60	b	2.58	11.71	c	0.21	0.23	b	0.00	0.18
106	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.38	b,c,d	0.00	0.06	a,b	0.00	0.00
107	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
108	0.00	0.20	a,b	0.00	0.00	0.00	0.00	0.57	a,b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
109	0.00	0.00	b	0.00	0.03	0.03	0.04	0.08	b	0.13	0.18	b	0.00	1.36	c	0.01	0.01	b	0.00	0.01
110	0.00	0.00	b	0.05	0.38	0.38	0.68	0.94	b	1.92	2.97	a,b	7.59	9.29	c	1.25	3.32	a,b	0.36	0.42
111	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
112	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
113	0.00	0.01	a,b	0.00	0.00	0.00	0.00	0.48	a,b	0.00	3.53	a,b	0.00	0.01	b,c,d	0.00	0.01	a,b	0.00	0.00
114	0.00	0.00	b	0.00	0.01	0.02	0.03	0.05	b	0.00	0.12	a,b	0.01	0.65	c	0.00	0.03	a,b	0.00	0.00
115	0.00	0.00	b	0.00	0.01	0.01	0.03	0.05	b	0.11	0.11	b	0.00	3.26	c	0.00	0.00	b	0.00	0.00
116	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
117	0.00	0.00	b	0.00	0.00	0.01	0.02	0.04	b	0.09	0.10	b	0.00	3.26	c	0.00	0.00	b	0.00	0.00
118	0.00	0.00	b	0.08	0.28	0.29	0.51	0.78	b	0.00	2.35	a	5.38	13.59	c	0.45	1.86	a,b	0.14	0.17
119	0.00	0.00	b		0.00	0.00	0.00	0.00	b	0.06	0.06	b	0.00	0.72	c	0.00	0.00	b	0.00	0.00
120	0.00	0.00	a,b		0.00	0.00	0.00	0.38	a,b	0.00	0.00	a,b	0.00	0.14	b,c,d	0.00	2.80	a,b	0.00	0.00
121	0.00	0.00	a,b	0.00	0.00	0.00	0.00	1.14	a,b	0.00	4.92	a,b	0.00	3.34	b,c,d	0.00	0.53	a,b	0.00	0.00
122	0.00	0.00	b	0.00	0.00	0.00	0.01	0.02	b	0.05	0.06	b	0.00	0.36	c	0.00	0.00	b	0.00	0.00
123	0.00	0.00	a,b		0.00	0.00	0.02	0.45	a,b	0.07	0.08	b	0.06	1.36	c	0.00	0.00	b	0.00	0.00
124	0.00	0.00	b	0.00	0.00	0.01	0.02	0.03	b	0.07	0.10	b	0.00	0.64	c	0.01	0.01	b	0.00	0.00
125	0.00	0.00	b	0.00	0.01	0.01	0.02	0.02	b	0.00	0.04	a,b	0.00	0.72	c,d	0.00	1.75	a,b	0.00	0.00
126	0.00	0.00	a,b	0.00	0.00	0.00	0.00	0.04	a,b	0.00	0.18	a	0.00	1.51	c	0.00	0.00	a,b	0.00	0.00
127	0.00	0.00	a,b	0.00	0.00	0.00	0.00	0.06	a,b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
128	0.00	0.00	b	0.00	0.00	0.00	0.00	0.04	b	0.00	0.12	a,b	0.72	1.98	c	0.48	0.56	a,b	0.17	0.20
129	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.02	b	0.38	1.46	c	0.12	0.15	b	0.03	0.04
130	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.01	0.04	b	0.00	1.00	c	0.21	0.23	b	0.03	0.06
131	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.27	c	0.01	0.08	a,b	0.00	0.00
132	0.00	0.00	b		0.02	0.02	0.03	0.05	b	0.00	0.15	a,b	1.50	6.94	c	2.84	2.96	b	1.07	1.35
133	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	1.42	a,b	0.00	0.11	b,c,d	0.06	0.08	b	0.03	0.05
134	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.14	a,b	0.00	0.45	c	0.31	1.04	a,b	0.11	0.14
135	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.04	a	0.21	1.25	c	0.30	1.14	a,b	0.65	0.67
136	0.00	0.00	b	0.00	0.00	0.01	0.00	0.00	b	0.05	0.25	a,b	0.00	0.94	c	1.15	1.48	a,b	0.99	1.02
137	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.02	0.03	b	0.00	0.68	c	0.02	0.02	b	0.01	0.01
138	0.00	0.00	a,b	0.00	0.05	0.06	0.05	0.16	b	0.24	0.41	a	4.38	7.64	c	5.15	6.73	a,b	2.33	3.14
139	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.25	c	0.00	0.00	b	0.00	0.00
140	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
141	0.00	0.00	b	0.00	0.00	0.00	0.00	0.01	b	0.07	0.09	b	0.69	1.29	c	2.57	2.68	b	1.63	1.69
142	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
143	0.00	0.00	a,b	0.00	0.00	0.00	0.00	0.10	a,b	0.00	0.00	b	0.00	0.25	c	0.00	0.00	b	0.00	0.00
144	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.01	b	0.00	0.32	c	0.61	0.61	b	0.41	0.41
145	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
146	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.04	0.05	b	0.45	1.05	c	1.11	1.17	b	0.57	0.61
147	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	3.68	c	0.00	0.00	b	0.00	0.00
148	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.15	a,b	0.00	0.07	b,c,d	0.00	0.06	a,b	0.00	0.00
149	0.00	0.00	b	0.00	0.05	0.05	0.04	0.07	b	0.24	0.97	a,b	1.29	4.24	c	8.73	9.78	a,b	6.36	6.44
150	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
151	0.00	0.00	b	0.00	0.01	0.01	0.00	0.01	b	0.00	0.08	a	0.00	0.90	c	0.06	3.04	a,b	2.81	3.14
152	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
153	0.00	0.00	a,b	0.00	0.05	0.05	0.03	0.09	a,b	0.16	0.43	a	3.06	6.94	c	8.44	9.91	a,b	6.78	7.42
154	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.15	c,d	0.00	0.00	a,b	0.00	0.00
155	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
156	0.00	0.00	b	0.00	0.00	0.00	0.00	0.02	b	0.00	0.06	a,b	0.00	4.60	c	0.42	0.54	a,b	0.14	0.18
157	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.01	a,b	0.04	2.37	c	0.02	0.03	a,b	0.00	0.00
158	0.00	0.00	b	0.00	0.00	0.00	0.00	0.02	b	0.00	0.04	a,b	0.00	1.46	c	0.18	0.60	a,b	0.18	0.21
159	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.79	b,c,d	0.00	1.52	a,b	0.00	0.00
160	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
161	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
162	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
163	0.00	0.00	b	0.00	0.02	0.02	0.00	0.02	b	0.00	0.08	a	0.00	7.64	c	0.00	2.44	a,b	1.50	1.55
164	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.02	0.03	b	0.00	1.00	c	0.66	0.72	b	0.23	0.30
165	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.80	c	0.00	0.00	b	0.00	0.00

***Tab. B** (continued)*

PCB	A 1016			1221	A 1232 b		A 1242			A 1248			A 1254			A 1260			A 1262 b	
	min	max		b	min	max	min	max		min	max		min	max		min	max		min	min
166	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.08	c	0.00	0.00	b	0.00	0.00
167	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.01	a,b	0.00	0.54	c	0.17	0.20	b	0.02	0.05
168	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.70	a,b	0.00	4.45	b,c,d	0.00	0.61	a,b	0.00	0.00
169	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
170	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.08	a,b	0.31	0.63	c	0.70	4.36	a,b	3.05	3.47
171	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.35	c	1.08	4.85	a,b	0.85	0.89
172	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.10	c	0.69	0.71	b	0.62	0.63
173	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.16	c,a,b,c	0.09	0.11	b	0.03	0.05
174	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.08	a,b	0.00	3.16	c	0.10	4.99	a,b	6.10	6.56
175	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.02	a,b,c,d	0.17	0.18	b	0.16	0.19
176	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.12	a,b	0.00	0.07	c	0.58	0.64	a,b	0.66	0.73
177	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.03	a,b	0.00	0.28	c	0.00	2.64	a,b	2.73	2.82
178	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.08	c	0.79	0.86	b	1.10	1.31
179	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.02	a,b	0.00	0.64	c	0.93	2.05	a,b	3.01	3.64
180	0.00	0.00	b	0.00	0.01	0.02	0.00	0.00	b	0.00	0.21	a	0.41	1.07	c	8.10	12.05	a,b	13.72	14.53
181	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.32	b,c,d	0.01	3.06	a,b	0.00	0.00
182	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.00	b,c,d	0.00	0.53	a,b	0.00	0.00
183	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.06	a,b	0.09	1.34	c	2.33	2.90	a,b	2.86	2.89
184	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.00	0.00	b	0.00	0.00
185	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	1.28	cb,c,d	0.53	6.36	a,b	0.81	0.93
186	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.00	b,c,d	0.00	0.42	a,b	0.00	0.00
187	0.00	0.00	b	0.00	0.00	0.01	0.00	0.00	b	0.00	0.09	a,b	0.04	0.55	c	1.26	5.44	a,b	8.76	9.55
188	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.00	a,b,c,d	0.00	0.15	a,b	0.00	0.00
189	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.05	c	0.02	0.12	a,b	0.03	0.04
190	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.11	c	0.80	0.85	b	0.74	0.77
191	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.04	a,b,c,d	0.16	0.17	b	0.13	0.13
192	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.23	b,c,d	0.00	1.09	a,b	0.00	0.00
193	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	2.65	b,c,dc	0.00	0.57	a,b	0.65	0.67
194	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.01	a,b,c,d	2.03	2.70	a,b	3.79	4.32
195	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.00	a,b,c,d	0.00	0.86	a,b	1.39	1.46
196	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.00	a,b,c,d	0.97	1.21	a,b	2.12	2.41
197	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.00	a,b,c,d	0.07	0.37	a,b	0.13	0.14
198	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	1.25	b,c,d	0.09	0.18	a,b	0.22	0.24
199	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.01	a,b,c,d	0.46	1.87	a,b	4.57	4.91
200	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.00	b,c,d	0.18	0.26	a,b	0.60	0.69
201	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	b	0.00	0.00	a,b,c,d	0.23	0.25	b	0.58	0.66
202	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.00	b,c,d	0.28	0.38	a,b	0.96	1.20
203	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.02	a,b,c,d	0.10	1.50	a,b	4.11	4.37
204	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.00	b,c,d	0.00	0.16	a,b	0.00	0.00
205	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.00	a,b,c,d	0.01	0.10	a,b	0.16	0.18
206	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.03	a,c,d	0.31	0.67	a,b	1.19	1.33
207	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.00	a,b,c,d	0.03	1.52	a,b	0.17	0.18
208	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.01	a,c,d	0.06	2.17	a,b	0.26	0.29
209	0.00	0.00	b	0.00	0.00	0.00	0.00	0.00	b	0.00	0.00	a,b	0.00	0.00	a,b,c,d	0.26	0.26	a	0.00	0.00

Appendix C

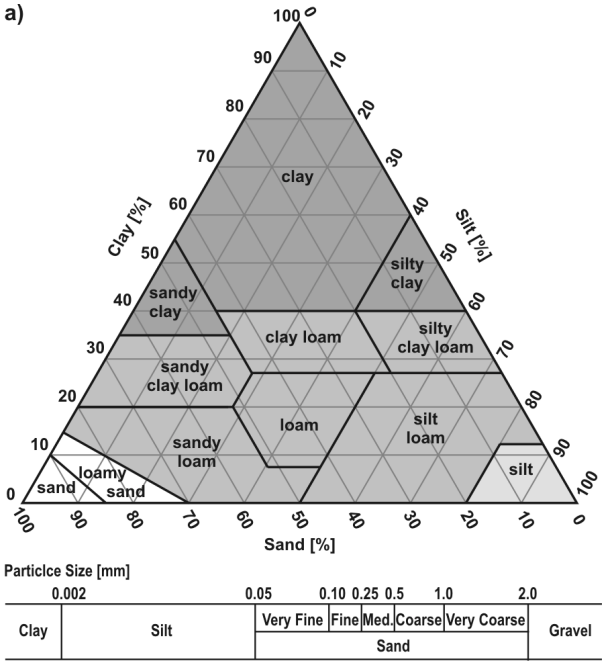
Derivation of soil and aquifer parameters

The literature of this appendix is cited in the Overall References list.

