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Comparison of different methodologies for selecting PELMO input parameters for groundwater modelling of plant protection products including current EU guidance (SANCO/12117/2014 - final, 2014)

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Comparison of different methodologies for selecting PELMO input parameters for groundwater modelling of plant protection products including current EU guidance (SANC0/12117/2014 - final, 2014)

by

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Kurzbeschreibung

Im Rahmen des Zulassungsverfahrens von Pflanzenschutzmitteln in Deutschland wird das Versickerungsrisiko von Wirkstoffen und deren Abbauprodukten in das Grundwasser in der ersten Stufe auf Basis von Computerberechnungen mit dem Simulationsmodell FOCUS-PELMO unter Verwendung des FOCUS-Szenarios Hamburg ermittelt. Freilandlysimeterstudien, die nach der BBA-Richtlinie IV 4-3 durchgeführt wurden, werden i.d.R. als höherstufige Studien akzeptiert. Die in diesen Studien gemessenen Sickerwasserkonzentrationen von Wirkstoffen und deren Abbauprodukten können die Ergebnisse der Modellierungen überschreiben.

Ziel dieses Vorhabens war es, zu untersuchen, ob die Modellierungen hinreichend konservativ sind und die berechneten Grundwasserkonzentrationen höher sind als die unter Freilandbedingungen im Sickerwasser von Lysimetern gemessenen Konzentrationen. Zu diesem Zweck wurden drei verschiedene Ansätze zur Auswahl der Eingabeparameter für die Modellierungen geprüft. Es handelte sich um zwei EU-Ansätze (bisheriger Ansatz auf Basis des arithmetischen Mittels und der neuer Ansatz basierend auf dem geometrischen Mittel für den Modellierungsendpunkt Kfoc) und den nationalen Ansatz (Holdt et al. 2011).

Der Vergleich der Modellierungen untereinander zeigte, dass das deutsche Auswahlverfahren zu etwas konservativeren Ergebnissen führte als der EU-Ansatz basierend auf dem geometrischen Mittelwert für den Kfoc (DE: 82%, EU: 79% der Simulationen oberhalb der entsprechenden Konzentrationen im Sickerwasser der Lysimeter). Dieses Ergebnis war unabhängig von der Art der Substanz (Wirkstoff oder Abbauprodukt). Die Verwendung des arithmetischen Mittels (bisheriger EU-Ansatz) führte zu noch weniger Situationen, bei denen die Ergebnisse der PELMO-Simulationen oberhalb entsprechender Lysimeterergebnisse blieben (74%). Außerdem waren die Ergebnisse davon abhängig, ob Wirkstoffe (79%) oder Abbauprodukte (72%) untersucht wurden.

Für eine Analyse möglicher regulatorischer Auswirkungen wurden die drei Ansätze zur Auswahl der Eingabeparameter für die Modellierungen im Hinblick auf falsch-negative Ergebnisse (gemessene Konzentration ≥ 0,1 µg/L bzw. ≥ 10 µg/L und modellierte Konzentration < 0,1µg/L bzw. < 10 µg/L) und falsch-positive Ergebnisse (modellierte Konzentration ≥ 0,1 µg/L bzw. ≥ 10 µg/L und gemessene Konzentration < 0,1µg/L bzw. < 10 µg/L) untersucht.

Die Analyse der falsch-negativen Ergebnisse zeigte keine signifikanten Unterschiede. Unabhängig vom Verfahren fielen 3% der Wirkstoffe und 6% bis 7% der Abbauprodukte in diese Kategorie.

Ein Vergleich der falsch-positiven Ergebnisse, die regulatorisch die Forderung weiterer Studien nach sich ziehen können, zeigte Unterschiede zwischen Wirkstoffen und Metaboliten. Bei Auswahl der Eingabeparameter für die Modellierungen nach den beiden EU-Ansätzen wurden für Wirkstoffe zwei- bis dreimal weniger falsch-positive Ergebnisse ermittelt als bei Auswahl der Eingabeparameter entsprechend dem nationalen Ansatz. Für Abbauprodukte traten keine Unterschiede zwischen dem nationalen und dem neuen EU-Ansatz (geometrischer Mittelwert für den Kfoc) auf. Für beide Ansätze wurden vergleichbare Prozentwerte für falsch-positive Ergebnisse für diese Substanzgruppe ermittelt. Simulationsergebnisse basierend auf dem bisherigen EU-Verfahren (arithmetischer Mittelwert für den Kfoc) führten dagegen für Abbauprodukte zu einer geringeren Anzahl von falsch-positiven Ergebnissen.

Abstract

For registration of plant protection products in Germany the groundwater risk assessment at lower tier is based on modelling results using simulated leaching concentrations of the Hamburg scenario from the FOCUS PELMO model. Measured leachate concentrations for active compounds and transformation products from outdoor lysimeter studies are accepted as higher tier endpoints and could overwrite modelling results. The objective of this project was to determine, whether lower tier calculations are still more conservative than higher tier results from lysimeter studies. For this purpose three different methodologies for selecting input parameters for modelling were considered: two variations of the EU methodology (previous: Kfoc value based on the arithmetic mean and new: Kfoc value based on the geometric mean according to EFSA 2014) and the national input parameter selection procedure (Holdt et al. 2011).

Overall, the German methodology was found to be slightly more conservative than the EU methodology based on the geometric mean Kfoc value (DE: 82%, EU: 79% simulations above lysimeter results). The results did not depend on the type of substance (active compound, transformation product). In contrast, results based on the previous EU methodology using the arithmetic mean Kfoc value showed less situations where PELMO simulations were above respective lysimeter results (74%). Furthermore, results were dependent whether active compounds (79%) or transformation products (72%) were analysed. When evaluating the regulatory impact of the different methodologies for selecting input parameters no significant differences were found when focusing on false negative results (lysimeter showed a problem which PELMO could not determine): independent on the input parameter selection procedure 3% of the active compounds and 6% to 7% of the transformation products belonged to that class. Comparing the three methodologies with regard to false positive comparisons (regulatory necessity for additional higher tier studies) the results were dependent whether active compounds or transformation products were simulated. For active compounds both EU methodologies led to 2 to 3 three times lower false positive results than the national input parameter selection. For transformation products the situation was different, since the new EU methodology (geometric mean Kfoc value) resulted in similar percentages as the national parameter input selection procedure. In contrast, the previous EU methodology (arithmetic mean Kfoc value) was characterized by lower deviations of these false positive results.

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1/n	Freundlich exponent (-)
ar m.	arithmetic mean value
DegT50	Time to reach 50% degradation (d)
EFSA	European Food Safety Authority
FOCUS	FOrum for the Coordination of pesticide fate models and their USe
geo m.	geometric mean value
Kf	Freundlich sorption constant in soil (L/kg)
Kfoc	Freundlich sorption constant related to organic carbon in soil (L/kg)
MA	Comparison of experimental and predicted data for metabolites (M): Group A: PELMO below 0.1 µg/L (trigger class 0) and lysimeter below 0.1 µg/L (trigger class 0), (acceptable risk in lower and higher tier)
MB	Comparison of experimental and predicted data for metabolites (M): Group B: PELMO below 0.1 µg/L (trigger class 0) and lysimeter in the range (trigger class 1), (no risk in lower tier, but relevance assessment triggered from higher tier study)
MC	Comparison of experimental and predicted data for metabolites (M): Group C: PELMO below 0.1 µg/L (trigger class 0) and lysimeter above/equal 10 µg/L (trigger class 2), (no risk in lower tier, but risk indicated in higher tier study)
MD	Comparison of experimental and predicted data for metabolites (M): Group D: PELMO in the range (trigger class 1) and lysimeter below 0.1 µg/L (trigger class 0), (acceptable risk in higher tier, finally no relevance assessment from lower tier necessary)
ME	Comparison of experimental and predicted data for metabolites (M): Group E: PELMO in the range (trigger class 1) and lysimeter in the range (trigger class 1), (relevance assessment triggered from both lower and higher tier)
MF	Comparison of experimental and predicted data for metabolites (M): Group F: PELMO in the range (trigger class 1) and lysimeter above/equal 10 µg/L (trigger class 2), (unacceptable risk indicated from higher tier study only)
MG	Comparison of experimental and predicted data for metabolites (M): Group G: PELMO above/equal 10 µg/L (trigger class 2) and lysimeter below 0.1 µg/L (trigger class 0), (unacceptable risk indicated in lower tier, but finally no risk by higher tier results)
MH	Comparison of experimental and predicted data for metabolites (M): Group H: PELMO above/equal 10 µg/L (trigger class 2) and lysimeter in the range (trigger class 1), (unacceptable risk indicated in lower tier, but finally only relevance assessment necessary by higher tier results)
MI	Comparison of experimental and predicted data for metabolites (M): Group I: PELMO above/equal 10 µg/L (trigger class 2) and lysimeter above/equal 10 µg/L (trigger class 2), (risk indicated in both lower and higher tier)
MRG I	Main regulatory group (MRG) I: agreement between PELMO and lysimeter (MA, ME, MI)

MRG II	Main regulatory group (MRG) I PELMO more conservative than lysimeter i.e. false positive
MRG III	Main regulatory group (MRG) III: lysimeter > 0.1 µg/L PELMO < 0.1 µg/L i.e. false negative, no risk in lower tier, but relevance assessment triggered from higher tier study
MRG IV	Main regulatory group (MRG) III: lysimeter > 10 µg/L PELMO < 0.1 µg/L i.e. false negative, no risk in lower tier, but risk indicated in higher tier study
MRG V	Main regulatory group (MRG) I: Lysimeter > 10 µg/L PELMO > 0.1 µg/L i.e. false negative, unacceptable risk indicated from higher tier study only
PA	Comparison of experimental and predicted data for parent compounds (P): Group A: lysimeter < 0.1 µg/L PELMO < 0.1 µg/L
PB	Comparison of experimental and predicted data for parent compound (P)s: Group B: lysimeter < 0.1 µg/L PELMO > 0.1 µg/L
PC	Comparison of experimental and predicted data for parent compound (P)s: Group C: lysimeter > 0.1 µg/L PELMO < 0.1 µg/L
PD	Comparison of experimental and predicted data for parent compounds (P): Group D: lysimeter > 0.1 µg/L PELMO> 0.1 µg/L
PELMO	PEsticide Leaching MOdel

Zusammenfassung

In Deutschland wird die Risikoabschätzung für den Bereich Grundwasser im Rahmen der Zulassung von Pflanzenschutzmitteln in der ersten Stufe auf Basis von Computerberechnungen mit FOCUS-PELMO (Version 5.5.3) und dem FOCUS-Szenario Hamburg durchgeführt. Freilandlysimeterstudien, die nach der BBA-Richtlinie Teil IV, 4-3 (1990) durchgeführt wurden, werden i.d.R. als höherstufige Studien akzeptiert. Die dort gemessenen Sickerwasserkonzentrationen von Wirkstoffen und deren Abbauprodukten können die Ergebnisse der Modellierungen überschreiben. Ziel dieses Vorhabens war es, zu untersuchen, ob die Ergebnisse aus Modellrechnungen hinreichend konservativ sind, d.h. berechnete Grundwasserkonzentrationen sind höher als die unter entsprechenden Freilandbedingungen im Sickerwasser von Lysimetern gemessenen Konzentrationen.

Zu diesem Zweck wurden drei verschiedene Ansätze zur Auswahl der Eingabeparameter für die Modellierungen mit FOCUS-PELMO überprüft. Es handelte sich um zwei EU-Ansätze (bisheriger Ansatz auf Basis des arithmetischen Mittels und neuer Ansatz basierend auf dem geometrischen Mittel für den Modellierungsendpunkt Kfoc) und dem bisherigen nationalen Ansatz (Holdt et al. 2011). Nach EFSA (2014) beschreibt der geometrische Mittelwert die Variation von Parametern besser als der arithmetische Mittelwert oder der Median. Liegen DegT50-Werte aus Feld- und Laborstudien vor, beschreibt EFSA (2014) außerdem ein statistisches Verfahren, mit dem entschieden werden kann, ob ein gemeinsamer DegT50-Endpunkt für die Modellierung aus Feld- und Labordaten abgeleitet werden kann oder diese getrennt berücksichtigt werden sollen. Voraussetzung dafür ist, dass die Feldstudien gemäß EFSA (2014) durchgeführt bzw. ältere Feldstudien nach EFSA (2014) ausgewertet werden. Da für das vorliegende Projekt derartige Daten aus Freilandstudien nicht vorlagen, wurden die Labor- und Felddaten für die Ableitung des Modellierungsendpunktes DegT50 separat betrachtet.

In dem vorliegenden Projekt wurde für die Evaluierung derselbe Datensatz – der die Datensituation aus dem Jahr 2011 wiedergibt – von 104 Substanzen (33 Wirkstoffe und 71 Abbauprodukte) verwendet, wie bereits in dem vorherigen Forschungsprojekt Klein (2016). Für den Fall, dass weniger als 4 Kfoc-Werte vorlagen, wurden für die Modellierungen anstelle von arithmetischen bzw. geometrischen Mittelwerten die kleinsten Kfoc-Werte als konservative Annahme verwendet.

In der vorliegenden Auswertung wurde die 80. Perzentile der Sickerwasserkonzentrationen basierend auf Simulationen mit FOCUS-PELMO 5.5.3 über 20 Jahre unter Verwendung des FOCUS-Szenarios Hamburg mit den maximalen jährlichen Durchschnittskonzentrationen gemessen im Sickerwasser von Lysimetern verglichen. Für alle 104 Stoffe (33 Wirkstoffe und 71 Abbauprodukte) wurden die normalisierten Endpunkte zu Abbau und Sorption nach den beiden EU-Ansätzen und dem nationalen Ansatz (Holdt et al. 2011) bestimmt. Bei 38 der 104 Substanzen (8 Wirkstoffe und 30 Metaboliten) wichen EU- und nationale Endpunkte voneinander ab, sei es aufgrund unterschiedlicher Sorptionskonstanten (29%) und/oder Halbwertszeiten (13%). Von diesen Substanzen wurden 30 Stoffe im Rahmen einer weiteren Analyse untersucht. Abbauprodukte, die von Muttersubstanzen abstammten, deren Sorptions- oder Abbaudaten ebenfalls eine hohe Streuung zeigten, wurden nicht in diese Analyse einbezogen. Dies betraf insgesamt 8 Metaboliten.

