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# Protection of the groundwater against loads of plant protection products: validation of the new EU-simulation model FOCUS PELMO 4 for a reliable prediction of the leaching potential of PPP into groundwater

## Part A I: Validation of the national groundwater modelling approach based on results of outdoor lysimeter studies

## Part A II: Results of inverse modelling optimisation using InversePELMO

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# Protection of the groundwater against loads of plant protection products: validation of the new EU-simulation model FOCUS PELMO 4 for a reliable prediction of the leaching potential of PPP into groundwater

Part A I: Validation of the national groundwater modelling approach based on results of outdoor lysimeter studies
Part A II: Results of inverse modelling optimisation using InversePELMO

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## Kurzbeschreibung

Seit 2012 wird das Computerprogramm FOCUS PELMO eingesetzt um das Versickerungspotential von aktiven Substanzen und ihren Abbauprodukten innerhalb des deutschen Zulassungsverfahrens für Pflanzenschutzmittel zu berechnenen. Aufgrund damit verbundener verschiedener Modifizierungen des nationalen Bewertungsverfahrens blieb allerdings die Frage offen, in wie weit das Schutzniveau immer noch ausreichend ist. Deshalb wurde in diesem Projekt die erste Stufe des nationalen Bewertungsverfahrens (FOCUS PELMO) mit Hilfe von 104 Substanzen darunter 33 Wirkstoffen, zu denen jeweils auch Lysimeterstudien unter Freilandbedingungen vorlagen, validiert. Unter Berücksichtigung aller Aspekte der Analyse weisen die Ergebnisse darauf hin, dass die FOCUS PELMO Simulatonen basierend auf beiden untersuchten Methoden zur Input Parameterbestimmung (national und EU) für die meisten der untersuchten Substanzen eine sichere und konservative Abschätzung des Grundwasserrisikos ermöglichen besonders, wenn Unsicherheiten aufgrund analytischer Probleme und Modellunsicherheiten unterhalb von 0.01 µg/L ignoriert werden. Unsicherheiten in der modellbasierten Vorhersage von Sickerwasserkonzentrationen wurden vor allem bei Abbauprodukten identifiziert. Im zweiten Teil des Projekts wurde überprüft, ob inverse Modellierungen mit Lysimeterstudien mit PELMO zu sinnvollen Optimierungen führen. Dies sollte dazu unter anderem dazu dienen, die Ergebnisse einer Freilandlysimeterstudie auch auf andere Bedingungen (insbesondere Laufzeitverlängerung, jährlich wiederholende Applikationsmuster) zu extrapolieren. Angesichts der Auswahl der Lysimeterstudien in dieser Analyse und unter Berücksichtigung der hohen Anzahl von Optimierungen, bei der das Standard FOCUS PELMO Modell nicht in der Lage war, das Substanzverhalten adäquat zu beschreiben, können inverse Modellierungen nicht als Standardinstrument für die Verfeinerung empfohlen werden. Für eine Reihe von Studien deuten die inversen Modellierungen außerdem darauf hin, dass die Ergebnisse von Lysimeterstudien durch präferentiellen Fluss beeinflusst waren. In Kombination mit Expert judgment könnte die Technik der inversen Modellierung daher eingesetzt werden, um entsprechende Experimente zu filtern.

## Abstract

Since 2012 the computer model FOCUS PELMO is used to calculate the leaching potential of active substances and their degradation products within the German national registration of plant protection products. Due to further modifications in the national groundwater risk assessment the question remains still open and needs to be answered if the level of protection of the new modelling approach is still sufficient. Therefore, the new national groundwater modelling approach at the lower tier and its protection level was validated considering 104 substances (33 active compounds) for which the results of lysimeter studies under field conditions were available. Looking at all aspects of the analysis the results indicate, that both used methodologies for lower tier groundwater modelling (national and EU) ensure for the majority of investigated compounds a safe and conservative estimation of the groundwater risk assessment especially when uncertainties correlated with analytical determinations and model haziness below 0.01 µg/L are are ignored. Uncertainties with regard to a safe prediction of leachate concentrations by modelling partly remain for degradation products. In the second part of the project it was analysed whether inverse modelling based on lysimeter studies and PELMO leads to meaningful optimisations. Aim was to evalulate whether the results of outdoor lysimeter studies can be transferred to other conditions (e.g. prolongation, repeated applications). Given the selection of lysimeter studies used in this evaluation and considering the significant number of optimisations where the standard FOCUS PELMO model could not adequately describe the substance transport in the lysimeter the use of inverse modelling cannot be recommended as a standard tool/approach for the refinement of tier 1 simulations. For a couple of studies inverse modelling showed evidence that the lysimeter study was influenced by preferential flow. In combination with expert judgement this technique could therefore be used to identify respective experiments.

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# 1 Zusammenfassung

## 1.1 Hintergrund und Ziele

Über viele Jahre wurde das Computerprogramm PELMO Version 3.0 (Klein 1995, Jene et. al. 1998) eingesetzt um das Versickerungspotential von aktiven Substanzen und ihren Abbauprodukten innerhalb des deutschen Zulassungsverfahrens für Pflanzenschutzmittel zu berechnen. Die Auswahl der Eingabeparameter erfolgte nach den Empfehlungen von MICHALSKI et al. (2004a). Wird nach den Ergebnissen derartiger Berechnungen der vom Trinkwassergrenzwert abgeleitete Grundwasserwert für Pflanzenschutzmittel von 0,1 µg/L für den Wirkstoff erreicht oder überschritten, so ist das Pflanzenschutzmittel nicht zulassungsfähig oder es sind Freilandlysimeterstudien nach der BBA RICHTLINIE TEIL 4-3 (1990) durchzuführen, deren Ergebnisse als regulatorische Endpunkte in die Bewertung eingehen.

Allerdings werden seit 2012 entsprechende Simulationsrechnungen auf Basis des Programms FOCUS PELMO und seiner europäischen Szenarien durchgeführt (FOCUS 2009/2014). Hintergrund des Wechsels war die Verordnung 1107/2009 (EG) nach der die Risikoabschätzung mit harmonisierten Verfahren durchzuführen ist, aber spezifische nationalen Bedingungen in einer angemessenen Weise berücksichtigt werden sollen. Aufgrund dieser Anforderungen wurde das existierende nationale Bewertungsverfahren entsprechend angepasst.

Nach dem Erscheinen des FOCUS Grundwasserberichts (FOCUS 2009/2014) hat das UBA gemeinsam mit Vertretern des Industrieverbandes Agrar (IVA) im Rahmen des Arbeitskreises Ökochemie den bisherigen nationalen Bewertungsansatz überarbeitet (Holdt et al. 2011).

Aufgrund verschiedener Modifizierungen des nationalen Bewertungsverfahrens unter Berücksichtigung von FOCUS (2009/2014) ist allerdings die Frage, in wie weit das Schutzniveau immer noch ausreichend ist, noch offen. Deshalb wurde die erste Stufe des neuen nationalen Bewertungsverfahrens (FOCUS PELMO Simulationen) im Rahmen dieses Projekts mit Hilfe von Lysimeterstudien unter Freilandbedingungen validiert, die als höherwertige Studien im nationalen Bewertungsverfahren akzeptiert sind.

Ziel dieses Projekts war es daher, dem Umweltbundesamt wissenschaftliche Hintergründe für mögliche Änderungen oder Erweiterungen des aktuellen Verfahrens zum Grundwasserschutz bereitzustellen.

Konkret wurden folgende Punkte in dem Projekt adressiert:

- Validierung des nationalen Bewertungsverfahrens: Vergleich der Ergebnisse des Hamburg-Szenarios von FOCUS PELMO (Version 5.5.3) mit experimentellen Ergebnissen von Freilandlysimeterstudien.
- Evaluierung der Lysimeterstudien im Hinblick auf die Frage, ob sie geeignet sind, das Versickerungsverhalten von Aktivsubstanzen und ihrer Abbauprodukte mit Hilfe der Technik der inversen Modellierung zu beschreiben.
- Evaluierung des Schutzniveaus der aktuellen FOCUS Standardszenarien Hamburg und Kremsmünster und Ihrer Repräsentativität für Umweltbedingungen in Deutschland. (Die Ergebnisse dieses Ziels wurden in einem separaten Dokument zusammengestellt.)
- Empfehlungen für ein protektives nationales gestuftes Bewertungsverfahren, dass sowohl harmonisierte EU-Prinzipien als auch nationale Besonderheiten berücksichtigen.

## 1.2 Ergebnisse

### 1.2.1 Teil A I: Validierung des nationalen Bewertungsverfahrens für Grundwasser mit Hilfe von Freilandlysimeterstudien

Im Rahmen des nationalen Zulassungsverfahren für Pflanzenschutzmittel (PSM) haben Modellierungen mit dem Simulationsmodell FOCUS PELMO eine Schlüsselfunktion für den nationalen Bewertungsansatz in der Risikobewertung Grundwasser. Im ersten Teil des Projekts erfolgte eine Validierung der ersten Stufe des Verfahrens (Simulationen mit dem FOCUS Hamburg Szenario) mit Hilfe von Lysimeterstudien, die unter Freilandbedingungen nach der BBA Richtlinie IV 4-3 durchgeführt wurden. Diese Validierung wurde erforderlich, weil seit 2012 das Modell FOCUS PELMO (Version 5.5.3) anstelle der älteren Version PELMO 3.0 für die Vorhersage von Sickerwasserkonzentrationen eingesetzt wird, um eine stärkere Harmonisierung in der Risikobewertung Grundwasser zwischen dem EU- und dem nationalen Bewertungsverfahren zu erreichen. Zusätzlich wurde im Rahmen des Modellwechsels auch die Auswahl von Modell-EIngabeparametern modifiziert (Holdt et al. 2011). Ein Ziel des Projekts war es daher, die Größe und Ursache von Unterschieden zwischen experimentellen und berechneten Konzentrationen im Sickerwasser zu bestimmen. Dabei lag der Fokus auf der Fragestellung, ob die Simulationen immer noch zu hinreichend konservativeren Ergebnissen als entsprechende experimentelle Ergebnisse führen und so das nationale Verfahren zum Grundwasserschutz eine sichere Vorhersage des Versickerungsverhaltens für aktive Substanzen und deren Abbauprodukten gewährleistet.

Im ersten Schritt wurden für 33 Wirkstoffe und 71 Metaboliten geeignete Lysimeterstudien ausgewählt und die erforderlichen Modell-Eingabeparameter für eine Risikoabschätzung nach der deutschen Methodik zusammengestellt. Es wurde für diesen Zweck eine eigene Datenbank für die relevanten Daten unter Verwendung von Microsoft Visual Basic entwickelt. Diese Datenbank enthält einerseits aggregierte Daten (z.B. mittlere Sorptionskonstanten) aber auch spezifische Information über individuelle Sorptions- und Abbaustudien (Labor und Feld). Die zusätzlichen Informationen zu individuellen Studien können direkt über die Datenbankmasken abgerufen werden. Insgesamt sind in der Datenbank 104 Substanzen (33 Aktivsubstanzen und 71 Abbauprodukte) enthalten. Die Ableitung der für die Modellierung erforderlichen Endpunkte zur Adsorption und zum Abbau in Böden erfolgte nach dem derzeit gültigen nationalen Bewertungsansatz (Holdt et al., 2011) mit dem EXCEL Tool Input Decision (Version 3.3).

Im nächsten Schritt wurde von allen Substanzen das 80. Perzentil über 20 Jahre der mit FOCUS PELMO 5.5.3 berechneten Grundwasserkonzentrationen berechnet. Dabei erfolgte die Parameterauswahl sowohl entsprechend dem nationalem also auch dem EU-Verfahren.

Darüber hinaus wurden Simulationen nach dem deutschem Bewertungsansatz für alle Substanzen zunächst basierend nur auf Laborabbaudaten und anschließend zusätzlich auf Freilandabbaudaten durchgeführt, um einen zusätzlichen Vergleich der Simulationsergebnisse zwischen Labor- und Freilanddaten zu ermöglichen. In allen Fällen der Modellierung entsprachen die Applikationsdaten und die Kulturbedingungen denen der entsprechenden Lysimeterstudien.

Für 38 der 104 Substanzen (37%, 8 Wirkstoffe und 30 Metabolite) ergaben sich unterschiedliche Eingabedaten (EU- und nationales Verfahren) in 29% der Fälle aufgrund unterschiedlicher

Sorptionskonstanten, in 13% aufgrund unterschiedlicher Abbauraten. Im weiteren Verlauf der Analyse wurden allerdings 6 dieser Transformationsprodukte nicht weiter verfolgt, weil bereits die jeweiligen Elternsubstanzen durch unterschiedliche Eingabeparameter bei beiden Verfahren (EU und national) charakterisiert waren.

In der Mehrheit der Fälle lagen die mit dem Simulationsmodell FOCUS PELMO berechneten Konzentrationen über denen in Freilandlysimeterstudien gemessenen maximalen Jahresdurchschnittskonzentrationen. Allerdings ergaben sich konservativere Ergebnisse für das nationale Verfahren (PELMO oberhalb Lysimeter: 72%) als für das EU-Verfahren (PELMO oberhalb Lysimeter: 64%). Dieses Ergebnis zeigt, dass die Kriterien des nationalen Bewertungsansatzes (Holdt et al (2011)) eine hinreichend sichere und konservative Abschätzung der Risikobewertung Grundwasser für 72% aller untersuchten Substanzen gewährleisten, wenn man Freilandlysimeterstudien mit experimentellen Ergebnissen als Basis für die Überpüfung des Schutzziels heranzieht. Das Schutzniveau erhöht sich auf 82%, wenn Unsicherheiten aufgrund analytischer Bestimmungsgrenzen und Modellunsicherheiten unterhalb von 0.01 µg/L ignoriert werden.

Ein Vergleich der Simulationen mit Labor- und Freilandabbaudaten, basierend auf dem nationalen Bewertungsschema, zeigte keine wesentlichen Unterschiede in Bezug auf das Schutzniveau. 84.5% der Simulationsergebnisse basierend auf Labordaten und 83.9% der Simulationsergebnisse basierend auf Felddaten waren höher als die entsprechenden Sickerwasserkonzentrationen der Freilandlysimeterstudien.

Die Analyse zeigte, dass sich das nationale Bewertungsverfahren durch ein leicht höheres Schutzniveau auszeichnet als der europäische Ansatz mit EU-Endpunktfestlegung (79% sichere Vorhersagen für Aktivsubstanzen, 72% sichere Vorhersagen für Abbauprodukte).

Obwohl die Computersimulationen grundsätzlich konservative Abschätzungen im Vergleich zum Lysimeterergebnis darstellen, könnte der Anteil der Substanzen mit einer nicht sicheren Vorhersage höher sein, aufgrund einer möglicherweise zu kurzen Laufzeit der experimentellen Studie sowie der häufig nur einmaligen Applikation.

Da von diesem direkten Vergleich zwischen berechneten und experimentell gemessenen jährlichen Sickerwasserkonzentrationen kein abschließendes Fazit über die Auswirkungen auf regulatorische Entscheidungen gezogen werden konnte, wurde eine weitere Analyse durchgeführt basierend auf unterschiedlichen Grenzwerten für Aktivsubstanzen und Abbauprodukten.

Der EU-weite Grundwassergrenzwert (abgeleitet aus dem Trinkwassergrenzwert) für Wirkstoffe und relevante Metaboliten beträgt 0.1 µg/L. Da es am Ende für nationale Zulassungsentscheidungen nicht zwingend relevant ist, ob Computersimulationen oberhalb oder unterhalb vom Lysimeterergebnis liegen, so lange das Verhältnis zum Trigger 0.1 µg/L gleich ist, wurde eine weitere Analyse gemacht, die diesen Umstand berücksichtigt.

Basierend auf dieser zusätzlichen Analyse konnte gefolgert werden, dass in nahezu allen Fällen das Verhältnis zum Grenzwert richtig beschrieben wurde. Unabhängig von der Endpunktbestimmung (EU oder national) wurden für Wirkstoffe nur 3% falsch-negative Ergebnisse (eine Substanz) gefunden.

Der Vergleich der zwei Auswahlmethoden (EU und national) zeigte, dass das EU-Verfahren zu einer geringeren Anzahl falsch-positiver Ergebnisse führt, ohne dass sich die Anzahl der falsch-negativen Resultate erhöht. Ursache hierfür ist die Auswahl konservativerer Endpunkte für die Modellierungen, wenn die Varianzen der Sorptions- und Abbauwerte hoch sind.

Wie bereits erwähnt, wurden auch für Abbauprodukte grundsätzlich konservative Abschätzungen erhalten. Allerdings lagen in etwa 18% (nationales Verfahren) bzw. 28% (EU-Verfahren) der Fälle die berechneten Konzentrationen unterhalb der gemessenen Jahresdurchschnittskonzentrationen der Lysimeterstudien. Eine vergleichbare Analyse möglicher Auswirkungen dieser Fehler auf regulatorische Entscheidungen wurde auch für die Abbauprodukte durchgeführt. Allerdings ist die Situation hier komplizierter, weil nicht nur der Triggergrenzwert 0.1 µg/L für relevante Metaboliten, sondern auch der Bereich zwischen 0.1 µg/L und 10 µg/L für nichtrelevante Metaboliten überprüft werden muss.

Unabhängig von der Art der Ableitung der Endpunkte wurde in der Mehrheit der Fälle eine Übereinstimmung zwischen den Simulationsergebnissen und den gemessenen Konzentrationen in Lysimeterstudien auch für Abbauprodukte gefunden.

Als unkritisch für die regulatorische Bewertung werden die Fälle betrachtet, bei denen die Modellierungen ein Risiko voraussagen, das durch die Ergebnisse einer Freilandlysimeterstudie nicht bestätigt wird (falsch-positiv), d.h. der berechnete Wert liegt entweder > 0.1 µg/L (Triggerwert für relevante Metaboliten) oder > 10 µg/L (Triggerwert für nicht relevante Metaboliten), während die gemessenen Konzentrationen unterhalb dieser Triggerwerte liegen. Dies traf auf etwa ein Drittel der Fälle zu. Der Unterschied zwischen beiden Auswahlverfahren liegt bei 35% im nationalen Verfahren entsprechend Holdt et al. (2011) und 28% im EU-Verfahren.

Im Gegensatz dazu sind die Fälle als kritisch für die regulatorische Bewertung zu betrachten, bei denen die Lysimeterergebnisse ein Risiko anzeigen, d.h. die gemessene Jahresdurchschnittskonzentration beträgt > 0.1 µg/L bzw. > 10 µg/L, obwohl das Simulationsergebnis unterhalb des jeweiligen Triggerwerts liegt. Die Wahrscheinlichkeit für ein solches falsch-negatives Ergebnisse betrug beim EU-Verfahren 7%, während bei dem konservativeren Verfahren auf Basis von Holdt et al. (2011) ein geringfügig niedrigerer Wert von 5.6% gefunden wurde. Allerdings lagen alle falsch-negativen Resultate im Bereich 0.1 µg/L bis 10 µg/L. In allen Fällen, bei denen Konzentrationen oberhalb von 10 µg/L in der Lysimeterstudie gemessen wurde, konnte die PELMO Simulation dies bestätigen (keine Abweichung unabhängig vom Auswahlverfahren).

Entsprechend des nationalen Bewertungsansatzes zur Risikoabschätzung für den Bereich Grundwasser (und im Unterschied zum EU-Verfahren) werden höhere Varianzen bei den Parametern $Kf_{oc}$ und $DegT_{50}$ bei der Festlegung der Modell-Inputparameter besonders berücksichtigt. So wird der Kf anstelle des $Kf_{oc}$ Werts für die Adsorption verwendet, wenn der Variationskoeffizient des $Kf_{oc}$ 60% überschreitet und keine Korrelation zwischen dem organischen Kohlenstoffgehalt im Boden und der Sorptionskonstante vorliegt. In diesen Fällen werden die Korrelationen des Kf Werts zu anderen Bodenparametern (pH, Ton, KAK) überprüft und spezifische Kf-Werte können für die Modellierung verwendet werden. Wenn keine Korrelation besteht und der Variationskoeffizient des Kf ist ≤ 100%, sollte der arithmetische Mittelwert, im anderen Fall das 10. Perzentile der Kf-Werte für die Simulationsrechnungen verwendet werden. Für den Abbau sollte das 90. Perzentil der $DegT_{50}$-Werte anstelle des geometrischen Mittelwerts verwendet werden, wenn der Variationskoeffizient oberhalb von 100% liegt.

Die Auswirkungen der Parameterauswahl bei einer hohen Streuung der Daten auf die Ergebnisse der Simulationsberechnungen wurden in einer gesonderten Analyse betrachtet. Dazu wurden alle Substanzen, bei denen die Kf-Werte (nationales Verfahren in Deutschland) anstelle des $Kf_{oc}$-Werts (EU Verfahren) oder das 90. Perzentil des $DegT_{50}$-Wertes (deutsches Verfahren) anstelle des geometrischen Mittelwerts (EU Verfahren) verwendet wurden, selektiert. Insgesamt 38 der 104 Substanzen (37%, 8 Wirkstoffe und 30 Transformationsprodukte) erfüllten prinzipiell die geforderten Bedingungen hinsichtlich der hohen Streuung der Adsorptions- und/oder der Abbaudaten, so dass daher anstelle eines Mittelwertes (EU-Ansatz) ein anderer Endpunkt abgeleitet und für Modellierungen verwendet wurde. Allerdings wurden 6 der 30 Transformationsprodukte nicht weiter verfolgt, weil sie bereits durch Elternsubstanzen gebildet wurden, die sich ihrerseits durch eine unterschiedliche Auswahl der Eingabeparameter bei EU und nationalem Verfahrem auszeichneten.

Unter den 32 weiter verfolgten Substanzen befanden sich acht Wirkstoffe. Die Analyse zeigte für diese Substanzen bis auf eine Ausnahme, dass die Modellierungsergebnisse höher als die gemessenen Lysimeterendpunkte waren und somit eine sichere und konservative Abschätzung ermöglicht wurde. Nur für einen Wirkstoff wurden maximale jährliche Konzentrationen im Lysimeter oberhalb des entsprechenden PELMO-Ergebnisses gefunden. Für diese Substanz wurde entsprechend dem nationalen Auswahlschema ein arithmetischer Kf-Mittelwert zusammen mit dem geometrischen $DT_{50}$ –Mittelwert für die Modellierung verwendet. In diesem Fall führte die entsprechende Simulation basierend auf dem $Kf_{oc}$-Wert (EU Methodik) zum gleichen Resultat.

Wenn allerdings die EU Methodik (grundsätzlich gemittelte Werte) verwendet wurde, ergab sich eine weitere Situation, bei der höhere Konzentrationen in der Lysimeterstudie beobachtet wurden als in der PELMO Simulation. Die entsprechende Aktivsubstanz zeichnete sich durch einen hohen Variationskoeffizienten der Abbaudaten aus, der beim nationalen Verfahren zur Auswahl des konservativeren 90. Perzentil der $DT_{50}$ –Werte führte.

Da kein abschließendes Fazit über die Auswirkungen auf regulatorische Entscheidung von diesem direkten Vergleich zwischen berechneten und experimentellen jährlichen Konzentrationen gezogen werden konnte, wurde eine weitere Analyse für Aktivsubstanzen durchgeführt.

Es bestätigte sich, dass beide Auswahlmethoden (EU und nationale Prozedur entsprechend Holdt et al. 2011) eine sichere und konservative Abschätzung des Grundwasserrisikos ermöglichen. Keine falsch-negativen Resultate wurden gefunden, ganz gleich ob das EU-Verfahren oder das nationale Verfahren angewendet wurde. Der Vergleich der falsch-positiven Situationen zeigte, dass der deutsche Bewertungsansatz im Vergleich zum EU-Ansatz zu einer dreifach höheren Anzahl dieser Fälle führt (EU: 13%, national: 38%).