C.1 Hydraulic parameters and soil bulk density

The U.S. Department of Agriculture (USDA 1993) defines 12 soil textural classes (Fig. C1). Specific to these classes, average values for a number of hydraulic parameters are provided by the estimation program ROSETTA (Schaap et al. 2001, see Tab. C1). The hydraulic parameters shown in Tab. C1 were fitted to a dataset of 1209 soil samples (for the retention parameters) and a subset of 620 samples (for saturated hydraulic conductivity; Schaap et al. 1998).

a)



b) **Percentage of sand, silt and clay**

	sand	*silt*	*clay*
Clay	< 45	< 40	≥ 40
C loam	20 -45		27 -40
Loam	< 52	28 -50	7 -27
L Sand	70 -91	[s]+1.5[c] ≥ 15 and [s]+2[c] < 30	
Sand	≥ 85	[s]+1.5[c] ≤ 15	
S Clay	≥ 45		≥ 35
S C L	> 45	< 28	20 -35
S loam	> 52	[s]+2[c] ≥ 30	7 -20
	> 43	< 50	< 7
Silt	< 20		27 -40
Si Clay		≥ 80	< 12
Si C L		≥ 50	12 -27
		50 -80	< 12
Si Loam		≥ 40	≥ 40

Fig. C1*: Soil textural classification according to USDA (1993). a) texture classes and particle size range, b) definition, Med.: medium, C: clay, L: loam, S: sand, Si: silt, [si] and [c]: percentage of silt and clay, respectively.*

Mean or typical water saturation $\theta_{w,m}$ in Tab. C1 was estimated from residual water content and water content at 1/3 bar or 33 kPa suction (or approximately field capacity) as recommended e.g. by the US EPA (2004a):

$$\theta_{w,m} = \frac{\theta_{1/3\,bar} + \theta_r}{2} \qquad \text{(C1)}$$

$\theta_{1/3\,bar}$: measured vol. water content at 330 cm suction [cm^3/cm^3]
θ_r, θ_s: residual and saturated water content [cm^3/cm^3]

$\theta_{1/3\,bar}$ can be calculated with the van Genuchten (1980) equation:

$$\theta(h) = \theta_r + \frac{\theta_S - \theta_r}{\left[1 + (\alpha \cdot h)^N\right]^{1-1/N}} \qquad \text{(C2)}$$

$\theta(h)$: measured vol. water content at suction h [cm^3/cm^3]
h: suction [cm]
α: parameter related to the inverse of air entry suction [1/cm]
N: measure of the pore-size distribution [-]

Tab. C1: *Class average values for the USDA textural classes (in parentheses: standard deviations), compare to Fig. C1. n: number of samples, θ_r and θ_S: residual and saturated water content, α and N: van Genuchten-parameters, K_S: saturated hydraulic conductivity, $\theta_{w,m}$: calculated mean water saturation (average of θ_r and water saturation at field capacity), ρ_b: soil bulk density. a: values taken from Schaap et al. (1998), b: average values from Ley et al. (1994).*

Texture Class	N	θ_r (a) [cm³/cm³]		θ_s (a) [[cm³/cm³]		$\theta_{w,m}$ [cm³/cm³]		log α (a) [log 1/cm]		log *N* (a) [log10]		log K_S (a) [log cm/day]		ρ_b (b) [g/cm³]
Clay	84	0.098	(0.107)	0.459	(0.079)	0.22	(0.10)	-1.825	(0.68)	0.098	(0.07)	1.169	(0.92)	1.43
C loam	140	0.079	(0.076)	0.442	(0.079)	0.17	(0.08)	-1.801	(0.69)	0.151	(0.12)	0.913	(1.09)	1.48
Loam	242	0.061	(0.073)	0.399	(0.098)	0.15	(0.08)	-1.954	(0.73)	0.168	(0.13)	1.081	(0.92)	1.59
L Sand	201	0.049	(0.042)	0.390	(0.070)	0.08	(0.04)	-1.459	(0.47)	0.242	(0.16)	2.022	(0.64)	1.62
Sand	308	0.053	(0.029)	0.375	(0.055)	0.05	(0.03)	-1.453	(0.25)	0.502	(0.18)	2.808	(0.59)	1.66
S Clay	11	0.117	(0.114)	0.385	(0.046)	0.20	(0.10)	-1.476	(0.57)	0.082	(0.06)	1.055	(0.89)	1.63
S C L	87	0.063	(0.078)	0.384	(0.061)	0.15	(0.08)	-1.676	(0.71)	0.124	(0.12)	1.120	(0.85)	1.63
S loam	476	0.039	(0.054)	0.387	(0.085)	0.10	(0.06)	-1.574	(0.56)	0.161	(0.11)	1.583	(0.66)	1.35
Silt	6	0.050	(0.041)	0.489	(0.078)	0.17	(0.04)	-2.182	(0.30)	0.225	(0.13)	1.641	(0.27)	1.38
Si Clay	28	0.111	(0.119)	0.481	(0.080)	0.22	(0.11)	-1.790	(0.64)	0.121	(0.10)	0.983	(0.57)	1.37
Si C L	172	0.090	(0.082)	0.482	(0.086)	0.20	(0.08)	-2.076	(0.59)	0.182	(0.13)	1.046	(0.76)	1.49
Si Loam	330	0.065	(0.073)	0.439	(0.093)	0.18	(0.07)	-2.296	(0.57)	0.221	(0.14)	1.261	(0.74)	1.62

Values from the ROSETTA database were statistically analysed, and value ranges were evaluated for different soil types. Probability density functions (PDF) were fitted to the analysed data sets using the software package Crystal Ball (Decisioneering 2001). The texture classes were grouped to sand and loamy sand (Group 1) and to clays, loams and silt (Group 2, corresponding to the 10 USDA textural classes remaining). These groups of soil types comprise characteristic ranges of values. This especially applies for $\theta_{w,m}$ and K_S, and also for *N* (Fig. C2). Values of α, ρ_b, θ_r and θ_s vary over the whole spectrum of textural classes, but nevertheless Group 1 (sand and loamy sand) reveals upper values for α and ρ_b and lower ranges for θ_r and θ_S.
Results of the database analysis were compared with the class average values given in Tab. C1. Adjustments were made to obtain a dataset that represents soil properties specific to soil texture classes and in addition contain information on the statistical distribution that is typically found. Results are summarised in Tab. C2.

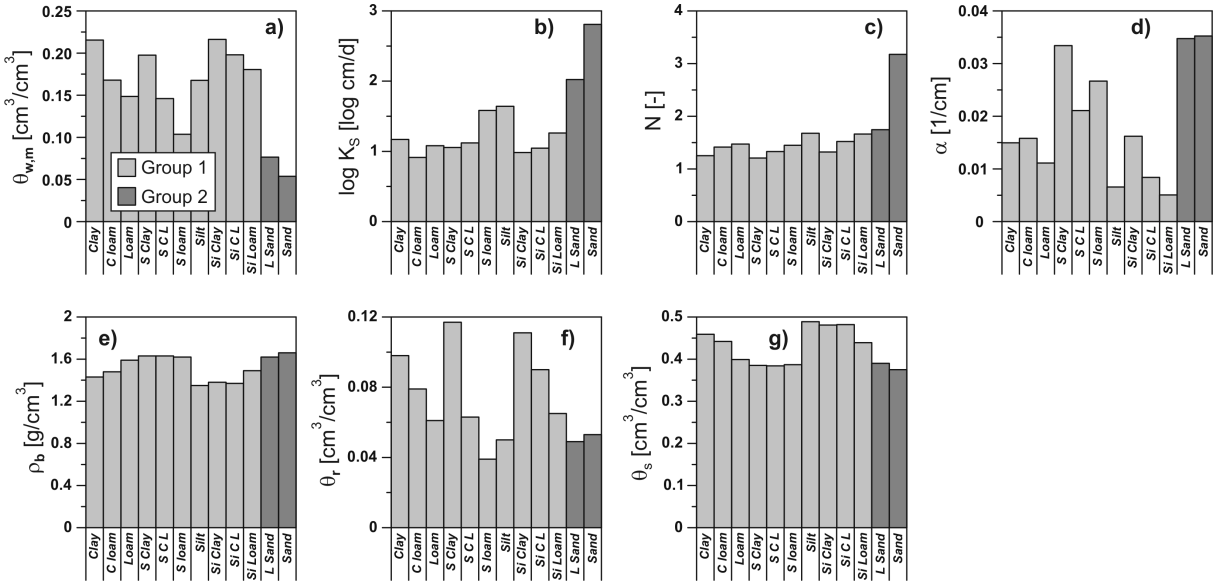


Fig. C2: *Average soil property values specific to groups of soil textural classes (according to Tab. C1). a): calculated mean water saturation, b): saturated hydraulic conductivity, c) and d): van Genuchten N and α, e): soil bulk density, f) and g): residual and saturated water content.*

Beside the methodology described above (see Eq. C1 and C2), water saturation can also be estimated as a function of the infiltration rate, following the unit gradient approach. Accordingly, Darcy's equation can be written as:

$$q_W = k_r \cdot K_S \qquad \text{(C3)}$$

q_W: infiltration rate [cm/d]
K_S: saturated hydraulic conductivity [cm/d]
k_r: relative permeability [-]

The relative permeability k_r is a function of moisture content θ_w, residual water content θ_r and the pore size distribution parameter γ(Brooks and Corey 1964):

$$k_r = \left[\frac{\theta_w - \theta_r}{\theta_w - \theta_r}\right]^{\gamma} \qquad \text{(C4)}$$

The pore size distribution parameter γ[-] can be estimated from the van Genuchten parameter N as follows (Lenhard et al. 1989):

$$\gamma = 3 + \frac{2}{(N-1)\cdot\left(1 - 0.5^{\left(\frac{N}{N-1}\right)}\right)} \qquad \text{(C5)}$$

Solving Eq. (C4) for θ_W and inserting k_r from Eq. (C3) yields an estimate of water saturation that depends on infiltration. Respective values are indicated in Tab. C2 for Group 1 and 2.

Tab. C2: *Fitted distributions and statistical parameters for soil properties, specific to Group 1 and 2. a: mode, b: scale. θ_w: moisture content as a function of infiltration rate; Extr. value: extreme value, Min.: minimum, Max.: maximum, St.dev.: standard deviation, other abbreviations according to Tab. C1.*

	Group 1 (sand, loamy sand)					Group 2 (clays, loams, silt)				
	Distribution	**Mean**	**St.dev.**	**Min.**	**Max.**	**Distribution**	**Mean**	**St.dev.**	**Min.**	**Max.**
ρ_b [g/cm^3]	Lognormal	1.64	0.138	1.13	1.965	Lognormal	1.497	0.313	0.459	1.97
θ_r [cm^3/cm^3]	Lognormal	0.051	0.0233	0.0251	0.280	Lognormal	0.0773	0.0419	0.0150	0.359
θ_s [cm^3/cm^3]	Lognormal	0.383	0.0391	0.261	0.508	Lognormal	0.435	0.0757	0.268	0.716
α [1/cm]	Lognormal	0.0350	6.67 x 10^{-3}	0.0264	0.0649	Lognormal	0.0159	6.08 x 10^{-3}	0.0121	0.131
K_s [cm/d]	Lognormal	373.94	401.94	9.560	1918.6	Lognormal	18.05	40.64	0.688	296.19
$\theta_{w,m}$ [cm^3/cm^3]	Lognormal	0.065	0.035	0.016	0.26	Lognormal	0.174	0.0663	0.0176	0.472
θ_w [cm^3/cm^3]	Lognormal	0.128	0.026	0.064	0.27	Lognormal	0.281	0.066	0.10	0.69
N [-]	Uniform			1.746	3.177	Extr. value	(a) 1.431	(b) 0.237	1.121	5.193

C.2 Organic carbon content in soil

The fraction of soil organic carbon f_{OC} varies significantly between and also within soil textural classes, as function of geological background and geochemical conditions, climate and vegetation (Scheffer and Schachtschabel 1998). Figure C3 gives an overview on typical f_{OC}-percentages for a variety of soil units, at depths below the upper soil horizon. The values were taken from a soil mapping survey performed over the total area of Germany (BÜK 1000), where 72 representative soil profiles (LBE) are defined. In this survey, horizons are specified for a) upper soil unit (agricultural use, high density of roots; depth < 30 cm or < 10 cm, depending on soil use), b) lower soil unit (30 cm/ 10 cm < depth < 120 cm), c) subsurface unit (depth > 120 cm). Based on these 72 profiles, 16 relevant soil units were extracted (Henzler et al. 2006). This classification is based on geological aspects and soil characteristics of lower soils and subsurface. The units of lower soil and subsurface were summarised when appropriate, i.e. for all soils covering loose sediments and for deeply weathered soils covering clay rocks, sandy and granular rocks. Upper soil units were not considered. Data from different LBE profiles and soil horizons were averaged considering the frequency of LBE profiles and the thickness of the profile horizons. The resulting 16 profiles are assumed to be representative for approximately 90% of the area of Germany (not considered are the soil units of marshes, moors and strongly anthropogenic influenced soils in cities and abandoned mining areas).

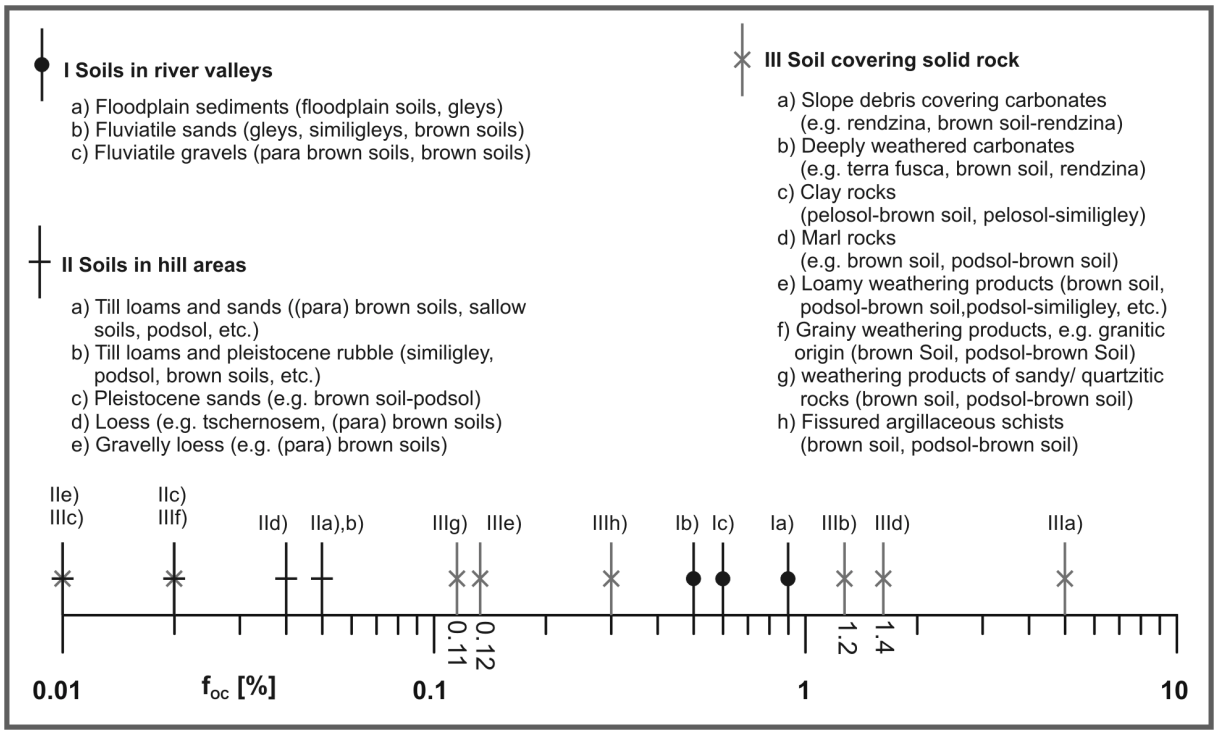


***Fig. C3**: Soil organic carbon content representative for 16 lower soil units in Germany, based on data from BÜK 1000 (average values, depths < 10 cm and < 30 cm).*

C.3 Aquifer parameters

Few studies are available that report ranges and statistical characteristics of effective hydraulic conductivity and organic carbon content in aquifers. Also, data on the variation of hydraulic gradients *i* and the effective porosities n_e can rarely be found in literature. Tab. C3 summarise results of two studies in Germany, Tab. C4 indicates ranges of f_{OC} found in Canadian, US and UK aquifers.