Die beiden folgenden Tabellen zeigen die wesentlichen Ergebnisse dieses Projekts.

In Tabelle 1-1 sind Ergebnisse des direkten Vergleichs von berechneten und gemessenen Konzentrationen für alle Substanzen dargestellt. Tabelle 1-2 zeigt die Ergebnisse für Substanzen, bei denen nach dem nationalen Ansatz zur Auswahl von Endpunkten eine hohe Variabilität der DT50- und Kfoc-Werte festgestellt wurde. Es stellte sich heraus, dass der deutsche Ansatz im Allgemeinen zu etwas konservativeren Ergebnissen führte als der EU-Ansatz basierend auf dem geometrischen Mittelwert für den

Kfoc. Demgegenüber zeigten Simulationen basierend auf dem bisherigen EU-Ansatz mit dem arithmetischen Mittelwert des Kfoc weniger Situationen, bei denen die Ergebnisse der PELMO-Simulationen oberhalb entsprechender Lysimeterergebnisse blieben.

Tabelle 1-1: Ergebnisse des Vergleichs von berechneten Konzentrationen* mit gemessenen jährlichen Durchschnittskonzentrationen im Sickerwasser von Lysimeterstudien (Konzentrationen unterhalb von 0,01 µg/L auf 0,01 µg/L gesetzt)

Parameterauswahl entsprechend	33 Wirkstoffe		71 Transformationsprodukte	
	PELMO ≥ Lysimeter	PELMO < Lysimeter	PELMO ≥ Lysimeter	PELMO < Lysimeter
EU (Kfoc: arithmetischer Mittelwert)	78,8%	21,2%	71,8%	28,2%
EU (Kfoc: geometrischer Mittelwert)	78,8%	21,2%	78,9%	21,1%
DE	81,8%	18,2%	81,7%	18,3%

* alle PELMO Simulationen basierend auf dem FOCUS Hamburg Szenario (80. zeitliches Perzentil)

Tabelle 1-2: Ergebnisse des Vergleichs von berechneten Konzentrationen* mit gemessenen jährlichen Durchschnittskonzentrationen im Sickerwasser von Lysimeterstudien für Substanzen mit hoher Variabilität von Eingabeparametern (Konzentrationen unterhalb von 0,01 µg/L auf 0,01 µg/L gesetzt)

Parameterauswahl entsprechend	8 Wirkstoffe		22 Transformationsprodukte	
	PELMO ≥ Lysimeter	PELMO < Lysimeter	PELMO ≥ Lysimeter	PELMO < Lysimeter
EU (Kfoc: arithmetischer Mittelwert)	75,0 %	25,0%	59,1%	40,9%
EU (Kfoc: geometrischer Mittelwert)	75,0 %	25,0%	68,2%	31,8%
DE	87,5%	12,5%	77,3%	22,7%

* alle PELMO Simulationen basierend auf dem FOCUS Hamburg Szenario (80. zeitliches Perzentil)

Für eine Analyse möglicher regulatorischer Auswirkungen wurden die drei Ansätze zur Auswahl der Eingabeparameter für die Modellierungen mit FOCUS-PELMO im Hinblick auf falsch-negative Ergebnisse (gemessene Konzentration ≥ 0,1 µg/L bzw. ≥ 10 µg/L, modellierte Konzentration < 0,1µg/L bzw. < 10 µg/L) und falsch-positive Ergebnisse (modellierte Konzentration ≥ 0,1 µg/L bzw. ≥ 10 µg/L, gemessene Konzentration < 0,1µg/L bzw. < 10 µg/L) untersucht.

In den nachfolgenden Tabellen sind die Ergebnisse dieser Analyse für alle Substanzen (Tabelle 1-3) und für Substanzen mit hoher Variabilität der Eingabeparameter (Tabelle 1-4) dargestellt. Grundsätzlich wurden keine Unterschiede zwischen den verschiedenen Ansätzen festgestellt, wenn die falsch-negativen Ergebnisse (Lysimeter zeigt ein Problem, das PELMO nicht angezeigt hatte) verglichen werden. Wenn die drei Ansätze zur Auswahl der Eingabeparameter im Hinblick auf falsch-positive Ergebnisse verglichen werden, hängen die Ergebnisse davon ab, ob Wirkstoffe oder Abbauprodukte untersucht wurden. Für Wirkstoffe führen beide EU-Ansätze zu zwei- bis dreimal niedrigeren falsch-positiven Ergebnissen als der nationale Ansatz. Für Abbauprodukte ist die Situation anders, da kaum Unterschiede zwischen dem neuen EU- und dem nationalen Ansatz gefunden wurden. Im Gegensatz dazu werden mit dem bisherigen EU-Ansatz basierend auf dem arithmetischen Mittelwert des Kfoc geringere Abweichungen dieses Typs gefunden.

Tabelle 1-3: Ergebnisse zum Vergleich berechneter Konzentrationen mit gemessenen jährlichen Konzentrationen im Sickerwasser von Lysimeterstudien (regulatorische Auswirkungen)

Parameterauswahl entsprechend	Wirkstoffe (33 Substanzen)				Transformationsprodukte (71 Substanzen)				
Lysimeter	< 0,1 µg/L	< 0,1 µg/L	> 0,1 µg/L	> 0,1 µg/L	Lysimeter	Lysimeter	> 0,1 µg/L	> 10 µg/L	> 10 µg/L
PELMO	< 0,1 µg/L	> 0,1 µg/L	< 0,1 µg/L	> 0,1 µg/L	= Pelmo	< Pelmo	< 0,1 µg/L	< 0,1 µg/L	> 0,1 µg/L
EU (Kfoc: arithmetischer Mittelwert)	75,8%	18,2%	3,0%	3,0%	64,8%	28,2%	7,0%	0,0%	0,0%
EU (Kfoc: geometrischer Mittelwert)	75,8%	18,2%	3,0%	3,0%	57,7%	35,2%	7,0%	0,0%	0,0%
DE	60,6%	33,3%	3,0%	3,0%	59,2%	35,2%	5,6%	0,0%	0,0%

Tabelle 1-4: Ergebnisse zum Vergleich berechneter Konzentrationen mit gemessenen jährlichen Konzentrationen im Sickerwasser von Lysimeterstudien für Substanzen mit hoher Variabilität von Eingabeparametern (regulatorische Auswirkungen)

Parameterauswahl entsprechend	Wirkstoffe (8 Substanzen)				Transformationsprodukte (22 Substanzen)				
Lysimeter	< 0,1 µg/L	< 0,1 µg/L	> 0,1 µg/L	> 0,1 µg/L	Lysimeter	Lysimeter	> 0,1 µg/L	> 10 µg/L	> 10 µg/L
PELMO	< 0,1 µg/L	> 0,1 µg/L	< 0,1 µg/L	> 0,1 µg/L	= Pelmo	< Pelmo	< 0,1 µg/L	< 0, 1 µg/L	> 0,1 µg/L
EU (Kfoc: arithmetischer Mittelwert)	87,5%	12,5%	0,0%	0,0%	63,6%	27,3%	9,1%	0,0%	0,0%
EU (Kfoc: geometrischer Mittelwert)	87,5%	12,5%	0,0%	0,0%	50,0%	40,9%	9,1%	0,0%	0,0%
DE	62,5%	37,5%	0,0%	0,0%	45,5%	45,5%	9,1%	0,0%	0,0%

Summary

For registration of plant protection products in Germany the groundwater risk assessment at lower tier is based on modelling results using simulated leaching concentrations of the Hamburg scenario from the FOCUS PELMO model (version 5.5.3). Measured leachate concentrations for active compounds and transformation products from outdoor lysimeter studies performed according to BBA (1990) are still accepted as higher tier endpoints to assess the risk of plant protection products to groundwater in certain cases. The objectives of this project were to determine, whether lower tier calculations are still more conservative than higher tier results from lysimeter studies and to investigate discrepancies and their possible causes between simulated and experimentally derived leachate concentrations dependent on the input parameter selection procedure for modelling.

Three different methodologies for selecting input parameters for modelling with FOCUS PELMO were considered: the national input parameter selection procedure according to Holdt et al. (2011), the previous EU methodology based on the arithmetic mean Kfoc value and the new EU methodology based on the geometric mean Kfoc value. According to EFSA (2014) the geometric mean should better describe the variation of parameters. If the DegT50 was analysed in field and laboratory studies in EFSA (2014) a procedure is also described for deciding whether or not the DegT50 values from laboratory and field dissipation databases can be treated separately or can be pooled. With regard to this procedure the current guidance was not followed in this evaluation. Instead laboratory and field degradation half-lives were kept separately and either geometric mean DegT50 from laboratory or field studies was used. This is because the available field studies were not performed according to the requirements outlined in EFSA (2014). Due to the limitations with regard to DegT50 the presented results will only be preliminary.

For the evaluation in this project the same data sets of 104 substances (33 active compounds, 71 metabolites) have been considered as given in Klein et al. (2016), which were based on the data available in 2011. It is current practice in registration to use the worst case sorption constant if less than 4 Kfoc values are available. Therefore, the same values for the geometric and arithmetic simulation were used in this analysis even if the geometric and arithmetic mean values were different. In so far, the present evaluation generally followed the rules in the current registration process rather than the methodologies of pure statistical analyses.

The 80th percentile of predicted groundwater concentrations for the Hamburg scenario simulated over 20 years with FOCUS PELMO 5.5.3 and the maximum average annual leachate concentrations from lysimeter experiments were compared for 33 active substances and 71 metabolites, both for simulations with national and EU endpoints. Normalised degradation and sorption endpoints were defined for all 104 compounds according to the national input parameter selection procedure (Holdt et al. 2011) and the EU methodologies. For 38 of the 104 substances (37%, 8 active compounds and 30 metabolites) EU and national input parameters deviated caused by different sorption constants (29%) and/or half-lives (13%). However, 8 of these 30 transformation products were not considered further since they were already formed by parent compounds characterised by different national and EU input parameter selection.

As already explained in this evaluation no re-evaluation of the field studies was performed and so the requirements of EFSA (2014) were only followed with regard to the selection of Kfoc values. Therefore, the results do not exactly reflect the same level of protection as described in EFSA (2014).

The following two tables show the key results of this project.

In Table 1-5 and Table 1-6 the results of the direct comparison between the calculated and the observed concentrations for all substances and for substances with high variability of input parameters

are presented. Overall, the German input parameter selection procedure is slightly more conservative than the new EU methodology based on the geometric mean Kfoc value according to EFSA (2014). In contrast results based on the previous EU methodology using the arithmetic mean Kfoc value show more situations where lysimeter results were above respective PELMO simulations. Compounds with high variability of input parameters and especially transformation products are affected.

Table 1-5: Summary of the comparison of calculated concentration* with observed annual average concentrations in the leachates of lysimeter studies
(concentration below 0.01 µg/L set to 0.01 µg/L)

Parameter setting according to	33 Parent compounds		71 Transformation products	
	PELMO ≥ Lysimeter	PELMO < Lysimeter	PELMO ≥ Lysimeter	PELMO < Lysimeter
EU (Kfoc: arithmetic mean)	78.8%	21.2%	71.8%	28.2%
EU (Kfoc: geometric mean)	78.8%	21.2%	78.9%	21.1%
DE	81.8%	18.2%	81.7%	18.3%

* all PELMO simulations based on FOCUS Hamburg scenario (80th temporal percentile)

Table 1-6: Summary of the comparison of calculated concentration* with observed annual average concentrations in the leachates of lysimeter studies for substances with high variability of input parameters
(concentration below 0.01 µg/L set to 0.01 µg/L)

Parameter setting according to	8 Parent compounds		22 Transformation products	
	PELMO ≥ Lysimeter	PELMO < Lysimeter	PELMO ≥ Lysimeter	PELMO < Lysimeter
EU (Kfoc: arithmetic mean)	75.0 %	25.0%	59.1%	40.9%
EU (Kfoc: geometric mean)	75.0 %	25.0%	68.2%	31.8%
DE	87.5%	12.5%	77.3%	22.7%

* all PELMO simulations based on FOCUS Hamburg scenario (80th temporal percentile)

In Table 1-7 and Table 1-8 information about the regulatory impact of the different selection methodologies for all substances and for substances with high variability of input parameters are presented. Basically, no differences between the methodologies were found when comparing the false negative results (lysimeter showed a problem which PELMO did not determine, see also Table 1-5 and Table 1-6). When comparing the three input parameter selection procedures with regard to false positive comparisons the results depend on whether active compounds or transformation products are simulated. For active compounds both EU methodologies led to 2 to 3 three times lower false positive results than the national input parameter selection procedure. For transformation products the situation is different, since there were no big differences between the new EU methodology based on the geometric mean Kfoc value according to EFSA (2014) and the national input parameter selection procedure according to Holdt et al. (2011). In contrast the previous EU methodology based on arithmetic mean Kfoc value is characterized by lower deviations of this type.