Zusätzlich zu den acht Wirkstoffen wurden 24 Abbauprodukte analysiert, bei denen aufgrund einer hohen Streuung der Daten anstelle von Mittelwerten andere Endpunkte entsprechend dem nationalen Bewertungsansatz entsprechend Holdt et al. (2011) abgeleitet wurden. Unter diesen 24 Metaboliten befinden sich nur solche Abbauprodukte, deren Ausgangssubstanzen keine Abweichungen der Abbau- und Adsorptionsendpunkte zwischen EU- und nationalem Verfahren aufweisen. Das heißt, in den Modellierungen der Sickerwasserkonzentrationen für diese 24 Metaboliten wurden immer Mittelwerte der $DT_{50}$ und $Kf_{oc}$-Werte für die Muttersubstanzen entsprechend dem EU-Ansatz eingesetzt.

Es bestätigte sich, dass die Kriterien entsprechend Holdt et al. (2011) für nationale Grundwassermodellierungen im allgemeinen eine sichere und konservative Abschätzung des

Grundwasserrisikos auch für Abbauprodukte gewährleisten, die eine hohen Varianz von $Kf_{oc}$- und $DegT_{50}$– Werten aufweisen. Allerdings wurden für 6 der 24 Metaboliten jährliche Konzentrationen in Lysimetern oberhalb der entsprechenden Simulationsergebnisse gefunden. Für alle diese Fälle konnte keine Korrelation zwischen organischem Kohlenstoffgehalt im Boden und verfügbaren Sorptionwerten gefunden werden, und die Simulationen basierten auf dem Mittelwert oder 10. Perzentil des Kf-Werts. In einigen Fällen wurden auch Korrelationen des Kf-Werts mit CEC und pH verwendet. Die entsprechenden Simulationen auf Basis des $Kf_{oc}$-Werts (EU Verfahren) führten zum gleichen Resultat. Das EU Verfahren (stets gemittelte $Kf_{oc}$-Werte) führte allerdings bei weiteren Abbauprodukten (insgesamt 9) zu Situationen, bei denen höhere Konzentrationen im Lysimeter gefunden wurden als in der Simulation berechnet.

Auch für die 24 im nationalen Verfahren von der EU-Bewertung abweichenden Abbauprodukte wurde eine zusätzliche Analyse durchgeführt, um die Relevanz auf mögliche regulatorische Entscheidungen festzustellen. Es zeigte sich, dass nur in 8% der Fälle (2 von 24 Substanzen) falsch-negative Resultate auftraten, unabhängig, ob das EU oder das nationale Auswahlverfahren angewendet wurde. Dieser Prozentsatz ist nur geringfügig höher als die entsprechenden Zahlen für alle untersuchten Abbauprodukte (5.6% für das nationale Verfahren bzw. 7% für das EU Verfahren).

Der Vergleich der falsch-positiven Situationen zeigte, dass der deutsche Ansatz fast zu einer doppelten Anzahl dieser Fälle gegenüber der Auswahlmethode für Endpunkte im EU-Verfahren führt (EU: 25%, national: 42%).

Alle PELMO-Simulationen wurden mit und ohne Berücksichtigung des Pflanzenaufnahmefaktors (PUF = 0.5) durchgeführt. Unabhängig von der Art der Substanz (Aktivsubstanz oder Abbauprodukt) und des Verfahren (EU oder national) hatte der PUF nur einen geringen Einfluss auf den Vergleich. In etwa 3 bis 5% der Fälle wechselte das Ergebnis von PELMO > Lysimeter (PUF=0) zu PELMO < Lysimeter (PUF=0.5). Bei der zusätzlichen Analyse unter Berücksichtigung des Grenzwerts von 0.1 µg/L zeigte sich gar kein Einfluss des Pflanzenaufnahmefaktors.

Unter Berücksichtigung aller Aspekte der detaillierte Analyse weisen die Ergebnisse darauf hin, dass beide Methoden (national und EU) eine sichere und konservative Abschätzung des Grundwasserrisikos ermöglichen besonders, wenn Unsicherheiten aufgrund analytischer Bestimmungsgrenzen und Modellunsicherheiten unterhalb von 0.01 µg/L ignoriert werden.

Unter Berücksichtigung der Tatsache, dass keine Methodik in der Lage ist, eine 100%ige Sicherheit zu garantieren und unter Berücksichtigung der Tatsache, dass die Gesamtunterschiede zwischen beiden Verfahren nicht signifikant sind (PELMO Simulationen waren in 81.7% [national] bzw. 74% [EU] der Vergleiche konservativer als Lyismeterexperimente) und sogar identisch, wenn die Ergebnisse mit dem regulatorischen Trigger verglichen werden (3% falsch-negative Resultate für Aktivsubstanzen unabhängig vom Verfahren), wird empfohlen, Optionen für eine weitergehende Harmonisierung der nationalen Endpunktbestimmung mit dem EU Verfahren zu prüfen.

### 1.2.2 Teil A II: Evaluierung von Lysimeterstudien – Ergebnisse von inversen Modellierungen mit InversePELMO

Seit vielen Jahren werden Lysimeterstudien als höherwertige Studien für die Abschätzung des Versickerungspotentials in der deutschen Zulassung eingesetzt. Die Voraussetzung für die Akzeptanz dieser Freilandstudien ist, dass konservative Bedingungen für die Abschätzung des Versickerungspotentials festgelegt werden: ein sandiger Boden mit geringem Kohlenstoffgehalt und eine jährliche Niederschlagsmenge von etwa 800 mm, die als repräsentativ und „realistic worst case“ für nationale Bedingungen in Deutschland angesehen werden. Allerdings wurden in der Vergangenheit die Repräsentativität der Lysimeterstudien häufig kontrovers diskutiert, und ihre Eignung als direkte Entscheidungsbasis („Endpunktstudie“) wurde hinterfragt. Die Bedenken bezogen sich auch auf die relativ kurze Studiendauer mit normalerweise zwei oder drei Jahren in Kombination mit einer einmaligen Anwendung des Wirkstoffs zu Beginn der Studie. Das steht im Widerspruch zu den Ergebnissen der Versickerungsmodelle, die signifikante Versickerungen häufig erst nach längerer Zeit und wiederholten Anwendungen vorhersagen.

Da aber die Eigenschaften des FOCUS Hamburg Szenarios zu einem großen Teil auf den in der BBA-RICHTLINIE IV TEIL 4-3 (BBA1990) festgelegten Boden- und Klimabedingungen basieren, akzeptieren die deutschen Behörden bis heute Lysimeterstudien als „Endpunktstudien“. Daher soll in einer speziellen Analyse die Bedenken im Zusammenhang mit der kurzen Laufzeit und der einmaligen Applikation in Lysimeterstudien überprüft werden. Die Evaluierung wurde mit Hilfe der Technik der inversen Modellierung unter Verwendung des Softwaretools inversePELMO durchgeführt, welches das Simulationsmodell PELMO mit dem Optimierungstool „PEST“ kombiniert (Klein 2011). Der Ansatz besteht darin, Schlüsselparameter für die Risikobewertung wie $Kf_{oc}$ (Freundlich Sorptionskonstante relativ zum organischen Kohlenstoffgehalt) und $DegT_{50}$ (Zeit bis zu dem 50% des Abbaus erreicht sind) direkt aus den Ergebnissen der Lysimeterstudien abzuleiten und die Studie somit prozessorientiert interpretieren zu können. Dadurch soll ein tieferer Einblick in die Studienergebnisse gewonnen werden. Inverse Modellierungen werden von FOCUS (2009/2014) empfohlen, um die Qualität von Standardsimulationen zu verbessern, indem in diese zusätzliche Ergebnisse in Form von Abbauraten und Adsorptionswerten von höherwertigen Freilandstudien einfließen.

Für die Evaluierung wurden nur Lysimeterstudien an 4 deutschen Standorten zwischen 1989 und 1999 berücksichtigt, die nach der BBA Richtlinie IV Teil 4-3 (1990) durchgeführt wurden. Dies geschah vor dem Hintergrund, dass dadurch am ehesten vergleichbare Bedingungen zum FOCUS Hamburg Szenario sichergestellt werden können. Außerdem würden fehlende detaillierte Wetterdaten für diese Standorte leichter beschafft werden können. Die Lysimeterstandorte waren Neustadt (Rheinland-Pfalz), Schmallenberg, Monheim (beide Nordrhein-Westfalen) und Hamburg. Weiterhin wurden nur Lysimeterstudien berücksichtigt, bei denen es auch zu einer messbaren Versickerung von Substanzen gekommen ist (Wirkstoff oder zumindest ein Metabolit). Insgesamt wurden acht verschiedene Wirkstoffe und sechs Abbauprodukte analysiert (einige der Substanzen tauchten in mehreren Optimierungen auf). Leider lagen entscheidende Modell-Inputparameter bei den meisten Lysimeterstudien nicht vor, die für eine inverse Modellierung mit ausreichender Qualität benötigt werden. Dabei handelte es sich um folgende Datendefizite:

- Nicht ausreichende Wetterdaten (Auflösung nur monatlich)
- Beregnung nur in monatlicher Auflösung aufgezeichnet
- Keine Angaben zur potentiellen Evapotranspiration
- Nicht alle Proben analysiert (teilweise nur Radioaktivität untersucht)

Einige dieser Defizite sind dem Umstand geschuldet, dass die Lysimeterrichtlinie (BBA 1990) ursprünglich mit dem Ziel erarbeitet wurde, den Datenbedarf für inverse Modellierungen abzudecken. Besonders fehlende Angaben zur Evapotranspiration führten am Ende dazu, dass Parameteroptimierungen außerhalb des erwarteten Bereichs erfolgten.

Bevor die Substanzparameter optimiert wurden, wurde die Hydrologie im Boden mit Hilfe des Anfangswassergehalts und kulturspezifischer Kc-Faktoren angepasst. Diese Faktoren werden benutzt, um die generische potentielle Evapotranspiration in kulturspezifische Werte umzustellen. So lang der visuelle Eindruck und der FOCUS chi²-Test für das kumulative Perkolat zufriedenstellende Übereinstimmung aufwiesen, wurde die Optimierung nicht zurückgewiesen, nur weil sich optimierte Parameter vom üblichen Werteberich unterschieden.

Für die Optimierung der Parameter $Kf_{oc}$ und $DegT_{50}$ wurden die kumulativen Substanzeinträge im Perkolat verwendet. In einigen Situationen, bei denen die Substanz zu keiner Zeit im Sickerwasser aufgetreten ist, wurden auch die Bodenrückstände am Ende der Studie berücksichtigt, um die Aussagekraft entsprechender inverser Modellierungen zu überprüfen.

Für eine signifikante Anzahl von Optimierungen konnte das Standard FOCUS PELMO Modell den Substanztransport im Lysimeter nicht adäquat beschreiben. Unter Berücksichtigung der totalen Speicherkapazität des Bodenkerns waren diese Studien durch einen sehr frühen Substanzdurchbruch gekennzeichnet. Es wurde gefolgert, dass diese Studien teilweise durch präferentiellen Fluss beeinflusst waren. Obwohl dieser Prozess eher häufig bei schweren Tonböden beobachtet wurde, gibt es auch Berichte, die dieses Phänomen in Sandböden beschreiben. So wurde zum Beispiel in einer parallelen Feld- und Lysimeterstudien (Jene et al. 1998) das Auftreten von Matrixfluss in oberen und präferentiellen Fluss in unteren Schichten postuliert.

Um den Effekt einer längeren Studiendauer zu überprüfen, wurden für einige Studien „verlängerte“ Simulationen durchgeführt. Diese Rechnungen sollten die Frage beantworten, ob die Länge der Studien ausreichend ist und ob die experimentelle Studie nicht abgebrochen wurde, bevor das Maximum der Substanz den unteren Lysimeterboden bzw. das Sickerwasser erreicht hat. Ein weiterer Aspekt dieser Simulationen war die Untersuchung des Effekts von Mehrfachanwendungen auf langjährige Substanzkonzentrationen im Perkolat. Vor allem jene Studien wurden für weitere Extrapolationen ausgewählt, bei denen angenommen wurde, dass sie kaum durch präferentiellen Fluss beeinflusst waren. Um die Auswirkungen von Mehrfachanwendungen zu erkennen, wurden diese Simulationen sowohl mit einmaliger als auch mit jährlichen Applikationen durchgeführt.

Leider konnte diese Analyse nicht alle offenen Fragen im Hinblick auf die notwendige Studiendauer und Mehrfachanwendungen beantworten. Allerdings gab es folgende allgemeine Beobachtungen

- Die Versuchsdauer entsprechend BBA (1990) scheint für Substanzen mit niedrigen Sorptionskonstanten auszureichen, da die maximalen Konzentrationen innerhalb der Versuchsdauer abgedeckt werden. Außerdem schien für diese Substanzen der Effekt von Mehrfachanwendungen vernachlässigbar zu sein.
- Substanzen mit hohen Sorptionskonstanten erreichen nicht während der standardmäßigen Versuchsdauer entsprechend BBA (1990) die maximale Konzentration. Außerdem scheint der Effekt von Mehrfachanwendungen für diesen Substanztyp erheblich zu sein. Dabei ist die maximale Konzentration als auch die Zeitdauer bis zum Peak stark abhängig vom Anwendungsmuster.
- Keine Korrelation zwischen Sorption und notwendiger Studiendauer wurde für Substanzen im mittleren Sorptionsbereich gefunden, weil die aktuellen Wetterbedingungen und die Unterschiede zwischen den Lysimeterexperimenten zu hoher Variabilität führten.
- Die Abbaurate sollte hauptsächlich für Konzentrationsunterschiede bei Einfach- und Mehrfachanwendungen verantwortlich sein. Das konnte auch für zwei Substanzen gezeigt werden, bei denen erhebliche Unterschiede für beide Varianten auftraten. Allerdings wurden aufgrund der Kombination von Halbwertszeit und Sorptionskonstante und Applikationsmenge nur Konzentrationen deutlich unterhalb des Grenzwerts von 0.1 µg/L berechnet. Dennoch zeigten diese Simulationen, dass Mehrfachanwendungen die Konzentrationen von Subtanzen mit einer Halbwertszeit von etwa 60 Tagen stark beeinflussen können.

Dieses Fazit bezieht sich allerdings nur auf eine begrenzte Anzahl von untersuchten Studien und nur für diese Studien stellten verlängerte Simulationen eine sinnvolle Ergänzung des Experiments dar. Für diese Studien führten anschließende FOCUS PELMO Simulationen mit dem Standardszenario aber basierend auf optimierten Parametern zu niedrigeren Konzentrationen als mit entsprechenden Simulationen basierend auf Standard-Inputparametern. Nur in einem einzigen Fall, der durch präferentiellen Fluss beeinflusst war, wurden Konzentrationen oberhalb vom regulatorischen Endpunkt berechnet, der sich in der Studie nicht bestätigte.

Obwohl die Anzahl der experimentellen Datensätze begrenzt war, wurden weitere Simulationen durchgeführt, um das Verständnis für den Einfluss der Boden- und Wetterbedingungen für die berechneten Perkolatkonzentrationen besser zu verstehen. Das ist ein wichtiger Aspekt, wenn Lysimeterstudien auf andere Situationen extrapoliert werden sollen. Folgende Simulationen wurden zusätzlich berücksichtigt:

- Kombination von Lysimeterboden (inkl. Applikationsmuster) mit dem Standardwetter des FOCUS Hamburg Szenarios
- Kombination des Lysimeterwetters mit dem Standardboden des FOCUS Hamburg Szenarios

Basierend auf diesen Simulationen konnten einige Aussagen über maximale Konzentrationen in Lysimeterstudien mit folgenden Trends getroffen werden:

- In den Fällen, wo die Lysimeterstudie in Schmallenberg (Nordrhein-Westfalen) durchgeführt wurde, führt die Kombination FOCUS Hamburg Boden mit dem Lysimeter Klima zu höheren Konzentrationen im Sickerwasser als die Kombination FOCUS Hamburg Klima mit dem Lysimeterboden. Das kann dadurch erklärt werden, dass sich das Klima in Schmallenberg durch höhere Niederschlage als in Hamburg auszeichnet, während der Boden im FOCUS Szenario Hamburg und in den Schmallenberger Lysimeterstudien vergleichbar war. Letzteres ist nicht überraschend, da das FOCUS Hamburg Szenario basierend auf dem Boden Borstel, der für diese Lysimeterstudien verwendet wird, parametrisiert wurde.

- In den Fällen, wo die Lysimeterstudien in Neustadt (Rheinland-Pfalz) oder Monheim (Nordrhein-Westfalen) durchgeführt wurde, führte die Kombination FOCUS Hamburg Boden mit Lysimeter Wetter zu niedrigeren Perkolatkonzentrationen als die Kombination FOCUS Hamburg Klima mit dem Lysimeterboden. Das zeigt, dass das Klima von FOCUS Hamburg höhere effektive Niederschläge aufweist als das Lysimeterklima, während sich die Böden an den beiden Standorten eine stärkere Substanzverlagerung ermöglichen als im Standardszenario. Dies war nicht überraschend, wenn man die mittleren Kohlenstoffgehalte der Lysimeterböden mit dem des FOCUS Hamburg Szenarios vergleicht (FOCUS Hamburg: 0.78%, Neustadt: 0.49%, Monheim: 0.60%).

Für andere mögliche Kombinationen (z.B. verlängerte Simulationen mit reinen Lysimeter- oder reinen FOCUS-Simulationen) galten diese Regeln nur zu einem gewissen Grad mit einigen Ausnahmen, entweder verursacht durch besonders ungünstige Wetterbedingungen während der Studie oder aufgrund von Unterschieden bei der Auswahl der Zielkonzentration (maximale Konzentrationen / 80. zeitliches Perzentil). Wie bereits zuvor erläutert war ein Ziel des Projekts, verschiedene Fragen im Hinblick auf die Eignung von Lysimeterstudien entweder als "Endpunktstudie" oder als "Prozessstudie" zu adressieren. Allerdings konnten die meisten dieser offenen Fragen nicht adäquat aufgrund verschiedener Einschränkungen der vorliegenden Studien beantwortet werden. Folgendes Fazit wird dennoch basierend auf der Analyse gezogen:

- Der Vergleich von Simulationen mit Anwendungen über viele Jahre gegenüber Einfachapplikationen aber verlängerter Simulationszeit zeigte keine eindeutige Tendenz (6 Fälle ohne Effekt, 6 Fälle mit höheren Konzentrationen bei Mehrfachanwendungen, im Durchschnitt 70%, Bereich 15% bis 270%). Da die Eingabeparameter der entsprechenden Substanzen sich alle durch geringe Sorption und schnellem Abbau auszeichneten war nicht zu erwarten, dass sich selbst bei jährlichen Anwendungen ein Plateau ausbilden würde. Stattdessen waren höhere Konzentrationen eher durch eine höhere Wahrscheinlichkeit ungünstiger Wetterbedingungen verursacht.
- Falls Substanzen nicht während der Studie im Sickerwasser auftraten, so wurden bei den verlängerten Simulationen lediglich geringe Konzentrationen weit unterhalb des Grenzwerts (nicht messbar) berechnet.
- Es wurde bereits festgestellt, dass Simulationen mit Lysimeter-Wetterbedingungen zu geringeren Konzentrationen im Sickerwasser führten, wenn die Studie an Standorten mit geringerem Niederschlag als im FOCUS Hamburg Szenario vorgegeben, stattgefunden hatte (Neustadt, Monheim). Daraus folgt, dass auch das vorgegebene Beregnungsmanagement (BBA 1990) nicht in der Lage ist, die Differenzen zwischen dem FOCUS Klima und dem Klima am Standort auszugleichen.
- Der Boden aus dem Ort „Borstel“ aus Norddeutschland, der in Schmallenberger Lysimeterstudien eingesetzt wird, ist vor allem hinsichtlich des organischen Kohlenstoffgehalts sehr ähnlich dem des FOCUS Hamburg Szenarios. Dies liegt daran, dass dieser Boden die Basis für die Definition des FOCUS Szenarios Hamburg darstellte. Insofern sind Unterschiede von Simulationen mit dem FOCUS Hamburg Szenario und dem

Lysimeterboden aus Studien in Schmallenberg aufgrund unterschiedlicher Kulturparametrisierung verursacht.

- Im Gegensatz dazu zeichnen sich die Lysimeterböden der anderen beiden deutschen Standorte Neustadt und Monheim durch niedrigere Kohlenstoffgehalte als im FOCUS Hamburg Szenario aus. Deshalb werden wie erwartet häufig höhere Konzentrationen mit FOCUS PELMO (Hamburg) berechnet, wenn dieser Lysimeterboden anstelle des Standardbodens im FOCUS Hamburg Szenario verwendet wird.
- Abschließend wird festgestellt, dass die Studiendauer zukünftiger Lysimeterstudien von den Eigenschaften der Substanz abhängig sein sollte und auf Basis von Standardsimulationen festgelegt werden könnte.

Im Hinblick auf die allgemeine Verwendbarkeit von inversen Modellierungen als Option zur Durchführung von höherwertigen Studien wird folgendes Fazit gezogen:

- Angesichts der Auswahl der Lysimeterstudien in dieser Analyse und unter Berücksichtigung der hohen Anzahl von Optimierungen, bei der das Standard FOCUS PELMO Modell nicht in der Lage war, das Substanzverhalten adäquat zu beschreiben, können inverse Modellierungen nicht als Standardinstrument für die Verfeinerung von Standardsimulationen empfohlen werden.
- Für eine Reihe von Studien deuten die inversen Modellierungen darauf hin, dass die Ergebnisse von Lysimeterstudien durch präferentiellen Fluss beeinflusst waren. In Kombination mit Einzelfallentscheidungen könnte die Technik der inversen Modellierung daher eingesetzt werden, um entsprechende Experimente zu filtern.
- Wenn eine Lysimeterstudie offensichtlich durch präferentiellen Fluss beeinflusst war, so sind wahrscheinlich deren Ergebnisse zusätzlich konservativ und nicht direkt vergleichbar mit Standardsimulationen. Es wird empfohlen, im Einzelfall zu überprüfen, ob derartige Studien nicht dennoch für die regulatorische Entscheidungen verwendet werden können (z.B. wenn die Ergebnisse trotz konservativer Ergebnisse unter dem Grenzwert bleiben).
- Eine simple Verwendung des FOCUS chi² Fehlers (FOCUS 2006) als Qualitätskriterium für eine inverse Modellierung, wie es das Tool inversePELMO vorschlägt, erscheint nicht sinnvoll, da die individuellen experimentellen Ergebnisse durch höhere Variabilität gekennzeichnet sein können als entsprechende Ergebnisse von Standardabbauversuchen. Das war besonders der Fall, wenn Substanzen nicht während der Studie im Perkolat aufgetreten sind und die Bodenrückstände als Basis für die Optimierung gedient hatten.
- Anstelle der Verwendung des FOCUS chi² Fehlers könnten maximal akzeptable Abweichungen von vorliegenden Sorptions- und Abbaustudien verwendet werden, um die Ergebnisse von Optimierungen durch inverse Modellierung zu bewerten. Ein Vorschlag wäre der Bereich zwischen dem 10. und 90. Perzentil der Verteilung der Parameter. Wenn optimierte Werte deutlich jenseits dieses Bereichs liegen, könnte die Verwendung für die Risikoabschätzung abgelehnt werden.

# 2 Summary

## 2.1 Background and objectives

For many years PELMO version 3.0 (Klein 1995, Jene et. al. 1998) was used to calculate the leaching potential of active substances and their degradation products within the German national registration of plant protection products. The selection of input parameters was performed according to the recommendations of Michalski et al. (2004). If according to the results of PELMO simulations the threshold of 0.1 µg/L for the active compound was exceeded the plant protection product could not be registered unless lysimeter studies according to BBA (1990) were performed which demonstrate that the use of the product is safe and the concentrations are below the trigger of 0.1 µg/L.

However, since 2012 simulations are performed using FOCUS PELMO and the European FOCUS scenarios (FOCUS 2009/2014). The background to this change was the new regulation 1107/2009 (EG) which states that the risk assessment should be performed with harmonised methodologies but specific national conditions should be as well considered in an appropriate way. Due to these requirements the existing national assessment scheme had to be adjusted accordingly.