***Tab. C3**: Fraction of organic carbon f_{OC}, effective hydraulic conductivity K_f and hydraulic gradient i. Data from two sites in Germany, a: Site Buchholz/ Nordheide (Boorboor 2004), b: Site Testfeld Süd (Herfort 2000). Not det.: not determined, #: numerically modelled values, based on drainage experiments. Loc, Sc, Sh: Weibull parameters (Loc: location, Sc: Scale, Sh: Shape), other abbreviations according to Tab. C1.*

	Distribution	Min.	Max.	Mean or Loc	St.dev. or Sc, Sh	Site
f_{oc} [%]	Lognormal	0.01	0.39	0.10	0.19	(a)
i [%]	Weibull	0.125	0.157	Loc 0.0364	Sc 0.111 Sh 15	(a)
K_f [cm/d]	Lognormal	1115	8813	3655	2696	(a)
K_f [cm/d]	Not det.			136.5	234.3	(b)
n_e [%]	Not det.			21		(a)
n_e [%]	Not det.	6	25	13.6	4.5	(b) #

***Tab. C4**: Fraction of organic carbon in aquifer material: value ranges reported for Canadian, US and UK aquifers (Steventon-Barnes 2001).*

Aquifer	Aquifer type	f_{oc} [%]
Borden, Ontario (Can)	Medium to fine sand	0.02-0.1
Gloucester, Ontario (Can)	Silts, sands, gravels	0.0-0.06
Moffat Base, California (US)	Coarse gravel	0.11
Otis Base, Mass'ts (US)	Sand & gravel	0.0-0.75
Coventry (UK)	Carb. sandstone	0.08
Liverpool (UK)	Triassic sandsone	0.01-0.04
Chalk (UK)	Chalk	0.05-0.2
Triassic Sandstone (UK)	Triassic sandsone	0.01-0.15
Jurassic Limestone (UK)	Jurassic limestone	0.2-2

The effective porosity n_e is defined as the porosity available for fluid flow (e.g. Fetter 1994). Figure C4a shows the relation between total porosity, drainable porosity and specific retention reported by Eckis (1934) for quaternary fluviatile sediments in the coastal plain of southern California. Similar results are reported by Davis and de Wiest (1966). In Fig. C4b, the portion of sand, silt and clay in natural grain compositions is plotted against drainable porosity (according to Johnson 1967).
Drainable porosity or specific yield is the ratio of the volume of water that drains from a saturated rock owing to the attraction of gravity to the total volume of rock (Langguth and Voigt 1980). Values of drainable porosity obtained by drainage experiments can be regarded as the lower limit of effective porosity (e.g. Herfort 2000). Castany (1967) reports porosity components as a function of grain size (Fig. C5).

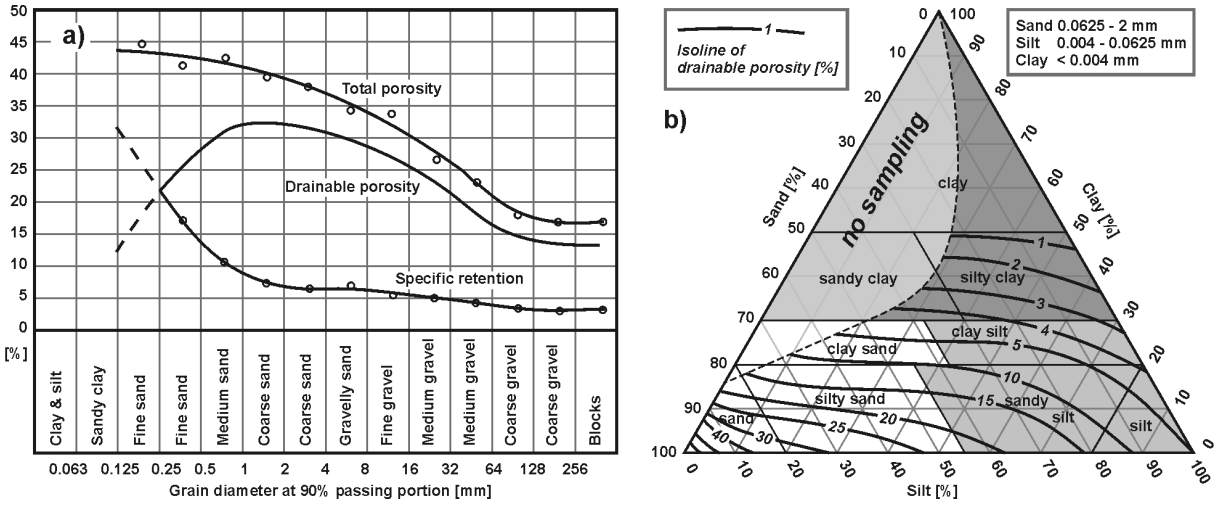


***Fig. C4**: a) Total porosity, drainable porosity and specific retention (Eckis 1934), b) drainable porosity of clastic sediments as a function of grain composition (according to Klein 1954, cited by Johnson 1967). a) and b) are cited by Langguth and Voigt (1980).*

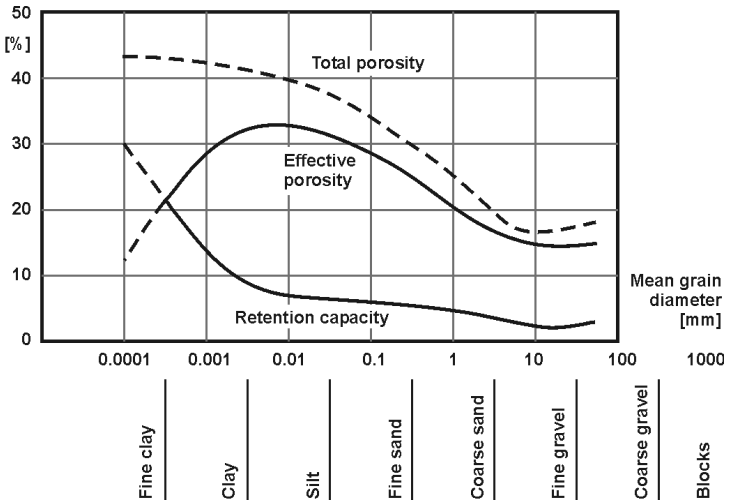


***Fig. C5**: Porosity components as a function of grain size (according to de Marsily 1986, following Castany 1967).*

Appendix D

Contaminant concentrations – Deterministic results for Group II

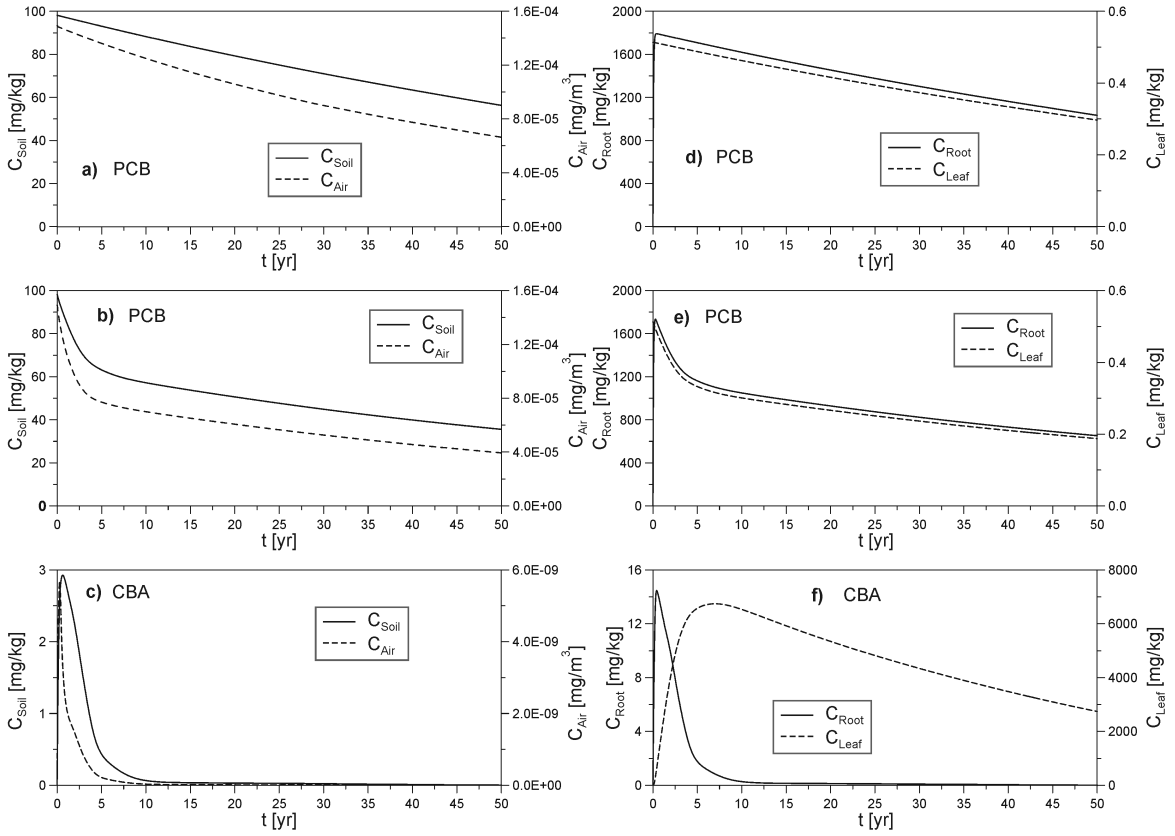


Fig. D1: *Compound concentrations, Group II. a) to c): soil and air; d) to f): root and leaf; a), d): PCB for conditions without biodegradation; b), e): PCB considering biodegradation; c), f): CBA.*

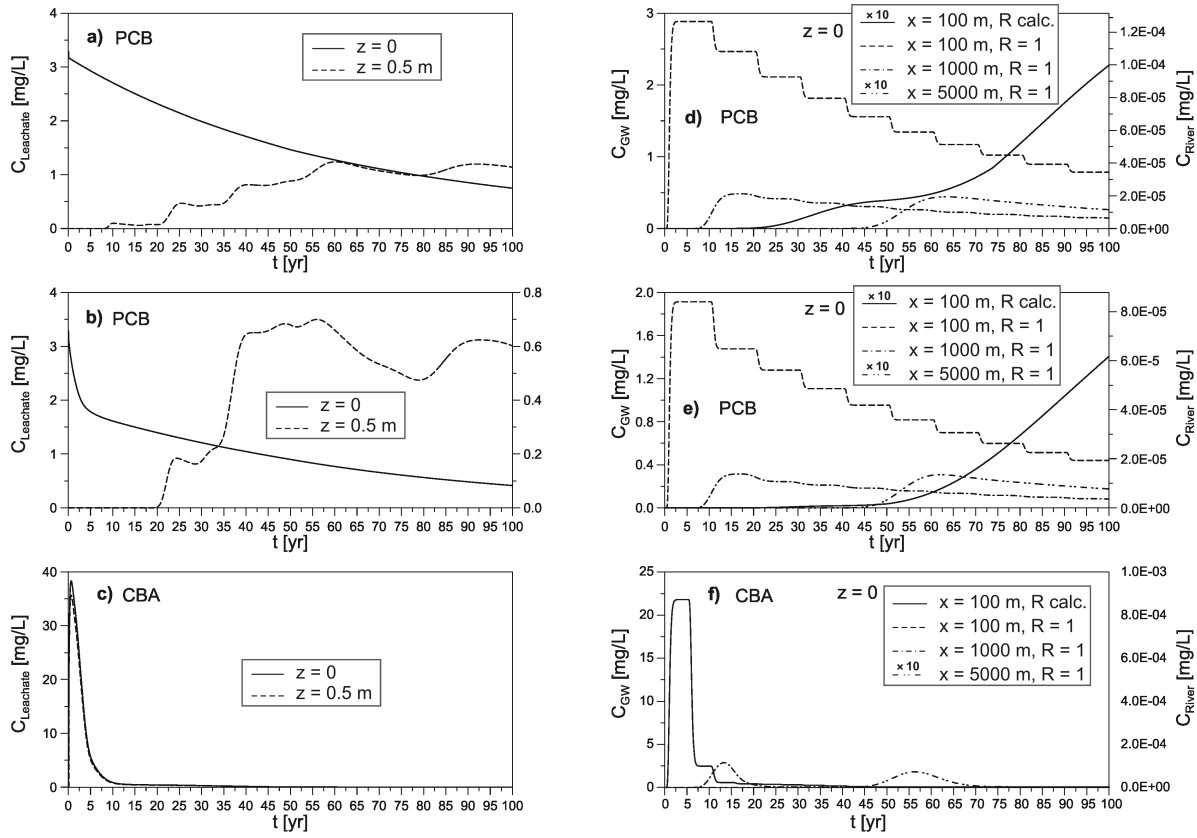


Fig. D2: *Compound concentrations, Group II. a) to c): leachate at the source bottom (z = 0) and beneath (z = 0.5 m); d) to f): groundwater and river water (referring to z = 0); a), d): PCB for conditions without biodegradation; b), e): PCB considering biodegradation; c), f): CBA; x: downstream distance; R: retardation coefficient; calc.: calculated; x 10: curves are 10 fold exaggerated.*