Table 1-7: Summary of the comparison of calculated with observed annual leaching concentrations (regulatory impact)

Input parameter selection according to	Parent compounds (33 substances)				Transformation products (71 substances)				
Lysimeter	< 0.1 µg/L	< 0.1 µg/L	> 0.1 µg/L	> 0.1 µg/L	Lysim.	Lysim.	> 0.1 µg/L	> 10 µg/L	> 10 µg/L
PELMO	< 0.1 µg/L	> 0.1 µg/L	< 0.1 µg/L	> 0.1 µg/L	= Pelmo	< Pelmo	< 0.1 µg/L	< 0.1 µg/L	> 0.1 µg/L
EU (Kfoc: arithm. mean)	75.8%	18.2%	3.0%	3.0%	64.8%	28.2%	7.0%	0.0%	0.0%
EU (Kfoc: geom. mean)	75.8%	18.2%	3.0%	3.0%	57.7%	35.2%	7.0%	0.0%	0.0%
DE	60.6%	33.3%	3.0%	3.0%	59.2%	35.2%	5.6%	0.0%	0.0%

Table 1-8: Summary of the comparison of calculated with observed annual leaching concentrations for substances with high variability of input parameters (regulatory impact)

Input parameter selection according to	Parent compounds (8 substances)				Transformation products (22 substances)				
Lysimeter	< 0.1 µg/L	< 0.1 µg/L	> 0.1 µg/L	> 0.1 µg/L	Lysim.	Lysim.	> 0.1 µg/L	> 10 µg/L	> 10 µg/L
PELMO	< 0.1 µg/L	> 0.1 µg/L	< 0.1 µg/L	> 0.1 µg/L	= Pelmo	< Pelmo	< 0.1 µg/L	< 0.1µg/L	> 0.1 µg/L
EU (Kfoc: arithm. m.)	87.5%	12.5%	0.0%	0.0%	63.6%	27.3%	9.1%	0.0%	0.0%
EU (Kfoc: geom. mean)	87.5%	12.5%	0.0%	0.0%	50.0%	40.9%	9.1%	0.0%	0.0%
DE	62.5%	37.5%	0.0%	0.0%	45.5%	45.5%	9.1%	0.0%	0.0%

1 Introduction

For many years PELMO 3.0 (Klein 1995, Jene et al. 1998) was used as a model in the national groundwater risk assessment for active substances and metabolites from plant protection products. PELMO 3.0 was validated based on several studies (Klein et al. 1997, 2000). The last validation initiated by the Industrieverband Agrar (IVA) was made by Hardy et al. (2008). It was investigated whether the input parameter selection procedure for modelling according to Michalski et al. (2004) is sufficiently conservative for triggering lysimeter studies performed according to the German lysimeter guidance (BBA 1990). The authors of this project conclude that PELMO 3.0 in combination with the input parameter selection procedure according to Michalski et al. (2004) fulfil this requirement for parent compounds as well as for transformation products.

The FOCUS groundwater report (2009) was released and resulted in new FOCUS PELMO versions 4.4.3 and 5.5.3. In order to achieve more harmonisation of the assessment especially with regard to the new regulation 1107/2009 EG such as zonal registration the Federal Environment Agency in Germany (UBA) in co-operation with German industry (Industrieverband Agrar, IVA) revised the national risk assessment procedure for groundwater (Holdt et al. 2011).

Due to these various modifications in the national registration procedure of plant protection products the following open issues were addressed within a recent research project (Klein et al., 2016) with regard to the level of protection of the new FOCUS Hamburg scenario in combination with a new input parameter selection procedure for modelling compared to the results of lysimeter studies as higher tier studies.

- FOCUS PELMO Hamburg scenario
  Although the soil properties (soil type, soil texture, organic carbon content, pH) did not change when changing from PELMO 3.0 to FOCUS PELMO, different biodegradation factors at different depths are considered in both models. Furthermore, the FOCUS weather service (26 years) compared to the two PELMO 3.0 weather years (Hamburg wet and normal) led to a major change and more complexity in the PEC calculation.

- Calculation of the endpoint
  The simulated percolate concentrations in the previous procedure were based on the maximum annual concentrations of the two selected weather years. However, the results of FOCUS PELMO are based on the 80th temporal percentile of 20 subsequent weather years.

- pH-dependency of degradation and/or sorption
  In the current national assessment procedure simulations based on the neutral to alkaline FOCUS Kremsmünster soil scenario are required for compounds which show pH-dependent degradation and/or sorption caused by dissociation of the respective compound. It was the intention of the project to check these compounds as well. However, as only one substance in the dataset belonged to that group, an investigation of pH dependency was not possible.

However, in May 2015 a new European guidance (EFSA 2014) was endorsed with new selection criteria for the important modelling endpoints DegT50 and Kfoc which are going to be used for groundwater simulations on EU level (active substances) as well as in the zonal authorization procedure (product registration). Therefore, the influence of the new requirements on the results of standard simulations has to be investigated as well and compared with the existing German procedure with regard to the level of protection. In this report the following aspects of the new European guidance will be checked.

- According to the new guidance the geometric mean Kfoc value should be used instead of the arithmetic mean Kfoc value (EFSA 2014). The geometric mean should better describe the variation of individual results. Therefore, the geometric mean is used for the calculations in this report.

- If degradation data from field and laboratory are available in EFSA (2014) a procedure is described for deciding whether or not the DegT50 values from laboratory and field dissipation databases can be treated separately or can be pooled. With regard to this procedure the current guidance was not followed in this evaluation. Instead laboratory and field degradation half-lives were kept separately and either geometric mean DegT50 from laboratory or field studies was used. This is because the available field studies were not performed according to the requirements outlined in EFSA (2014).

Due to the limitations with regard to DegT50 the presented results will only be preliminary. Nevertheless, the influence of the change to the geometric mean Kfoc value on the level of protection will be analysed in detail.

It should be noted that the evaluation generally followed the rules in the current registration process rather than the methodologies of pure statistical analyses. The consequence was that the statistics couldn't deliver the maximum differences between different approaches since in some cases the same values for the geometric and arithmetic simulation were used (e.g. selection of the worst case number because less than 4 Kfoc values were available).

In the following the three different procedures for the selection of input parameters are named:

DE:	selection according to Holdt et al. (2011)
EU (Kfoc: ar. m.):	selection according to the previous EU methodology based on the arithmetic mean Kfoc value
EU (Kfoc: geo. m.):	selection according to the current EU methodology (EFSA 2014) based on the geometric mean Kfoc value

2 Data collection and preparation

For the validation of the national modelling approach the same data sets of 104 substances (33 active compounds, 71 metabolites) have been considered as given in Klein et al. (2016), which were based on the data available in 2011.

For all compounds outdoor lysimeter studies performed according to the German guideline (BBA 1990) were available, where the selected substances were also detected in the percolate. PELMO's most important processes are mobility (driven by the sorption constant Kfoc and the Freundlich exponent 1/n) and degradation (driven by the DegT50 and its moisture, temperature and depth dependency). These parameters are not purely substance dependent (as for example water solubility) but also dependent on environmental conditions (e.g., soil properties). Therefore, the values as obtained from the selection methodology which were used in the computer simulations do not necessarily reflect the situation in the field studies Important influencing soil properties are, for example, organic carbon content, pH as well as clay, sand and silt content. As the degradation rate also depends on temperature and soil moisture, these parameters must also be considered when using the results. Of course, in addition to mobility and degradation there are further pesticide input parameters that influence leaching of substances (e.g. vapour pressure, photolysis rate, degradation on plant surfaces, plant uptake).

For all 104 compounds (33 parent compounds and 71 metabolites) the geometric mean Kfoc values were calculated, whereas the other parameters (Freundlich exponent, DegT50) were used as documented in Klein et al. (2016). Table 7-1 in the appendix shows the geometric and arithmetic mean Kfoc values for all compounds considered in this project.

In contrast to the EU methodology the German methodology outlines that a high variance of Kfoc and DegT50 should be taken into account when selecting input parameters for modelling. For adsorption a Kf value should be used instead of an arithmetic mean Kfoc value if the coefficient of variation Kfoc exceeds 60% and if there is no correlation between the organic carbon content and the sorption constant. For degradation the 90th percentile of DegT50 values should be used instead of the geometric mean value, when the coefficient of variation is > 100 %. Detailed information is given in

Table 7-2 and Table 7-3 in the appendix for active compounds and transformation products, respectively.

In order to check the impact of these differences between the national and the EU input parameter selection on the performance of the simulation models a further evaluation was performed: Therefore,,all substances were selected from the database where Kf values (German methodology) were used instead of Kfoc values (EU methodology) or 90th percentiles (German methodology) of the degradation values were used instead of the geometric mean (EU methodology, EFSA 2014). In total 32 substances (31 %) were found that matched the required conditions.

For comparison the results of the new simulations based on the geometric mean Kfoc value are presented together with results given by Klein et al. (2016). However, the evaluation presented in this report is performed without considering plant uptake (PUF=0) because it was demonstrated by Klein et al. (2016) that this parameter has only a minor influence on the results.

3 Direct comparison of modelling and lysimeter results

3.1 Evaluation based on all substances

In the present chapter direct comparisons between the leachate concentrations in 1 m soil depth simulated with the FOCUS Hamburg scenario and corresponding information from outdoor lysimeter studies are presented. However, in this comparison the results are not directly linked to regulatory questions (e.g. compared to regulatory important trigger values). According to the analysis with 104 substances the national approach for the selection of modelling endpoints differs in 39% from the EU methodology (31% because of different sorption constants, 13% because of different half-lives). For the comparisons the concentrations below 0.01 µg/L were set to 0.01 µg/L independent whether they were based on lysimeter results or computer predictions. That was done since uncertainties correlated with analytical determinations and model haziness below 0.01 µg/L can be significant but the overall conclusions would be nevertheless the same.

For all selection methodologies, in most of the cases FOCUS PELMO calculated higher concentrations than determined in the lysimeter studies. However, the national input parameter selection procedure was found to be more conservative (PELMO above lysimeter: 81.7%) than the previous EU methodology based on arithmetic mean Kfoc value (PELMO above lysimeter: 74%). The new EU methodology based on geometric mean Kfoc value according to EFSA (2014) is more conservative than the previous EU methodology (PELMO above lysimeter: 78.8%) and well comparable with the national input parameter selection procedure according to Holdt et al. (2011).

Table 3-1 shows the results of the comparisons between the calculated concentrations and the annual average concentrations in the leachates of lysimeter studies.

Table 3-1: Summary of the comparison of calculated concentrations* with observed annual average concentrations in the leachates of lysimeter studies (concentrations below 0.01 µg/L set to 0.01 µg/L)

Parameter setting according to	PELMO ≥ Lysimeter	PELMO < Lysimeter
EU (Kfoc: arithmetic mean)	77 (74.0%)	27 (26.0%)
EU (Kfoc: geometric mean)	82 (78.8%)	22 (21.2%)
DE	85 (81.7%)	19 (18.3%)

* all PELMO simulations based on FOCUS Hamburg scenario (80th temporal percentile)

These results indicate that if experimental outdoor lysimeter data are used to investigate the protection level, the criteria in Holdt et al. (2011) as well as the new EU methodology for lower tier groundwater modelling on a national scale ensure a safe and conservative estimation of the groundwater risk assessment in about 82% and 79% of the investigated cases, respectively.

As a consequence, a safe prediction of the leaching concentration was not possible for 18% of the analysed compounds by using national input parameters, for 21% by using new EU methodology and for 26% of the compounds by using the previous EU methodology. All comparison were based on the FOCUS Hamburg scenario.

The individual results for three selection variations are also presented in the following figures.

The visualisations demonstrate that especially for parent compounds there are only few exceptions where the simulation was below the experimental result. For parent compounds, there is only one example where FOCUS PELMO calculated concentrations below the trigger of 0.1 µg/L whereas the lysimeter study showed leaching above 0.1 µg/L (see the red circles in Figure 3-1 to Figure 3-3). This was a lysimeter study performed with substance 72 where 0.272 µg/L was detected in the leachate, but where the model did not predict any leachate independent whether the EU or the national parameter selection criteria were considered. Obviously, the study cannot be described adequately based on the available information on mobility and degradation, possibly because fast transport processes (e.g. preferential flow) were dominant. Furthermore, the soil was characterised by lower organic carbon content (< 1%) than in the FOCUS PELMO Hamburg scenario. For other cases (e.g. substances 4, 31, 55, 60, 74) the lysimeter study results were at least below the trigger of 0.1 µg/L.

Figure 3-1: Comparison of calculated leaching concentrations over 20 years with observed annual leaching concentrations in lysimeter studies (concentration below 0.01 µg/L set to 0.01 µg/L, DE)

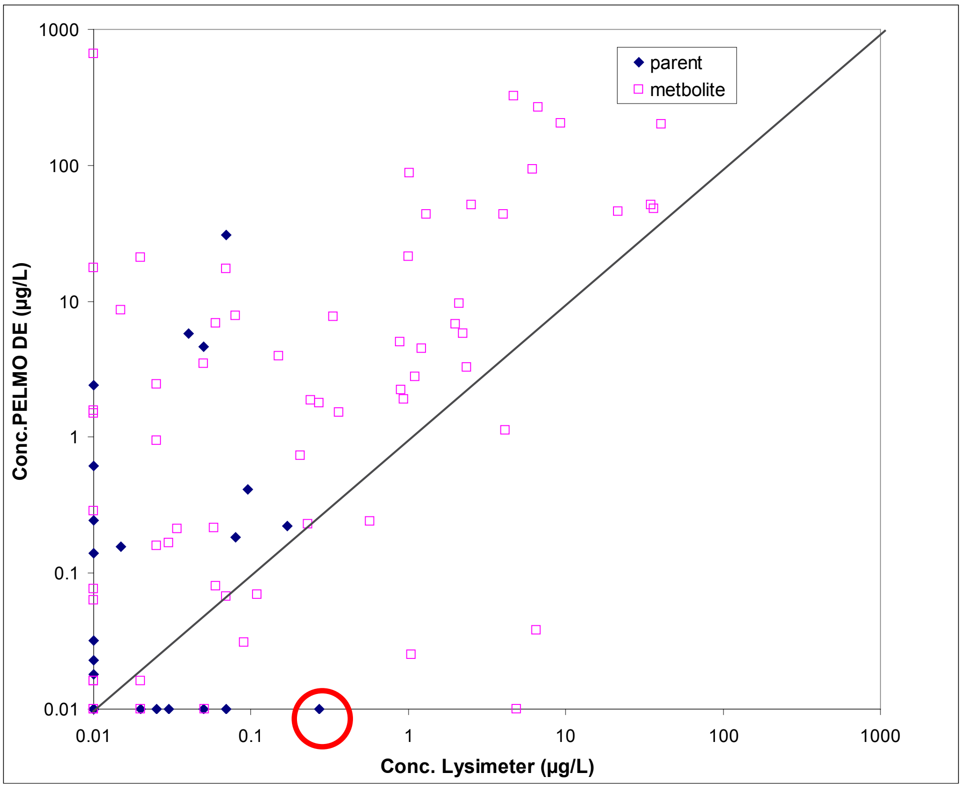


Figure 3-2: Comparison of calculated leaching concentrations over 20 years with observed annual leaching concentrations in lysimeter studies (concentration below 0.01 µg/L set to 0.01 µg/L, EU Kfoc geo m.)