After the FOCUS groundwater report (FOCUS 2009/2014) was released the Umweltbundesamt (UBA) in co-operation with the German plant protection industry (Industrieverband Agrar, IVA) revised the national assessment procedure (Holdt et al. 2011). Due to various modifications in the national groundwater risk assessment based on the recommendations given in FOCUS (2009/2014) the question remains still open and needs to be answered if the level of protection of the new modelling approach is still sufficient. Therefore, the new national groundwater modelling approach at the lower tier and its protection level was validated on results of lysimeter studies under field conditions, which are still accepted as higher tier studies in the national registration procedure.

The aim of the project was to provide the Umweltbundesamt with a scientific background for potential changes and extensions of the current procedure for the registration of plant protection products concerning groundwater protection.

The following points were addressed in this project:

- Validation of the national assessment procedure: comparison of results obtained with FOCUS PELMO (version 5.5.3) Hamburg scenario with experimental results from outdoor lysimeter studies.
- Evaluation of lysimeter studies with regard to the question whether they are suitable to assess the leaching behaviour of active compounds and their metabolites by using inverse modelling.
- Evaluation of the protection level of the currently used FOCUS standard scenarios Hamburg and Kremsmünster and how representative they are for the national conditions in Germany (the results of this task was summarised in a separate document, part 2 of this report).
- Recommendations based on the results of the evaluation for a protective and suitable national tiered groundwater risk assessment scheme which considers harmonised methodologies and national environmental conditions.

## 2.2 Main results

### 2.2.1 Part A I: Validation of the national assessment procedure for groundwater based on available outdoor lysimeter studies

The modelling with FOCUS PELMO has a key role in the German tiered groundwater assessment scheme for national authorisation of plant protection products. The first project part includes a validation of the current national groundwater modelling approach with the FOCUS Hamburg scenario at the lower tier in comparison with results from available outdoor lysimeter studies according to BBA (1990). This became necessary since the new FOCUS PELMO model (version 5.5.3) is used in the national authorisation procedure instead of PELMO 3.0 in terms of harmonisation between the EU and the national procedure. Additionally, a revised approach to select modelling endpoints which differs in some cases from the EU recommendations has been implemented. One objective was to determine discrepancies and their possible causes between simulated PECs and experimentally derived leachate concentrations. The main objective was to determine whether tier 1 and 2 calculations are still more conservative than higher tier results from lysimeter studies and thus the national groundwater modelling approach ensures a safe prediction of leachate concentrations for both active substances and their transformation products.

In a first step for 33 active compounds and 71 metabolites, suitable lysimeter studies were selected and necessary input data to perform the current national risk assessment by modelling for the respective pesticides was gathered. A database for collecting all relevant FOCUS PELMO input parameters was developed using Microsoft Visual Basic. The database provides aggregated data (e.g. mean sorption constants) as well as specific information about individual sorption or degradation studies (laboratory or field). The additional information on individual sorption studies can be directly selected from the form containing the aggregated data. In total 104 compounds, 33 parent compounds and 71 metabolites are listed in the database. All necessary input data were obtained using the software tool input decision (version 3.3), which is recommended by Holdt et al. (2011) to derive compound-specific input parameter (degradation and adsorption values) for groundwater modelling.

In the next step, 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 national requirements (Holdt et al. 2011) and according to the EU risk assessment. Additional simulations were performed according to the German decision scheme using either exclusively laboratory degradation data or field degradation data to compare the outcomes. In all cases simulation runs were conducted considering the application rates and crop conditions from corresponding lysimeter studies. For 38 of the 104 substances (37%, 8 active compounds and 30 metabolites) EU and national input deviated caused by different sorption constants (29%) or half-lives (13%). However, 6 of these 30 transformation products were not considered further since they were formed already by parent compounds characterised by different national and EU parameter selection.

For both methodologies (simulation runs with national and EU endpoints), in most of the cases FOCUS PELMO calculated higher concentrations than the respective maximum annual average concentrations in the field lysimeter studies according to BBA (1990). However, the national procedure was found to be more conservative (PELMO above lysimeter: 72%) than the EU system (PELMO above lysimeter: 64%).

This result indicate, 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 for about 72% of all analysed compounds, if experimental outdoor lysimeter data are used to investigate the protection level. The level of protection increases up to 82% if uncertainties correlated with analytical determinations and model haziness below 0.01 µg/L are ignored (national procedure: 81.7%, EU: procedure 74%).

The comparison of simulations based on the national assessment scheme according to Holdt et al. (2011) but exclusively considering the results of field or laboratory degradation tests showed no significant differences: 84.5% (laboratory data) and 83.9% (field data) of the simulations were above the respective lysimeter results.

The analysis demonstrated that the model simulations represent conservative estimations when comparing with lysimeter results. Nevertheless, the portion of compounds with a non-safe prediction might be still higher against the background, that uncertainties still remain and have to be taken into account related to single applications in and the short duration of lysimeter studies.

The national lower tier groundwater risk assessment is more protectable compared to FOCUS modelling with averaged EU endpoints. A marginal smaller percentage of 79% and a lower percentage of 72% have been determined based on the EU methodology for a safe prediction of active substances and metabolites, respectively.

As no 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 and relevant metabolites with respect to groundwater is 0.1 µg/L (based on the EU drinking water limit). 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 a further analysis was performed taken 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 selection methodology (EU or national) only 3% false negative results (one active substance, only) were found.

When comparing the two selection methods (EU and German) the EU methodology showed less false-positive comparisons without increasing the number of false negative cases. That was caused by the more conservative national input parameter setting for modelling if the variances of the adsorption and/or degradation values are high.

As already mentioned also for transformation products the comparisons of PELMO simulations with lysimeter studies resulted in general in conservative estimations. However, in about 18% of the comparisons PELMO simulated lower concentrations than observed annual average concentrations in lysimeter studies if the national approach was followed. A higher percentage of 28% was calculated using averaged endpoints like in the EU assessment.

A similar regulatory impact analysis as for the active substances was also performed for the transformation products. However, the situation was more complicated, since not only the trigger of 0.1 µg/L for relevant metabolites has to be checked but also the concentration range between 0.1 µg/L and 10 µg/L for non-relevant metabolites.

Independent of the input selection methodology the majority of cases (transformation products) showed agreement in the PELMO simulation and lysimeter study (EU 64.8%, DE: 59.2%).

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 for relevant metabolites or above 10 µg/L for non-relevant) but the experiment 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 German methodology according to Holdt et al. (2011) the number of false positive results is higher (35%) than for the EU methodology (28%).

In contrast the critical situations when the lysimeter results indicated a risk (i.e. the annual average concentrations were above 0.1 µg/L or above 10 µg/L) which PELMO did not determine, was found to be 7% when considering the EU methodology. A slightly lower percentile (5.6%) belonged to these cases when the simulation was based on the more conservative national approach 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 it as well (never any disagreement independent on the input parameter selection).

According to the national groundwater risk assessment and in contrast to the EU approach a high variance of the parameters $Kf_{oc}$ and $DT_{50}$ is taken into account when selecting input parameters for modelling (Holdt et al. 2011). For adsorption a Kf value is used instead of an arithmetic mean $Kf_{oc}$ value if the coefficient of variation $Kf_{oc}$ exceeds 60% and if there is no correlation between the organic carbon content in soil and the 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%, an arithmetic mean, otherwise the 10th percentile of all available Kf values should be used for modelling. For degradation the 90th percentile $DT_{50}$ value instead of the geometric mean value should be used, when the coefficient of variation is > 100%.

In order to check the impact of this different selection method for substances where high variation of input data was observed on the performance of the simulation models a special evaluation was performed. Therefore, all substances where Kf-values (German regulation) instead of $Kf_{oc}$-values (EU regulation) or 90th percentiles $DegT_{50}$-values (German regulation) instead of the geometric mean $DegT_{50}$ (EU regulation) were selected from the database. 38 out of 104 substances (37%, 8 active compounds and 30 metabolites) were found that principally matched the required conditions. However, 6 of these 30 transformation products were not considered further since they were formed already by parent compounds characterised by different national and EU parameter selection.

Eight parent compounds were identified where parameter selection according to Holdt et al. (2011) deviated from the 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 $Kf_{oc}$ and $DT_{50}$ have been considered. Only for a single parent compound the maximum average annual concentration in the lysimeter experiment was found to be above respective simulation results. For that compound according to the national scheme the average Kf-value was selected together with the geometric $DT_{50}$. For the respective simulation based on the $Kf_{oc}$ (EU-methodology) the comparison led to the same result.

However, when using the EU methodology (always average values) one additional situation was found where higher concentrations were observed in lysimeter studies than in the PELMO simulation. For this respective active substance the $DegT_{50}$ value was characterised by a high coefficient of variation of the degradation data (selection of the more conservative 90th percentile $DegT_{50}$ 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 performed for active substances.

It was confirmed that both selection methodologies (EU and German procedure according to Holdt et al. 2011), ensure a safe and conservative estimation of the groundwater risk. No false negative results independent whether EU or the national selection approach was followed. When comparing the false positive situations (regulatory necessity for additional higher tier studies) the German approach led to 3 times more results that belonged to group MB (EU: 13%, national: 38%).

In addition to the parent compounds also 24 transformation products were analysed where parameter selection according to Holdt et al. (2011) deviated from the EU methodology. All these selected transformation products were formed by parents where no deviations occurred between EU and national methodology. That means, that in the simulations of the percolate concentrations for this 24 metabolites, always averaged degradation and adsorption values have been used for the respective parent compounds.

It was confirmed 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 $Kf_{oc}$ and $DT_{50}$ have been considered. However, for 6 of 24 metabolites annual concentrations in the lysimeter experiment were found to be above respective simulation results. For all these transformation products no correlations between organic carbon content in soil and sorption were found and the simulation was based on the average Kf-value. For the respective simulation based on the $Kf_{oc}$ (EU-methodology) the comparison led to the same result. When using the EU methodology (always average $Kf_{oc}$ -values) further metabolites (all together 9 metabolites) were found where higher concentrations were observed in lysimeter studies than in the PELMO simulation.

Also for these 24 transformation products where input parameter selection differed between EU and national methodology a regulatory impact analysis was performed to evaluate possible registration decisions. It was demonstrated that only in 8% (2 of 24 compounds) false negative results were obtained independent whether the EU or the national selection approach was followed. That percentage is only slightly higher than the corresponded value based on the evaluation of all transformation products (5.6% and 7% for national selection and EU selection, respectively).

When comparing the false positive situations the German approach led to 2 times more results that belonged to that group (EU: 25%, national: 42%).

All PELMO simulations were done both with and without considering plant uptake (PUF=0.5). Independent on the type of compound (parent or metabolite) and the selection criteria (EU or national methodology) the plant uptake factor only had a minor influence on the comparison. In about 3 to 5% of the simulations the comparison changed from PELMO > lysimeter (no plant uptake) to PELMO < lysimeter (including plant uptake). However, the additional impact analysis using the regulatory limit of 0.1 µg/L did not show any effect of the plant uptake factor.

Looking at all aspects of the detailed analysis the results indicate, that both methodologies, the national criteria as described in Holdt et al. (2011) as well as the EU methodology for lower tier groundwater modelling ensure a safe and conservative estimation of the groundwater risk assessment especially when uncertainties correlated with analytical determinations and model haziness below 0.01 µg/L are is ignored.

Considering the fact that both methodologies are not able to guarantee 100% safe predictions and considering also that the overall differences between both methodologies are not significant (national methodology: 81.7%, EU methodology: 74% more conservative than lysimeter) and even identical when comparing the calculation against the trigger (EU and national methodology: 3% false negative results for parent compounds) it is recommended to check further options for the harmonisation of the national input parameter selection with the European methodology.

### 2.2.2 Part A II: Evaluation of lysimeter studies - Results of inverse modelling using InversePELMO

For many years lysimeter studies were considered in German pesticide regulation as a higher tier study for the assessment of leaching potential. The presupposition of this approach is that conservative conditions for leaching: a sandy soil with low organic carbon content and approximately 800 mm precipitation per year are representative as “realistic worst case” for national conditions in Germany. In the past the representativeness of lysimeter studies was often controversially discussed and questioned with regard to their suitability as a direct trigger for decisions ("endpoint study"). Major concerns are related to the relatively short study time of normally two or three years in combination with single applications at the beginning of the experiment. This is often not in line with results of leaching models which predict significant leaching only after long time periods of repeated applications.

The specifications of the FOCUS Hamburg scenario are to a large extent based on the soil and climate conditions for lysimeter studies according to BBA Part 4.3 (BBA 1990) and the German authorities are therefore still accepting lysimeter studies as endpoint studies. Therefore, the suitability of lysimeter studies as a "process study" in this analysis mainly concentrated on the major concerns with regard to the short study time in combination with single applications at the beginning of the experiment.

This evaluation was conducted based on inverse modelling using the software tool “inversePELMO” which combines the simulation model PELMO with the optimisation tool “PEST” (Klein 2011). The idea was to obtain key parameters for risk assessment such as $Kf_{oc}$ (Freundlich sorption constant related to organic carbon) and $DegT_{50}$ (degradation time to 50%) directly from lysimeter studies. The aim of such a study is to get a deeper look into the processes that led to a certain lysimeter result. According to FOCUS (2009/2014) inverse modelling is recommended to be used to improve the standard modelling at tier 1 by considering additional information from higher tier studies.

For the evaluation only lysimeter studies according to BBA (1990) and performed between 1989 and 1999 at in total 4 different lysimeter sites were considered none of which were outside of Germany. It was assumed that this limitation would generally lead to comparable conditions as in the FOCUS Hamburg scenario. The lysimeter sites were located in Neustadt (Rhineland-Palatinate), Schmallenberg, Monheim (both North Rhine-Westphalia) and Hamburg.

Furthermore, only lysimeter studies were included which showed some leaching of the active compound or at least of one metabolite.

- In five lysimeter cores only parent residues were available (no metabolites).
- In two lysimeter cores only metabolite residues were detected.
- In eight lysimeter cores parent and metabolite residues were available.

In total degradation rates and adsorption values of eight different parent compounds and six metabolites were analysed by inverse modelling (some of the substances were considered in several optimisations). Unfortunately, key input data was not available from most lysimeter studies to perform inverse modelling with high quality. The issues were

- weather information not sufficient (only monthly values available)
- irrigation sometimes recorded on a monthly basis
- data on potential evapotranspiration not reported
- not all samples analysed (only radioactivity reported )

Some deficiencies of the lysimeter studies for inverse modelling could be explained by the fact that the lysimeter guideline (BBA 1990) does not consider the needs of inverse modelling optimisations. Especially, the lack of data on daily potential evapotranspiration led to fitting outside the expected range for the respective parameters.

Before the substance parameters were optimised the hydrology in soil was fitted based on initial soil moisture and crop specific Kc-factors. These factors are used to transpose the generic potential evaporation data to crop specific values. As long as the visual representation and the FOCUS chi$^2$ test of the cumulative leachate showed satisfactorily agreement with the experimental data an optimisation of the percolate was not rejected just because parameters deviated from normal parameterisation.

When optimising the parameters $Kf_{oc}$ and $DegT_{50}$ the cumulative substance amounts fluxes determined in the percolate were considered. In some situations the soil residues in the soil core after the study were used for the optimisation when the substance was never detected in the leachate. That was done to check whether still meaningful results can be obtained. However, based on these results it can be concluded that respective inverse modelling should not be performed since percolate concentrations are essential for an adequate optimisation of the results.

For a significant number of optimisations the standard FOCUS PELMO model could not adequately describe the substance transport in the lysimeter. Considering the total water storage capacity of the cores these studies were characterised by very early breakthrough of substances. It was concluded that these studies were partly influenced by preferential flow. Though this process is mostly happening in heavy soils preferential flow has been reported also in sandy soils. For example, an extensive study of 14C-Benazolin-ethyl in a parallel field and lysimeter study (Jene et al. 1998) was conducted. This study demonstrated that the solute transport exhibited through the upper part of the soil profile was dominated by matrix flow, whereas preferential flow occurred in the lower part. The authors additionally found that the travel time and the transformation behaviour of the reactive chemical were different in pathways which were only a few centimetres apart. It was assumed by Jene et al. (1998) that the collection and transport of the lysimeter cores may have induced disturbances of the soil structure which led to the formation of macro-pores within the soil core. Cracks may also exist between the lysimeter wall and the soil core.

In order to check the effect of longer study periods "prolonged" simulations were performed for some lysimeter studies previously considered for inverse modelling optimisation. These “prolonged" simulations should answer the question whether the length of a certain study was sufficient and the experimental study was not stopped before the bulk of the chemicals reached the bottom of the soil core or accordingly the percolate. Another aspect of these prolonged simulations was to investigate the effect of multiple applications on long-term concentrations in the percolate. Mainly those studies were selected for further extrapolation modelling, in which the influence of preferential flow is assumed to be low and no major time lag of the substance break through between experimental and inverse modelling results occurred. However, two lysimeter studies in this selection could have still been influenced by fast transport processes in soil such as preferential flow. They were included in the analysis to check in how far extrapolation results are influenced by these processes. The optimised parameters for these two studies were not based on the preferential flow module. Simulations were performed using the optimised sorption and degradation parameters in combination with periodical climate as observed during the study. As only a limited number of weather years were available and as annual precipitation including irrigation during the study was at least 800 mm (lysimeter guideline BBA 1990) the first complete weather file (i.e. year 2) was always considered for the additional “prolonged” simulation period. In order to definitively estimate the time between application and the maximum concentration in the percolate pesticide was applied only in the first year according to the information given in the lysimeter study. Consequently, for the additional simulation period the crop rotation in the first experimental year was used. Furthermore, in order to analyse the maximum concentration in leachate for repeated applications an additional simulation was performed with annual applications.

Unfortunately this analysis could not answer all open questions with regards to minimum study duration and multiple application patterns. However some general observations were

- For substances with low sorption constants the experimental period according to BBA (1990) seems to be sufficient as it covers the maximum annual concentrations within the experimental period. Additionally, for this substance type the effect of multiple applications can be considered negligible.
- For substance with high sorption constants the maximum concentrations would not be observed during the standard study period according to BBA (1990). Additionally, the effect of multiple applications seems to be significant for this substance type. The maximum concentrations as well as the time the peaks occurred are strongly dependent on the pattern.

- No correlation could be found for substances in the medium sorption range between the sorption constant and the necessary study duration because the actual weather conditions and the differences in the lysimeter soils led to too much variability.
- The degradation rate should mainly influence the percolate difference for single and multiple applications. This was shown for two substances where significant differences were simulated for both situations. However, due to the combination of application rate, half-life and sorption in soil only concentrations far below the trigger of 0.1 µg/L were simulated. Nevertheless the simulations demonstrate that multiple applications have a significant impact on the percolate concentrations for substances with $DegT_{50}$ above 60 days.

However, all these conclusions were only based on a limited number of analysed studies and finally apply only for these studies. Prolonged simulations can be a meaningful addition tool to describe the lysimeter experiment over a longer period of time. When considering only these few studies standard FOCUS PELMO simulations based on optimised parameters led to concentrations below the respective simulations with standard Tier 1 input parameters. However, in a single exceptional situation the optimised parameters resulted in concentrations above the regulatory relevant trigger but not in the experimental studies.

Although the number of experimental data sets was limited further simulations were performed in order to improve the understanding about the influence of the soil and weather conditions on the predicted concentrations in the percolate which is necessary for the extrapolation of lysimeter results. The following additional simulations were performed:

- Combination of the lysimeter soil (and application pattern) with standard (FOCUS Hamburg) scenario weather pattern.
- Combination of the lysimeter weather with standard (FOCUS Hamburg) soil and application pattern.

Based on the results of this evaluation it can be concluded that the maximum concentration for a certain combination depends mainly on the lysimeter study with the following trends:

- If the lysimeter study was performed in Schmallenberg (North Rhine Westphalia) the combination of FOCUS Hamburg soil and lysimeter weather condition leads to a higher leachate concentration than the combination of FOCUS Hamburg climate and lysimeter soil conditions. This provides evidence that the Schmallenberg climate has in general higher rainfall than the FOCUS Hamburg climate but the soil conditions are more or less identical. This is not surprising since the FOCUS Hamburg scenario soil was parameterised based on the Borstel soil which is also used for the lysimeter studies performed in Schmallenberg
- If the lysimeter study was performed in Neustadt (Rhineland-Palatinate) or Monheim (Nordrhein-Westfalen) the combination FOCUS Hamburg soil and lysimeter weather condition leads to lower leachate concentration than the combination FOCUS Hamburg climate and lysimeter soil conditions. This provides evidence that the FOCUS Hamburg climate has higher effective rainfall than the lysimeter climate whereas the lysimeter soils in Neustadt/Monheim lead to more substance transport since they are characterised by less organic carbon than the FOCUS Hamburg soil conditions (as shown also by the

average organic carbon contents in the top metre of the soils at FOCUS Hamburg, Neustadt and Monheim with 0.78%, 0.49% and 0.60%, respectively).

For other comparisons (e.g. taking into account prolonged simulations with pure lysimeter conditions or pure FOCUS simulations) these rules hold still to some extent but with exceptions caused either by unfavourable weather conditions during the study or because of differences in the target concentration (maximum versus 80th percentile). As explained previously several questions with regard to the use of lysimeter studies either as "endpoint study" or "process study" were addressed. However, most of these open issues could not be adequately addressed due to various limitations of the existing studies. Nevertheless some conclusions could be drawn based on the analyses:

- The effect of repeated annual versus single applications from PELMO computer simulations with prolonged lysimeter conditions showed no clear tendency (6 cases with no effect, 6 cases with higher concentrations than the respective single concentration, on average 70%, range 15% to 270%). As optimised input parameters of the related substances were all characterised by low sorption and fast degradation a significant plateau is not expected to be formed even if these compounds are applied repeatedly over a longer study time. Instead, it is more likely that the increased concentrations were simply caused by the higher probability of unfavourable weather conditions for prolonged studies.
- For the compounds that did not occur in the leachate during the experimental studies in the prolonged simulations small concentrations far below the trigger were simulated with prolonged study time (not measurable).
- It was previously concluded that simulations with lysimeter weather conditions lead to lower leachate concentrations than simulations with FOCUS Hamburg weather if the lysimeter study was performed at locations with smaller annual precipitation than in the FOCUS Hamburg scenario (Neustadt, Monheim). Based on this result, it can also be concluded that the irrigation requirements in the guideline for lysimeter studies (BBA 1990) are not able to account for differences between the climate at the site and the FOCUS scenario.
- The soil (in particular the organic carbon content) used for studies in Schmallenberg is quite comparable to the FOCUS Hamburg scenario since the respective soil from the location “Borstel” in northern Germany was also used for the parameterisation of the FOCUS Hamburg scenario. Differences between respective simulations are therefore related to different crop parameterisation.
- In contrast, the organic carbon contents of the lysimeter soils from the other two locations (Neustadt, Monheim), where lysimeter studies have also been conducted in Germany, are characterised by lower organic carbon content than in the FOCUS Hamburg scenario. As expected higher concentrations were often simulated with PELMO when using the lysimeter soil instead of the FOCUS scenario soil.
- Finally, the study period of future lysimeter studies should depend on the properties of the substance and could be based on tier 1 simulations.

With regard to the general use of inverse modelling as a higher tier option in national groundwater risk assessment the following conclusions can be drawn:

- Given the selection of lysimeter studies used in this evaluation and considering the significant number of optimisations where the standard FOCUS PELMO model could not adequately describe the substance transport in the lysimeter The use of inverse modelling cannot be recommended as a standard tool/approach for the refinement of tier 1 simulations,
- For a couple of studies inverse modelling showed evidence that the lysimeter study was influenced by preferential flow. This technique could therefore be used to identify respective experiments on a case by case basis.
- If a lysimeter study was obviously influenced by preferential flow the results of such an experiment are probably additionally conservative and are not directly comparable with Tier 1 simulations. It is recommended that in these situations the respective studies are further checked whether they could be nevertheless used for regulatory purposes (e.g. if their conservative results are still below the trigger).
- Simple considerations of the FOCUS chi² error (FOCUS 2006) as quality criteria for invers modelling as it is used by inversePELMO as a criteria doesn't seems to be appropriate since the individual experimental results could be more affected by higher variability than respective results from standard degradation studies. That was especially the case when substances were never detected in the percolate and optimisations were based only on soil residues after the study.
- Instead of focusing on FOCUS chi² error maximum acceptable deviations from existing tier 1 data on sorption and degradation should be defined which are considered acceptable to be used as higher tier information from inverse modelling. They should be defined in view of the distribution of existing laboratory data on degradation and sorption. A possible procedure could be to check whether the optimised parameters meet the range between the 10th and 90th percentile of the distribution of these standard studies. If optimised parameters are clearly beyond these ranges their use in the risk assessment should be rejected.