Appendix E

Contaminant concentrations – Probabilistic results and comparison to best estimate values

E1 Group I

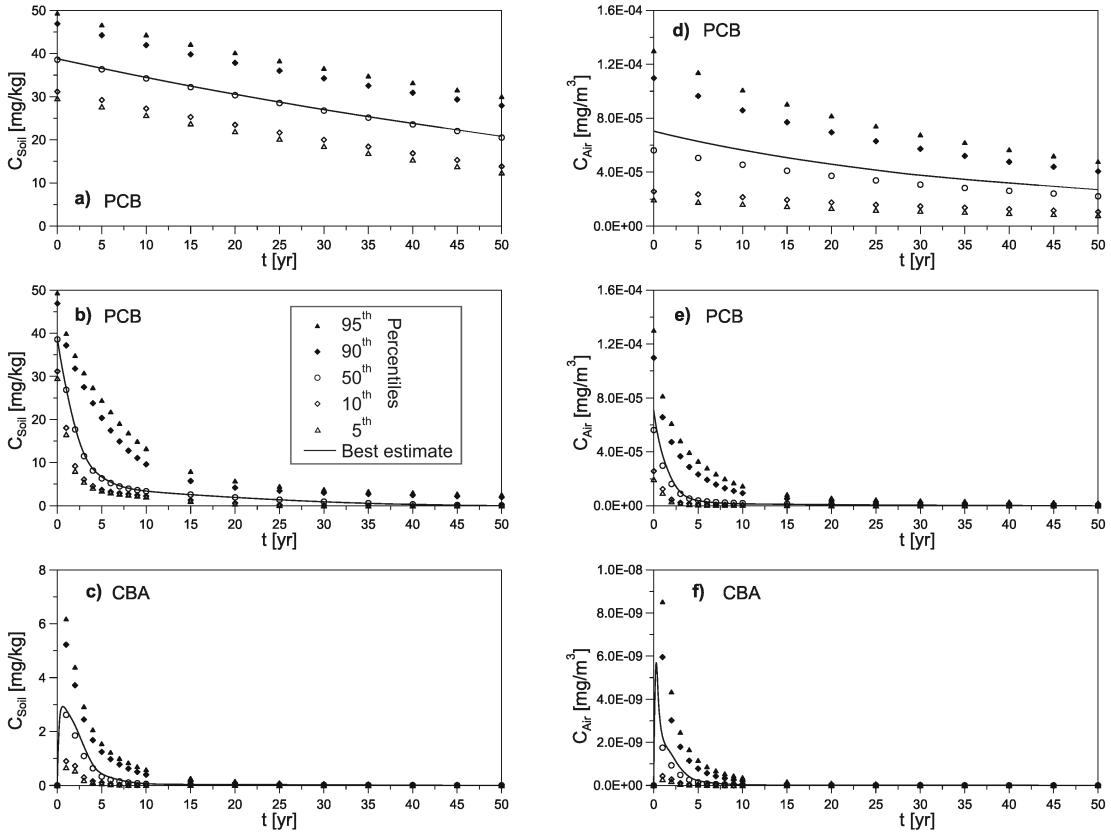


Fig. E1: *PCB concentrations (Group I) for conditions without biodegradation (a and d) and considering biodegradation (b and e), CBA concentrations (c and f); a) to c):* ***soil****, d) to f):* ***air****.*

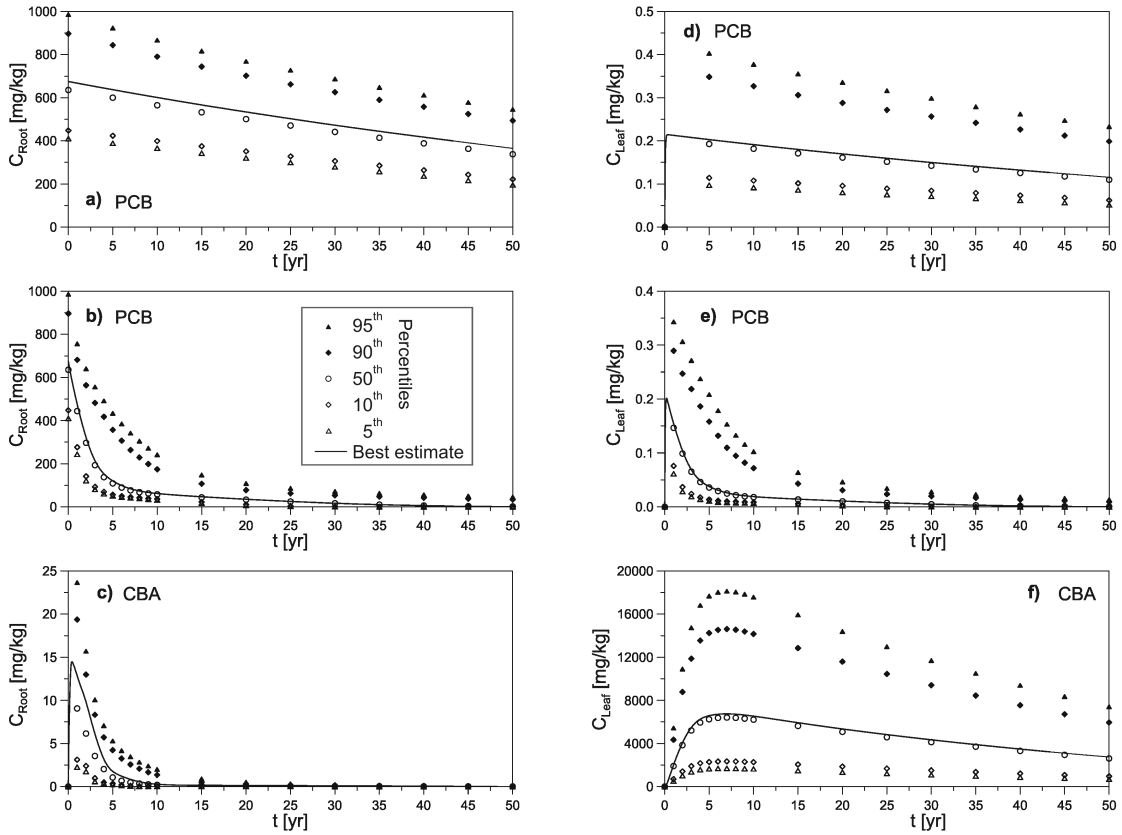


Fig. E2: *PCB concentrations (Group I) for conditions without biodegradation (a and d) and considering biodegradation (b and e), CBA concentrations (c and f); a) to c):* ***root****; d) to f):* ***leaf****.*

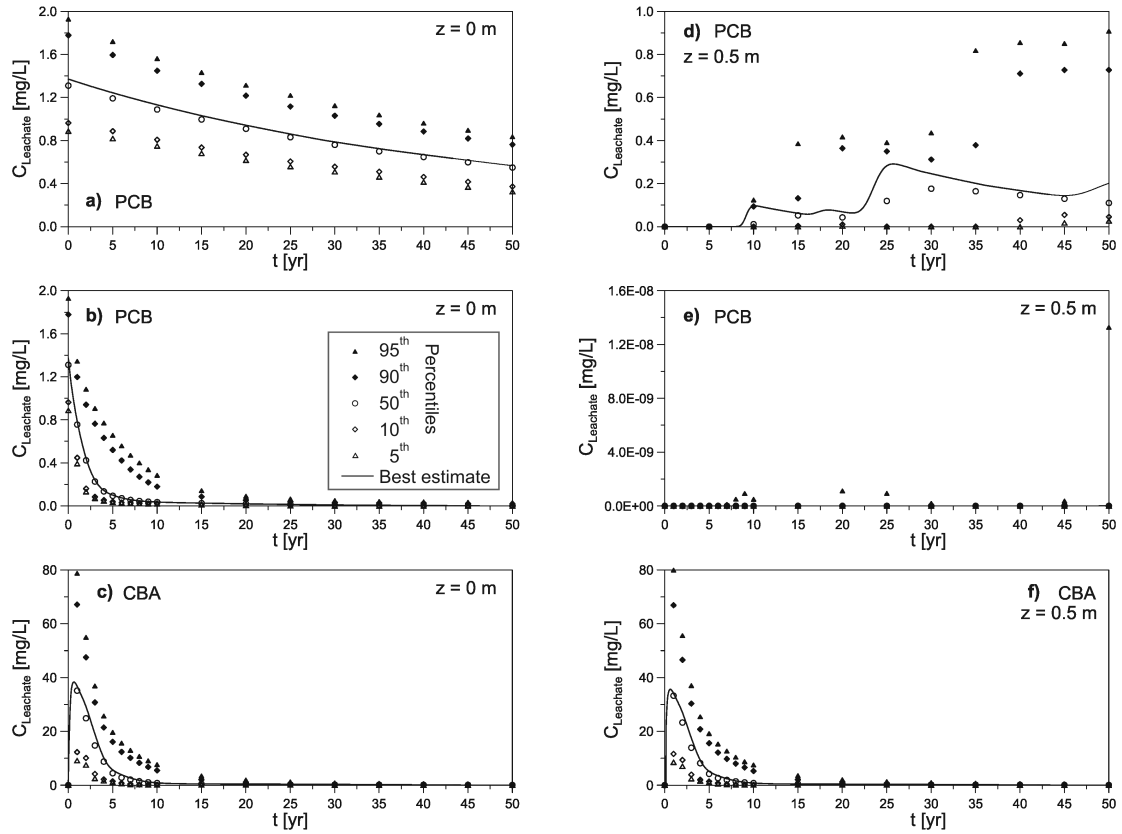


Fig. E3: Leachate *concentrations (Group I). a) to c): directly below the source bottom (depth z = 0 m); d) to f): mean depth z = 0.5 m; PCB without biodegradation (a and d) and considering biodegradation (b and e); CBA (c and f).*

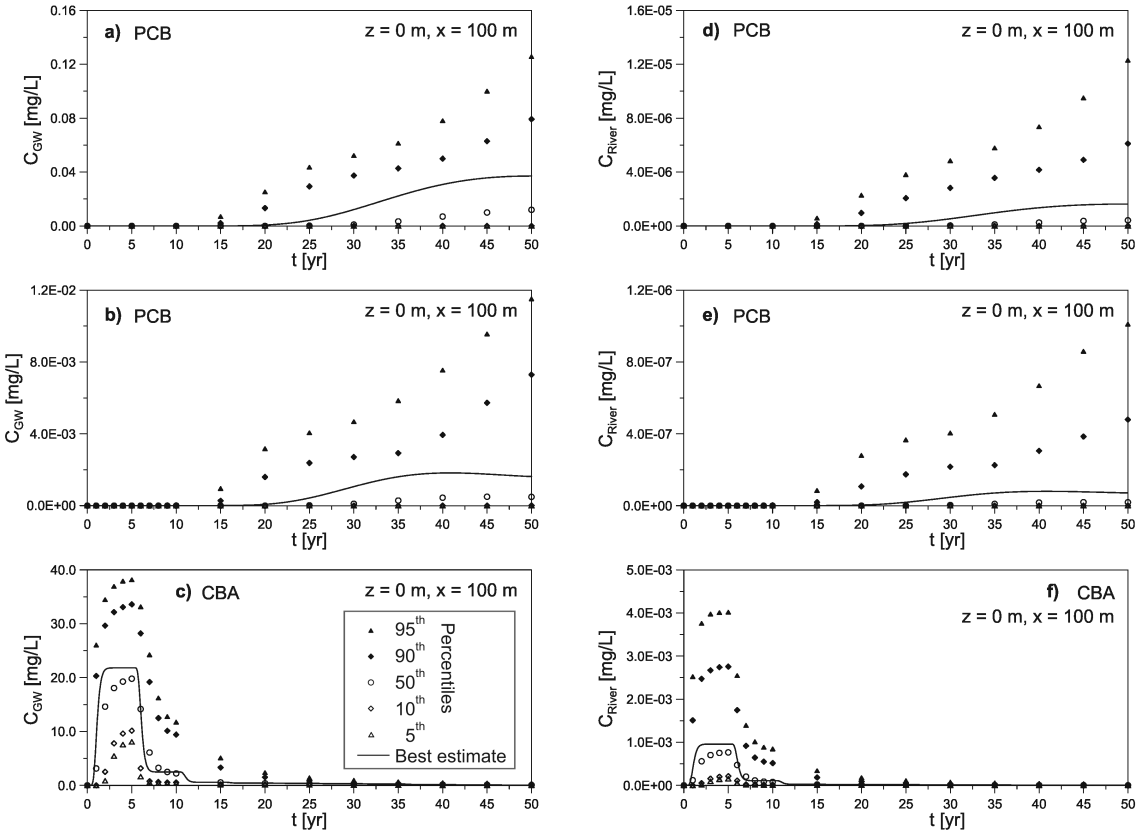


Fig. E4: Groundwater *concentrations (Group I; receptor point directly below the source and 100 m downstream) and mixing with surface water (**river**): PCB without biodegradation (a and d) and considering biodegradation (b and e); CBA (c and f).*