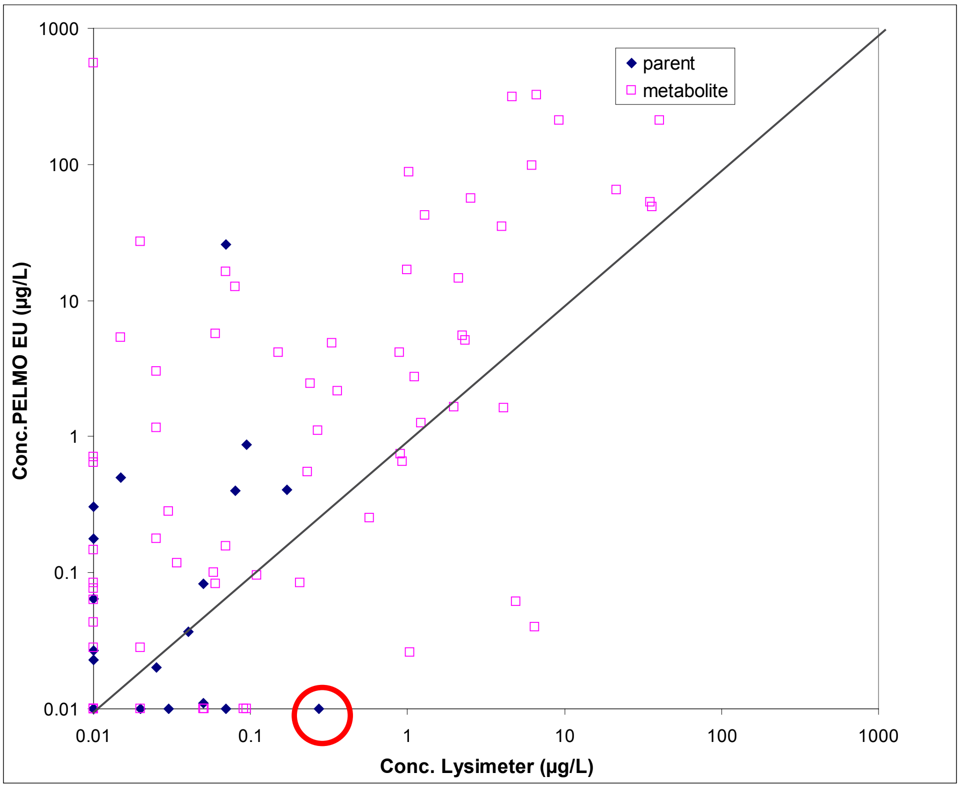
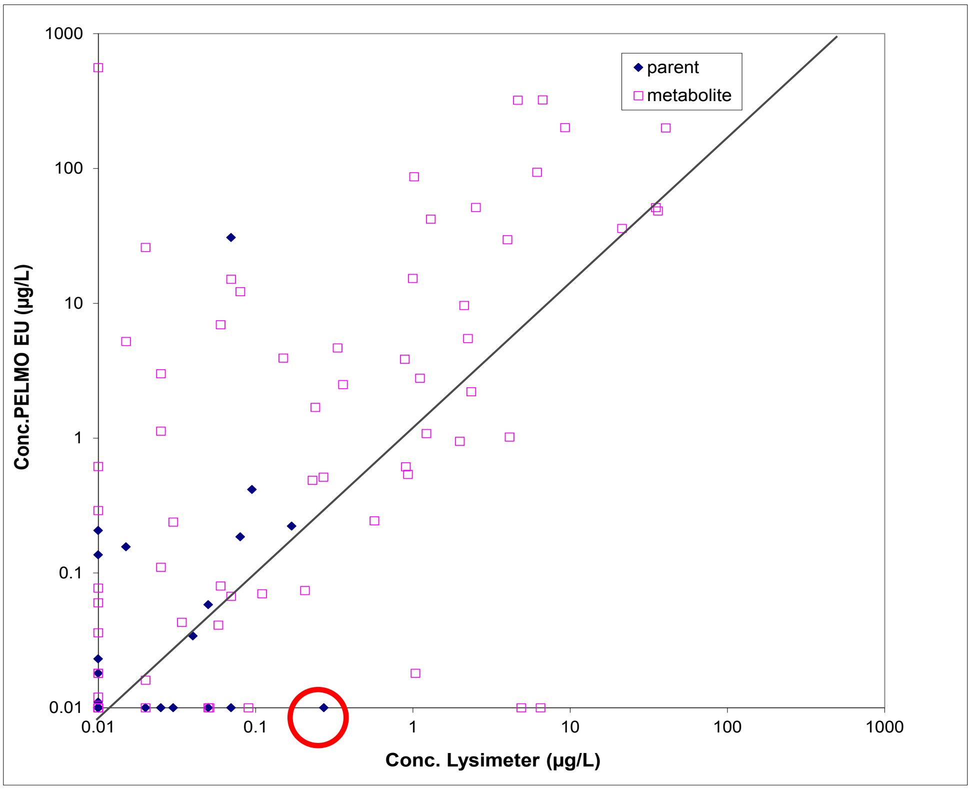


Figure 3-3: Comparison of calculated leaching concentrations over 20 years with observed annual leaching concentrations in lysimeter studies (concentration below 0.01 µg/L set to 0.01 µg/L, EU Kfoc: ar m.)



The statistical analysis presented so far in the tables do not distinguish between active compounds and metabolites. However, compared to simulations of the applied parent compounds the calculation of transformation products is characterised by higher uncertainty. This is caused by an additional estimation step in the simulation, the formation of transformation products. Whereas the application of the pesticide is an experimentally available defined parameter the formation of transformation is calculated based on the degradation of the parent compound and the formation fraction. If formation fractions are not known as a worst case assumption the formation fraction is set to 1 which is estimated to result in more conservative PEC´s compared with parent compounds.

3.2 Evaluation based on active substances only

In the following Table 3-2 a similar evaluation is done as before only for the parent compounds.

Table 3-2: Summary of the comparison of calculated concentration* with observed annual average concentrations in the leachates of lysimeter studies (only active substances, concentration below 0.01 µg/L set to 0.01 µg/L

Parameter setting according to	PELMO ≥ Lysimeter	PELMO < Lysimeter
EU (Kfoc: arithmetic mean)	26 (78.8%)	7 (21.2%)
EU (Kfoc: geometric mean)	26 (78.8%)	7 (21.2%)
DE	27 (81.8%)	6 (18.2%)

* all PELMO simulations based on FOCUS Hamburg scenario (80th temporal percentile)

Similar results as for all substances were also observed for parent compounds (see Table 3-1) when selecting model input parameters according to the German national methodology or the new EU methodology based on the geometric mean. However, the comparison for the previous EU methodology (based on arithmetic mean Kfoc value) shows relatively more situations (about 79%) where PELMO simulated higher concentrations than observed in lysimeter studies when looking only at the parent compounds (all substances: 74%). It can be concluded that the Kfoc values of active compounds do not depend so much on the type of averaging (geometric or arithmetic mean) presumably because the variations of the experimental data are relatively small.

For active compounds these results confirm the previous conclusion, that the criteria in Holdt et al. (2011) for lower tier groundwater modelling on a national scale ensure a safe and conservative estimation of the groundwater risk assessment (82%). But also FOCUS PELMO simulations performed according to the EU methodology (both type of averaging) result in estimations of similar conservativeness (79%).

3.3 Evaluation based on transformation products only

In the following Table 3-3 the respective evaluation is done as before only for transformation products.

Table 3-3: Summary of the comparison of calculated concentration* with observed annual average concentrations in the leachates of lysimeter studies (only metabolites, concentration below 0.01 µg/L set to 0.01 µg/L)

Parameter setting according to	PELMO ≥ Lysimeter	PELMO < Lysimeter
EU (Kfoc: arithmetic mean)	51 (71.8%)	20 (28.2%)
EU (Kfoc: geometric mean)	56 (78.9%)	15 (21.1%)
DE	58 (81.7%)	13 (18.3%)

* all PELMO simulations based on FOCUS Hamburg scenario (80th temporal percentile)

It confirms the previous conclusion that the criteria in Holdt et al. (2011) for lower tier groundwater modelling on a national scale as well as the new EU methodology (geometric mean Kfoc value, EFSA 2014) ensure a safe and conservative estimation of the groundwater risk assessment which does not depend on the type of compound (parent compounds and metabolites: 82% (DE) and 79% (EU) safe predictions). However, the comparison for metabolites simulated using the previous EU methodology shows relatively more situations (about 28%) where higher concentrations were observed in lysimeter studies than in PELMO simulations.

3.4 Deviations between the national and European approach

In contrast to the EU methodologies according to the German national scheme a high variance of the parameters Kfoc and DegT50 should be taken into account when selecting input parameters for modelling. For adsorption a Kf value should be used instead of an arithmetic mean Kfoc value if the coefficient of variation Kfoc exceeds 60% and if there is no correlation between the organic carbon content and the sorption constant according to the German input parameter selection procedure (input decision). In these cases the correlations between Kf values and other soil properties (pH, clay, CEC) have to be checked. Furthermore, specific Kf values can be used for modelling. If there is no correlation observed and the coefficient of variation Kf is ≤ 100% the arithmetic mean, otherwise the 10th percentile Kf value should be used for modelling. For degradation the 90th percentile DegT50 value instead of the geometric mean value should be used, when the coefficient of variation is > 100 % (see Holdt et al., 2011).

In order to check the impact of this difference in the national input parameter selection procedure on the performance of the simulation models a special evaluation is performed. Therefore, all substances were selected from the database where Kf values (German methodology) were used instead of Kfoc values (EU methodology) or 90th percentiles (German methodology) of the degradation values were used instead of the geometric mean (EU methodology, EFSA 2014). In total 38 cases (37% of 104 substances, 8 active compounds and 30 transformation products) were found that matched the required conditions.

Table 3-4 shows the comparison of FOCUS PELMO simulations with observed annual average concentrations in the leachates of lysimeter studies for active substances when selecting different sorption constants and degradation half-lives. The simulations were based on the FOCUS Hamburg scenario and the 80th percentile of average annual concentrations. The detailed results are also presented in the appendix, Table 7-2 and Table 7-3.

Table 3-4: Summary of the comparison of PELMO simulations (based on FOCUS Hamburg scenario and 80th temporal percentile) with observed annual average concentrations in the leachates of lysimeter studies of active substances when selecting different sorption constants and degradation half-lives (Plant uptake = 0)

Modelling end-points		**Comparison**						
Kfoc /Kf	**DegT50**	**Total no.**	**PELMO DE ≥ Lysim.**	**PELMO DE < Lysim.**	**PELMO EU Kfoc:ar m. ≥ Lysim.**	**PELMO EU Kfoc:ar m. < Lysim.**	**PELMO EU Kfoc:geo m. ≥ Lysim.**	**PELMO EU Kfoc:geo m. < Lysim.**
Kf_{oc}(ar m.)	90thp.	2	2	0	1	1	1	1
Kf (ar m.)	geo m.	3	2	1	2	1	2	1
Kf(10thp.)	geo m.	1	1	0	1	0	1	0
Kf (ar m.)	90thp.	0	0	0	0	0	0	0
Kf(10thp.)	90thp.	2	2	0	2	0	2	0
Kf (CEC)	geo m.	0	0	0	0	0	0	0
Kf (pH)	pH	0	0	0	0	0	0	0
Total		8	7	1	6	2	6	2

p. = percentile
pH =average of acid and neutral/basic soils (Kf arithmetic mean, DegT50 geometric mean)
Kf(CEC) = Kf dependent on cation exchange capacity

Eight parent compounds were identified where input parameter selection according to Holdt et al. (2011) deviated from the EU methodology. They were grouped in Table 3-4 into 7 different input classes according to the type of deviation. However, no active substance could be grouped into input classes with an average sorption constant Kf and a 90th percentile of DegT50 values (Table 3-4, line 6), with a Kf value dependent on CEC (Table 3-4, line 8) and Kf/ DegT50 values dependent on pH (Table 3-4, line 9).

- <u>Average sorption constant Kfoc and 90th percentile of DegT50 values (Table 3-4, line 3)</u>:
  Two situations were found that fitted into this class. In both cases PELMO simulated higher concentrations than observed in the lysimeter study. In contrast, in the simulations based on the EU methodology (geometric mean and arithmetic mean) one simulation (of two) was below the respective experimental result. As parameterisation according to Holdt et al. (2001) is usually more conservative no situation could be found where "EU-type" simulations were above simulations according to Holdt et al (2011).
- <u>Average sorption constant Kf and average DegT50 value (Table 3-4, line 4)</u>:
  Three substances were found that fitted into this class. The result of the comparison was independent on the methodology: In two cases PELMO simulated higher concentrations than observed in lysimeter studies and in one case the simulation result was below the corresponding lysimeter value.