# 3 Introduction

This project tries to address the implications of recent modifications in the German national registration procedure with regard to the level of protection of the new scenarios and the importance of lysimeters as higher tier studies.

In its structure this report follows the three major questions raised in chapter 2:

**Part A I: Validation of the national groundwater modelling approach based on results of outdoor lysimeter studies.**

After the FOCUS groundwater report (2009) was released the UBA in co-operation with German industry (Industrieverband Agra, IVA) revised the national assessment procedure in order to achieve a harmonisation of the assessment especially with regard to the zonal registration under the regulation 1107/2009 EG (Holdt et al. 2011).

The revised national assessment procedure is based on FOCUS PELMO taking into account the FOCUS scenarios Hamburg and Kremsmünster. Similar to the EU scheme the 80th temporal percentiles of 20, 40, or 60 years for annual, biennial and triennial applications are calculated as relevant predicted environmental concentrations. In accordance with the EU procedure all simulations start with 6 warming-up years which are not considered for the percentile calculations. Averaged degradation and adsorption values comparable to the EU assessment are normally recommended as national input parameter for modelling, unless there is evidence of dependency of those compound properties to different soil properties (pH, CEC, clay content) or the statistical variability of all available values is high. The revised assessment procedure therefore differentiates between dissociating and non-dissociating substances. Especially, if a dependency between degradation and/or sorption with pH in soil is determined the selection of input parameter has to reflect it. In addition to the FOCUS scenario Hamburg additional simulations using the Kremsmünster scenario may then be necessary. And besides, a percentile selection deviating from the average value is recommended, if the variability of measured degradation or sorption values exceeds a certain trigger value. (Holdt et al. 2011).

The following hypothesis will be checked as a consequence of the new national assessment approach for groundwater modelling according to Holdt et al. 2011.

- For non-dissociating substances (parent and metabolites) the FOCUS Hamburg scenario can be considered a realistic worst case for Germany, and corresponding lysimeter concentrations according to BBA Part 4-3 (1990) show the same or lower concentrations than the model simulations.
- For dissociating substances (parent and metabolites) for which degradation or sorption is significantly lower at low pH than at high pH the FOCUS Hamburg-scenario can be considered a realistic worst case scenario.
- For dissociating substances (parent and metabolites) for which degradation or sorption is significantly lower at high pH lysimeter experiments do not represent a worst case situation because the soil used in lysimeter studies is comparable to the Borstel soil (low pH). Therefore, calculated concentrations could be higher for the Kremsmünster than for

the FOCUS Hamburg scenario. Furthermore, calculated concentrations could be lower than the results of lysimeter studies for these compounds.

- The national assessment scheme gives a more realistic and sufficiently conservative PEC calculation compared to the EU-assessment scheme for substances for which degradation and/or sorption show significant dependency on relevant soil properties other than the organic carbon content. However, for some substances more harmonization between the two schemes could be achieved.

**Part 2: Evaluation of lysimeter studies with regard to the question whether they are suitable to assess the leaching behaviour of active compounds and their metabolites by using the method of inverse modelling.**

For many years lysimeter studies according to BBA (1990) are considered in German pesticide regulation as higher tier for the assessment of the leaching potential of plant protection products. They are used as “endpoint studies” which means that the measured maximum averaged annual percolate concentrations are directly used for regulatory decision making. However, in the past the representativeness of lysimeter studies was often controversial discussed and criticised with regard to their suitability as endpoint studies for regulatory decision-making (see e.g. FOCUS 2009/2014). Major concerns are related to the relatively short study time of two or three years in combination with single applications at the beginning of those experiments. This is often not in line with expected repeated application pattern over a longer time period as in reality. Therefore this is not comparable with probably more conservative results of leaching models which predict leachate concentrations after 20 years and repeated applications.

Considering these deficiencies of the lysimeter studies with regard to repeated applications and durations the use of these experiments as “endpoint studies” may be put into question. Nevertheless, lysimeter studies could be used to increase the understanding of leaching under field conditions ("process study") when the results of lysimeter studies are further evaluated using the FOCUS leaching models. This was the background as to why the current FOCUS groundwater report (FOCUS 2009/2014) recommends these evaluations and suggests the inverse modelling technique as an appropriate methodology. FOCUS explicitly mentions inverse modelling as an appropriate methodology to interpret lysimeter studies. Inverse modelling optimisations are usually in regulatory context performed to obtain key parameters for risk assessment such as $Kf_{oc}$ and $DegT_{50}$ from lysimeter or other higher tier studies. Once optimised adsorption and degradation values are obtained for the single lysimeter experiment, model based extrapolations of the experiment (longer time period and/or different application amounts) are than possible in a second step. The aim of inverse modelling is therefore on one hand to get a deeper look into the processes that led to a certain lysimeter result. On the other hand inverse modelling can be used to improve the standard modelling at tier 1 by considering additional information from higher tier studies.

If the model was able to mimic the processes in one lysimeter study the lysimeter study results could then in principle be transposed to other conditions e.g. different soil types, climate or application pattern. In the national context of groundwater risk assessment for pesticides it is in general assumed, that the soil and climate conditions in lysimeter studies according to BBA (1990) are comparable to the conditions of the FOCUS Hamburg scenario.

In the following chapters the suitability of lysimeter studies as a "process study" to assess the leaching behaviour of pesticides and their metabolites is analysed.

Special focus will be on in how far the short study period (2 to 3 years) in combination with applications in the first year limits the value of the lysimeter study for meaningful conclusions about leaching under outdoor conditions.

In order to check in how far the lysimeter conditions can be extrapolated to other conditions like the effect of the changing climatic conditions and soil profiles is analysed.

Further questions which will be addressed in this chapter are:

- Could inverse modelling of field lysimeter studies be routinely used as a higher tier option when assessing leaching to groundwater in the national regulatory context?
- Is it possible to assess a range of substance properties (sorption, degradation) for which the current study period of 2 to 3 years is sufficient to still use field lysimeter studies as higher tier endpoint studies in the national regulatory context?
- Are the measured maximum annual percolate concentrations in lysimeter studies principally comparable to their respective simulated percolate concentrations performed with FOCUS PELMO and optimised parameter setting?
- Do simulations with FOCUS Hamburg soil result in similar concentrations as in lysimeter studies if the lysimeter climate and optimised parameter setting is used?
- Do simulations with FOCUS Hamburg climate result in similar concentrations as in lysimeter studies if the lysimeter soil and optimised parameter setting are used?
- Do simulations with FOCUS Hamburg (endpoint: 80th temporal percentile) result in similar concentrations as maximum concentrations in lysimeter studies if optimised parameter setting is used?

In order to achieve the different objectives different calculations with extended simulation periods of the lysimeter experiments (and optimised adsorption and degradation values, which represent the lysimeter experiment) are performed in this chapter such as:

1) Simulations over 20 years considering the lysimeter conditions (soil and weather) with repeated and single application patterns.
2) Simulations over 20 years considering the lysimeter soil conditions but in combination with FOCUS Hamburg weather scenario
3) Simulations over 20 years considering the lysimeter weather conditions but in combination with FOCUS Hamburg soil scenario
4) Simulations over 20 years considering the FOCUS weather and soil scenarios

# 4 Part A I: Validation of the national groundwater modelling approach based on results of outdoor lysimeter studies

## 4.1 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 and 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 selection according to Michalski et al. (2004) is sufficiently conservative to be used in PELMO 3.0 for triggering lysimeter studies 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 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 from which resulted in the new FOCUS PELMO versions 4.4.3 and 5.5.3 followed. 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 the various modifications in the national registration procedure the following open issues were addressed with regard to the level of protection of the new FOCUS Hamburg scenario in combination with a new selection procedure of input parameters for modelling compared to the results of lysimeter studies as higher tier studies.

FOCUS PELMO Hamburg scenario

Though the soil properties (soil type, soil texture, and organic carbon content, pH-values) 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 old procedure were based on the maximum annual concentrations of the both selected weather years. However, the results of FOCUS PELMO are based on the 80th temporal percentile of 20 subsequent weather years.

Special substances

In the new national assessment procedure simulations based on the neutral to alkaline FOCUS Kremsmünster soil scenario are required for compounds which show pH dependency of sorption and degradation caused by dissociation of the respective compound. The influence of this parameter will also be checked.

Due to these modifications in the national groundwater risk assessment the question remains still open and needs to be answered if the level of protection of the new modelling approach according to Holdt et al. (2011) is still sufficient. Therefore, the new national groundwater modelling approach at the lower tier and its protection level will be validated on results of lysimeter studies under field conditions, which are still accepted as higher tier studies in the national registration procedure in Germany.

The simulations will be based on endpoint selection criteria as recommended by Holdt et al. (2011). Additional simulations will be performed based on endpoints derived from the EU-assessment procedure. The aim is to evaluate the level of protection of both methodologies compared to lysimeter studies.

## 4.2 Data collection and preparation

Background of this part is to make available all data necessary to validate FOCUS PELMO 5.5.3 for the national risk assessment procedure for groundwater.

For the validation of the national modelling approach 104 substances (33 active compounds, 71 metabolites) were selected for which lysimeter studies were available according to the German guideline (BBA 1990). It was checked that the selected substances were also detected in the percolate of the lysimeter studies.

Finally, dossier information for all 104 substances was collected which are necessary to run FOCUS PELMO to predict the leaching concentration in 1 m soil depth. PELMO's most important processes are mobility (driven by the sorption constant $Kf_{oc}$ and the Freundlich exponent 1/n) and degradation (driven by the $DegT_{50}$ and its moisture, temperature and depth dependency). As these parameters are not only substance dependent (as for example water solubility) there may be differences between the value as obtained from the selection methodology (e.g. the geometric mean) which was used in the computer simulations and the actual value in the experimental study which was not available. Important influencing soil properties are, for example, the organic carbon content, pH-value as well as the clay, sand and silt content. As the degradation rate also depends on temperature and moisture these parameters have to be considered as well 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).

Since it was planned to use all 104 compounds in the analysis, and with regard to dependencies of many pesticide input parameters on soil properties, a database was created to simplify the data management. The database is designed in a way that it shows the final modelling input parameters for all 104 compounds. It further provides all background information, which led to decisions on national input parameters if they are different from averaging like in the EU assessment.

The detailed national approach how to select input parameters from dossier information was followed by using the new version of the Excel tool "Input Decision" (version 3.3), which was developed by the Umweltbundesamt and the IVA (Holdt et al. 2011).

In total 104 compounds, 33 parent compounds and 71 metabolites are listed in the database. The $Kf_{oc}$, Kf and $DegT_{50}$ values were found using the EXCEL tool input decision 3.3. Table 7-1 (appendix 2) lists the identities of parent compounds and their metabolites, Table 7-2 (appendix 3) summarises the available information on sorption properties of the compounds, and Appendix 4: Information on degradation for the compounds in the data base

Table 7-3 (appendix 4) shows the degradation endpoints for the different compounds.

Only four active substances (no 35, 77, 78, and 85) and four transformation products with pH dependency of adsorption and/or degradation in soil, for which lysimeter studies have been conducted, could be identified during the data evaluation. Consequently due to the small number of cases no separate statistical analysis of the protection level of the modelling approach for these compounds were performed. Therefore, the revised national assessment scheme regarding pH dependency could not be adequately addressed within this project.

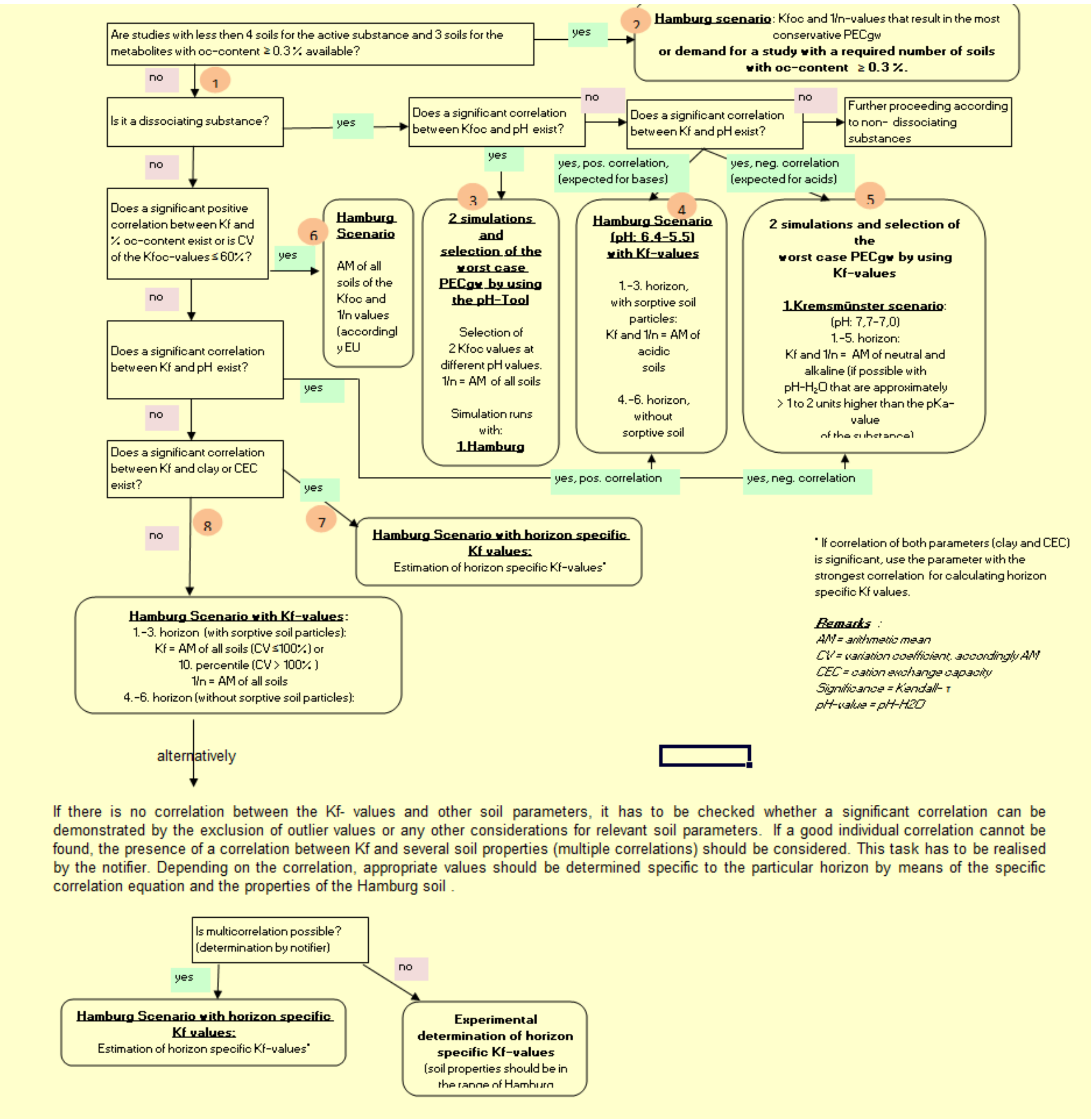
## 4.3 Selection of modelling endpoints

Based on the results of the analysis presented previously standard FOCUS leaching simulations were performed with the Hamburg (and in some cases the Kremsmünster) scenario of FOCUS PELMO 5.5.3. Calculations were performed using the EU endpoints for $DegT_{50}$ and $Kf_{oc}$ as well as the endpoints according to the German national decision scheme (Holdt et al. 2011).

Conditions for calculating the EU-endpoint:

| | |
|---|---|
| $Kf_{oc}$: | arithmetic mean (parent: n>3, metabolite: n>2) or<br>minimum value (parent: n<4, metabolite: n<3) |
| 1/n: | arithmetic mean (if $Kf_{oc}$ based on arithmetic mean) or<br>individual related study result (if $Kf_{oc}$ based on minimum value) or<br>default 1.0 (if $K_{oc}$ is based on kd values or based on QSAR) or<br>default 0.9 (if 1/n below 0.7 or above 1.0) |
| $DegT_{50}$: | geometric mean (parent: n>3, metabolite: n>2) or maximum value (parent: n<4, metabolite: n<3),<br>SFO kinetics or re-calculated SFO-kinetics of normalised laboratory data or normalised field data (if available). If field and laboratory half-lives were available field data was as preferred option for the risk assessment. |

The decision scheme to select modelling endpoints which are used in the German national lower tier groundwater risk assessment is presented in Figure 4-1 for sorption constants and in Figure 4-2 for $DegT_{50}$ values. One major difference between the procedure for calculating EU endpoints and the German decision scheme for endpoint derivation is the use of Kf-values instead of $Kf_{oc}$-values when the correlation of sorption with organic carbon is statistically poor. And the 10th and 90th percentiles for sorption and degradation are used, respectively, when the coefficients of variation are above 60% for $Kf_{oc}$ values and 100% for Kf or $DegT_{50}$ values. Further details of the German methodology are presented in Holdt et al. (2011) and in the following figures.



* If correlation of both parameters (clay and CEC) is significant, use the parameter with the strongest correlation for calculating horizon specific Kf values.

***Remarks*** :
*AM = arithmetic mean*
*CV = variation coefficient, accordingly AM*
*CEC = cation exchange capacity*
*Significance = Kendall- τ*
*pH-value = pH-H2O*

If there is no correlation between the Kf- values and other soil parameters, it has to be checked whether a significant correlation can be demonstrated by the exclusion of outlier values or any other considerations for relevant soil parameters. If a good individual correlation cannot be found, the presence of a correlation between Kf and several soil properties (multiple correlations) should be considered. This task has to be realised by the notifier. Depending on the correlation, appropriate values should be determined specific to the particular horizon by means of the specific correlation equation and the properties of the Hamburg soil .

Figure 4-1: Decision scheme for calculating sorption endpoints according to input decision 3.3 used in the lower tier groundwater risk assessment relating to the German national registration of plant protection products

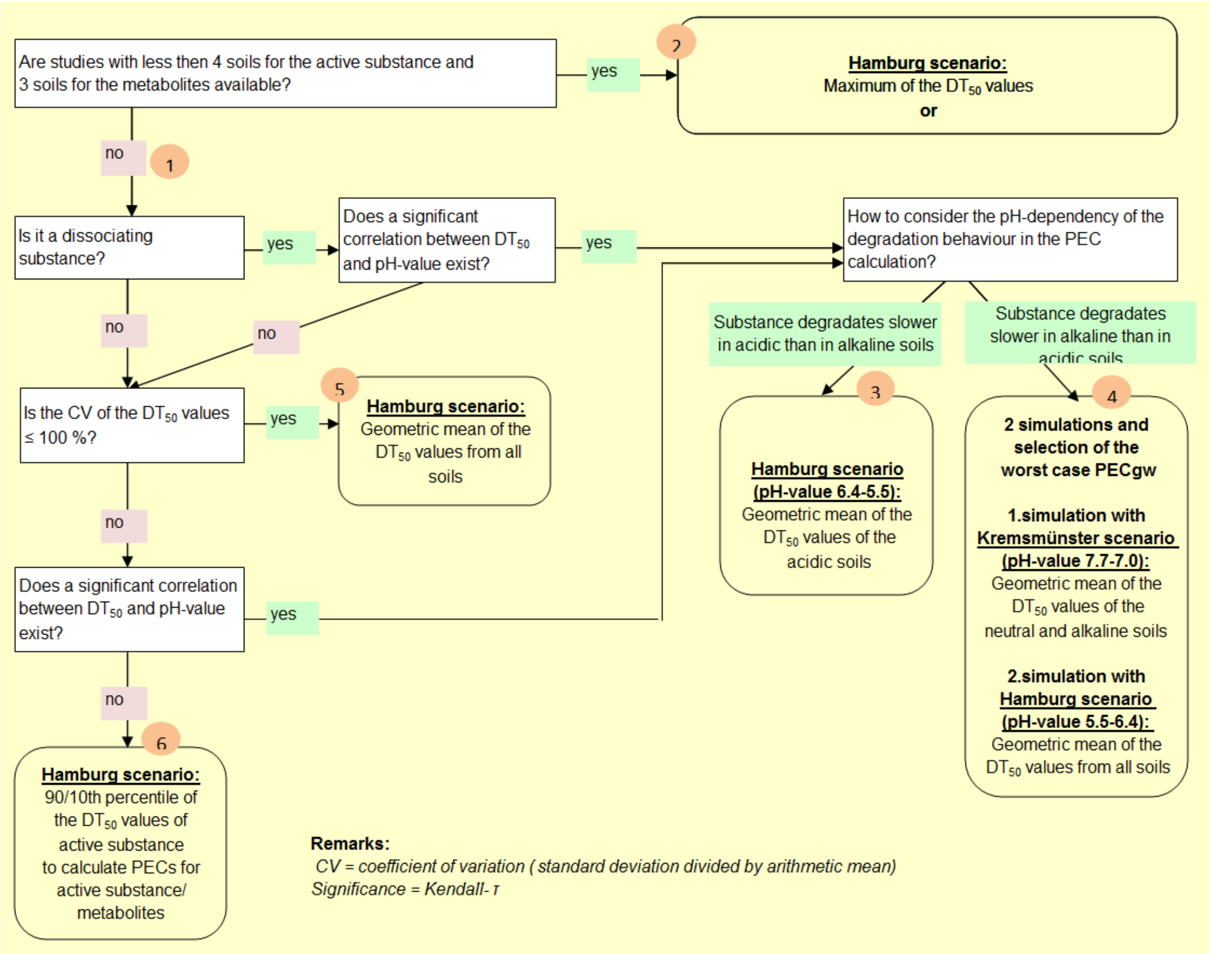


Figure 4-2: Decision scheme for calculating endpoints for degradation in soil according to input decision 3.3 used in the lower tier groundwater risk assessment relating to the German national registration of plant protection products

The application pattern (crop, rate, and timing) for groundwater modelling with FOCUS PELMO were based on the results of lysimeter studies with the same compounds. If several lysimeter studies or lysimeter cores were available, the worst case result from the experimental study with the highest measured average annual leachate concentration was used for comparison.

In order to take into account the influence of the plant uptake factor (PUF) on the predicted environmental concentrations two variations were evaluated for modelling, first FOCUS groundwater modelling was provided considering a plant uptake of zero (PUF = 0) and second simulations were provided considering the FOCUS default of 0.5 as plant uptake factor (PUF = 0.5).

The information presented in Table 7-5 (appendix 4) was taken from the respective database. The table shows 104 detailed comparisons between lysimeter results and calculations with FOCUS PELMO. The FOCUS PELMO results based on Hamburg are based on the 80th temporal percentile at 1 m depth (FOCUS standard) which is currently selected for regulatory decision-making on national level and in the EU.

## 4.4 Comparison of modelling and lysimeter results

### 4.4.1 Evaluation based on all substances

In Table 4-1 the direct comparisons are presented between the leachate concentrations in 1 m soil depth simulated with the FOCUS Hamburg scenario and corresponding information from outdoor lysimeter studies. In this chapter, the results are not directly linked to regulatory questions (e.g. compared to regulatory important trigger values). The first two rows in Table 4-1 show simulated concentrations in the percolate compared to the lysimeter data when using the EU or the national parameter setting, respectively. According to the analysis with 104 substances the national approach for the selection of modelling endpoints differs in 39% from the EU procedure (31% because of different sorption constants, 13% because of different half-lives).

For both methodologies, simulations were performed with a plant uptake factor of 0 and 0.5.