E2 Group II

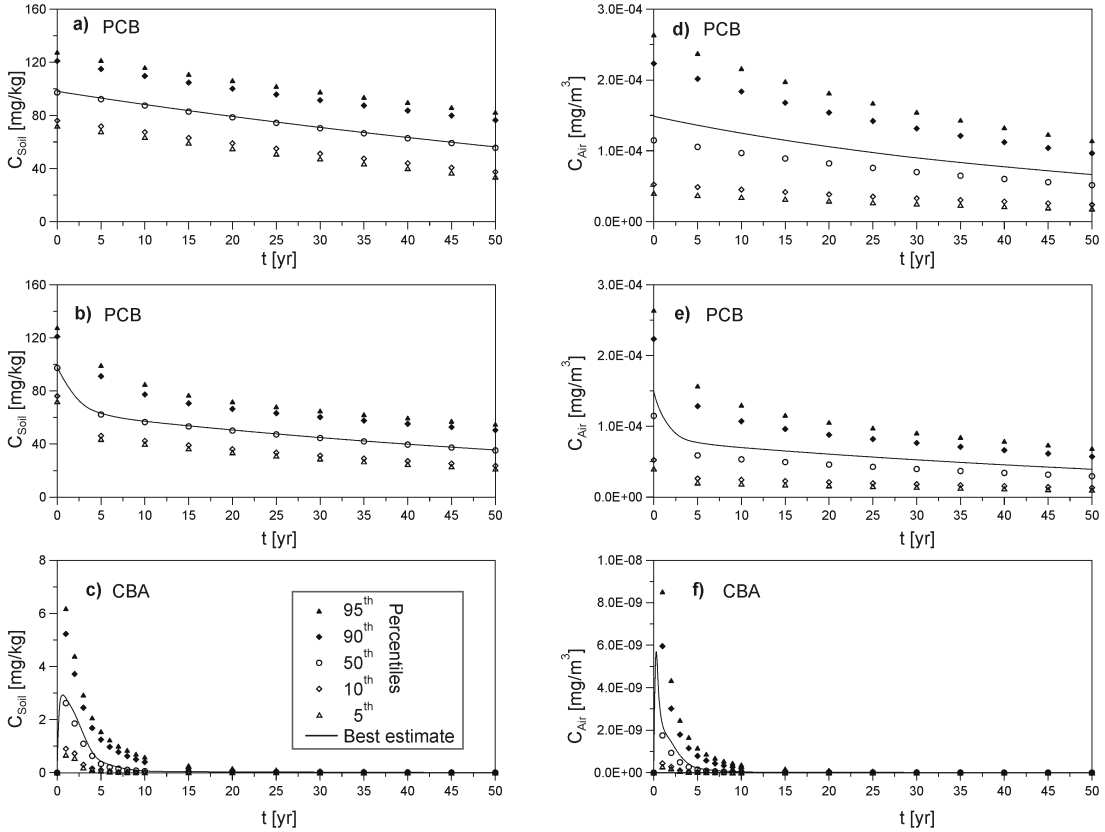


***Fig. E5: Soil** (a to c) and **air** (d to f) concentrations (Group II). a), d): PCB without biodegradation; b), e): PCB considering biodegradation; c), f): CBA.*

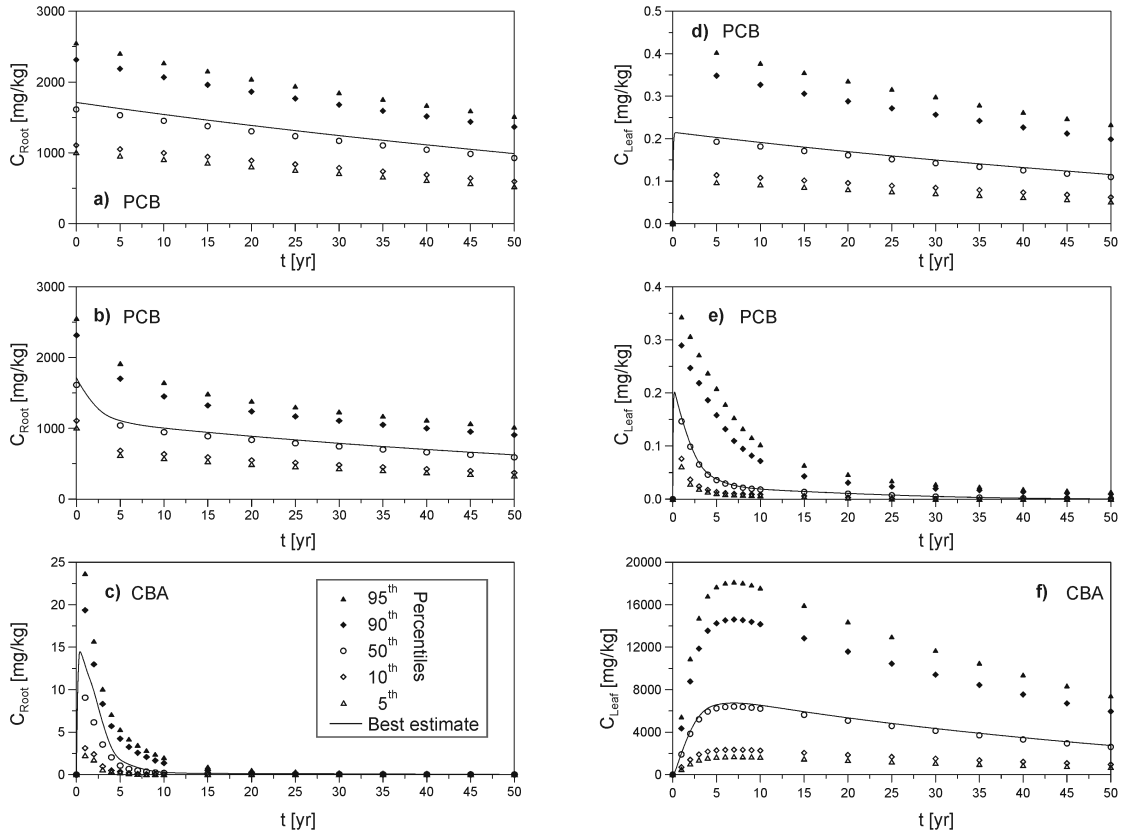


***Fig. E6: Root** (a to c) and **leaf** (d to f) concentrations (Group II). a), d): PCB without biodegradation; b), e): PCB considering biodegradation; c), f): CBA.*

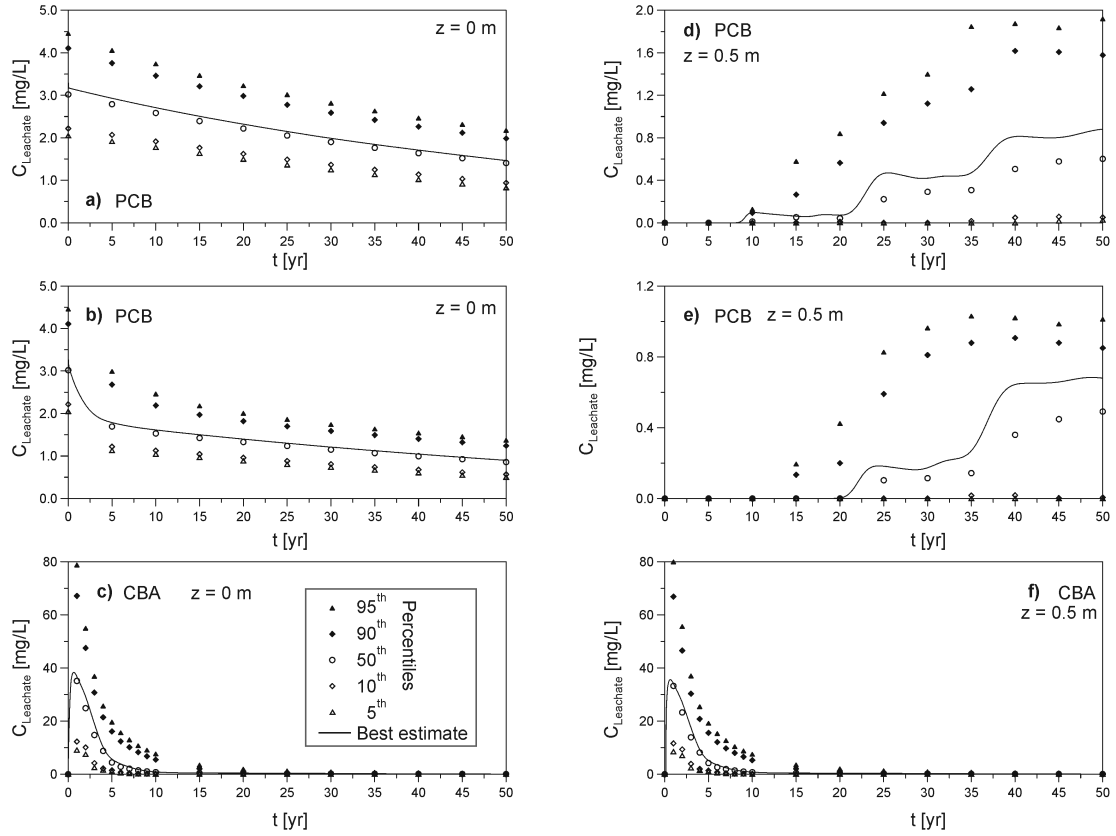


Fig. E7: Leachate *concentrations (Group II). a) to c): at the source bottom, d) to f): at a mean depth of z = 0.5 m; a), d): PCB without biodegradation; b), e): PCB considering biodegradation; c), f): CBA.*

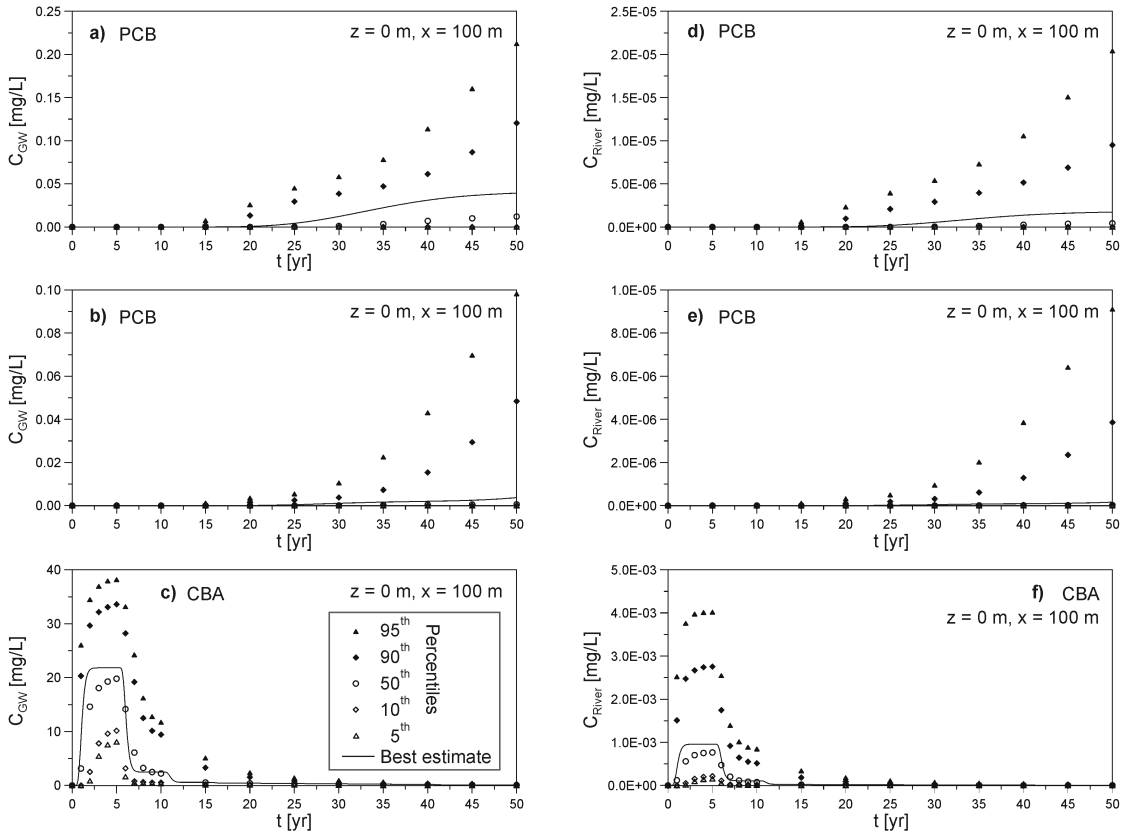


Fig. E8: Groundwater *(a to c) and* ***river*** *(d to f) concentrations (Group II), referring to z = 0 and receptor points at a distance of x = 100 m downstream of the source. a), d): PCB without biodegradation; b), e): PCB considering biodegradation; c), f): CBA.*