- 10th percentile of Kf values and average DegT50 value (Table 3-4, line 5):
  Only a single parent compound was found that fitted into this class. The result of the comparison was independent on the methodology: PELMO simulated higher concentrations than observed in the lysimeter study.
- 10th percentile of Kf values and 90th percentile of DegT50 values (Table 3-4, line 7):
  Two substances were found that fitted into this class. The result of the comparison was independent on the methodology: PELMO simulated higher concentrations than observed in the lysimeter study.

Table 3-4 confirms the previous conclusion that the criteria in Holdt et al. (2011) for lower tier groundwater modelling on a national scale ensure a safe and conservative estimation of the groundwater risk assessment also for parent compounds, for which a high variance of the input parameters Kfoc and DegT50 has been considered. Only for a single substance the annual concentration in the lysimeter experiment was found to be above respective simulation results. For that compound no correlation between organic carbon content and sorption was found and the simulation was based on the average Kf value. For the respective simulation based on the Kfoc (EU methodology) the comparison led to the same result.

However, when using the EU methodology (geometric or arithmetic mean Kfoc value) one additional situation was found where higher concentrations were observed in lysimeter studies than in the PELMO simulation. For this respective substance the DegT50 values were characterised by a high coefficient of variation (selection of the more conservative 90th percentile DegT50 according to Holdt et al. 2011).

Table 3-5 shows the comparison of PELMO simulations with observed annual average concentrations in the leachates of lysimeter studies for transformation products when selecting different sorption constants and degradation half-lives. The simulations were based on the FOCUS Hamburg scenario and the 80th percentile of annual concentrations. All transformation products considered for this comparison were formed by “ordinary” parents (no deviations between EU and German methodology for the parent).

In total 30 transformation products were found where EU and national inputs deviate caused by different sorption constants (32%) or half-lives (13%). However, 8 of these substances were not considered further since they were already formed by parent compounds which were characterised by different national and EU parameter selection.

Table 3-5: Summary of the comparison of PELMO simulations (based on FOCUS Hamburg scenario and 80th temporal percentile) with observed annual average concentrations in the leachates of lysimeter studies of transformation products when selecting different sorption constants and degradation half-lives (Plant uptake = 0)

Modelling end-points		**Comparison**						
Kfoc /Kf	**DegT50**	**Total no.**	**PELMO DE ≥ Lysimeter**	**PELMO DE < Lysimeter**	**PELMO EU (arith) ≥ Lysimeter**	**PELMO EU (arith) < Lysimeter**	**PELMO EU (geo)≥ Lysimeter**	**PELMO EU (geo) < Lysimeter**
Kf_{oc}(ar m.)	90thp.	6	6	0	6	0	6	0
Kf (ar m.)	geo m.	8	4	4	3	5	4	4
Kf(10thp.)	geo m.	4	4	0	2	2	3	1
Kf (ar m.)	90thp.	2	2	0	0	2	0	2
Kf(10thp.)	90thp.	0	0	0	0	0	0	0
Kf (CEC)	geo m.	1	1	0	1	0	1	0
Kf (pH)	pH	1	0	1	1	0	1	0
Total		22	17	5	13	9	15	7

* for parent: Kfoc = ar m. and DegT50 (lab+field) = geo m.
p. = percentile
pH =average of acid and neutral/basic soils (Kf arithmetic mean, DegT50 geometric mean)
CEC = dependent on cation exchange capacity

In Table 3-5 the remaining 22 substances were grouped into 7 different input classes according to the type of deviation. However, no transformation can be grouped into input classes with a 10th percentile of the sorption constant Kf and a 90th percentile of DegT50 values (Table 3-5, line 7).

- Average sorption constant Kfoc and 90th percentile of DegT50values (Table 3-5, line 3):
  Six situations were found that fitted into this class. The result of the comparison was independent on the methodology: PELMO always simulated higher concentrations than observed in the lysimeter study.
- Average sorption constant Kf and average DegT50 value (Table 3-5, line 4):
  8 compounds were found that fitted into this class. The result of the comparison was the same when following the German input parameter selection procedure or the new EU methodology: in 4 cases PELMO simulated higher concentrations than observed in the lysimeter study and in 4 cases it was the opposite. However, following the previous EU methodology (arithmetic mean Kfoc value) in only 3 cases PELMO simulated concentrations above the lysimeter result whereas in 5 cases it was the opposite.
- 10th percentile of Kf values and average DegT50 value (Table 3-5, line 5):
  Four transformation products belonged to this class. In all cases PELMO simulated higher concentrations than observed in the lysimeter study whereas in the simulation based on the previ-

ous EU methodology two simulations were below the respective experimental result. The result for the new EU methodology (Kfoc based on geometric mean value) was again between the other methodologies (3 above, 1 below the lysimeter result).

- Average sorption constant Kf and 90th percentile of DegT50 values (Table 3-5, line 6):
  2 transformation products belonged to this class. When following the German input parameter selection procedure PELMO simulated higher concentrations than observed in the lysimeter study whereas in the simulation based on both EU methodologies it was the opposite. Due to the DegT50 value the German methodology is clearly more conservative.
- Kf based on CEC and average DegT50 values (Table 3-5, line 8):
  Only a single transformation product belonged to this class. The result of the comparison was independent on the methodology: PELMO always simulated higher concentrations than observed in the lysimeter study.
- Sorption and Degradation dependent on pH (Table 3-5, line 9):
  Only a single transformation product belonged to this class. When following the EU-methodologies (new or previous) PELMO simulated higher concentrations than observed in the lysimeter study whereas in the simulation based on the German methodology it was opposite. This is not surprising, since the German methodology is not necessarily more conservative here, just different.

Table 3-5 confirms the previous conclusion that the criteria in Holdt et al. (2011) for lower tier groundwater modelling on a national scale ensure in general a safe and conservative estimation of the groundwater risk assessment also for transformation products for which a high variance of the input parameters Kfoc and/or DegT50 has been considered. However, for 5 of 22 substances annual average concentrations in the lysimeter experiment were found to be above respective simulation results. For these compounds no correlations between organic carbon content and sorption were found and the simulation was based on the average Kf in 4 cases and in one case adsorption was depended on CEC. In 4 of the 5 situations the respective simulations based on the Kfoc (both EU methodologies) the comparison led to the same result.

However, when using the previous EU methodology (Kfoc values always based on arithmetic mean) 4 more compounds were found where higher concentrations were observed in lysimeter studies than in the PELMO simulation. For two of these substances the 10th percentile of Kf values had to be considered according to the German methodology, for the third one it was the 90th percentile of DegT50 values. The final case was based on average Kf values when following the German methodologies. These more conservative selections finally resulted in higher simulated concentrations than observed in the lysimeter.

The new EU input parameter selection procedure was found to be more conservative than the previous EU methodology: compared to the national input parameter procedure only 2 more situations were found were lysimeter studies were above simulation results. In both cases the more conservative 90th percentile of DegT50 values was considered in the national simulations according to Holdt et al. (2011).

4 Analysis based on regulatory triggers

The analysis in the previous chapter demonstrated that the computer simulations represent in general conservative estimations. However, even when the input parameter selection was based on the (compared to the EU selection methodologies) more conservative national procedure in about 18% of the comparisons PELMO still simulated lower concentrations than observed in the higher tier study. Aim of this chapter is to perform an additional analysis based on different regulatory limits to evaluate the possible impact of these cases on regulatory decisions.

The EU wide trigger value for active compounds with respect to groundwater is 0.1 µg/L. As from the point of registration it does not necessarily matter whether the computer simulation is above or below the lysimeter result as long as their ratio to the trigger of 0.1 µg/L is the same. Therefore, the results were evaluated according to the following groups for parent compounds (P):

- Group PA: PELMO < 0.1 µg/L and lysimeter < 0.1 µg/L (acceptable risk in lower and higher tier)
- Group PB: PELMO > 0.1 µg/L and lysimeter < 0.1 µg/L (acceptable risk in higher tier only)
- Group PC: PELMO < 0.1 µg/L and lysimeter > 0.1 µg/L (no risk in lower tier, but in higher tier studies)
- Group PD: PELMO > 0.1 µg/L and lysimeter > 0.1 µg/L (risk indicated in both lower and higher tier)

Comparing the four cases above, group PC can be considered as most critical, because it would mean that the simulation underestimates measured concentrations from field experiments (as represented by the lysimeter study). Such cases would lead to the conclusion that the FOCUS Hamburg scenario in combination with the national input parameter for modelling may not be conservative enough to ensure a realistic worst case scenario approach.

In contrast, group PB is principally less critical when focusing on the level of protection. However, if group PB is dominant it will reduce the usefulness and acceptability of the initial tier as it indicates the need for higher tier studies when they are unnecessary.

Generally, the sum of the groups PA, PB and PD represents the level of protection, for which a safe prediction of the leaching concentration compared to lysimeter results can be ensured.

For transformation products the situations are more complicated, since the concentration range between 0.1 µg/L and 10 µg/L (in the following just expressed as "trigger class 1") for metabolites is also conducted. This is important since metabolites for which the prediction shows leaching in this range have to be assessed whether or not they are relevant in groundwater.

However, checking the range is more complicate than a simple check against a threshold as more than four comparisons have to be considered. The concentration ranges for the comparison have to be split into 3 trigger classes for metabolites:

- Trigger class 0: < 0.1 µg/L
- Trigger class 1: ≥ 0.1 < 10 µg/L
- Trigger class 2: ≥ 10 µg/L

This ends up into 9 different groups for metabolites (M) of simulation and experimental result:

- Group MA: PELMO below 0.1 µg/L (trigger class 0) and lysimeter below 0.1 µg/L (trigger class 0), (acceptable risk in lower and higher tier)
- Group MB: PELMO below 0.1 µg/L (trigger class 0) and lysimeter in the range (trigger class 1), (no risk in lower tier, but relevance assessment triggered from higher tier study)
- Group MC: PELMO below 0.1 µg/L (trigger class 0) and lysimeter above/equal 10 µg/L (trigger class 2), (no risk in lower tier, but risk indicated in higher tier study)
- Group MD: PELMO in the range (trigger class 1) and lysimeter below 0.1 µg/L (trigger class 0), (acceptable risk in higher tier, finally no relevance assessment from lower tier necessary)
- Group ME: PELMO in the range (trigger class 1) and lysimeter in the range (trigger class 1), (relevance assessment triggered from both lower and higher tier)
- Group MF: PELMO in the range (trigger class 1) and lysimeter above/equal 10 µg/L (trigger class 2), (unacceptable risk indicated from higher tier study only)
- Group MG: PELMO above/equal 10 µg/L (trigger class 2) and lysimeter below 0.1 µg/L (trigger class 0), (unacceptable risk indicated in lower tier, but finally no risk by higher tier results)
- Group MH: PELMO above/equal 10 µg/L (trigger class 2) and lysimeter in the range (trigger class 1), (unacceptable risk indicated in lower tier, but finally only relevance assessment necessary by higher tier results)
- Group MI: PELMO above/equal 10 µg/L (trigger class 2) and Lysimeter above/equal 10 µg/L (trigger class 2), (risk indicated in both lower and higher tier)

4.1 Evaluation based on all substances

As the regulatory concentrations and consequences for active compounds and metabolites are different, no special evaluation is performed with all substances included.

4.2 Evaluation based on active substances only

In Table 4-1the results of the comparison are presented. As explained above the columns group PA and PD represent the same classification of the result (= above or below the trigger of 0.1 µg/L) in the simulation and lysimeter experiment. This does not depend on the input parameter selection procedure, which was followed.

Table 4-1: Summary of the comparison of calculated with observed annual leaching concentrations (33 active substances, no plant uptake, trigger: 0.1 µg/L)

Group Comparison (n=33)	PA Lysimeter <0.1 µg/L PELMO < 0.1 µg/L	PB Lysimeter <0.1 µg/L PELMO > 0.1 µg/L	PC Lysimeter > 0.1 µg/L PELMO < 0.1 µg/L	PD Lysimeter >0.1 µg/L PELMO > 0.1 µg/L	Total
EU (Kfoc: arith. m.)	25 (75.8%)	6 (18.2%)	1 (3.0%)	1 (3.0%)	33 (100%)
EU (Kfoc: geom. m.)	25 (75.8%)	6 (18.2%)	1 (3.0%)	1 (3.0%)	33 (100%)
DE	20 (60.6%)	11 (33.3%)	1 (3.0%)	1 (3.0%)	33 (100%)

Figure 4-1 highlights the differences between the PELMO variations for the applied substance (active compounds). Again, better agreement between simulation and experiment was reached when using the EU input parameter selection procedures (based on geometric or arithmetic mean Kfoc value) compared to the more conservative German procedure. The figure also shows that in many of the selected cases for the analysis the applied active substances do not leach which is reflected by the lysimeter results as well as with model simulations (group PA).