Table 4-1: Summary of the comparison of calculated concentrations* with observed annual average concentrations in the leachates of lysimeter studies (all compounds)

| Comparison | no Plant uptake | | including Plant uptake 0.5 | |
|---|---|---|---|---|
| Parameter setting according to | PELMO ≥ Lysimeter | PELMO < Lysimeter | PELMO ≥ Lysimeter | PELMO < Lysimeter |
| EU | 67 (64.4%) | 37 (35.6%) | 62 (59.6%) | 42 (40.4%) |
| DE | 75 (72.1%) | 29 (27.9%) | 70 (67.3%) | 34 (32.7%) |
| DE (lab)° | 78 (75.7%) | 25 (24.3%) | 72 (69.9%) | 31 (30.1%) |
| DE (field)° | 24 (77.4%) | 7 (22.6%) | - | - |

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

° analysis exclusively based on field or laboratory data on degradation (national procedure)

For both methodologies, in most of the cases FOCUS PELMO calculated higher concentrations than which were determined in the lysimeter studies. However, the national procedure was found to be more conservative (PELMO above lysimeter: 72%) than the EU system (PELMO above lysimeter: 64%).

This result indicate, 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 for about 72% of all analysed compounds, if experimental outdoor lysimeter data are used to investigate the protection level. The level of protection increases up to 82% if uncertainties correlated with analytical determinations and model haziness below 0.01 µg/L are ignored (see Table 4-2).

Table 4-2: Summary of the comparison of calculated concentrations* with observed annual average concentrations in the leachates of lysimeter studies (concentration below 0.01 µg/L set to 0.01 µg/L)

| Comparison | no Plant uptake | | including Plant uptake 0.5 | |
|---|---|---|---|---|
| Parameter setting according to | PELMO ≥ Lysimeter | PELMO < Lysimeter | PELMO ≥ Lysimeter | PELMO < Lysimeter |
| EU | 77 (74.0%) | 27 (26.0%) | 73 (70.2%) | 31 (29.8%) |
| DE | 85 (81.7%) | 19 (18.3%) | 81 (77.9%) | 23 (22.1%) |
| DE (lab)° | 87 (84.5%) | 16 (15.5%) | 82 (79.6%) | 21 (20.4%) |
| DE (field)° | 26 (83.9%) | 5 (16.1%) | - | - |

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

° analysis exclusively based on field or laboratory data on degradation (national procedure)

As a consequence, a safe prediction of the leaching concentration was not possible for 18% of the analysed compounds by using national input parameters and the FOCUS Hamburg scenario and for 26% of the compounds by using the EU input parameters.

Dependent on the available data the results of field or laboratory tests may be selected for the PELMO simulations. If the national procedure according to Holdt et al. (2011) was followed the influence of the type of data on the simulation result was insignificant (84.5% and 83.9% for simulations based on laboratory and field data, respectively, (see Table 4-2)).

The individual results for the variations without plant uptake are also presented in the following four 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 4-3 and Figure 4-4). 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 in the study. 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.

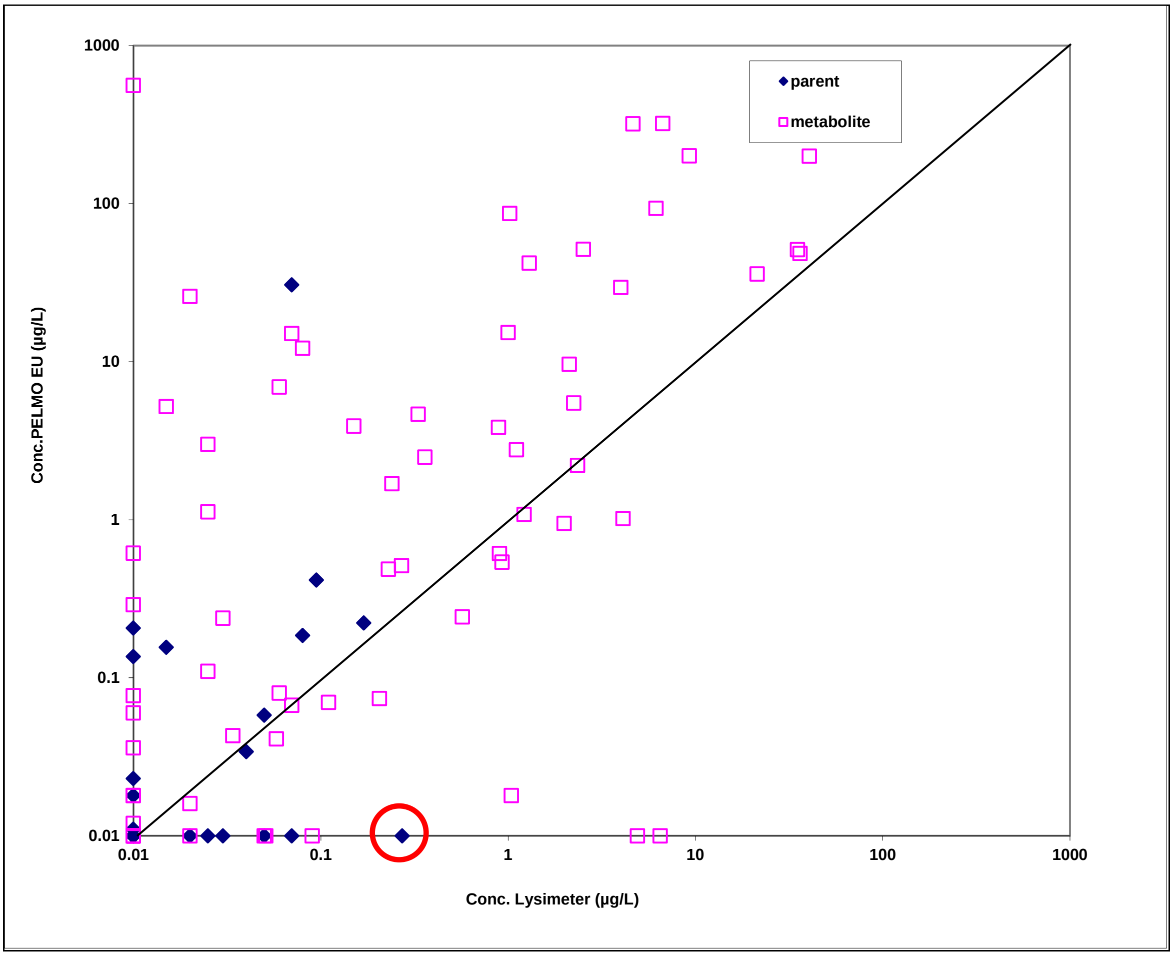


Figure 4-3: Comparison of calculated with observed annual leaching concentrations (concentration below 0.01 µg/L set to 0.01 µg/L, EU parameter selection, no plant uptake)

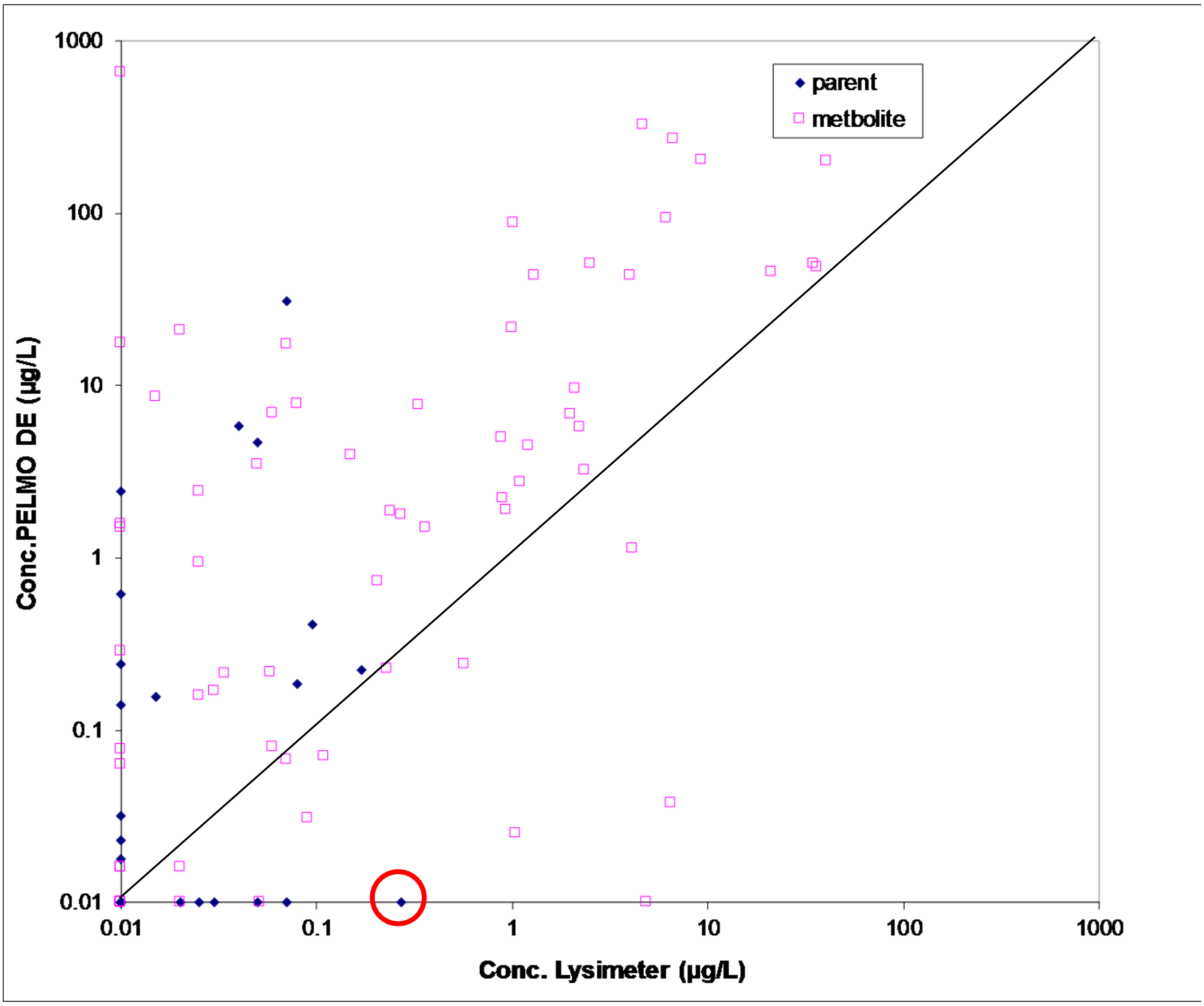


Figure 4-4: Comparison of calculated with observed annual leaching concentrations (concentration below 0.01 µg/L set to 0.01 µg/L, German parameter selection, no plant uptake)

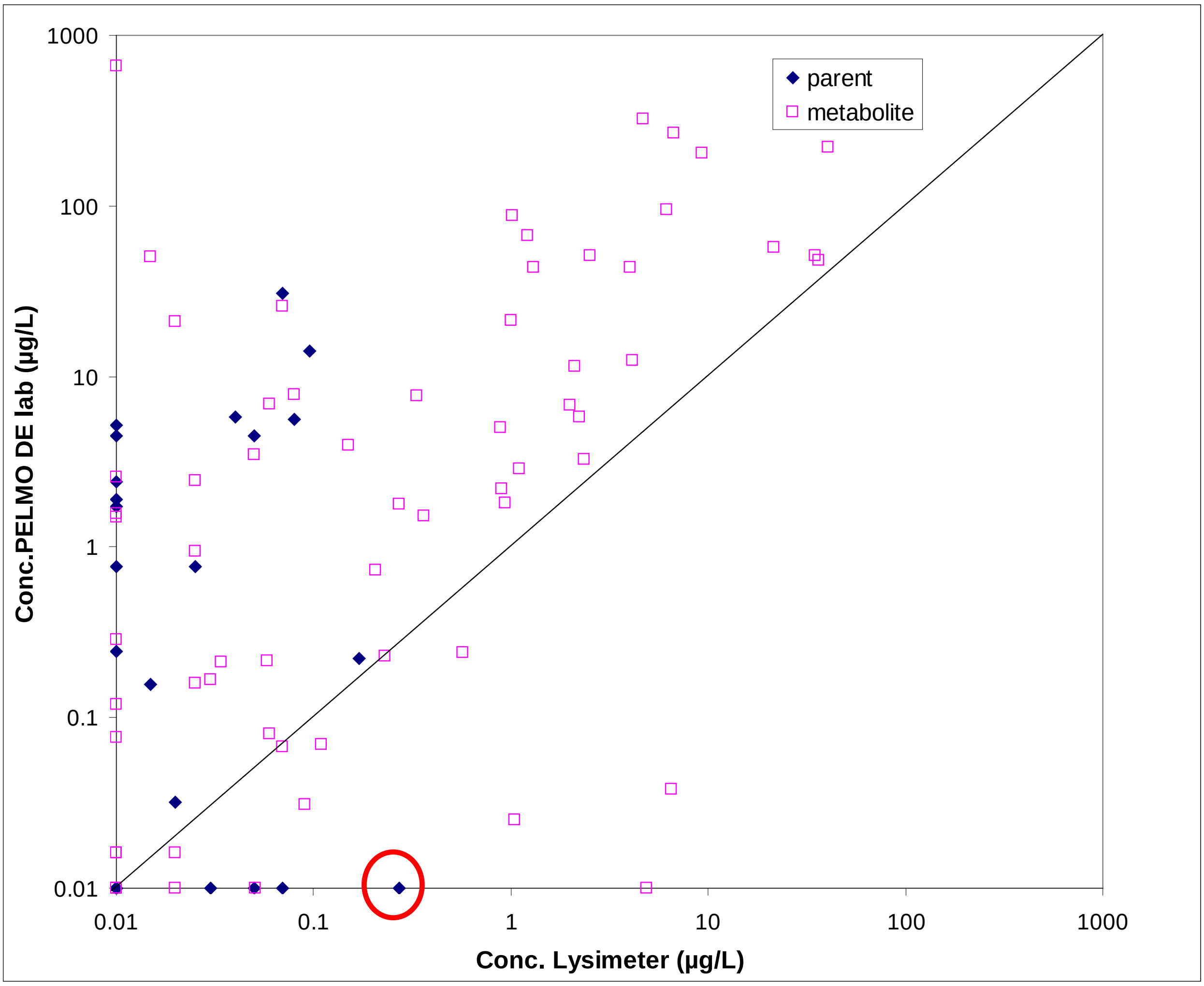


Figure 4-5: Comparison of calculated with observed annual leaching concentrations (concentration below 0.01 µg/L set to 0.01 µg/L, German parameter selection with lab values, no plant uptake)

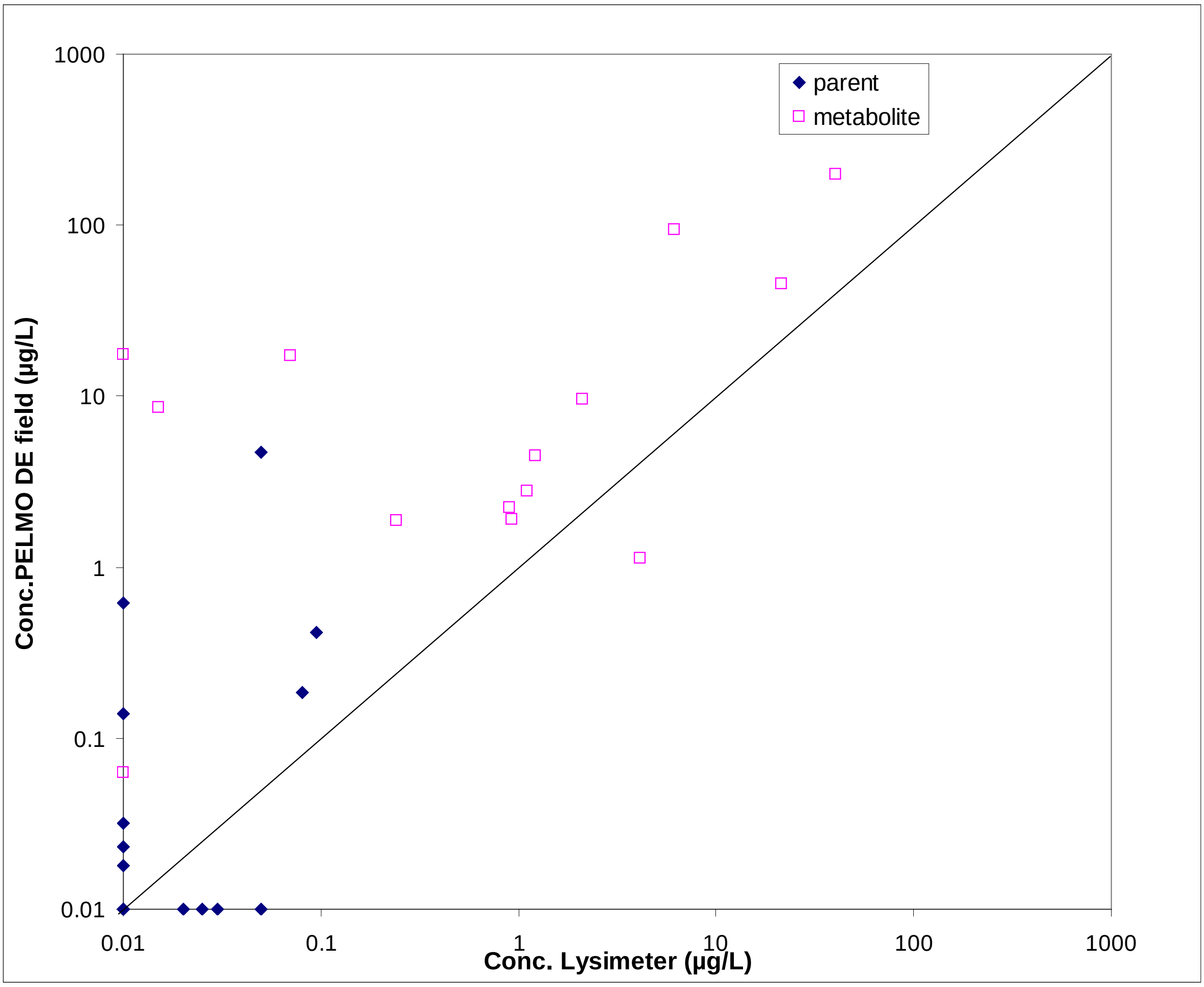


Figure 4-6: Comparison of calculated with observed annual leaching concentrations (concentration below 0.01 µg/L set to 0.01 µg/L, German parameter selection with field values, no plant uptake)

The statistical analysis presented so far in the tables does 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 than for parent compounds.

### 4.4.2 Evaluation based on active substances only

In the following Table 4-3 a similar evaluation is done as before only for the parent compounds.

Table 4-3: 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)

| Comparison | no Plant uptake | | including Plant uptake 0.5 | |
|---|---|---|---|---|
| Parameter setting according to | PELMO ≥ Lysimeter | PELMO < Lysimeter | PELMO ≥ Lysimeter | PELMO < Lysimeter |
| EU | 26 (78.8%) | 7 (21.2%) | 25 (75.8%) | 8 (24.2%) |
| DE | 27 (81.8%) | 6 (18.2%) | 26 (78.8%) | 7 (21.2%) |
| DE (lab)° | 29 (87.9%) | 4 (12.1%) | 27 (81.8%) | 6 (18.2%) |
| DE (field)° | 12 (75.0%) | 4 (25.0%) | - | - |

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

° analysis exclusively based on field or laboratory data on degradation (national procedure)

As shown in Table 4-3 the comparison for parent compounds shows similar results compared to Table 4-2 (all compounds) when selecting model input parameters according to the German national methodology. However, the comparison for the EU methodology 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%).

For active compounds this result 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 (82%). But also FOCUS PELMO simulations performed according to the EU assessment result in estimations of similar conservativeness (79%).

### 4.4.3 Evaluation based on transformation products only

In the following Table 4-4 the respective evaluation is done as before only for transformation products.

Table 4-4: 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)

| Comparison | no Plant uptake | | including Plant uptake 0.5 | |
|---|---|---|---|---|
| Parameter setting according to | PELMO ≥ Lysimeter | PELMO < Lysimeter | PELMO ≥ Lysimeter | PELMO < Lysimeter |
| EU | 51 (71.8%) | 20 (28.2%) | 48 (67.6%) | 23 (32.4%) |
| DE | 58 (81.7%) | 13 (18.3%) | 55 (77.5%) | 16 (22.5%) |
| DE (lab)° | 59 (83.1%) | 12 (16.9%) | 56 (78.9%) | 15 (21.1%) |
| DE (field)° | 14 (93.3%) | 1 (6.7%) | - | - |

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

° analysis exclusively based on field or laboratory data on degradation (national procedure)

Table 4-4 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 which does not depend on the type of compound (parent compounds and metabolites: 82% safe predictions). However, the comparison for metabolites simulated using the EU methodology shows relatively more situations (about 28%) where higher concentrations were observed in lysimeter studies than in PELMO simulations.

### 4.4.4 Deviations between the national and European approach

In contrast to the EU rules according to the German national scheme a high variance of the parameters $Kf_{oc}$ and $DT_{50}$ should be taken into account when selecting input parameters for modelling. For adsorption a Kf-value should be used instead of an arithmetic mean $Kf_{oc}$-value if the coefficient of variation $Kf_{oc}$ exceeds 60% (see Figure 4-1) and if there is no correlation between the organic carbon content and the sorption constant according to the German parameter selection rules (input decision). In these 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 %, an arithmetic mean, otherwise the 10th percentile Kf should be used for modelling. For degradation the 90th percentile $DT_{50}$ -value instead of the geometric mean value should be used, when the coefficient of variation is > 100 % (see Figure 4-2).

In order to check the impact of this difference in the national input parameter selection on the performance of the simulation models a special evaluation is performed. Therefore, all substances were selected from the database where Kf-values (German regulation) were used instead of $Kf_{oc}$-values (EU regulation) or 90th percentiles (German regulation) of the degradation values were used instead of the geometric mean (EU regulation). In total 32 cases (31 % of 104 substances) were found that matched the required conditions.

Table 4-5 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. Plant uptake was not considered for the simulations (see also Table 7-6 and Table 7-7).

Table 4-5: 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 active substances when selecting different sorption constants and degradation half-lives (Plant uptake = 0)

| Modelling endpoints | | | Comparison | | | | | |
|---|---|---|---|---|---|---|---|---|
| $Kf_{oc}$ / Kf | $DegT_{50}$ | Total no. | PELMO DE ≥ Lysimeter | PELMO DE < Lysimeter | PELMO EU ≥ Lysimeter | PELMO EU < Lysimeter | PELMO DE ≥ PELMO EU | PELMO DE < PELMO EU |
| $Kf_{oc}$(AM) | 90th p. | 2 | 2 | 0 | 1 | 1 | 2 | 0 |
| Kf (AM) | GM | 3 | 2 | 1 | 2 | 1 | 3 | 0 |
| Kf (10th p.) | GM | 1 | 1 | 0 | 1 | 0 | 1 | 0 |
| Kf (AM) | 90th p. | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Kf (10th p.) | 90th p. | 2 | 2 | 0 | 2 | 0 | 2 | 0 |
| Kf (CEC) | GM | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Kf (pH) | pH | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Total | | 8 | 7 | 1 | 6 | 2 | 8 | 0 |

AM = arithmetic mean
GM = geometric mean
p. = percentile
P = PELMO, L = Lysimeter
pH =average of acid and neutral/basic soils (Kf arithmetic mean, $DegT_{50}$ geometric mean)
CEC = dependent on cation exchange capacity

Eight parent compounds were identified where parameter selection according to Holdt et al. (2011) deviated from the EU methodology. In Table 4-5 they were grouped into 7 different input classes according to the type of deviation. However, no active substances can be grouped into input classes with an average sorption constant Kf and a 90th percentile of $DegT_{50}$ value (Table 4-5, line 6), with a Kf value dependent on CEC (Table 4-5, line 8)and Kf/ $DegT_{50}$ values dependent on pH (Table 4-5, line 9).