Appendix F

Risk evaluations – Supplemental data

F1 Non-carcinogenic effects

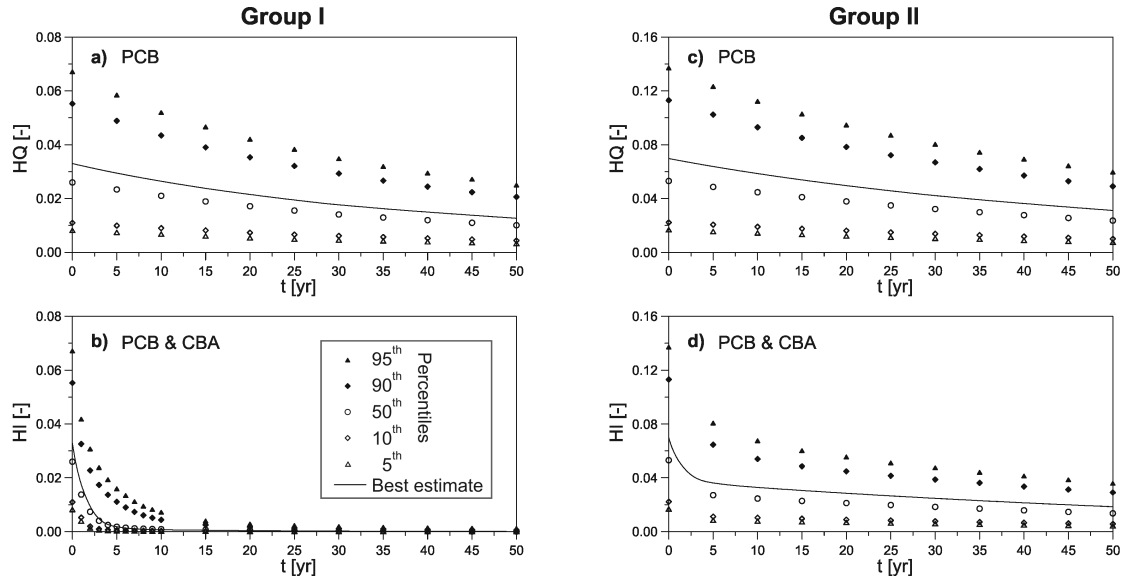


Fig. F1: *Non-carcinogenic effects from ambient air inhalation, sports activity scenario. a), b): Group I, c), d): Group II; a), c): hazard quotient (PCB, no biodegradation); b), d): hazard index (PCB and CBA, biodegradation).*

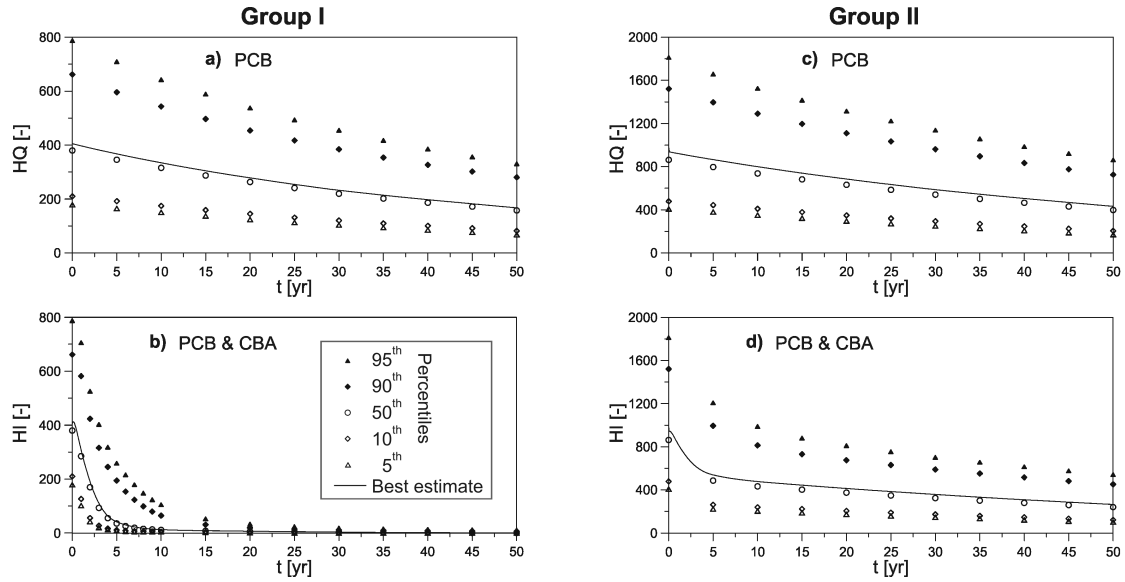


Fig. F2: *Non-carcinogenic effects from leachate ingestion (hypothetic domestic use as drinking water), receptor point at the source bottom. a), b): Group I; c), d): Group II; a), c): hazard quotient (PCB, no biodegradation); b), d): hazard index (PCB and CBA, biodegradation).*

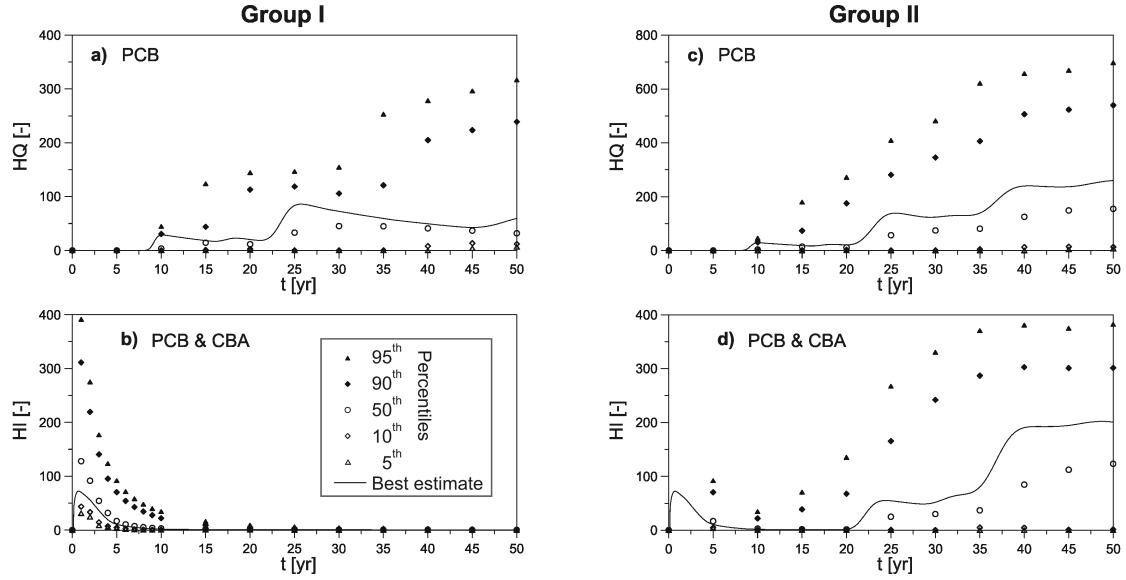


Fig. F3: *Non-carcinogenic effects from leachate ingestion (hypothetic domestic use as drinking water), receptor point at a depth z = 0.5 m beneath the source. a), b): Group I; c), d): Group II; a), c): hazard quotient (PCB, no biodegradation); b), d): hazard index (PCB and CBA, biodegradation).*

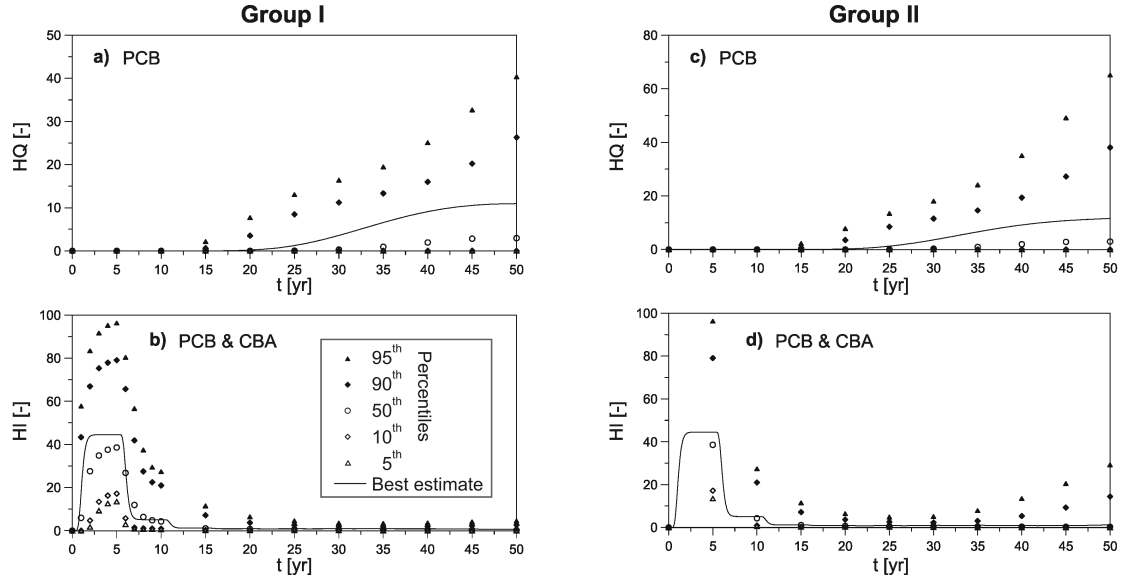


Fig. F4: *Non-carcinogenic effects from groundwater ingestion (domestic use as drinking water), groundwater well located 100 m downstream of the source. Groundwater level at the source bottom (z = 0); considering retardation in the aquifer; a), b): Group I; c), d): Group II; a), c): hazard quotient (PCB, no biodegradation); b), d): hazard index (PCB and CBA, biodegradation).*

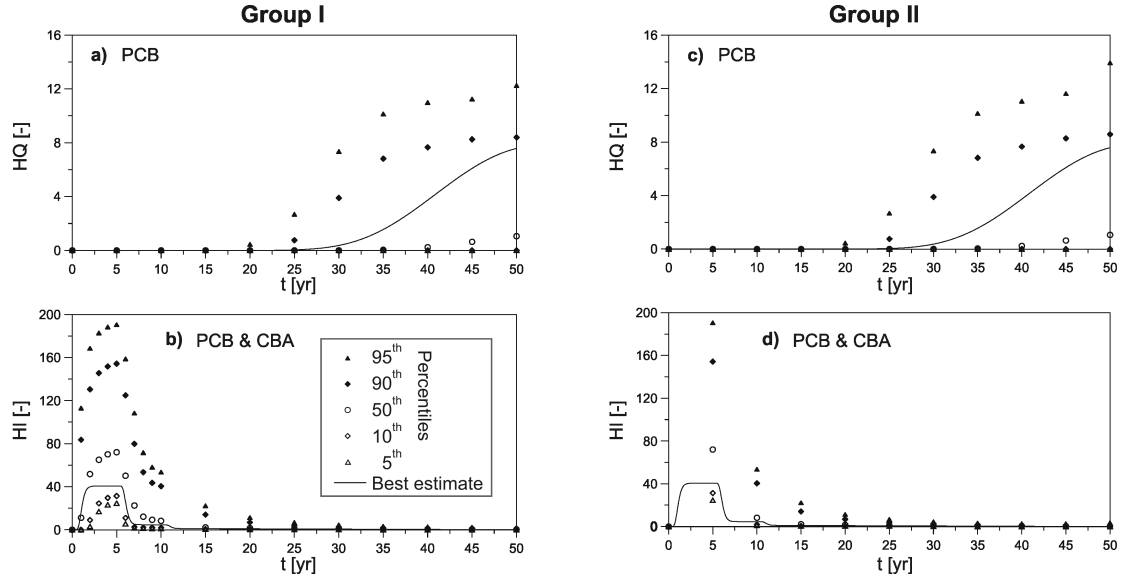


Fig. F5: *Non-carcinogenic effects from groundwater ingestion (domestic use as drinking water), groundwater well located 100 m downstream of the source. Groundwater level at a depth z = 0.5 m beneath the source; considering retardation in the aquifer; a), b): Group I; c), d): Group II; a), c): hazard quotient (PCB, no biodegradation); b), d): hazard index (PCB and CBA, biodegradation).*

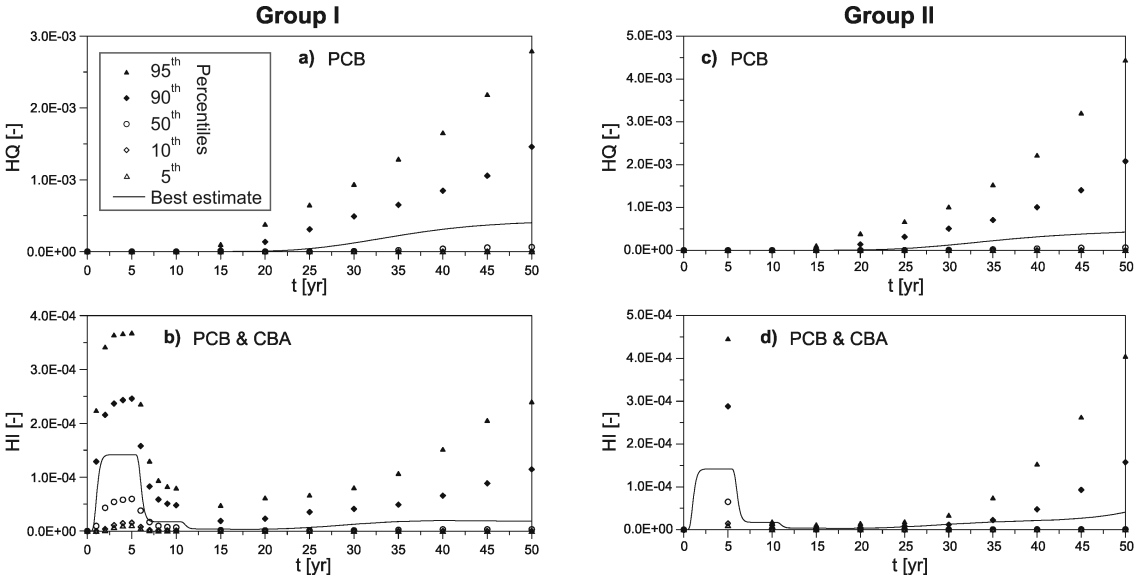


Fig. F6: *Non-carcinogenic effects from exposure to river water while swimming (river water mixing with groundwater). Based upon groundwater level GWL at the source bottom (z = 0); receptor point at x = 100 m downstream of the source; considering retardation in the aquifer; a), b): Group I; c), d): Group II; a), c): hazard quotient (PCB, no biodegradation); b), d): hazard index (PCB and CBA, biodegradation).*