Figure 4-1: Agreement between experiment and simulation for different simulation variations (active substances only, n=33)

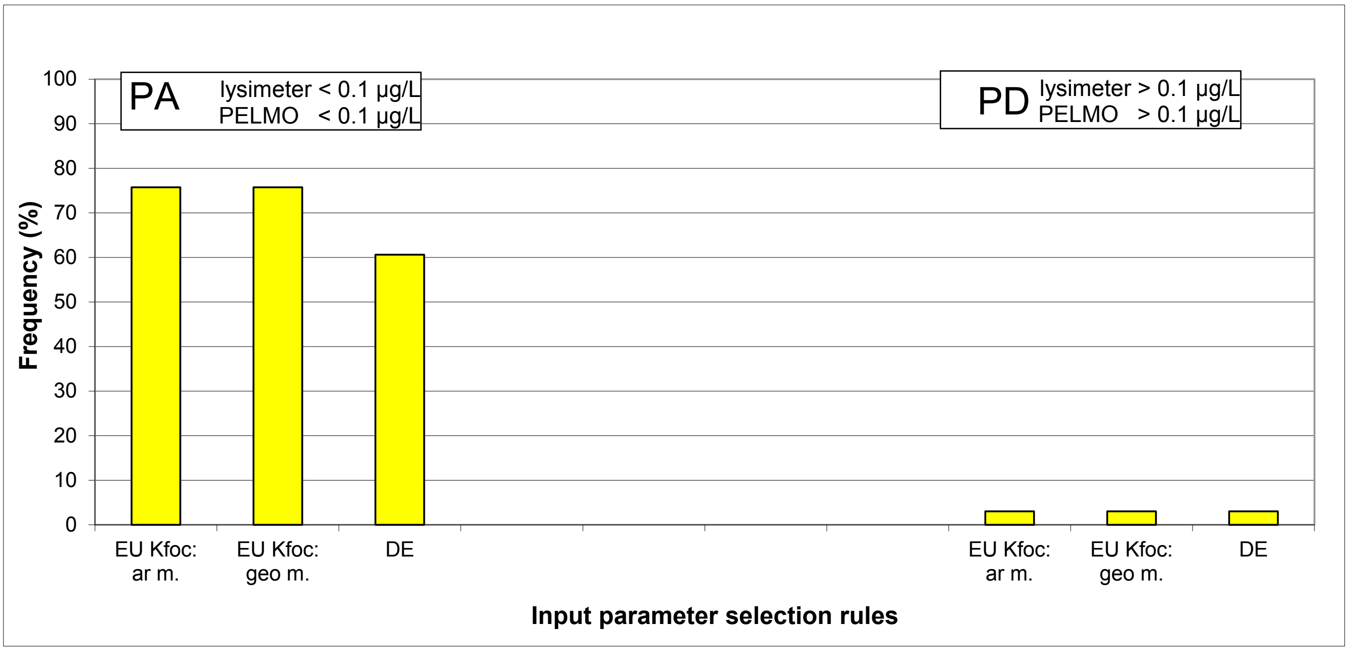
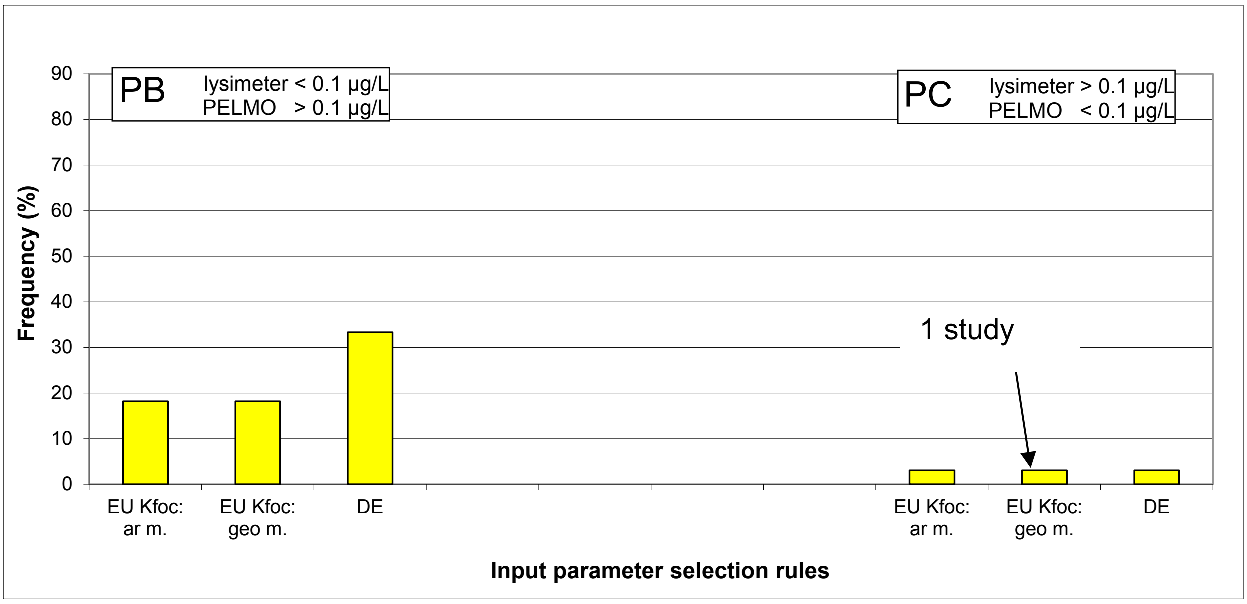


Figure 4-2 shows the situations which led to disagreements between experiments and simulations. The predominant number of cases are characterised by simulation results above the trigger and experimental studies below the trigger which indicates the conservative character of the standard leaching scenario. The remaining cases (group "PC": lysimeter > 0.1 µg/L and PELMO < 0.1 µg/L) hardly occur. The small bars in Figure 4-2 only represent the results of a single study with substance 72 (autumn application) where the findings in the lysimeter could not be explained even based on the generally very conservative German input parameter selection procedure for laboratory degradation studies. The study was already mentioned in the previous section (see red circles in Figure 3-1 to Figure 3-3).

Figure 4-2: Disagreement between experiment and simulation for different simulation variations (applied substances only, n=33)



The analysis in the previous chapter 3 demonstrated that the computer simulations represent in general conservative estimations. But even when the input parameter selection was based on the (compared to the EU methodology) more conservative national approach in about 18% of the comparisons PELMO still simulated lower concentrations than observed in the higher tier study for active substances (see Table 3-2). Based on this additional evaluation considering the regulatory endpoint of 0.1 µg/L it can be concluded that the impact of these situations was only minor: Independent on the input parameter selection procedure only 3% false negative results (group PC) were found for active substances.

Both EU methodologies showed less false positive comparisons without increasing the number of false negative cases. That may be caused by a more conservative national input parameter selection if the variances are high.

4.3 Evaluation based on transformation products

4.3.1 Methodology

Also for transformation products the analysis in chapter 3.3 demonstrated that the computer simulations represent in general conservative estimations. However, in at least 18% of the comparisons PELMO simulated lower concentrations than observed in the higher tier study considering the national input parameter selection. However, the comparison for metabolites simulated using the previous EU methodology shows relatively more situations (about 28%) where higher concentrations were observed in lysimeter studies than in PELMO simulations. With a result of 21% the new EU methodology (based on geometric mean Kfoc value) was rather similar to the German approach. An additional analysis based on different regulatory limits is also performed for metabolites to evaluate the possible impact of these cases on regulatory decisions.

However, as explained earlier checking the range is more complicated than a simple check against a threshold value because more than four comparisons have to be considered as shown in Table 4-2.

Table 4-2: Overview of the different groups (MA to MI) relevant for the comparison of three different trigger classes of simulated results with respective observed data for metabolites

	Trigger Class	PELMO < 0.1 µg/L	0.1 µg/L ≤ PELMO ≤ 10 µg/L	PELMO > 10 µg/L
Trigger class		**0**	**1**	**2**
Lysimeter < 0.1 µg/L	0	MA	MD	MG
0.1 µg/L ≤ lysimeter ≤ 10 µg/L	1	MB	ME	MH
Lysimeter > 10 µg/L	2	MC	MF	MI

In order to structure the detailed information presented in Table 4-3 better the various cases MA to MI are consolidated into 5 groups with regard to their relevance for regulatory risk assessment:

- Main regulatory group (MRG) I: agreement between PELMO and lysimeter (MA, ME, MI)
- Main regulatory group (MRG) II: PELMO more conservative than lysimeter i.e. false positive (MD, MG, MH)
- Main regulatory group (MRG) III: PELMO trigger class 0 and lysimeter trigger class 1 i.e. false negative, no risk in lower tier, but relevance assessment triggered from higher tier study (MB)
- Main regulatory group (MRG) IV: PELMO trigger class 0 and lysimeter trigger class 2 i.e. false negative, no risk in lower tier, but risk indicated in higher tier study (MC)
- Main regulatory group (MRG) V: PELMO trigger class 1 and lysimeter trigger class 2 i.e. false negative, unacceptable risk indicated from higher tier study only (MF)

4.3.2 Results

Table 4-3 shows the results of the comparisons.

Table 4-3: Summary of the comparison of calculated with observed annual leaching concentrations for transformation products with regard to the range 0.1 µg/L to 10 µg/L

Input parameter selection according to	MRG I Lysimeter. = Pelmo	MRG II Lysimeter < Pelmo	MRG III Lysimeter > 0.1 µg/L Pelmo < 0.1 µg/L	MRG IV Lysimeter > 10 µg/L Pelmo < 0. 1µg/L	MRG V Lysimeter > 10 µg/L Pelmo > 0.1 µg/L	Sum
EU (Kfoc: ar. m.)	46 (64.8%)	20 (28.2%)	5 (7.0%)	0	0	71
EU (Kfoc: geo m.)	41 (57.7%)	25 (35.2)	5 (7.0%)	0	0	71
DE	42 (59.2%)	25 (35.2)	4 (5.6%)	0	0	71

	MA	ME	MI	MD	MG	MH	MB	MC	MF	Sum
EU (Kfoc: ar. m.)	23	18	5	7	4	9	5	0	0	71
EU (Kfoc: geo m.)	19	17	5	11	4	10	5	0	0	71
DE	18	19	5	12	4	9	4	0	0	71

The following conclusions can be drawn based on the aggregated information in Table 4-3:

Independent of the input parameter selection procedure the majority of cases showed agreement between the PELMO simulation and lysimeter study (new EU: 57.7%, DE: 59.2%, MRG I, previous EU: 64.8%).

MRG II summarises the cases not critical in regulatory risk assessment when the simulation predicts a potential problem (PECgw either above 0.1 µg/L or 10 µg/L) but the experiment did not (false positive). About one third of the comparisons led to this result showing the conservatism of the PELMO simulations (FOCUS Hamburg). However, when using the German methodology according to Holdt et al. (2011) or the new EU methodology based on the geometric mean Kfoc value the number of false positive results is significantly higher compared to the previous EU methodology.

The probability of problematic false negative results (lysimeter showed a problem which PELMO did not determine, was found to be 7% when considering the EU methodologies. A slightly lower percentile (5.6%) belonged to this class when the simulation was based on the national input parameter selection procedure as described in Holdt et al (2011).

However, all false negative results were confined to experimental findings in the range of 0.1 µg/L to 10 µg/L. In all situations when leaching was observed above 10 µg/L in the lysimeter study PELMO predicted it as well (in none of the cases any disagreement independent on the input parameter selection procedure).

The analysis in the previous chapter 3 demonstrated that the computer simulations represent in general conservative estimations. But even when the input parameter selection was based on the (compared to the EU methodology) more conservative national approach in about 18% of the comparisons PELMO still simulated lower concentrations than observed in the higher tier studies (see Table 3-4).

Based on this additional evaluation considering the regulatory endpoints it can be concluded that the impact of these situations was less pronounced than indicated by the percentage of 18%. Dependent on the selection methodology only 7% (EU methodology) or 5.6% (national methodology) false negative results (MRG III) were found.

When comparing the three methodologies the previous EU methodology showed less false positive comparisons. That may be caused by a more conservative national input parameter selection if the variances of adsorption values are high.

4.4 Deviations between the national and European approach

The analysis performed in chapter 3.4 (Table 3-4 and Table 3-5) confirmed that the criteria in Holdt et al. (2011) for lower tier groundwater modelling on a national scale ensured a safe and conservative estimation of the groundwater risk assessment in most of the cases also for those active compounds and metabolites, for which a high variance of the input parameters Kfoc and DegT50 have been considered.

When using the EU methodologies (always average Kfoc values) more situations were found where higher concentrations were observed in lysimeter studies than in the PELMO simulation.

Aim of this chapter is to perform an additional analysis based on different regulatory limits to evaluate the possible impact of unfavourable cases on regulatory decisions.

Table 4-4 shows the results for parent compounds and the regulatory trigger of 0.1 µg/L. The simulations were based on FOCUS Hamburg and the 80th percentile of annual leachate concentrations.

Table 4-4: Summary of the comparison of calculated with observed annual leaching concentrations when selecting Kf or Kfoc values (active compounds, no plant uptake, trigger: 0.1 µg/L)

			PA			PB			PC			PD		
			Lysimeter < 0.1 µg/L			Lysimeter < 0.1 µg/L			Lysimeter > 0.1 µg/L			Lysimeter > 0.1 µg/L		
			Pelmo < 0.1 µg/L			Pelmo > 0.1 µg/L			Pelmo < 0.1 µg/L			Pelmo> 0.1 µg/L		
Kfoc /Kf	**DegT50**	**n**	**DE**	**EU**		**DE**	**EU**		**DE**	**EU**		**DE**	**EU**	
				ar. m.	**geo. m.**		**ar. m.**	**geo. m.**		**ar. m.**	**geo. m.**		**ar. m.**	**geo. m.**
Kfoc (ar. m.)	90th p.	2	1	2	2	1	-	-	-	-	-	-	-	-
Kf (ar. m.)	geo.m.	3	3	3	3	-	-	-	-	-	-	-	-	-
Kf (10th p.)	geo.m.	1	-	-	-	1	1	1	-	-	-	-	-	-
Kf (10th p.)	90th p.	2	1	2	2	1	-	-	-	-	-	-	-	-
total		8	5	7	7	3	1	1	-	-	-	-	-	-

p. = percentile

pH =average of acid and neutral/basic soils (Kf arithmetic mean, DegT50 geometric mean)

CEC = dependent on cation exchange capacity

Due to the analysis performed in chapter 3.4 there were a small number of cases where PELMO simulated lower concentrations for parent compounds than observed in experimental studies (EU methodologies: 2 out of 8, German methodology: 1 out of 8, see Table 3-4), none of them would have resulted in a problematic situation in registration as the experimental results were below the regulatory limit of 0.1 µg/L. Nevertheless the two methodologies lead to differences as demonstrated in Table 4-4. The table shows the same input classes as Table 3-4 in section 3.4.