1. Average sorption constant $Kf_{oc}$ but 90th percentile of $DegT_{50}$ values (Table 4-5, line 3):
   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 simulation based on the EU methodology one simulation (of two) was below the respective experimental result. As parameterisation according to Holdt et al. (2001) is definitively more conservative no situation could be found where “EU-type” simulations were above simulations according to Holdt et al (2011).
2. Average sorption constant Kf and average $DegT_{50}$ value (Table 4-5, line 4):
   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 is was the opposite. When comparing the two methodologies (last two columns in line 4) no EU-result was found to be higher than the respective simulation according to Holdt et al (2001). However, the German methodology is not necessarily more conservative here, just different.
3. 10th percentile of Kf values and average $DegT_{50}$ value (Table 4-5, line 5):
   Only a single parent compounds was found that fitted into this class. The result of the comparison was independent on the methodology: PELMO simulated higher concentrations than in the lysimeter study. When comparing the two methodologies (last two columns in line 4) no EU-result was found to be higher than the respective simulation according to Holdt et al (2001).
4. 10th percentile of Kf values and 90th percentile of $DegT_{50}$ values (Table 4-5, 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 in the lysimeter study. As parameterisation according to Holdt et al. (2001) is definitively more conservative no situation could be found where these simulations were below EU-type simulations (last two columns in Table 4-5, line 7)

Table 4-5 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 $Kf_{oc}$ and $DT_{50}$ 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 $Kf_{oc}$ (EU-methodology) the comparison led to the same result.

However, when using the EU methodology (always average values) one additional situation was found where higher concentrations were observed in lysimeter studies than in the PELMO simulation. For this respective substance the $DegT_{50}$ value was characterised by a high coefficient of variation (selection of the more conservative 90th percentile $DegT_{50}$ according to Holdt et al (2011)).

Table 4-6: 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 endpoints* | | | Comparison | | | | | |
|---|---|---|---|---|---|---|---|---|
| $Kf_{oc}$/Kf | $DegT_{50}$ DE | Total no. | PELMO DE ≥ Lysimeter | PELMO DE < Lysimeter | PELMO EU ≥ Lysimeter | PELMO EU < Lysimeter | PELMO DE ≥ PELMO EU | PELMO DE < PELMO EU |
| $Kf_{oc}$(AM) | 90thp. | 6 | 6 | 0 | 6 | 0 | 6 | 0 |
| Kf (AM) | GM | 9 | 5 | 4 | 3 | 6 | 6 | 3 |
| Kf (10thp.) | GM | 4 | 4 | 0 | 2 | 2 | 4 | 0 |
| Kf (AM) | 90thp. | 1 | 1 | 0 | 0 | 1 | 1 | 0 |
| Kf (10thp.) | 90thp. | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Kf (CEC) | GM | 3 | 2 | 1 | 3 | 0 | 2 | 1 |
| Kf (AM) | pH-dep. | 1 | 0 | 1 | 1 | 0 | 0 | 1 |
| Total | | 24 | 18 | 6 | 15 | 9 | 19 | 5 |

* for parent: $Kf_{oc}$ = AM and $DegT_{50}$ (lab+field) = GM
AM = arithmetic mean
GM = geometric mean
p. = percentile
P = PELMO, L = Lysimeter
pH =average of acid and neutral/basic soils (Kf arithmetic mean, $DegT_{50}$ geometric mean)
CEC = dependent on cation exchange capacity

Table 4-6 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 FOCUS Hamburg and the 80th percentile of annual concentrations. Plant uptake was not considered for the simulations. 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 input deviate caused by different sorption constants (29%) or half-lives (13%). However, 6 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.

In Table 4-6 the remaining 24 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 $DegT_{50}$ value (Table 4-5, line 7).

1. Average sorption constant $Kf_{OC}$ but 90th percentile of $DegT_{50}$values (Table 4-6, 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 in the lysimeter study. As parameterisation according to Holdt et al (2001) is definitively

more conservative no situation could be found where these simulations were below EU-type simulations (last two columns in Table 4-6).

2. Average sorption constant Kf and average $DegT_{50}$ value (Table 4-6, line 4):
   9 compounds were found that fitted into this class. The result of the comparison was dependent on the methodology: When following the German input selection methodology in five cases PELMO simulated higher concentrations than in the lysimeter study, and in 4 cases it was the opposite. However, following the EU methodology in only three cases PELMO simulated concentrations above the lysimeter result whereas in six cases it was the opposite. When comparing the two methodologies (last two columns in line 4) 3 EU-results were found to be higher than the respective simulation according to Holdt et al (2011). This is not surprising, since the German methodology is not necessarily more conservative here, just different.
3. 10th percentile of Kf values and average $DegT_{50}$ value (Table 4-6, line 5):
   Four transformation products belonged to this class. In all cases PELMO simulated higher concentrations than in the lysimeter study whereas in the simulation based on the EU methodology two simulations were below the respective experimental result. As parameterisation according to Holdt et al (2011) is definitively more conservative here, no situation could be found where these simulations were below EU-type simulations (last two columns in Table 4-6).
4. Average sorption constant Kf and 90th percentile of $DegT_{50}$ values (Table 4-6, line 6):
   Only a single transformation product belonged to this class. PELMO simulated higher concentrations than in the lysimeter study whereas in the simulation based on the EU methodology it was the opposite. As parameterisation according to Holdt et al (2011) is definitively more conservative, no situation was found where these simulations were below EU-type simulations (last two columns in Table 4-6).
5. Kf based on CEC and average $DegT_{50}$ values (Table 4-6, line 8):
   Three transformation products belonged to this class. When following the EU-methodology in all cases PELMO simulated higher concentrations than in the lysimeter study whereas in the simulation based on the German methodology a single simulation were below the respective experimental result. This is supported by the last column in the table which shows a situation where the simulation according to EU methodology was above the respective German simulation. This is not surprising, since the German methodology is not necessarily more conservative here, just different.
6. Sorption and Degradation dependent on pH (Table 4-6, line 9):
   Only a single transformation product belonged to this class. PELMO simulated lower concentrations than in the lysimeter study whereas in the simulation based on the EU methodology it was the opposite. As parameterisation according to Holdt et al (2011) is not more or less conservative (just different), these results were by coincidence below EU-type simulations (last two columns in Table 4-6).

Table 4-6 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 $Kf_{oc}$ and/or $DT_{50}$ has been considered. However, for 6 of 24 substances annual concentration 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-value. For the respective simulation based on the $Kf_{oc}$ (EU-methodology) the comparison led to the same result.

However, when using the EU methodology (always average $Kf_{oc}$ -values) further 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 $DegT_{50}$-values. These more conservative selections finally resulted in higher simulated concentrations than observed in the lysimeter.

However, that does not mean that the German methodology is necessarily more conservative in all cases. In 5 of 24 situations the EU-methodology led to higher concentrations than input parameter selection according to Holdt et al (2011). These situations were based on average Kf-values or considering pH or CEC dependent Kf values instead of $Kf_{oc}$-values. As explained the national parametrisation of the FOCUS Hamburg scenario with arithmetic mean Kf-values or Kf-values dependent on soil properties like pH or CEC is not necessarily more conservative than the parametrisation with arithmetic mean $Kf_{oc}$ values.

## 4.5 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 parameter selection was based on the (compared to the EU selection methodology) more conservative national approach in about 18% of the comparisons PELMO still simulated lower concentrations than 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 needs for higher tier studies when they are unnecessary.

Generally, the sum of the groups PA + PB + 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 is more complicated, since also the concentration range between 0.1 µg/L and 10 µg/L (in the following just expressed as "trigger class 1") for metabolites is 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 complicated 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)

### 4.5.1 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.

### 4.5.2 Evaluation based on active substances only

Table 4-7 shows the results of the comparison for the simulations with PUF = 0.

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 is independent of which parameter selection rules were followed.

Table 4-7: Summary of the comparison of calculated with observed annual leaching concentrations (active substances, no plant uptake, trigger: 0.1 µg/L)

| Group | PA | PB | PC | PD | |
|---|---|---|---|---|---|
| Comparison | Lysimeter <0.1 µg/L PELMO < 0.1 µg/L | Lysimeter <0.1 µg/L PELMO > 0.1 µg/L | Lysimeter > 0.1 µg/L PELMO < 0.1 µg/L | Lysimeter >0.1 µg/L PELMO > 0.1 µg/L | Total |
| PELMO EU | 25 (75.8%) | 6 (18.2%) | 1 (3.0%) | 1 (3.0%) | 33 (100%) |
| PELMO DE | 20 (60.6%) | 11 (33.3%) | 1 (3.0%) | 1 (3.0%) | 33 (100%) |
| PELMO DE Lab | 16 (48.5%) | 15 (45.5%) | 1 (3.0%) | 1 (3.0%) | 33 (100%) |
| PELMO DE field | 11 (68.8%) | 5 (31.3%) | 0 | 0 (0.0%) | 16 (100%) |

Figure 4-7 highlights the differences between the PELMO variations for the applied substance (active compounds) only. Again, better agreement between simulation and experiment was reached when using the EU parameter selection compared to the more conservative German procedure. Similar as before there is a general trend that the strict use of field data leads to a more realistic description of what happened in the lysimeter study compared to laboratory data. 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. The selection of the plant uptake factor does not have a dominant influence but leads to a more realistic description of the processes in the lysimeter study as indicated by the higher bars (group PA).

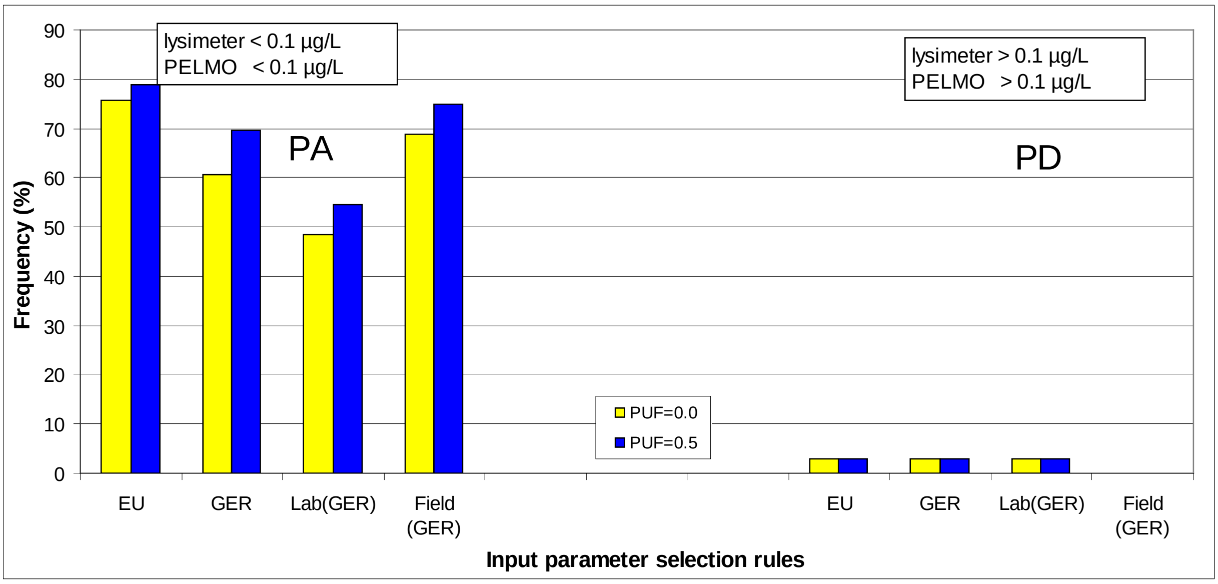


Figure 4-7: Agreement between experiment and simulation for different simulation variations (active substances only, n=33, field: n=16)

Figure 4-8 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 4-8 only represent the results of a single study with substance72 (autumn application) where the findings in the lysimeter could not be explained even based on the generally very conservative German rules for laboratory degradation studies. The study was already mentioned in section 4.4.1 (see red circles in Figure 4-3 to Figure 4-5). The reason that the field studies did not fail for this case was simply due to the fact that no simulation was performed as the field data on degradation was missing.

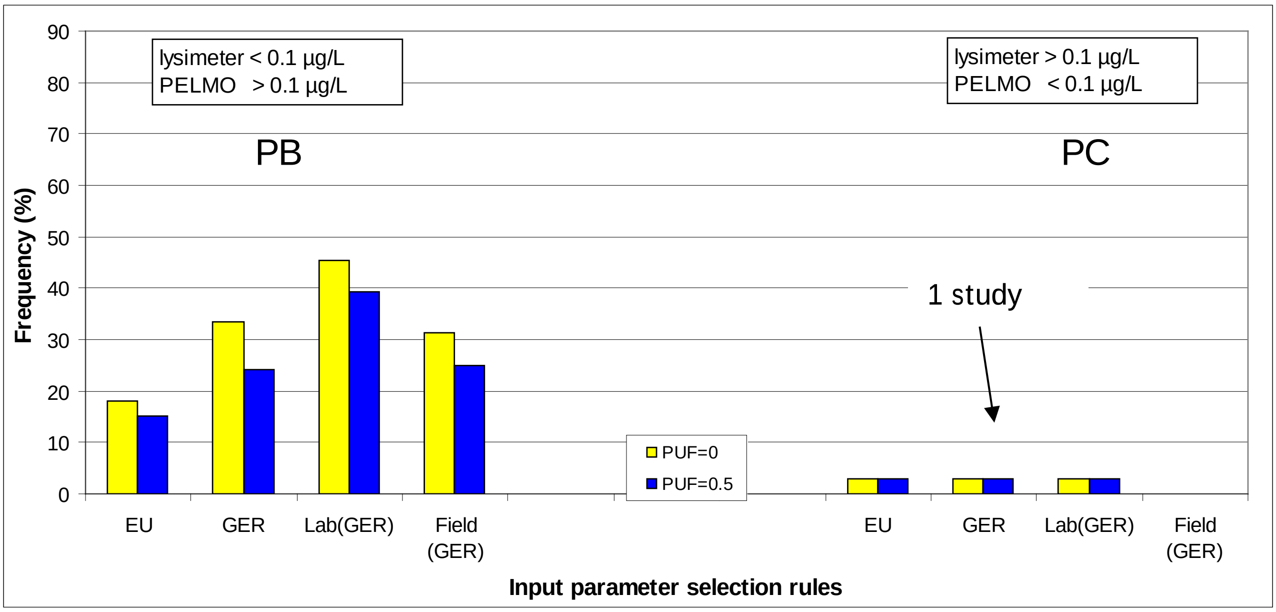


Figure 4-8: Disagreement between experiment and simulation for different simulation variations (applied substances only, n=33, field: n=16)

The analysis in the previous chapter 4.4 demonstrated that the computer simulations represent in general conservative estimations. But even when the parameter selection was based on the (compared to the EU selection methodology) more conservative national approach in about 18% of the comparisons PELMO still simulated lower concentrations than in the higher tier study for active substances. 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 selection methodology only 3% false negative results (group PC) were found for active substances.

When comparing the two selection variations (EU and German) the EU methodology showed less false-positive comparisons without increasing the number of false negative cases. That may be caused by more conservative national parameter setting if the variances are high.

As in the previous evaluations performed in chapter 4.4 the plant uptake factor did not play a dominant role for the comparison.

### 4.5.3 Evaluation based on transformation products

Also for transformation products the analysis in chapter 4.4 demonstrated that the computer simulations represent in general conservative estimations. However, in at least 18% of the comparisons PELMO simulated lower concentrations than in the higher tier study for national input parameter selection. However, the comparison for metabolites simulated using the EU methodology shows relatively more situations (about 28%) where higher concentrations were observed in lysimeter studies than in PELMO simulations. Therefore, also for metabolites an additional analysis based on different regulatory limits is performed 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 4-8.

Table 4-8: Overview on 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 |

Table 4-9 and Table 4-10 show the results for the simulations based on absolute numbers and percentages, respectively.

Table 4-9: 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 (values based on the absolute number of occurrences)

| | PUF | MA | MB | MC | MD | ME | MF | MG | MH | MI | Sum |
|---|---|---|---|---|---|---|---|---|---|---|---|
| EU | 0 | 23 | 5 | 0 | 7 | 18 | 0 | 4 | 9 | 5 | 71 |
| D | 0 | 18 | 4 | 0 | 12 | 19 | 0 | 4 | 9 | 5 | 71 |
| Lab | 0 | 17 | 4 | 0 | 14 | 14 | 0 | 3 | 13 | 5 | 70* |
| Field | 0 | 2 | 0 | 0 | 0 | 8 | 0 | 2 | 1 | 3 | 16 |
| EU | 0.5 | 24 | 5 | 0 | 7 | 19 | 0 | 3 | 8 | 5 | 71 |
| D | 0.5 | 21 | 5 | 0 | 9 | 18 | 0 | 4 | 9 | 5 | 71 |
| Lab | 0.5 | 21 | 5 | 0 | 10 | 15 | 0 | 3 | 11 | 5 | 70* |
| Field | 0.5 | 2 | 0 | 0 | 0 | 8 | 0 | 2 | 1 | 3 | 16 |

* reduced number because no laboratory data available for one substance

Table 4-10: 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 (values in %)

| | PUF | MA | MB | MC | MD | ME | MF | MG | MH | MI | Sum |
|---|---|---|---|---|---|---|---|---|---|---|---|
| EU | 0 | 32.4 | 7.0 | 0.0 | 9.9 | 25.4 | 0.0 | 5.6 | 12.7 | 7.0 | 100.0 |
| DE | 0 | 25.4 | 5.6 | 0.0 | 16.9 | 26.8 | 0.0 | 5.6 | 12.7 | 7.0 | 100.0 |
| Lab(DE) | 0 | 24.3 | 5.7 | 0.0 | 20.0 | 20.0 | 0.0 | 4.3 | 18.6 | 7.1 | 100.0 |
| Field(DE) | 0 | 12.5 | 0.0 | 0.0 | 0.0 | 50.0 | 0.0 | 12.5 | 6.3 | 18.8 | 100.0 |
| EU | 0.5 | 33.8 | 7.0 | 0.0 | 9.9 | 26.8 | 0.0 | 4.2 | 11.3 | 7.0 | 100.0 |
| DE | 0.5 | 29.6 | 7.0 | 0.0 | 12.7 | 25.4 | 0.0 | 5.6 | 12.7 | 7.0 | 100.0 |
| Lab(DE) | 0.5 | 30.0 | 7.1 | 0.0 | 14.3 | 21.4 | 0.0 | 4.3 | 15.7 | 7.1 | 100.0 |
| Field(DE) | 0.5 | 12.5 | 0.0 | 0.0 | 0.0 | 50.0 | 0.0 | 12.5 | 6.3 | 18.8 | 100.0 |

In order to structure the detailed information presented in Table 4-9 and Table 4-10 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)

Table 4-11: 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 (values in %)

| | PUF | MRG I | MRG II | MRG III | MRG IV | MRG V |
|---|---|---|---|---|---|---|
| EU | 0 | 64.8 | 28.2 | 7.0 | 0.0 | 0.0 |
| DE | 0 | 59.2 | 35.2 | 5.6 | 0.0 | 0.0 |
| Lab (DE) | 0 | 51.4 | 42.9 | 5.7 | 0.0 | 0.0 |
| Field (DE) | 0 | 81.3 | 18.8 | 0.0 | 0.0 | 0.0 |
| EU | 0.5 | 67.6 | 25.4 | 7.0 | 0.0 | 0.0 |
| DE | 0.5 | 62.0 | 31.0 | 7.0 | 0.0 | 0.0 |
| Lab | 0.5 | 58.6 | 34.3 | 7.1 | 0.0 | 0.0 |
| Field | 0.5 | 81.3 | 18.8 | 0.0 | 0.0 | 0.0 |

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 class 0 and Lysimeter 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 class 0 and Lysimeter 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 class 1 and Lysimeter class 2 i.e. false negative, unacceptable risk indicated from higher tier study only (MF)

The following conclusions can be drawn based on the aggregated information in Table 4-11:

Independent of the input selection methodology the majority of cases showed agreement in the PELMO simulation and lysimeter study (EU: 64.8%, DE: 59.2%, MRG I, no plant uptake).

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) the number of false positive results is significantly higher than for the 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 methodology. A slightly lower percentile (5.6%) belonged to this class when the simulation was based on the more conservative national approach as described in Holdt et al (2011).

However, all false-negative results were confined to experimental findings in the range 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 (never any disagreement independent on the input parameter selection).

The analysis in the previous chapter 4.4 demonstrated that the computer simulations represent in general conservative estimations. But even when the parameter selection was based on the (compared to the EU selection methodology) more conservative national approach in about 18% of the comparisons PELMO still simulated lower concentrations than in the higher tier studies. 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 less pronounced than indicated by the percentage of 18%. Dependent on the selection methodology only 7% (EU approach) or 5.6% (national approach) false negative results (MRG III) were found.

When comparing the two selection approaches (EU and German) the EU methodology showed less false-positive comparisons. That may be caused by more conservative national parameter setting if the variances of adsorption and/or degradation values are high.

As in the previous evaluations performed in chapter 4.4 the plant uptake factor did not play a dominant role for the comparison.

### 4.5.4 Deviations between the national and European approach

The analysis performed in chapter 4.4.4 (Table 4-5 and Table 4-6) 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 also for those active compounds and metabolites, for which a high variance of the input parameters $Kf_{oc}$ and $DT_{50}$ have been considered.

When using the EU methodology (always average 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 4-12 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. Plant uptake was not considered for the simulations.

Table 4-12: Summary of the comparison of calculated with observed annual leaching concentrations when selecting Kf or $Kf_{oc}$ values (active compounds, no plant uptake, trigger: 0.1 µg/L)

| Group | | | PA | PB | PC | PD |
|---|---|---|---|---|---|---|
| Modelling endpoint | | | PELMO<br>< 0.1 µg/L<br>Lysimeter<br>< 0.1 µg/L | PELMO<br>> 0.1 µg/L<br>Lysimeter<br>< 0.1 µg/L | PELMO<br>< 0.1 µg/L<br>Lysimeter<br>> 0.1 µg/L | PELMO<br>> 0.1 µg/L<br>Lysimeter<br>> 0.1 µg/L |
| $Kf_{oc}$(AM) | 90thp. | EU | 2 (100%) | 0 (0%) | 0 (0%) | 0 (0%) |
| | | DE | 1 (50.0%) | 1 (50%) | 0 (0%) | 0 (0%) |
| Kf (AM) | GM | EU | 3 (100%) | 0 (0%) | 0 (0%) | 0 (0%) |
| | | DE | 3 (100%) | 0 (0%) | 0 (0%) | 0 (0%) |
| Kf (10thp.) | GM | EU | 0 (0%) | 1 (100%) | 0 (0%) | 0 (0%) |
| | | DE | 0 (0%) | 1 (100%) | 0 (0%) | 0 (0%) |
| Kf (AM) | 90thp. | EU | - | - | - | - |
| | | DE | - | - | - | - |
| Kf(10thp.) | 90thp. | EU | 2 (100%) | 0 (0%) | 0 (0%) | 0 (0%) |
| | | DE | 1 (50.0%) | 1 (50%) | 0 (0%) | 0 (0%) |
| Kf(CEC) | GM. | EU | - | - | - | - |
| | | DE | - | - | - | - |
| Kf(pH) | pH | EU | - | - | - | - |
| | | DE | - | - | - | - |
| Total | | EU | 7 (87%) | 1 (13%) | 0 (0%) | 0 (0%) |
| | | DE | 5 (62%) | 3 (38%) | 0 (0%) | 0 (0%) |

AM = arithmetic mean
GM = geometric mean
p. = percentile
P = PELMO, L = Lysimeter
pH =average of acid and neutral/basic soils (Kf arithmetic mean, $DegT_{50}$geometric mean)
CEC = dependent on cation exchange capacity

Due to the analysis performed in chapter 4.4.3 there were a small number of cases where PELMO simulated lower concentrations for parent compounds than observed in experimental studies (EU methodology: 2 out of 8, German methodology: 1 out of 8, see Table 4-5), 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 4-12. The table shows the input classes as Table 4-5 in section4.4.4.