F2 Carcinogenic effects

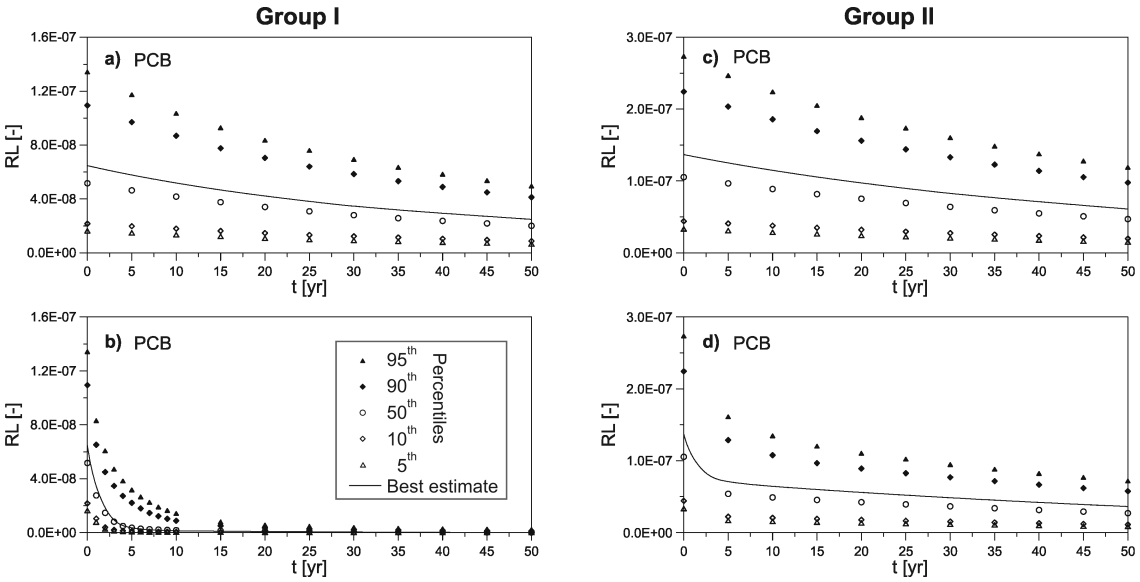


Fig. F7: *Carcinogenic effects from ambient air inhalation, sports activity scenario: cancer risk levels for PCB. a), b): Group I, c), d): Group II; a), c): no biodegradation; b), d): biodegradation.*

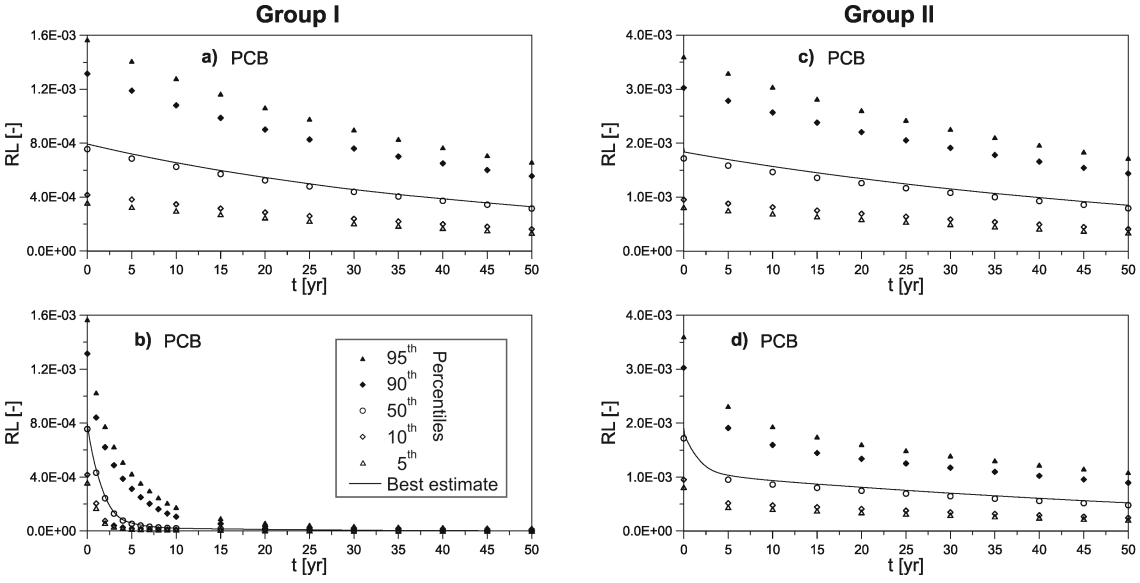


Fig. F8: *Carcinogenic effects from leachate ingestion (hypothetical domestic use as drinking water), receptor point at the source bottom. a), b): Group I; c), d): Group II; a), c): no biodegradation; b), d): biodegradation.*

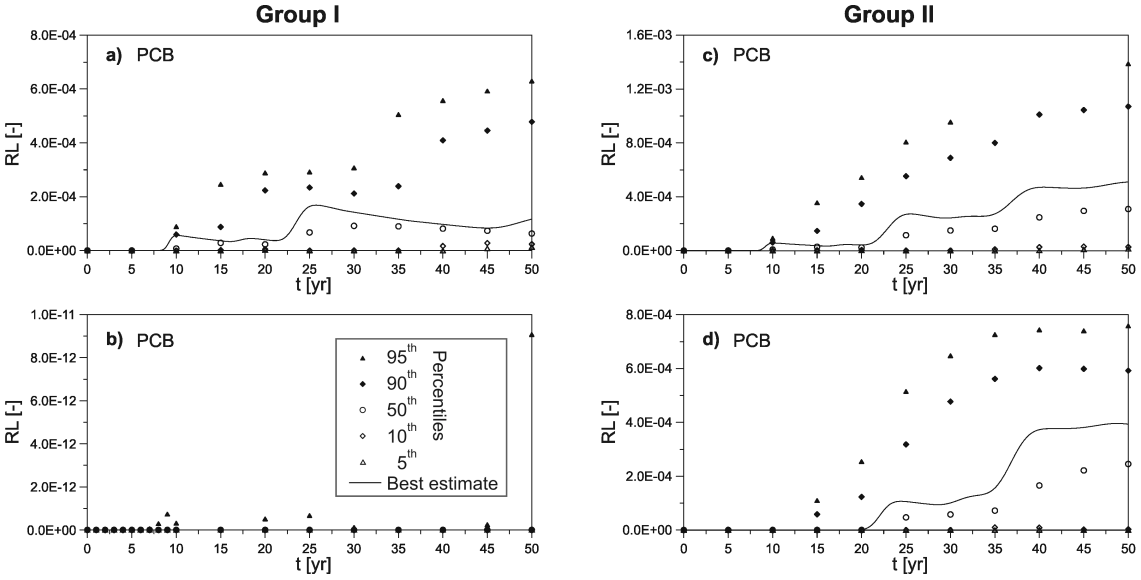


Fig. F9: *Carcinogenic effects from leachate ingestion (hypothetical domestic use as drinking water), receptor point at a depth z = 0.5 m beneath the source. a), b): Group I; c), d): Group II; a), c): no biodegradation; b), d): biodegradation.*

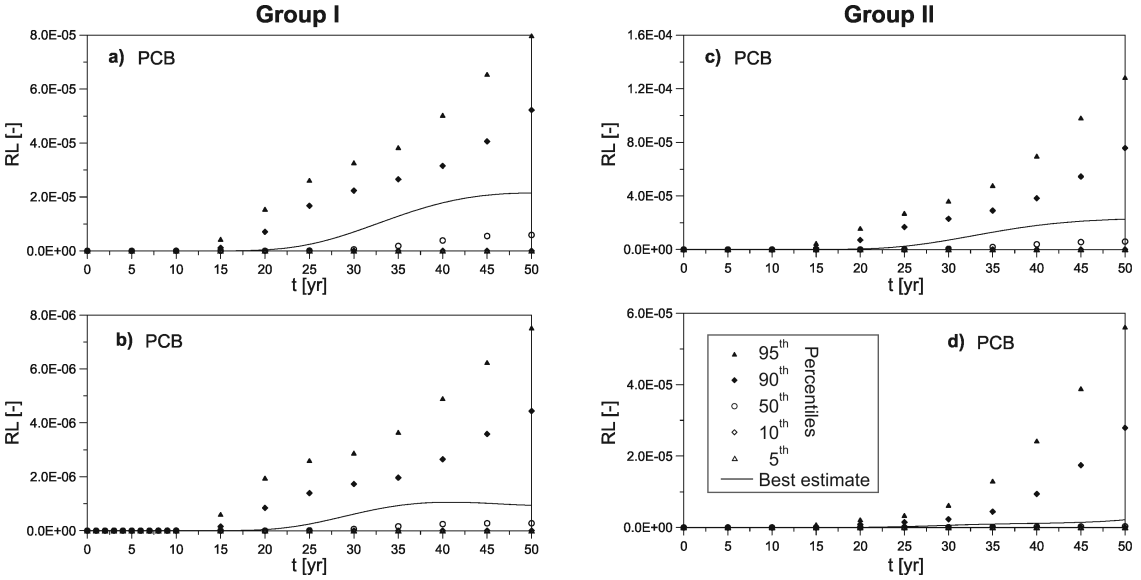


Fig. F10: *Carcinogenic effects from groundwater ingestion (domestic use as drinking water), groundwater well located 100 m downstream of the source. Groundwater level at the source bottom (z = 0); considering retardation in the aquifer; a), b): Group I; c), d): Group II; a), c): no biodegradation; b), d): biodegradation.*

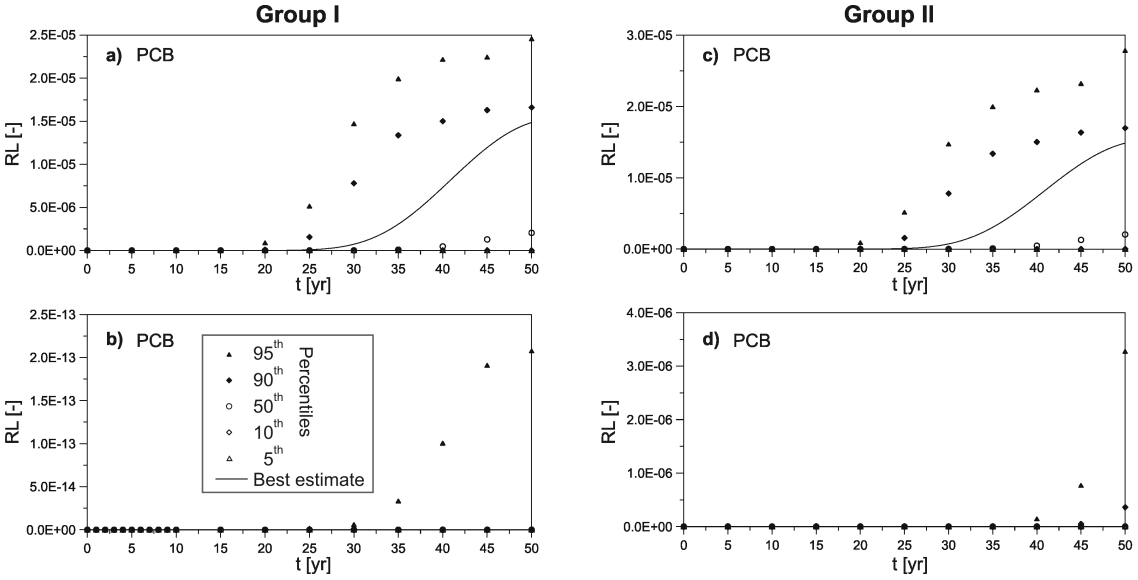


Fig. F11: *Carcinogenic effects from groundwater ingestion (domestic use as drinking water), groundwater well located 100 m downstream of the source. Groundwater level at a depth z = 0.5 m beneath the source; considering retardation in the aquifer; a), b): Group I; c), d): Group II; a), c): no biodegradation; b), d): biodegradation.*