- Average sorption constant Kfoc but 90th percentile of DegT50 values (Table 4-4):
  Two situations were found that fitted into this input class. Both active compounds were simulated correctly by the two EU-type simulations (group PA), whereas in the more conservative national simulation (selection of the 90th percentile of the DegT50) only one situation was correctly simulated (group PA). The other situation was classified as type "PB" (false positive). However, no false negative results (group PC) were observed independent on the selection criteria.

- Average sorption constant Kf and average DegT50 value (Table 4-4):
  Three substances were found that fitted into this input class. The result of the comparison was independent on the methodology: In all cases (EU and DE methodology) the simulation came to the same result as the experimental study (<0.1 µg/L, group PA). Consequently, no false negative results (group PC) were found.

- 10th percentile of Kf values and average DegT50 value (Table 4-4):
  Only a single parent compound was found that fitted into this input class. The result of the comparison was independent on the methodology: Both EU and DE simulation results were above the trigger whereas the experimental result was below (false positive, group PB). Again, no false negative results (group PC) were found.

- 10th percentile of Kf values and 90th percentile of DegT50 values (Table 4-4):
  Two situations were found that fitted into this input class. Both compounds were simulated correctly by the two EU-type simulations (group PA)), whereas in the more conservative national simulation (selection of the 90th percentile of the DegT50) one simulation were simulated below the trigger (group PA), the other one above (group PB, false positive).) only one situation was correctly simulated (group PA). The other situation was classified as type "PB" (false positive). However, no false negative results (group PC) were observed independent on the selection criteria.

No active substances can be grouped into input classes with an average sorption constant Kf and a 90th percentile of DegT50 value, with a Kf value dependent on CEC and Kf/ DegT50 values dependent on pH. Table 3-4 confirms that all input parameter selection procedures (EU and German) ensure a safe and conservative estimation of the groundwater risk. No false negative results are identified independent on the chosen input parameter selection procedure (EU or German).

There was of course a single assessment when PELMO simulated a lower concentration than observed in the lysimeter study (see section 3.4, Table 3-4). However, regarding the results presented in Table 4-4 for active substances (regulatory necessity for additional higher tier studies) the German approach led to 3 times more results that belonged to that group PB (both EU: 1 (13%), DE: 3(38%).

Table 4-5 shows the results for transformation products and the regulatory limits in the range of 0.1 µg/L to 10 µg/L. The simulations were based on FOCUS Hamburg and the 80th percentile of annual concentrations. All transformation products considered for this comparison were formed by "ordinary" parents (no deviations between EU and German methodology for the parent).

Table 4-5: Summary of the comparison of calculated with observed annual leaching concentrations when selecting Kf or Kfoc values for transformation products with regard to the range of 0.1 µg/L to 10 µg/L

			MRG I			MRG II			MRG III			MRG IV			MRG V		
Kfoc /Kf	DegT50	n	DE	EU		DE	EU		DE	EU		DE	EU		DE	EU	
				ar. m.	geo. m.		ar. m.	geo. m.		ar. m.	geo. m.		ar. m.	geo. m.		ar. m.	geo. m.
Kfoc (ar. m.)	90th p.	6	3	4	3	3	2	3	0	0	0	0	0	0	0	0	0
Kf (ar. m.)	geo. m.	8	4	4	4	2	2	2	2	2	2	0	0	0	0	0	0
Kf (10th p.)	geo. m.	4	1	3	1	3	1	3	0	0	0	0	0	0	0	0	0
Kf (ar. m.)	90thp.	2	1	2	3	1	0	0	0	0	0	0	0	0	0	0	0
Kf(CEC)	geo m.	1	0	0	0	1	1	1	0	0	0	0	0	0	0	0	0
Kf(pH)	pH	1	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0
total (number)		22	10	14	11	10	6	9	2	2	2	0	0	0	0	0	0
Total (%)			45.5	63.6	50.0	45.5	27.3	40.9	9.1	9.1	9.1	0	0	0	0	0	0

p. = percentile

pH =average of acid and neutral/basic soils (Kf arithmetic mean, DegT50 geometric mean)

CEC = dependent on cation exchange capacity

In total 22 cases were found where parameter selection according to Holdt et al. (2011) deviated from the EU methodology. They were in principal grouped in Table 4-5into 7 different input classes according to the type of deviation. However one group remained empty since no metabolite had respective properties (Kf: 10th percentile., DegT50: 90th percentile)

- Average sorption constant Kfoc and 90th percentile of DegT50 values:
  Six situations were found that fitted into this input class. 4 compounds were simulated correctly when input parameters were selected based on the previous EU-methodology (MRG I), the remaining 2 compounds resulted in MRG II classification (false positive). The more conservatives simulations according to the national approach (selection of the 90th percentile of the DegT50) or the selection of the geometric mean Kfoc value (new EU methodology) resulted in 3 simulations below the trigger (MRG I), the other 3 above (MRG II, false positive). No false negative results (MRG III, IV, V) were observed independent on the selection criteria.

- Average sorption constant Kf and average DegT50 value:
  9 compounds were found that fitted into this input class. Two false negative results were found (MRG III, 22%) independent on the input parameter selection procedure. However, the more conservative national approach according to Holdt et al. (2011) led to more false positive results (MRG II, 33%) compared to the EU methodologies (both 22%).

- 10th percentile of Kf values and average DegT50 value:
  Four transformation products belonged to this input class. No false negative results (MRG III, IV, V) were found independent on the input parameter selection procedure. However, the situation with regard to false positive results (MRG II) was completely different: 25% belonged to this group when following the previous EU methodology (based on arithmetic mean Kfoc value) whereas 75% belonged to this group when following the national or the new EU methodology.

- 10th percentile of Kf values and 90th percentile of DegT50 values:
  Only a single substance was found that fitted into this input class. The result of the comparison was independent on the methodology (MRG I, agreement). Consequently, no false negative results (MRG III, IV, V) were found.

- Kf based on CEC and average DegT50 values:
  Only a single substance was found that belonged to this input class. The result of the comparison was independent on the methodology MRG II (false positive). Consequently, no false negative results (MRG III, IV, V) were found.

- Sorption and degradation dependent on pH:
  Only a single substance was found that fitted into this input class. The result of the comparison was independent on the methodology (MRG I, agreement). No false negative results (MRG III, IV, V) were found.

According to the analysis performed in chapter 3.4 (Table 3-5, column 5) for 5 of 22 transformation products (23%) annual concentrations in the lysimeter experiments were found to be above respective simulation results. For these metabolites there was no correlation between organic carbon content and sorption (no transformation product belonged to input class 1) and so the simulation was based on Kf values. Nevertheless, the impact of this result on registration decisions may be less pronounced since only for 9% (2 of 22 compounds) false negative results were obtained independent on the chosen input parameter selection procedure (Table 4-5, MRG III). That percentage is only slightly higher than the corresponding percentage in the evaluation for all transformation products (5.6% and 7% for national and EU methodology, respectively, see section 4.3, Table 4-3, MRG III).

When comparing the false positive situations (regulatory necessity for additional higher tier studies) the German methodology led to 2 times more results that belonged to MRG II (previous EU: 27%, national: 45%). The number of these false positive results using the new EU methodology based on geometric mean Kfoc value was only slightly smaller than the number of false positive results using the national methodology (new EU: 41%).

5 Discussion and Conclusion

The protection level of the tiered groundwater risk assessment for plant protection products in Germany has been investigated in this project. Thereby, the main objectives were to determine, whether lower tier calculations using FOCUS PELMO 5.5.3 are still more conservative than higher tier results from outdoor lysimeter studies and thus the national groundwater modelling approach ensures a safe prediction of leachate concentrations for both active substances and their metabolites. Furthermore, the discrepancies and their possible causes between simulated and experimentally derived leachate concentrations dependent on the input parameter selection procedure for modelling should be investigated.

Three different methodologies for selecting input parameters for modelling with FOCUS PELMO were considered: the national input parameter selection procedure according to Holdt et al. (2011), the previous EU methodology based on the arithmetic mean Kfoc value and the new EU methodology based on the geometric mean Kfoc value. According to EFSA (2014) the geometric mean should better describe the variation of parameters. If the DegT50 was analysed in field and laboratory studies in EFSA (2014) a procedure is also described for deciding whether or not the DegT50 values from laboratory and field dissipation databases can be treated separately or can be pooled. With regard to this procedure the current guidance was not followed in this evaluation. Instead laboratory and field degradation half-lives were kept separately and either geometric mean DegT50 from laboratory or field studies was used. This is because the available field studies were not performed according to the requirements outlined in EFSA (2014). Due to the limitations with regard to DegT50 the presented results will only be preliminary.

For the evaluation in this project the same data sets of 104 substances (33 active compounds, 71 metabolites) have been considered as given in Klein et al. (2016), which were based on the data available in 2011. It is current practice in registration to use the worst case sorption constant if less than 4 Kfoc values are available. Therefore, the same values for the geometric and arithmetic simulation were used in this analysis even if the geometric and arithmetic mean values were different. In so far, the present evaluation generally followed the rules in the current registration process rather than the methodologies of pure statistical analyses.

The 80th percentile of predicted groundwater concentrations for the Hamburg scenario simulated over 20 years with FOCUS PELMO 5.5.3 and the maximum average annual leachate concentrations from lysimeter experiments were compared for 33 active compounds and 71 metabolites. For 38 of the 104 substances (37%, 8 active compounds and 30 metabolites) EU and national input parameters deviated caused by different sorption constants (29%) or half-lives (13%). However, 8 of these 30 transformation products were not considered further since they were already formed by parent compounds characterised by different national and EU input parameter selection.

For the comparison concentrations below 0.01 µg/L were set to 0.01 µg/L independent whether they were based on lysimeter results or simulations. This was done since uncertainties correlated with analytical determinations and model haziness below 0.01 µg/L can be significant but the overall conclusions would be nevertheless the same. For all three input parameter selection methodologies, in most of the cases FOCUS PELMO 5.5.3 calculated higher concentrations than determined in the outdoor lysimeter studies. However, the national input parameter selection procedure was found to be more conservative (PELMO above lysimeter: 81.7%) than the previous EU methodology (PELMO above lysimeter: 74.0%). However, results according to the new EU input parameter selection procedure based on the geometric mean Kfoc value were found to be in the range between the results of other two methodologies (78.8%, see chapter 3.1, Table 3-1).

The analysis demonstrated that the model simulations represent conservative estimations when comparing them with lysimeter results in most of the cases. Nevertheless, the portion of compounds with a non-safe prediction might be still higher considering that uncertainties still remain and have to be taken into account related to single applications and the short duration of lysimeter studies (see chapter 4 in FOCUS 2009/2014).

When comparing the results separately for active compounds and transformation products no differences can be found with regard to the level of protection. Both the national methodology and the new EU methodology (geometric mean of Kfoc) show the same percentages for both types of compounds. However the national lower tier groundwater risk assessment is slightly more protectable compared to FOCUS modelling with averaged EU endpoints based on the geometric mean Kfoc value.

As no final conclusions about the regulatory impact could be drawn from this direct comparison of predicted and measured average annual concentrations in 1 m soil depth a further analysis based on different limit values was performed for both active substances and transformation products.

The EU wide trigger value for active compounds with respect to groundwater is 0.1 µg/L. Since from the viewpoint of registration it does not necessarily matter whether the simulation is above or below the lysimeter result as long as their ratio to the trigger of 0.1 µg/L is the same a further analysis was performed taking into account this aspect.

Based on this additional analysis it could be concluded that the regulatory impact of these situations was only minor for active substances: Independent on the input parameter selection methodology (previous/new EU or national) only 3% false negative results (only one active substance) were found.

When comparing the three input parameter selection methodologies, both EU methodologies (Kfoc based on geometric value and arithmetic mean value) showed less false positive comparisons without increasing the number of false negative cases. That may be caused by the more conservative national input parameter selection for modelling if the variances of the adsorption and/or degradation values are high.

A similar regulatory impact analysis as for the active substances was also performed for the transformation products. However, the situation was more complex, since the concentration range between 0.1 µg/L and 10 µg/L for metabolites had also to be checked.

Independent of the input parameter selection methodology the majority of cases showed agreement for transformation products in the PELMO simulation and lysimeter study (main regulatory group MRG I). Thereby, the results for the new EU and the national methodology have the same order of magnitude (new EU 57.7%, DE: 59.2%). The agreement for the previous EU methodology based on arithmetic mean Kfoc value is even higher (64.8%, see Table 4-3).

The following results were obtained for the cases not critical in regulatory risk assessment when the simulation predicts a potential problem (either above 0.1 µg/L or 10 µg/L) but the leachate concentration did not (false positive): about one third of the comparisons for metabolites led to this result showing the conservatism of the PELMO simulations. However, when using the new EU methodology or the German methodology according to Holdt et al. (2011) the number of false positive results is higher (35.2%) than for the previous EU methodology (28.2%, see Table 4-3).

The probability of problematic false negative results for metabolites (lysimeter showed a problem which PELMO did not determine) was found to be 7% when considering both EU methodologies. A slightly lower percentage (5.6%) belonged to the main regulatory group MRG III when the simulation was based on the more conservative national methodology as described in Holdt et al. (2011).

However, all false negative results for metabolites were confined to experimental findings in the range of 0.1 µg/L to 10 µg/L. In all situations when leaching was observed above 10 µg/L in the lysimeter study PELMO predicted the same (in none of the cases disagreement occurred independent on the input parameter selection).

According to the national groundwater risk assessment in Germany and in contrast to the EU methodology a high variance of the parameters Kfoc and DegT50 is taken into account when selecting input parameters for modelling as described in chapter 4.3 (Holdt et al. 2011). For adsorption a Kf value is used instead of the arithmetic mean Kfoc value if the coefficient of variation Kfoc exceeds 60% and if there is no correlation between organic carbon content and sorption constant. In such cases the correlations between Kf values and other soil properties (pH, clay, CEC) have to be checked and specific Kf values can be used for modelling. If there is no correlation observed and the coefficient of variation Kf is ≤ 100% the arithmetic mean value, otherwise the 10th percentile of all available Kf values should be used for modelling. For degradation the 90th percentile DegT50 value instead of the geometric mean value should be used when the coefficient of variation is > 100%. This methodology for selecting national endpoints may have an effect on the groundwater modelling results.