1. Average sorption constant $Kf_{oc}$ but 90th percentile of $DegT_{50}$ values (Table 4-12):
   Two situations were found that fitted into this input class. Both active compounds were simulated correctly by the EU-type simulation (group MA) whereas in the more conservatives simulation according to the German decision scheme (selection of the 90th percentile of the $DegT_{50}$) one simulation were simulated below the trigger (group MA), the other one above (group MB, false positive). No false negative results (group MC) were observed independent on the selection criteria.
2. Average sorption constant Kf and average $DegT_{50}$ value (Table 4-12):
   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 procedure) the simulation came to the same result as the experimental study (<0.1 µg/L, group MA). Consequently, no false negative results (group MC) were found.
3. 10th percentile of Kf values and average $DegT_{50}$ value (Table 4-12):
   Only a single parent compounds 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 MB). Again, no false negative results (group MC) were found.
4. 10th percentile of Kf values and 90th percentile of $DegT_{50}$ values (Table 4-12):
   Two situations were found that fitted into this input class. Both compounds were simulated correctly by the EU-type simulation (group MA) whereas in the more conservatives simulation according to the German decision scheme (selection of the 90th percentile of the $DegT_{50}$) one simulation were simulated below the trigger (group MA), the other one above (group MB, false positive). No false negative results (group MC) 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 $DegT_{50}$ value (Table 4-12, line 6), with a Kf value dependent on CEC (Table 4-12, line 8) and Kf/ $DegT_{50}$ values dependent on pH (Table 4-12, line 9).

Table 4-12 confirms that both selection methodologies (EU and the German decision scheme), ensure a safe and conservative estimation of the groundwater risk. No false negative results are identified independent whether EU or the national selection approach was followed.

There was of course a single assessment when PELMO simulated lower concentration than observed in the lysimeter study (see chapter 4.4.4, Table 4-5). However, the results presented in Table 4-12 showed that this outcome had no impact on possible registration decisions as the result was below the trigger in simulation and experimental study.

When comparing the false positive situations for active substances (regulatory necessity for additional higher tier studies) the German approach led to 3 times more results that belonged to that group MB (EU: 13%, DE: 39%).

Table 4-13 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. Plant uptake was again not considered for the simulations.

All transformation products considered for this comparison were formed by “ordinary” parents (no deviations between EU and German methodology for the parent).

Table 4-13: Summary of the comparison of calculated with observed annual leaching concentrations when selecting Kf or $Kf_{oc}$ values (transformation products, no plant uptake, trigger: range of 0.1 µg/L to 10 µg/L)

| Modelling endpoint | | | MRG I | MRG II | MRG III | MRG IV | MRG V |
|---|---|---|---|---|---|---|---|
| $Kf_{oc}$(AM) | 90thp. | EU | 4 (67%) | 2 (33%) | 0 (0%) | 0 (0%) | 0 (0%) |
| | | DE | 3 (50%) | 3 (50%) | 0 (0%) | 0 (0%) | 0 (0%) |
| Kf (AM) | GM | EU | 5 (56%) | 2 (22%) | 2 (22%) | 0 (0%) | 0 (0%) |
| | | DE | 4 (44%) | 3 (33%) | 2 (22%) | 0 (0%) | 0 (0%) |
| Kf (10thp.) | GM | EU | 3 (75%) | 1 (25%) | 0 (0%) | 0 (0%) | 0 (0%) |
| | | DE | 1 (25%) | 3 (75%) | 0 (0%) | 0 (0%) | 0 (0%) |
| Kf(AM) | 90thp. | EU | 1 (100%) | 0 (0%) | 0 (0%) | 0 (0%) | 0 (0%) |
| | | DE | 1 (100%) | 0 (0%) | 0 (0%) | 0 (0%) | 0 (0%) |
| Kf(10thp.) | 90thp. | EU | - | - | - | - | - |
| | | DE | - | - | - | - | - |
| Kf(CEC) | GM | EU | 2 (67%) | 1 (33%) | 0 (0%) | 0 (0%) | 0 (0%) |
| | | DE | 2 (67%) | 1 (33%) | 0 (0%) | 0 (0%) | 0 (0%) |
| Kf(AM) | pH-dep. | EU | 1 (100%) | 0 (0%) | 0 (0%) | 0 (0%) | 0 (0%) |
| | | DE | 1 (100%) | 0 (0%) | 0 (0%) | 0 (0%) | 0 (0%) |
| Total | | EU | 16 (67%) | 6 (25%) | 2 (8%) | 0 (0%) | 0 (0%) |
| | | D | 12 (50%) | 10 (42%) | 2 (8%) | 0 (0%) | 0 (0%) |

AM = arithmetic mean
GM = geometric mean
p. = percentile
Main regulatory group (MRG) I: agreement between PELMO and lysimeter (A,E,I)
Main regulatory group (MRG) II: PELMO more conservative than lysimeter i.e. false positive (MD,MG,MH)
Main regulatory group (MRG) III: PELMO class 0 and Lysimeter 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 class 0 and Lysimeter 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 class 1 and Lysimeter class 2 i.e. false negative, unacceptable risk indicated from higher tier study only (MF)

In total 24 cases were found where parameter selection according to Holdt et al. (2011) deviated from the EU methodology. In Table 4-13 they were grouped into 7 different input classes according to the type of deviation.

1. Average sorption constant $Kf_{oc}$ but 90th percentile of $DegT_{50}$ values:
   Six situations were found that fitted into this input class. 4 compounds were simulated correctly by the EU-type simulation (MRG I), the remaining 2 compounds resulted in MRG II classification (false positive). The more conservatives simulation according to the national approach (selection of the 90th percentile of the $DegT_{50}$) 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.
2. Average sorption constant Kf and average $DegT_{50}$ value:
   9 compounds were found that fitted into this input class. Two false negative results were found (MRG III, 22%) independent on the 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 methodology (22%).
3. 10th percentile of Kf values and average $DegT_{50}$ value :
   Four transformation products belonged to this input class. No false negative results (MRG III,IV,V) were found independent on the selection approach. However, the situation with regard to false-positive results (MRG II) was completely different: 25% belonged to this group when following the EU approach whereas 75% when following the national approach.
4. 10th percentile of Kf values and 90th percentile of $DegT_{50}$ 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).
5. Kf based on CEC and average $DegT_{50}$ values:
   Three transformation products belonged to this input class. The result of the comparison was independent on the methodology. No false negative results (MRG III,IV,V) were found.
6. 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) and the percentage of false positive comparisons was 33%.

According to the analysis performed in chapter 4.4.4 (Table 4-6, column 5) for 6 of 24 transformation products (25%) annual concentration in the lysimeter experiment were found to be above respective simulation results. For these metabolites there was no correlation between organic carbon content and sorption (no transformation product was belonged to input class 1) and so the simulation was based on the Kf-values. Nevertheless, the impact of this result on registration decisions may be less pronounced since only in 8% (2 of 24 compounds) false negative results were obtained independent whether the EU or the national selection approach was followed (Table 4-13, 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 selection and EU selection, respectively, see chapter 4.5.3, Table 4-11, MRG III).

When comparing the false positive situations (regulatory necessity for additional higher tier studies) the German approach led to 2 times more results that belonged to that MRG II (EU: 25%, national: 42%).

## 4.6 Summary and Conclusions

The protection level of the tiered approach for the groundwater risk assessment in Germany has been investigated in this project. This became necessary since the new FOCUS PELMO model (version 5.5.3) is used in the national authorisation procedure instead of PELMO 3.0 in terms of harmonisation between EU member states since 2011 (Holdt et al. 2011). Additionally, a revised approach to select modelling endpoints which differs in some cases from the EU recommendations has been implemented for lower tier groundwater risk assessment since 2011. Besides, the maximum annual average leachate concentration from field lysimeter studies according to BBA (1990) is currently still accepted as higher tier measurement to assess the risk of plant protection products to groundwater. Therefore, one objective of the project was to determine discrepancies and their possible causes between simulated PECs and experimentally derived leachate concentrations. The main objective was to determine whether tier 1 and 2 calculations are still more conservative than higher tier results from lysimeter studies and thus the national groundwater modelling approach ensures a safe prediction of leachate concentrations for both active substances and their transformation products.

Therefore, 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 national requirements (Holdt et al. 2011) and according to the EU risk assessment. Additional simulations were performed according to the German decision scheme using laboratory degradation data in cases field degradation data was available to compare the outcomes. For 38 of the 104 substances (37%, 8 active compounds and 30 metabolites) EU and national input deviated caused by different sorption constants (29%) or half-lives (13%). However, 6 of these 30 transformation products were not considered further since they were formed already by parent compounds characterised by different national and EU parameter selection.

Simulation runs were conducted considering the application rates and crop conditions from corresponding lysimeter studies.

For both methodologies (simulation runs with national and EU endpoints), in most of the cases FOCUS PELMO calculated higher concentrations than determined in the field lysimeter studies according to BBA (1990). However, the national procedure was found to be more conservative (PELMO above lysimeter: 72%) than the EU system (PELMO above lysimeter: 64%) (see chapter 4.4.1, Table 4-1).

This result indicate, 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 for about 72% of all analysed compounds, if experimental outdoor lysimeter data are used to investigate the protection level. The level of protection increases up to 82% if uncertainties correlated with analytical determinations and model haziness below 0.01 µg/L are ignored (see Table 4-2, national procedure: 81.7%, EU: procedure 74%).

Dependent on the available data the results of field or laboratory degradation tests may be selected as input values for the PELMO simulations. If the national procedure for endpoint selection according to Holdt et al. (2011) was followed the influence of the type of data on the simulation result was insignificant (84.5% and 83.9% for simulations based on laboratory and field data, respectively).

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

The national lower tier groundwater risk assessment is more protectable compared to FOCUS modelling with averaged EU endpoints. A marginal smaller percentage of 79% and a lower percentage of 72% have been determined based on the EU methodology for a safe prediction of active substances and metabolites, respectively (see Table 4-3 and Table 4-4). Detailed comparisons between lysimeter and FOCUS PELMO taken from the database are summarised in appendix 2 (Table 7-5).

As no 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. 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 a further analysis was performed taken 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 selection methodology (EU or national) only 3% false negative results (one active substance, only) were found.

When comparing the two selection methods (EU and German) the EU methodology showed less false-positive comparisons without increasing the number of false negative cases. That may be caused by the more conservative national input parameter setting for modelling if the variances of the adsorption and/or degradation values are high.

As already mentioned also for transformation products the comparisons of PELMO simulations with lysimeter studies resulted in general in conservative estimations. However, in about 18% of the comparisons PELMO simulated lower concentrations than in the higher tier study if the national approach was followed. A higher percentage of 28% was calculated using averaged endpoints like in the EU assessment (see Table 4-4).

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

Independent of the input selection methodology the majority of cases (transformation products) showed agreement in the PELMO simulation and lysimeter study (main regulatory group MRG I: EU 64.8%, DE: 59.2%, see Table 4-11).

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 experiment 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 German methodology according to Holdt et al. (2011) the number of false positive results is higher (35%) than for the EU methodology (28%)(see Table 4-11).

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 the EU methodology. A slightly lower percentile (5.6%) belonged to the main regulatory group MRG III when the simulation was based on the more conservative national approach as described in Holdt et al. (2011).

However, all false-negative results for metabolites were confined to experimental findings in the range 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 (never any disagreement independent on the input parameter selection).

According to the national groundwater risk assessment and in contrast to the EU approach a high variance of the parameters $Kf_{oc}$ and $DT_{50}$ 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 an arithmetic mean $Kf_{oc}$ value if the coefficient of variation $Kf_{oc}$ exceeds 60% and if there is no correlation between the organic carbon content and the 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%, an arithmetic mean, otherwise the 10th percentile of all available Kf values should be used for modelling. For degradation the 90th percentile $DT_{50}$ value instead of the geometric mean value should be used, when the coefficient of variation is > 100%. This different rules to select national endpoints may have an effect on the groundwater modelling results.

In order to check the impact of this different selection method on the performance of the simulation models a special evaluation was performed. Therefore, all substances where Kf-values (German regulation) instead of $Kf_{oc}$-values (EU regulation) or 90th percentiles $DegT_{50}$-values (German regulation) instead of the geometric mean $DegT_{50}$ (EU regulation) were selected from the database. In total 32 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 endpoint selection in the EU assessment.

Eight parent compounds were identified where parameter selection according to Holdt et al. (2011) deviated from the 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 $Kf_{oc}$ and $DT_{50}$ have been considered. Only for a one parent compound the maximum average 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 $Kf_{oc}$ (EU-methodology) the comparison led to the same result.

However, when using the EU methodology (always average values) one additional situation was found where higher concentrations were observed in lysimeter studies than in the PELMO simulation. For this respective active substance the $DegT_{50}$ value was characterised by a high coefficient of variation (selection of the more conservative 90th percentile $\text{DegT}_{50}$ 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 performed for transformation products.

It was confirmed that both selection methodologies (EU and German procedure according to Holdt et al. 2011), ensure a safe and conservative estimation of the groundwater risk. No false negative results independent whether EU or the national selection approach was followed. When comparing the false positive situations (regulatory necessity for additional higher tier studies) the German approach led to 3 times more results that belonged to group MB (EU: 13%, national: 38%, see Table 4-12).

In addition to the parent compounds also 24 transformation products were found where parameter selection according to Holdt et al. (2011) deviated from the EU methodology. All these selected transformation products were formed by “ordinary” parents (no deviations between EU and German methodology for the parent).

It was confirmed 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 $\text{Kf}_{\text{oc}}$ and $\text{DT}_{50}$ have been considered. However, for 6 of 24 metabolites annual concentrations in the lysimeter experiment were found to be above respective simulation results. For all these transformation products no correlations between organic carbon content and sorption were found and the simulation was based on the average Kf-value. For the respective simulation based on the $\text{Kf}_{\text{oc}}$ (EU-methodology) the comparison led to the same result. When using the EU methodology (always average $\text{Kf}_{\text{oc}}$ -values) further metabolites (all together 9 metabolites) were found where higher concentrations were observed in lysimeter studies than in the PELMO simulation.

Also for these 24 transformation products a regulatory impact analysis was performed to evaluate possible registration decisions. It was demonstrated that only in 8% (2 of 24 compounds) false negative results were obtained independent whether the EU or the national selection approach was followed (see Table 4-13, 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 selection and EU selection, respectively, see chapter 4.5.3, Table 4-11, main regulatory group MRG III).

When comparing the false positive situations (relevant when asking for additional studies) the German approach led to 2 times more results that belonged to that group (EU: 25%, national: 42%, see Table 4-13, main regulatory group MRG II).

All PELMO simulations were done both with and without considering plant uptake (PUF=0.5). Independent on the type of compound (parent or metabolite) and the selection criteria (EU or national methodology) the plant uptake factor only had a minor influence on the comparison. In about 3 to 5% of the simulations the comparison changed from PELMO > lysimeter (no plant uptake) to PELMO < lysimeter (including plant uptake). However, the additional impact analysis using the regulatory limit of 0.1 µg/L did not show any effect of the plant uptake factor.

## 4.7 References

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# 5 Part A II: Results of inverse modelling optimisation using InversePELMO

## 5.1 Introduction

For many years lysimeter studies according to BBA (1990) are considered in German pesticide regulation as higher tier for the assessment of the leaching potential of plant protection products. They are used as “endpoint studies” which means that the measured maximum averaged annual percolate concentrations are directly used for regulatory decision making. However, in the past the representativeness of lysimeter studies was often controversial discussed and criticised with regard to their suitability as endpoint studies for regulatory decision-making (see e.g. FOCUS 2009/2014). Major concerns are related to the relatively short study time of two or three years in combination with single applications at the beginning of those experiments. This is often not in line with expected repeated application pattern over a longer time period as in reality. Therefore this is not comparable with probably more conservative results of leaching models which predict leachate concentrations after 20 years and repeated applications.

Considering these deficiencies of the lysimeter studies with regard to repeated applications and short durations the use of these experiments as “endpoint studies” may be put into question. Nevertheless, lysimeter studies could be used to increase the understanding of leaching under field conditions ("process study") when the results of lysimeter studies are further evaluated using the FOCUS leaching models. This was the background as to why the current FOCUS groundwater report (FOCUS 2009/2014) recommends these evaluations and suggests the inverse modelling technique as an appropriate methodology. FOCUS explicitly mentions inverse modelling as an appropriate methodology to interpret lysimeter studies. Inverse modelling optimisations are usually in regulatory context performed to obtain key parameters for risk assessment such as $Kf_{oc}$ and $DegT_{50}$ from lysimeter or other higher tier studies. Once optimised adsorption and degradation values are obtained for the single lysimeter experiment, model based extrapolations of the experiment (longer time period and/or different application amounts) are than possible in a second step. The aim of inverse modelling is therefore on one hand to get a deeper look into the processes that led to a certain lysimeter result. On the other hand inverse modelling can be used to improve the standard modelling at tier 1 by considering additional information from higher tier studies.

If the model was able to mimic the processes in one lysimeter study the lysimeter study results could then in principle be transposed to other conditions e.g. different soil types, climate or application pattern. In the national context of groundwater risk assessment for pesticides it is in general assumed, that the soil and climate conditions in lysimeter studies according to BBA (1990) are comparable to the conditions of the FOCUS Hamburg scenario.

In the following chapters the suitability of lysimeter studies as a "process study" to assess the leaching behaviour of pesticides and their metabolites is analysed.

Special focus will be on in how far the short study period (2 to 3 years) in combination with applications in the first year limits the value of the lysimeter study for meaningful conclusions about leaching under outdoor conditions.

In order to check in how far the lysimeter conditions can be extrapolated to other conditions like the effect of the changing climatic conditions and soil profiles is analysed.

Further questions which will be addressed in this chapter are:

- Could inverse modelling of field lysimeter studies be routinely used as a higher tier option when assessing leaching to groundwater in the national regulatory context?
- Is it possible to assess a range of substance properties (sorption, degradation) for which the current study period of 2 to 3 years is sufficient to still use field lysimeter studies as higher tier endpoint studies in the national regulatory context?
- Are the measured maximum annual percolate concentrations in lysimeter studies principally comparable to their respective simulated percolate concentrations performed with FOCUS PELMO and optimised parameter setting?
- Do simulations with FOCUS Hamburg soil result in similar concentrations as in lysimeter studies if the lysimeter climate and optimised parameter setting is used?
- Do simulations with FOCUS Hamburg climate result in similar concentrations as in lysimeter studies if the lysimeter soil and optimised parameter setting are used?
- Do simulations with FOCUS Hamburg (endpoint: 80th temporal percentile) result in similar concentrations as maximum concentrations in lysimeter studies if optimised parameter setting is used?

In order to achieve the different objectives different calculations with extended simulation periods of the lysimeter experiments (and optimised adsorption and degradation values, which represent the lysimeter experiment) are performed in this chapter such as:

5) Simulations over 20 years considering the lysimeter conditions (soil and weather) with repeated and single application patterns.
6) Simulations over 20 years considering the lysimeter soil conditions but in combination with FOCUS Hamburg weather scenario
7) Simulations over 20 years considering the lysimeter weather conditions but in combination with FOCUS Hamburg soil scenario
8) Simulations over 20 years considering the FOCUS weather and soil scenarios

## 5.2 Methodology

### 5.2.1 Inverse modelling procedure

The inverse modelling was done using the software tool “inversePELMO” which combines the simulation model FOCUS PELMO with the optimisation tool “PEST” (Klein 2011). As the software was already developed in 2011 it is based on the previous FOCUS PELMO version 4.4.3.

Information on how to perform inverse modelling studies can be taken from FOCUS (2009/2014). Generally, two steps have to be conducted when performing inverse modelling optimisations:

The first part of the inverse modelling is a calibration step to adequately describe the soil hydrology of the leaching study, in terms of both temporal and total fluxes. In order to be able to evaluate pesticide behaviour, the water balance in the soil must firstly be meaningful simulated. This should include a comparable description of percolate volumes over the course of time in experiment and simulation. If a conservative tracer was applied to the study, it should also be evaluated during the calibration phase. In the second part the pesticide input parameters are optimised. Of course, the calibrated hydrology must not be changed anymore at this stage of the analysis. Appendix 6 gives some details about the software and the methodology.

### 5.2.2 Data requirements for inverse modelling optimisations

The following data should be made available to reduce uncertainty in the outcome of the modelling study:

- weather information on a daily basis (temperature, rainfall)
- irrigation on a daily basis
- information on potential evapotranspiration on a daily basis
- analyses of individual percolate samples (without mixing over long time periods)
- chemical analyses of all samples not just radioactivity

Furthermore, it could be helpful if tracers were used in the lysimeter study in order to improve the calibration of the soil hydrology.

Unfortunately, key input data was not available from most of the lysimeter studies to perform inverse modelling. The issues were

- weather information not sufficient (only monthly values available)
- irrigation sometimes recorded on a monthly basis
- data on potential evapotranspiration not reported
- not all samples analysed (only radioactivity reported)

These deficiencies could be explained by the fact that the lysimeter guideline (BBA 1990) does not consider the needs of inverse modelling optimisations.

As the majority of studies was affected by those deficiencies these experiments could not simply be sorted out. Instead, different workarounds have been implemented in the analysis of selected lysimeter studies on a case by case basis such as:

- calculation daily weather data based on monthly information
- calculation of meaningful irrigation dates based on monthly values
- calculation evapotranspiration data based on available weather information
- calculation concentration based on radioactivity information

According to BBA (1990) remaining pesticide concentrations in soil have to be determined at the end of the lysimeter study. However, based on the experiences in this project inverse modelling should not be performed if only these soil concentrations are available because substances were never detected in the percolate. Percolate concentrations are essential for adequate optimisation of the results.

### 5.2.3 Simulations with optimized parameters

This section evaluates whether special PELMO simulations with optimised parameters are a useful tool to assess the leaching behaviour of pesticides and their metabolites. Three variations with different simulation conditions are used to analyse in how far inverse modelling of lysimeter studies is a suitable strategy:

1) Prolonged simulations

These simulations should answer the question whether the duration of a certain lysimeter study was sufficient and the experimental study was not stopped before the maximum concentrations in leachate were reached.

In contrast to standard FOCUS PELMO simulations over 26 years data from only a small number of weather years were available from the lysimeter studies. Annual precipitation, including irrigation during the lysimeter studies, was at least 800 mm over the whole study period (requirement of the lysimeter test guideline: BBA 1990). Therefore, for the prolonged PELMO simulations always the first complete weather year (i.e. year 2) was repeated.

In order to definitively estimate the time between application and the maximum concentration in the percolate, the active substance was applied only in the first year according to the information given in the lysimeter study. Consequently, for the additional simulation period also the crop rotation during the first experimental year was used.

An additional simulation was performed in order to analyse the maximum concentration in leachate after repeated applications.

2) Comparison of the impact of standard FOCUS Hamburg scenario conditions and experimental lysimeter conditions for modelling results

In order to analyse the dependencies of the lysimeter conditions and the FOCUS scenario definitions on the PEC calculations further simulations were performed.

- Combination of the lysimeter soil (and application pattern) with standard (FOCUS Hamburg) scenario weather pattern.
- Combination of the lysimeter weather with standard (FOCUS Hamburg) soil and application pattern

These simulations should improve the understanding about the influence of the various input parameters on the predicted concentrations in the percolate. The final goal was to assess how conservative the FOCUS Hamburg scenario was in comparison with experimental lysimeter conditions.

As the FOCUS scenarios are based on the weather series over 26 years only repeated annual application patterns were considered for the comparison.

3) FOCUS Tier 1 simulations with optimised parameters

Independent of the quality of the inverse modelling results additional simulations were performed using the obtained optimised sorption and degradation parameters as input for so called "higher tier" simulations with the standard FOCUS Hamburg scenario.

## 5.3 Lysimeter studies used for the evaluation

Table 5-1 shows an overview about the lysimeter studies used for the inverse modelling optimisations.