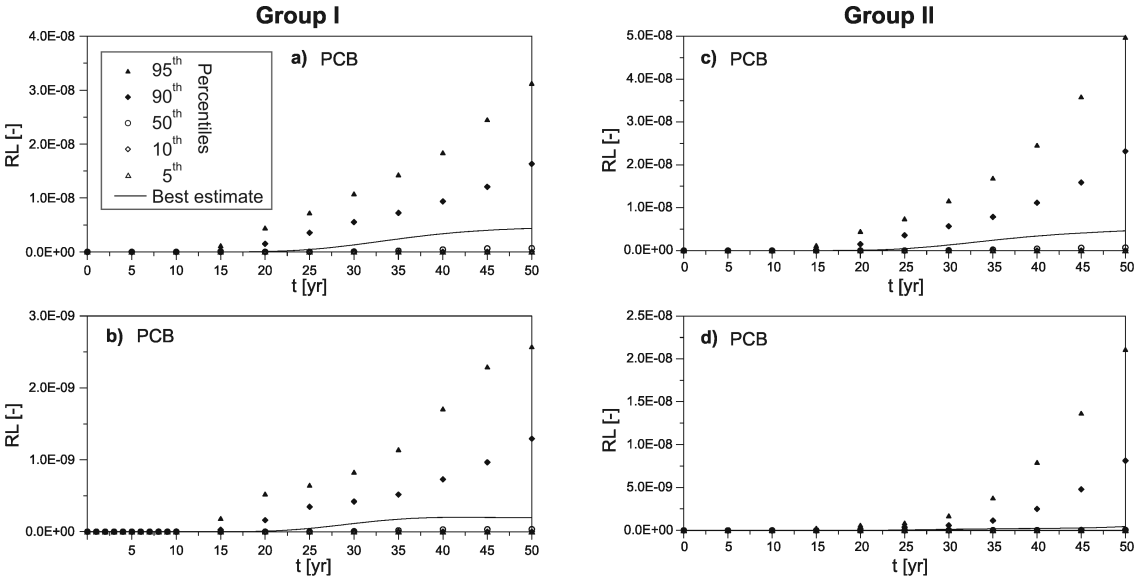


Fig. F12: *Carcinogenic effects from exposure to river water while swimming (river water mixing with groundwater). Based upon groundwater level at the source bottom (z = 0); receptor point at x = 100 m downstream of the source; considering retardation in the aquifer; a), b): Group I; c), d): Group II; a), c): hazard quotient (PCB, no biodegradation); b), d): hazard index (PCB and CBA, biodegradation).*

F3 Hazard to ecological receptors

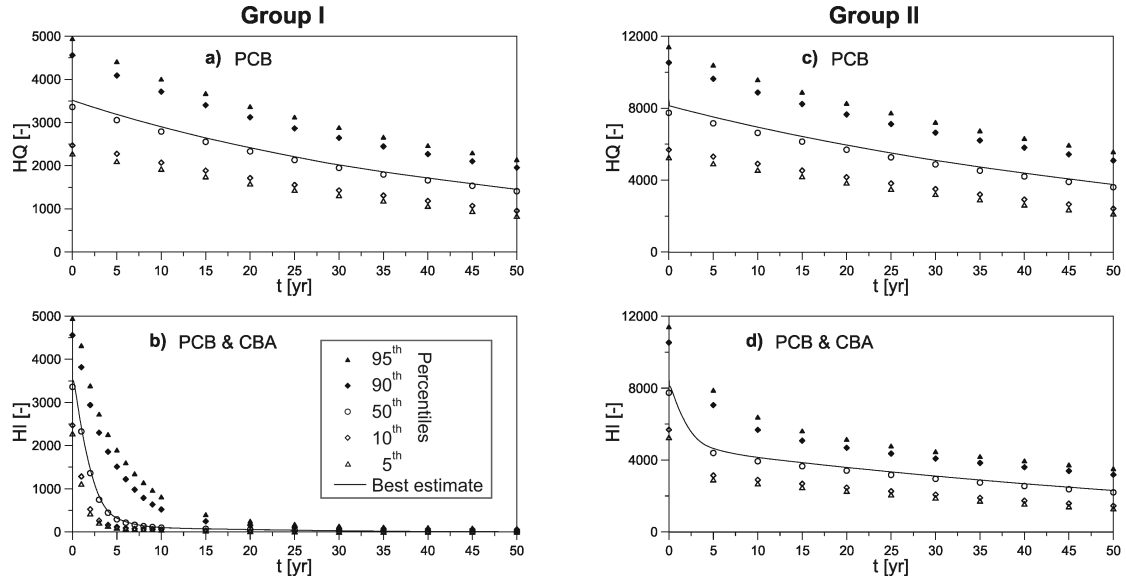


Fig. F13: *Hypothetical exposure of bluegill (Lepomis macrochirus) to contaminated leachate, receptor point at the source bottom; a), b): Group I; c), d): Group II; a), c): hazard quotient (PCB, no biodegradation); b), d): hazard index (PCB and CBA, biodegradation).*

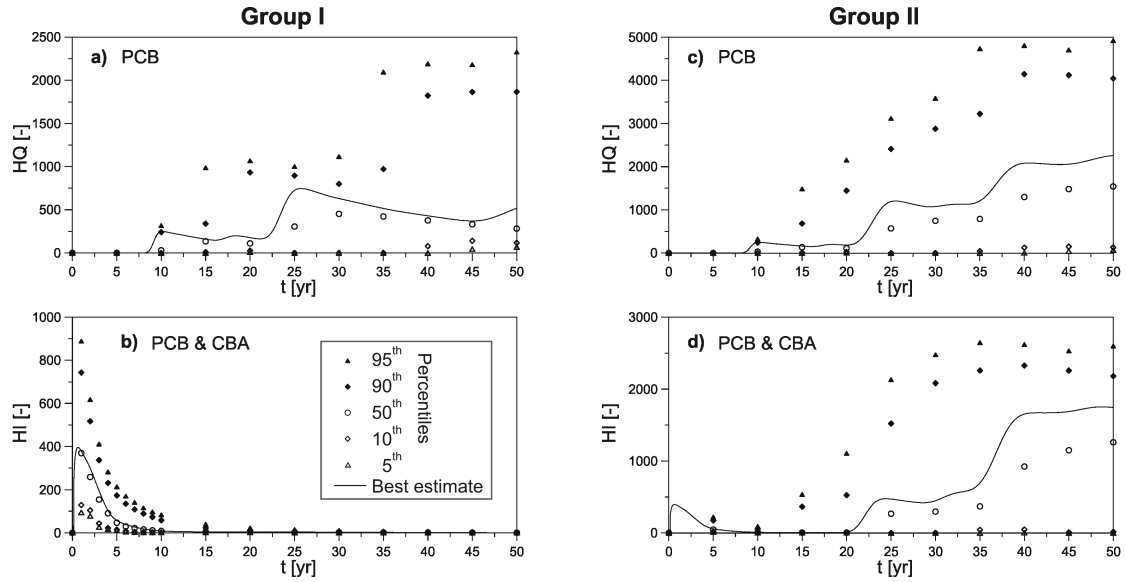


Fig. F14: *Hypothetical exposure of bluegill (Lepomis macrochirus) to contaminated leachate, receptor point at a depth z = 0.5 m beneath the source; a), b): Group I; c), d): Group II; a), c): hazard quotient (PCB, no biodegradation); b), d): hazard index (PCB and CBA, biodegradation).*

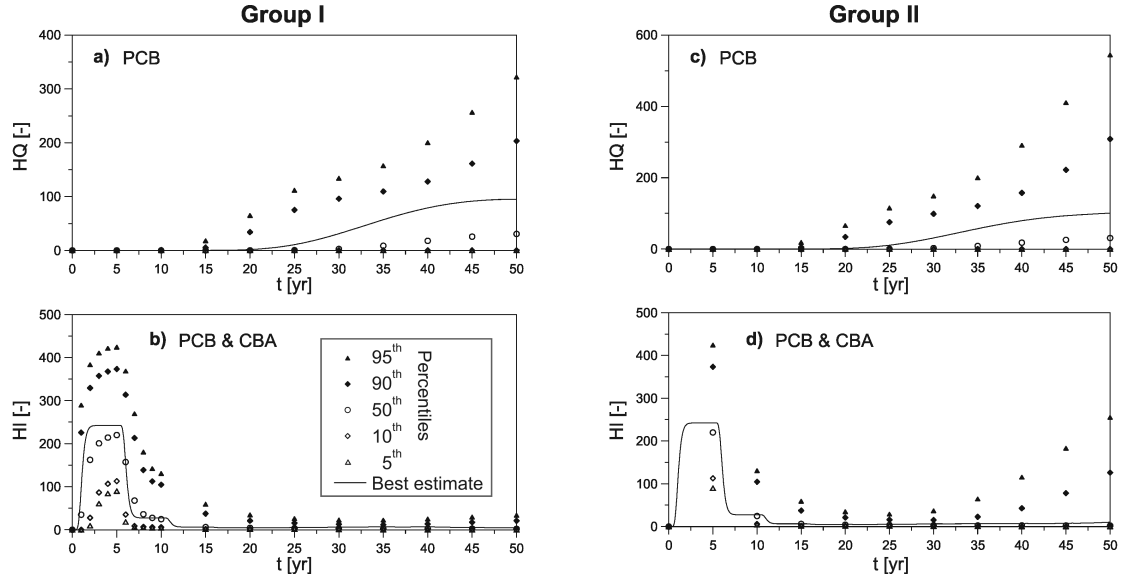


Fig. F15: *Hypothetical exposure of bluegill (Lepomis macrochirus) to contaminated groundwater. Groundwater level at the source bottom; receptor point at x = 100 m downstream of the source; considering retardation in the aquifer; a), b): Group I; c), d): Group II; a), c): hazard quotient (PCB, no biodegradation); b), d): hazard index (PCB and CBA, biodegradation).*

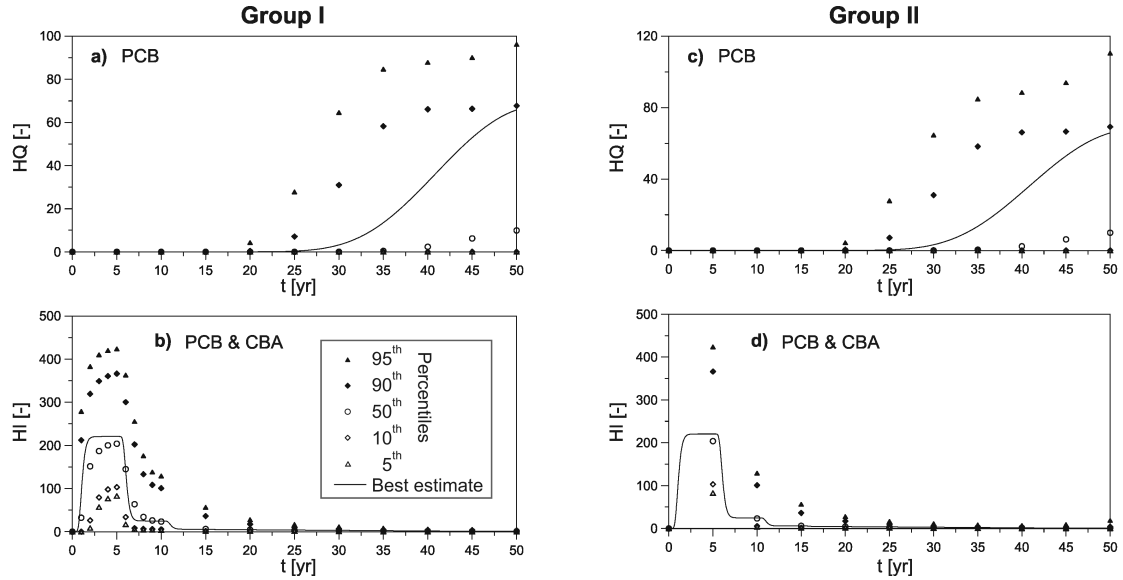


Fig. F16: *Hypothetical exposure of bluegill (Lepomis macrochirus) to contaminated groundwater. Groundwater level at a depth z = 0.5 m beneath the source; receptor point at x = 100 m downstream of the source; considering retardation in the aquifer; a), b): Group I; c), d): Group II; a), c): hazard quotient (PCB, no biodegradation); b), d): hazard index (PCB and CBA, biodegradation).*

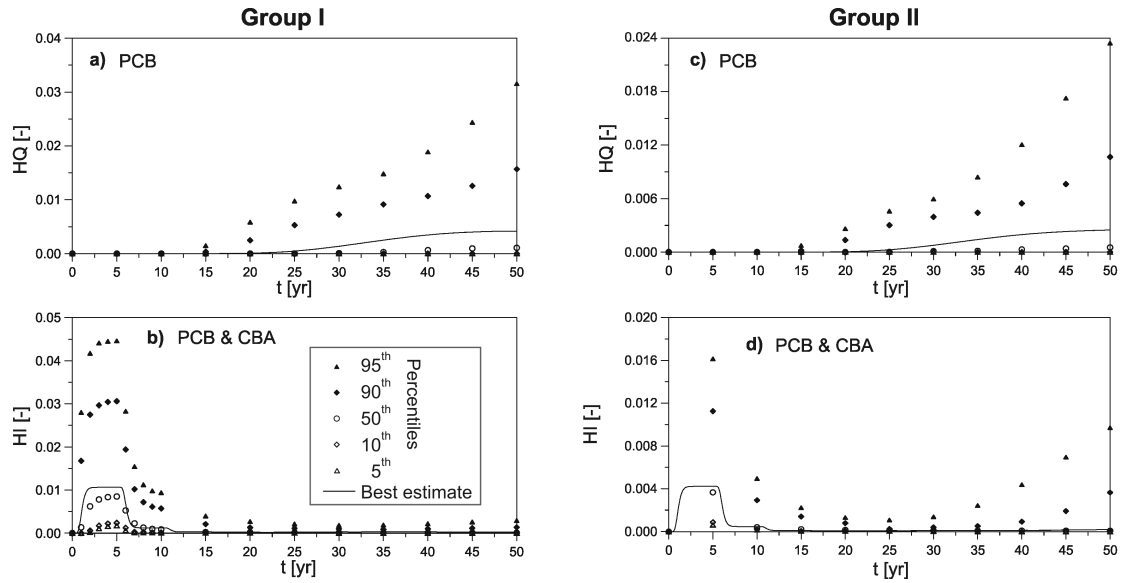


Fig. F17: *Exposure of bluegill (Lepomis macrochirus) to contaminated river water (river water mixing with groundwater). Based upon a groundwater level at the source bottom; receptor point at x = 100 m downstream of the source; considering retardation in the aquifer; a), b): Group I; c), d): Group II; a), c): hazard quotient (PCB, no biodegradation); b), d): hazard index (PCB and CBA, biodegradation).*

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