In order to compare the new EU input parameter selection procedure (geometric mean Kfoc value) with both other methodologies an additional evaluation was performed. Therefore, all substances were selected from the database where Kf values (German methodology) instead of Kfoc values (EU methodology) or 90th percentiles DegT50 values (German methodology) instead of the geometric mean DegT50 (EU methodology) should be used. In total 30 out of 104 cases were found that matched the required conditions and finally different national endpoints for modelling have been selected for that compounds compared to the typical input parameter selection in the EU assessment.

Eight parent compounds were identified where input parameter selection according to Holdt et al. (2011) deviated from the previous EU methodology. It was confirmed that the criteria in Holdt et al. (2011) for lower tier groundwater modelling on a national scale ensure a safe and conservative estimation of the groundwater risk assessment also for parent compounds, for which a high variance of the input parameters Kfoc and DegT50 have been considered. Only for one parent compound the maximum average annual concentration in the lysimeter experiment was found to be above respective simulation results (Table 3-4). For that compound no correlation between organic carbon content and sorption was found and the simulation was based on the average Kf value. For the respective simulation based on the Kfoc (EU methodology) the comparison led to the same result.

However, when using the EU methodologies (always average Kfoc values, either based on the arithmetic mean or on the geometric mean) one additional situation was found where higher concentrations were observed in lysimeter studies than in the PELMO simulation. For this respective active substance the DegT50 value was characterised by a high coefficient of variation (selection of the more conservative 90th percentile DegT50 according to Holdt et al. (2011)).

As no conclusions about the regulatory impact could be drawn from the direct comparison of predicted and measured average annual concentration in 1 m soil depth a further analysis based on different limit value concentrations was also performed for the eight active compounds.

It was confirmed that all three input parameter selection methodologies (previous/new EU and the German methodology according to Holdt et al. 2011) ensure a safe and conservative estimation of the groundwater risk. No false negative results were obtained independent whether the EU or the national input parameter selection procedure was followed. When comparing the false positive situations (regulatory necessity for additional higher tier studies) the German methodology led to 3 times more results that belonged to group PB (previous/new EU: 1 (13%), national: 3 (38%), see Table 4-4).

In addition to the parent compounds also 22 transformation products were found where input parameter selection according to Holdt et al. (2011) deviated from the EU methodology. All these selected transformation products were formed from parent compounds, for which no deviations between EU and German selection methodologies were observed and mean values for the input parameter could be used for the parent compounds.

It was confirmed that the new EU input parameter selection procedure based on the geometric mean (EFSA 2014) ensure in general a safe and conservative estimation of the groundwater risk assessment also for transformation products, for which a high variance of Kfoc and DegT50 was considered (see Table 3-5). However, for 7 of 22 metabolites annual concentrations in the lysimeter experiment were found to be above respective simulation results. Compared to the criteria in Holdt et al. (2011) for lower tier groundwater modelling on a national scale (5 of 22 lysimeter results were above respective simulations) the methodology is less conservative. For the respective simulation based on the arithmetic mean Kfoc value (previous EU methodology) even 9 of 22 lysimeter results were above the PELMO simulations.

Also for these 22 transformation products a regulatory impact analysis was performed to evaluate possible registration decisions. It was demonstrated that for only 9% (2 of 22 compounds) false negative results were obtained independent whether EU methodologies or the national input parameter selection procedure was followed (see Table 4-5, main regulatory group MRG III). That is only slightly higher than the corresponded value based on the evaluation of all transformation products (5.6% and 7% for national input parameter selection procedure and EU methodology, respectively, see chapter 4.3, Table 4-3, main regulatory group MRG III).

When comparing the false positive situations (relevant when asking for additional studies) the German methodology led to about 2 times more results that belonged to that group than the previous EU methodology (previous EU: 27%, national: 45%, see Table 4-5, main regulatory group MRG II). When using the new EU methodology (geometric mean Kfoc value according to EFSA 2014) also a relatively high number of false positive results were found (41%).

The following two tables show once more the key results of this project.

In Table 5-1 the results of the direct comparison of calculated and observed concentrations are presented. Overall, the German input parameter selection procedure is slightly more conservative than the new EU methodology based on the geometric mean Kfoc value according to EFSA (2014). In contrast results based on the previous EU methodology using the arithmetic mean Kfoc value show more situations where lysimeter results are above respective PELMO simulations. Especially transformation products and special compounds with high variability of input parameters are affected.

Table 5-1: Summary of the comparison of calculated concentration* with observed annual average concentrations in the leachates of lysimeter studies
(concentration below 0.01 µg/L set to 0.01 µg/L, numbers in brackets refer to special substances with high variability of input parameters)

	PELMO ≥ Lysimeter	PELMO < Lysimeter	PELMO ≥ Lysimeter	PELMO < Lysimeter
Parameter setting according to	**Parent compounds**		**Transformation products**	
EU (Kfoc: arithmetic mean)	78.8% (75.0%)	21.2% (75.0%)	71.8% (59.1%)	28.2% (40.9%)
EU (Kfoc: geometric mean)	78.8% (75.0%)	21.2% (25.0%)	78.9% (68.2%)	21.1% (31.8%)
DE	81.8% (87.5%)	18.2% (12.5%)	81.7% (77.3%)	18.3% (22.7%)

* all PELMO simulations based on FOCUS Hamburg scenario (80th temporal percentile)

In Table 5-2 and Table 5-3 information about the regulatory impact of the different methodologies are presented. Basically, no differences between the methodologies were found when comparing the false negative results (lysimeter showed a problem which PELMO did not determine, see also columns PC and MRG III in Table 5-2 and Table 5-3). When comparing the three input parameter selection procedures with regard to false positive comparisons (PB and MRG II in the same tables) the results depend on whether active compounds or transformation products are simulated. For active compounds both EU methodologies led to 2 to 3 three times lower false positive results than the national input parameter selection procedure. With respect to the group MRG II in these two tables the situation is different for transformation products, since the new EU methodology (EFSA 2014) results in similar percentages than the national input parameter selection procedure according to Holdt et al. (2011). In contrast the previous EU methodology is characterized by lower deviations of type MRG II.

Table 5-2: Summary of the comparison of calculated with observed annual leaching concentrations

Input parameter selection according to	Parent compounds (33 substances)				Transformation products (71 substances)				
group	PA	PB	PC	PD	MRG I	MRG II	MRG III	MRG IV	MRG V
Lysimeter	< 0.1 µg/L	< 0.1 µg/L	> 0.1 µg/L	> 0.1 µg/L	Lysim.	Lysim.	> 0.1 µg/L	> 10 µg/L	> 10 µg/L
PELMO	< 0.1 µg/L	> 0.1 µg/L	< 0.1 µg/L	> 0.1 µg/L	= Pelmo	< Pelmo	< 0.1 µg/L	< 0. 1µg/L	> 0.1 µg/L
EU (Kfoc: arithm. mean)	75.8%	18.2%	3.0%	3.0%	64.8%	28.2%	7.0%	0.0%	0.0%
EU (Kfoc: geom. mean)	75.8%	18.2%	3.0%	3.0%	57.7%	35.2%	7.0%	0.0%	0.0%
DE	60.6%	33.3%	3.0%	3.0%	59.2%	35.2%	5.6%	0.0%	0.0%

Table 5-3: Summary of the comparison of calculated with observed annual leaching concentrations for special substances with high variability of input parameters

Input parameter selection according to	Parent compounds (8 substances)				Transformation products (22 substances)				
group	PA	PB	PC	PD	MRG I	MRG II	MRG III	MRG IV	MRG V
Lysimeter	< 0.1 µg/L	< 0.1 µg/L	> 0.1 µg/L	> 0.1 µg/L	Lysim.	Lysim.	> 0.1 µg/L	> 10 µg/L	> 10 µg/L
PELMO	< 0.1 µg/L	> 0.1 µg/L	< 0.1 µg/L	> 0.1 µg/L	= Pelmo	< Pelmo	< 0.1 µg/L	< 0. 1µg/L	> 0.1 µg/L
EU (Kfoc: arithm. m.)	87.5%	12.5%	0.0%	0.0%	63.6%	27.3%	9.1%	0.0%	0.0%
EU (Kfoc: geom mean)	87.5%	12.5%	0.0%	0.0%	50.0%	40.9%	9.1%	0.0%	0.0%
DE	62.5%	37.5%	0.0%	0.0%	45.5%	45.5%	9.1%	0.0%	0.0%

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7 Appendix

Table 7-1: Overview about the geometric and arithmetic Kfoc values used in this evaluation

No.	Geometric mean Kfoc (L/kg)	Arithmetic mean Kfoc (L/kg)
1	138.00	138
2	46.90	49
3	68.36	92
4	186.41	200
5	10.58	11
6	9.65	10
7	46.00	62
8	410.87	780
9	350.39	364
10	25.58	37.1
11	43.42	50
12	48.01	50
13	32.00	32
14	26.62	27
15	13.68	14
16	22.26	29
17	36.63	46
18	7.14	8
19	6.42	9
20	122.42	277
21	3.94	5
22	5.38	8
23	224.70	232
24	74.86	78
25	180.09	187
26	122.55	195
27	46.63	58
28	110.60	133
29	79.36	93
30	22.97	24
31	22.31	41
32	113.92	142
33	112.00	118

No.	Geometric mean Kfoc (L/kg)	Arithmetic mean Kfoc (L/kg)
34	32.69	33
35	47.00	47
36	84.84	91
37	0.00	0
38	2288.18	2379
39	116.09	121
40	76.06	88
41	4.20	4.2
42	18.99	23
43	837.00	850
44	8.15	10
45	0.00	0
46	77.00	77
47	600.70	624
48	309.98	319
49	18.81	21
50	67.36	72
51	3.66	4
52	0.00	0
53	330.58	351
54	33.96	37
55	29.72	42
56	66.69	88
57	71.68	73
58	4936.00	6063
59	364.25	495
60	626.24	643
61	5.57	6
62	236.69	248
63	40.42	41
64	189.02	227
65	6.46	8
66	3.23	7
67	256.77	315
68	14.04	34
69	34.40	43
70	231.22	275

No.	Geometric mean Kfoc (L/kg)	Arithmetic mean Kfoc (L/kg)
71	27.07	32
72	113.65	126
73	136.96	147
74	47.44	86
75	12.08	16
76	0.00	0
77	64.23	74
78	31.61	37
79	26.00	26
80	19.00	19
81	8.50	8.5
82	65.03	124
83	7.34	25
84	10.95	15
85	29.39	47
86	16.49	31
87	38.92	72
88	25.08	73
89	14.32	24
90	46.52	53
91	70.55	83
92	298.94	357
93	10.61	16
94	32.09	34
95	5.08	6
96	74.30	86
97	33.28	46
98	28.64	30
99	69.66	79
100	63.21	73
101	303.21	321
102	4.20	6
103	21.09	26
104	2.17	6

Table 7-2: Results of lysimeter and PELMO simulation for active substances where different sorption constants and degradation half-lives are found based on the German and EU methodology

Input Class	Kf_{oc} /Kf DE	$DegT_{50}$ DE	No	Lysimeter (µg/L)	DE (µg/L)	EU Kfoc: ar m. (µg/L)	EU Kfoc: geo m. (µg/L)
1(n=2)	Kfoc(ar m.)	90th p	23	0.01	0.032	0.001	0.001
			53	0.05	4.666	0.058	0.083
2(n=3)	Kf (ar m.)	geo m.	58	0	0	0	0
			78	0	0	0	0
			88	0.01	0	0	0
3(n=1)	Kf (ar m.)	90th p	10	0.01	0.243	0.206	0.306
5(n=2)	Kf (10th p.)	90th p	43	0	0	0	0
			64	0	2.422	0.011	0.027

ar m. = arithmetic mean
geo m. = geometric mean
p. = percentile
P = PELMO, L = Lysimeter

Table 7-3: Results of lysimeter and PELMO simulation for transformation products where different sorption constants and degradation half-lives are found based on the German and EU methodology

Input Class	Kf_{oc} /Kf	$DegT_{50}$ DE	No	Lysimeter (µg/L)	DE (µg/L)	EU Kfoc: ar m. (µg/L)	EU Kfoc: geo m. (µg/L)
1 (n=6)	Kfoc (ar m.)	90th p.	9	0.01	1.582	0.036	0.146
			24	0.01	17.535	0.615	0.704
			30	0.332	7.669	4.656	4.877
			37	0	660.698	559.168	558.025
			79	0	0	0	0
			80	0	0.016	0	0
2 (n=8)	Kf (ar m.)	geo m.	21	0.03	0.168	0.238	0.28
			34	0.025	2.442	3.002	3.025
			56	6.49	0.038	0.01	0.04
			59	6.49	0	0.002	0.061
			68	2.35	3.244	2.207	5.066
			71	0.09	0.031	0	0
			100	0.005	0	0	0
			102	0	0.063	0.018	0.043
3 (n=4)	Kf (10thp.)	geo m.	32	0.025	0.159	0.11	0.178
			69	1.99	6.832	0.946	1.641
			86	0.058	0.216	0.041	0.1
			87	0.034	0.212	0.043	0.117
4 (n=2)	Kf (ar m.)	90th p.	103	0.902	2.193	0.613	0.749
			93	0.05	3.463	0	0.002
6 (n=1)	Kf (CEC)	geo m.	19	0.03	5.743	5.467	5.519
7 (n=1)	Kf (pH)	pH	8	0.01	0.006	0.012	0.063

p. = percentile
pH = average of acid and neutral/basic soils DegT50
Kf(pH) average of acid and neutral/basic soils arithmetic mean Kf
CEC = dependent on cation exchange capacity