Table 5-1: Lysimeter studies used for the inverse modelling optimisations

| Lysimeter Core No | Location | Time | Substance | Annual concentrations in the percolate (µg/L) | | | |
|---|---|---|---|---|---|---|---|
| | | | | Tier 1 EU° | Tier 1 D Lab° | Tier 1 D Field° | Lysimeter |
| 1 | Schmallenberg | 1990-1992 | Terbuthylazin | 0.001 | 0.772 | 0.000/ 0.032 | <0.01 |
| | | | Met. MT13 GS 23158 | 25.925 | 20.951 | - | 0.02 |
| 2 | Monheim | 1993-1995 | Flufenacetat | 0.000 | 0.000 | 0.000 | 0.03 |
| | | | Met FOE 5043-Sulfonic Acid | 5.208 | 50.299 | 8.652 | 0.015 |
| 3 | Monheim | 1993-1996 | Flufenacetat | 0.000 | 0.000 | 0.000 | 0.03 |
| | | | Met FOE 5043-Sulfonic Acid | 5.208 | 50.299 | 8.652 | 0.015 |
| 4 | Neustadt | 1995-1998 | Thiamethoxam | 0.415 | 14.071 | 0.414 | 0.095 |
| | | | Clothianidin | 0.513 | 1.770 | - | 0.27 |
| 5 | Neustadt | 1995-1998 | Thiamethoxam | 0.415 | 14.071 | 0.414 | 0.095 |
| | | | Clothianidin | 0.513 | 1.770 | - | 0.27 |
| 6 | Schmallenberg | 1990-1994 | Bentazon | 0.185 | 5.605 | 0.185 | 0.08 |
| 7 | Schmallenberg | 1990-1993 | Bentazon | 0.185 | 5.605 | 0.185 | 0.08 |
| 8 | Hamburg | 1989-1991 | Isoxaben | 0.058 | 4.457 | 4.666 / 0.000 | 0.05 |
| | | | Met Hydroxy-Isoxaben | 15.060 | 25.638 | 17.326/ 13.886 | 0.07 |
| 9 | Schmallenberg | 1995-1997 | Nicosulfuron | 0.222 | 0.222 | - | 0.17 |
| 10 | Neustadt | 1991-1994 | Met G27550 (of Diazinon) | 86.583 | 88.144 | - | 1.02 |
| 11 | Neustadt | 1991-1994 | Met G27550 (of Diazinon) | 86.583 | 88.144 | - | 1.02 |
| 12 | Neustadt | 1989-1992 | Isoproturon | 0 | 0 | - | 0.272 |
| 13 | Neustadt | 1989-1992 | Isoproturon | 0 | 0 | - | 0.272 |
| 14 | Neustadt | 1992-1994 | Metalaxyl | 0 | 0 | 0.004 | 0.05 |
| 15 | Neustadt | 1992-1994 | Metalaxyl | 0 | 0 | 0.004 | 0.05 |

° 80th percentile of the simulated annual concentrations over 20 years taken from part A I (chapter 4)

Not all compounds which were considered in part A I of this project were considered also for the inverse modelling of lysimeter results. Generally, lysimeter studies without significant amount of the substance leaching (parent or metabolite) were not considered.

Most of the lysimeter studies were performed in the nineties of the last century at in total 4 different lysimeter sites. Generally, a mismatch was observed between data available from the lysimeter study and necessary input data to perform inverse modelling:

- Weather information were not sufficient (only monthly values available),
- Irrigation sometimes were recorded on a monthly basis,
- Data on potential evapotranspiration were not reported,
- Not all samples were analysed (only radioactivity reported).

Although essential information to perform an inverse modelling was missing, the experimental data fulfilled all requirements of the BBA-test guideline (BBA 1990). The original intention of lysimeter studies and the BBA guideline was to establish a higher tier study, which can be directly used as an endpoint without transposing results to other situations using inverse modelling techniques. The lack of data on daily potential evapotranspiration led to fitting outside the expected range for the respective parameters. However, as long as the visual representation of the cumulative leachate shows satisfactory agreement with the experimental data an optimisation of the percolate was not rejected in this study just because parameters are deviating from normal parameterisation.

No lysimeter studies performed outside Germany were considered due to a lack of appropriate weather data required for inverse modelling. Beside, major deviations of the experimental conditions to the FOCUS Hamburg scenario might exist and would lead to more difficulties for the interpretation in the national regulatory context.

In five lysimeter cores shown in Table 5-1 only parent residues were analysed (6,7,9,14,15), in two lysimeter cores only metabolite residues were analysed (10,11) and in eight lysimeter cores parent and metabolite residues were analysed (1,2,3,4,5,8,12,13). The sites, where the lysimeter experiments have been conducted, were located in Neustadt, Schmallenberg, Monheim and Hamburg in Germany. In total eight different parent compounds and six metabolites were analysed (some of the substances were considered in several inverse modelling optimisations). Detailed information about the climate (temperatures, precipitation) and soil parameters (e.g. texture, organic carbon contents) are provided in appendix 7.

## 5.4 Results of the inverse modelling simulations

Detailed information about the results of the inverse modelling simulations including lysimeter conditions, input parameters and quality criteria can be found in appendix 7. As explained in appendix 6 inverse modelling always begins with a calibration step to adequately describe the soil hydrology of the leaching study, in terms of both temporal and total fluxes. PELMO is a capacity model. Compared to models that solve Richard's equation (e.g. PEARL) soil hydrology in PELMO is less complex programmed. As a consequence PELMO has only few parameters to calibrate hydrology in soil (e.g. the amount of percolate). The following input parameters are used by inversePELMO for the calibration:

- Initial soil moisture (a single value for the whole soil core),
- Minimum depth for evaporation,
- Crop specific Kc-factors.

The crop specific Kc-factors are used to transpose the generic potential evaporation data to crop specific values. These factors are available for no-crop condition, mid-season and late season.

Though PELMO has only limited possibilities to calibrate the hydrology in soil the level of agreement between the time dependent percolate in experiment and simulation was in general acceptable. As a quality criteria the FOCUS chi² error was used (FOCUS 2006). FOCUS chi² errors were found in the range 2.04 % to 10.24 % (arithmetic mean: 5.4 %, for more details see Table 5-4 or appendix 4).

In addition to statistical quality criteria appendix 7 also provides graphical comparison of calibrated cumulative percolate amounts. Two examples, one perfect (chi²: 2.8 %) the other one still adequate (chi²: 5.4 %) are given in the following figures.

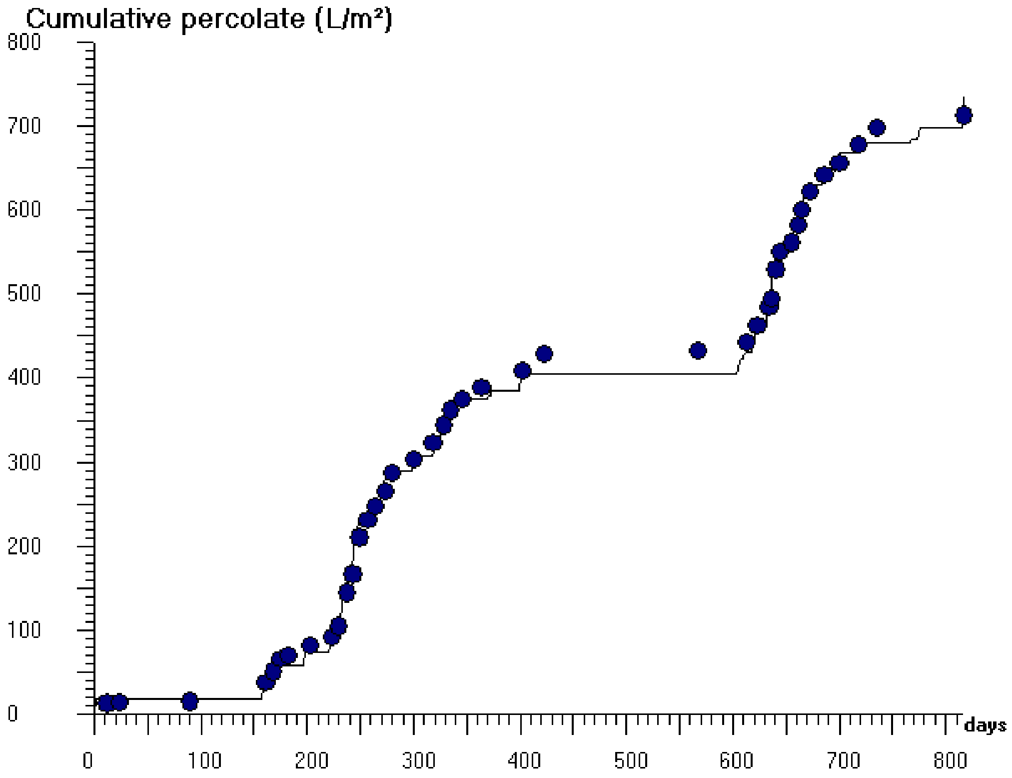


Figure 5-1: Example for a percolate optimisation (optimisation 3, FOCUS chi² 2.8 %)

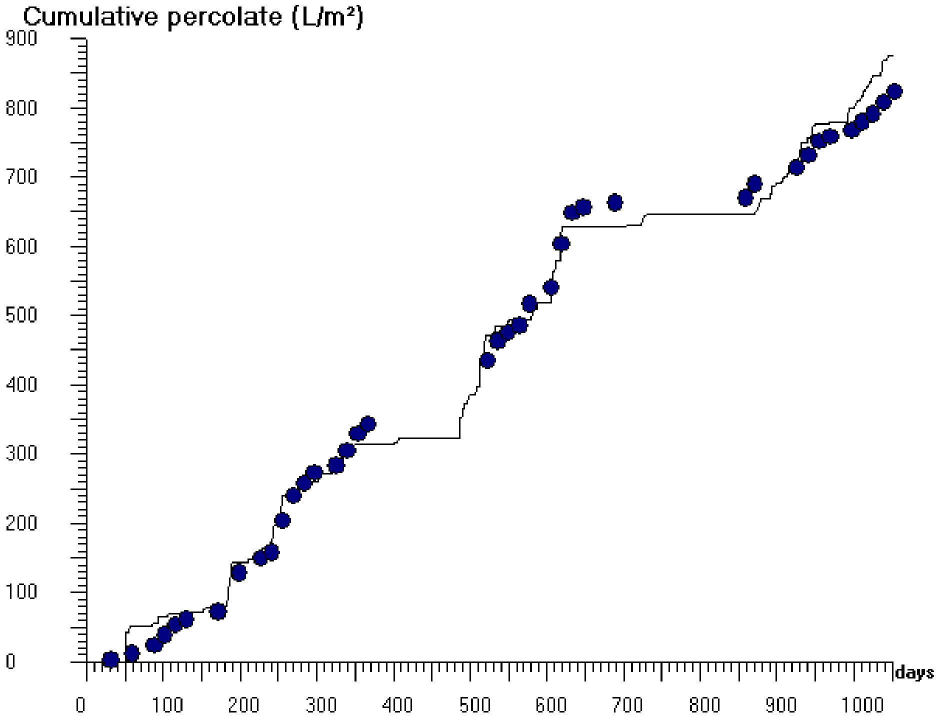


Figure 5-2: Example for a percolate optimisation (optimisation 5, FOCUS chi² 5.4 %)

After adjusting the water fluxes in the different lysimeter experiments and after performing the inverse modelling based on percolate concentrations it became obvious that about 50% of the investigated lysimeter cores showed a very early appearance of the active substance or metabolites in the leachate compared to the simulation with PELMO. FOCUS PELMO could not reproduce such a fast pesticide transport in 1 m soil depth by the common model assumptions of chromatographic flow in soil for four active substances and four metabolites. In those cases a fast transport through the soil core could probably only be reproduced by assuming preferential flow as an additional option during modelling. Four of these inverse modelling optimisations were therefore additionally checked assuming that preferential flow had occurred. This modelling procedure considering preferential flow is described in the following.

In PELMO a very simple descriptive approach to consider preferential flow is implemented. The concentration of pesticide entering macro pores at the soil surface is calculated using the mixing depth concept, whereby incoming rainfall is assumed to mix perfectly with the resident water in a shallow surface layer of soil according to following equation:

$$Q_1\left(\frac{z_d}{\Delta z}\right) = c_{ma}\left(R + z_d\left(\theta_{mi} + \rho\, k_f\, c_{ma}^{\frac{1}{n}-1}\right)\right) \qquad (1)$$

$c_{ma}$: concentration in the macro pore (g $cm^{-3}$)

$\Delta z$: thickness of the top numerical layer (cm)

$z_d$: mixing depth (cm)

$Q_1$: amount of pesticide stored in the top numerical layer at the previous time step (g $cm^{-2}$)

$R$: rainfall amount during the time step (cm)

$\theta_{mi}$ soil matrix water content ($cm^3$ $cm^{-3}$)

$\rho$ : the bulk density (g $cm^{-3}$)

$1/n$: Freundlich exponent (-)

$k_f$: Freundlich sorption coefficient ($cm^3$ $g^{-1}$)

The flux of pesticide into the macro pores is given by $c_{ma}$ multiplied by the infiltration rate into macro pores $I_{ma}$, and this amount of pesticide is extracted from the concentration in the matrix to maintain the mass balance.

$$J_{mar} = c_{ma} I_{ma} \qquad (2)$$

$c_{ma}$: concentration in the macro pore (g/cm³)

$I_{ma}$: Amount of water routed into macro pore (cm)

$J_{ma}$: Flux of pesticide into the macro pore (g/cm²)

A fixed number is defined for the depth of the macro pores. At that soil depth percolate is distributed in the soil matrix system again independent of the actual soil moisture conditions. The depth of macro pores used for the optimisation is documented in appendix 7 as part of the description of the calibration.

Before that depth there is no exchange between macro and micro pores domain. The substance is directly transported within one day from the surface (where the macro pore is filled with water and substance) to the end of the macro pore (where water and substance is released into the micro pore system).

Information about how the additional parameters were selected can be found in appendix 6. Some more information about the methodology followed in the inverse modelling optimisation is given in Table 5-2.

Table 5-2: Summary of options considered for the inverse modelling optimisations

| Parameter | Optimisation |
|---|---|
| Total number of lysimeter cores | 15 |
| Extremely early breakthrough of substance compared to PELMO | 8 |
| Additional check using preferential flow option of PELMO | 4 |
| Total number of inverse modelling optimisations | 27 |
| | |
| Optimisation of parent compound (standard FOCUS PELMO) | 13 |
| Optimisation of metabolites (standard FOCUS PELMO) | 6 |
| Optimisation of parent compound (PELMO's pref. flow option) | 4 |
| Optimisation of metabolites (PELMO's pref. flow option) | 4 |
| | |

Table 5-3: First appearance of substance in the percolate

| Optimisation | Substance | Location | Cumulative Percolate at time when first substance in the percolate (L/m²) |
|---|---|---|---|
| 1 | Terbuthylazin | Schmallenberg | 70 |
| 2 | Flufenacetat | Monheim | 15 |
| 3 | Flufenacetat | Monheim | 23 |
| 4 | Thiamethoxam | Neustadt | 4 |
| 5 | Thiamethoxam | Neustadt | 5 |
| 6 | Bentazon | Schmallenberg | 60 |
| 7 | Bentazon | Schmallenberg | 75 |
| 8 | Isoxaben | Hamburg | 8 |
| 9 | Nicosulufron | Schmallenberg | 9 |
| 10 | Diazinon | Neustadt | 10 |
| 11 | Diazinon | Neustadt | 11 |
| 12 | Isoproturon | Neustadt | 12 |
| 13 | Isoproturon | Neustadt | 13 |
| 14 | Metalaxyl | Neustadt | 14 |
| 15 | Metalaxyl | Neustadt | 15 |
| 16 | S-Metolachlor | Neustadt | 16 |

Table 5-3 connects the first appearance of the applied substance with the respective cumulative volume of water at this time. If this volume is significantly smaller than the dead volume of the lysimeter (i.e. the volume of the lysimeter which is able to store water) this is a strong indication for preferential flow processes. The volume can be calculated based on the difference of field capacity and wilting point (e.g. 21 % in optimisation 4). As the total volume of the lysimeter is 1 m³ the storage capacity for water should be 210 L. Consequently the first 210 L/m² percolate after application should consist of water present in the lysimeter before the application. In this estimation it is assumed that the soil moisture before application was field capacity. If the average soil moisture was below field capacity even more water is needed before the first substance should appear because percolation starts after the lysimeter has reached field capacity.

In Table 5-4 a comparison is made between Tier 1 input parameters for $Kf_{oc}$ and $DegT_{50}$ and the respective optimised values. As indicated optimisations led to unrealistic parameter settings even if the lysimeters, where an influence of preferential flow is additionally assumed, are not considered. Only for the active compounds in optimisations 1, 2 and 3 (all based on soil residue information at the end of the study) and optimisations 6 and 7 (bentazon) and 12 (isoproturon) meaningful parameters could be found considering the expected range of sorption and degradation values for these compounds. These results lead to the conclusion that it cannot be generally recommended to consider inverse modelling as a higher tier methodology for obtaining the key input parameters $Kf_{oc}$ and $DegT_{50}$ as it is recommended in FOCUS (2009/2014). Possibly the situation could be improved if more parameters are recorded in more detail in the lysimeter studies as explained earlier in this chapter. Also, it cannot be excluded that PELMO is not able to mimic the processes in the lysimeter adequately. However, that question could be definitely answered based only on lysimeter studies with complete data sets according to the recommendations in chapter5.2.2. Apart from these considerations the problem of early detections of active substances and metabolites in lysimeter studies may remain even if the collection of data during the study meets all necessary requirements for inverse modelling.

Principally, it should also be mentioned that only two substance parameters were optimised ($Kf_{oc}$ and $DegT_{50}$) whereas for many other substance related parameters such as Walker exponent and Q10 simply the scenario defaults were considered. Also, that could have had a minor impact on the results.

In addition to Table 5-4 all detailed results are presented in Appendix 7. Appendix 7 does also contain all relevant information about soil properties and climatic conditions.

Table 5-4: Results of the inverse modelling optimisation

| Optimisation | Substance | Lysimeter site | FOCUS chi² Percolate (%) | EU $Kf_{oc}$ (L/kg) | Optimised $Kf_{oc}$ (L/kg) | EU $DegT_{50}$ (d) | Optimised $DegT_{50}$ (d) | FOCUS chi² (%) | Remarks |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Terbuthylazin | Schmallenberg | 2.86 | 232 | 829 | 80 | 64 | 47.01 | based on soil residue information |
| 1 | Metabolite G23158 | Schmallenberg | 2.86 | 187 | 5.1 | 453 | 1.33 | 13.82 | unrealistic parameter optimisation |
| 2 | Flufenacetat | Monheim | 2.04 | 200 | 786.4 | 19.6 | 62 | 27.75 | based on soil residue information |
| 2 | Metabolite SAC | Monheim | 2.04 | 10 | 1 | 159.4 | 7.35 | 8.66 | unrealistic parameter optimisation |
| 3 | Flufenacetat | Monheim | 2.96 | 200 | 665 | 19.6 | 71 | 23.17 | based on soil residue information |
| 3 | Metabolite SAC | Monheim | 2.96 | 10 | 1.30 | 159.4 | 4.92 | 13.20 | unrealistic parameter optimisation |
| 4 | Thiamethoxam | Neustadt | 4.49 | 58 | 0.001 | 32.7 | 6.31 | 19.45 | not possible to calculate correct timing of break through |
| 4 | Thiamethoxam | Neustadt | 4.49 | 58 | 146 | 32.7 | 1.6 | 4.92 | preferential module considered for the optimisation |
| 4 | Metabolite Clothianidin | Neustadt | 4.49 | 133 | 142 | 103.6 | 2.9 | 11.7 | preferential module considered for the optimisation |
| 5 | Thiamethoxam | Neustadt | 5.42 | 58 | 7.7 | 32.7 | 7.92 | 11.91 | not possible to calculate correct timing of break through |
| 5 | Thiamethoxam | Neustadt | 5.42 | 58 | 546 | 32.7 | 10.98 | 5.61 | preferential module considered for the optimisation |
| 5 | Metabolite Clothianidin | Neustadt | 5.42 | 133 | 283 | 103.6 | 198042 | 26.7 | no meaningful $DegT_{50}$ optimised |

| Optimisation | Substance | Lysimeter site | FOCUS chi² Percolate (%) | EU $Kf_{oc}$ (L/kg) | Optimised $Kf_{oc}$ (L/kg) | EU $DegT_{50}$ (d) | Optimised $DegT_{50}$ (d) | FOCUS chi² (%) | Remarks |
|---|---|---|---|---|---|---|---|---|---|
| 6 | Bentazon | Schmallenberg | 7.38 | 23 | 54.91 | 9.5 | 14.09 | 10.08 | Reasonable optimisation |
| 7 | Bentazon | Schmallenberg | 6.96 | 23 | 38.23 | 9.5 | 23.12 | 14.06 | Reasonable optimisation |
| 8 | Isoxaben | Hamburg | 10.24 | 351 | 43.57 | 94.4 | 10.0 | 43 | unrealistic parameter optimisation |
| 8 | Isoxaben | Hamburg | 10.24 | 351 | 269 | 94.4 | 50 | 17.87 | preferential module considered for the optimisation |
| 8 | Met hydroxy-isoxaben | Hamburg | 10.24 | 37 | 53.8 | 92.7 | 5.8 |  | preferential module considered for the optimisation, nevertheless unrealistic $DegT_{50}$ optimised |
| 9 | Nicosulfuron | Schmallenberg | 5.1 | 29 | 0.001 | 22.8 | 4.46 | 34.91 | unrealistic parameter optimisation, presumably due to preferential flow |
| 9 | Nicosulfuron | Schmallenberg | 6.37 | 29 | 6.76 | 22.8 | 7.78 | 30.12 | unrealistic parameter optimisation, presumably due to preferential flow |
| 10 | Metabolite G27550 of Diazinon | Schmallenberg | 5.48 | 6 | 1.0 | 55.7 | 5.09 | 11.00 | unrealistic parameter optimisation |
| 11 | Metabolite G27550 of Diazinon | Schmallenberg | 5.50 | 6 | 1.95 | 55.7 | 8.01 | 5.70 | unrealistic parameter optimisation |
| 12 | Isoproturon | Neustadt | 4.77 | 126 | 101.3 | 7 | 14.52 | 21.37 | Reasonable optimisation |
| 13 | Isoproturon | Neustadt | 3.10 | 126 | 24.97 | 7 | 2.13 | 16.69 | unrealistic parameter optimisation, presumably due to preferential flow |
| 13 | Isoproturon | Neustadt | 3.10 | 126 | 139.3 | 7 | 3.98 | 6.20 | preferential module considered for the optimisation, Reasonable optimisation |

| Optimisation | Substance | Lysimeter site | FOCUS chi² Percolate (%) | EU $Kf_{oc}$ (L/kg) | Optimised $Kf_{oc}$ (L/kg) | EU $DegT_{50}$ (d) | Optimised $DegT_{50}$ (d) | FOCUS chi² (%) | Remarks |
|---|---|---|---|---|---|---|---|---|---|
| 14 | Metalaxyl | Neustadt | 4.24 | 86 | 5.13 | 14.6 | 10.10 | 25.30 | unrealistic parameter optimisation, presumably due to preferential flow |
| 15 | Metalaxyl | Neustadt | 4.41 | 126 | 0.001 | 14.6 | 5.71 | 33.72 | preferential module considered for the optimisation, Reasonable optimisation |

## 5.5 Simulations with optimised parameters

### 5.5.1 Extrapolation of the lysimeter study duration by modelling

Major critical points of the lysimeter study design as formulated by FOCUS (2009) are

- too short study time
- usually only single applications
- disturbance due to bottom boundary effects

Because of these deficiencies, uncertainties exist whether the maximum concentrations in the leachates can always be reached within the study period. Consequently FOCUS (2009/2014) questioned the direct utility of lysimeter results as regulatory endpoints.

To check the effect of longer study periods "prolonged" simulations are performed for some lysimeter studies previously considered for an inverse modelling optimisation. As mentioned above these "prolonged" simulations should answer the question whether the length of a certain study was sufficient and the experimental study was not stopped before the bulk of the chemicals reached the bottom of the soil core. Table 5-5 gives an overview about the lysimeter studies considered for these additional simulations. All simulations were performed with FOCUS PELMO 5.5.3.

Table 5-5: Overview on the prolonged simulations performed

| No | Substance | Lysimeter site | FOCUS chi² Percolate (%) | EU $Kf_{oc}$ (L/kg) | Optimised $Kf_{oc}$ (L/kg) | EU $DegT_{50}$ (d) | Optimised $DegT_{50}$ (d) | FOCUS chi² Substance (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | Terbuthylazin | Schmallenberg | 2.86 | 232 | 829 | 80 | 64 | 47.01 |
| 1 | Metabolite G23158 | Schmallenberg | 2.86 | 187 | 5.1 | 453 | 1.33 | 13.82 |
| 2 | Flufenacetat | Monheim | 2.04 | 200 | 786.4 | 19.6 | 62 | 27.75 |
| 2 | Met. SAC | Monheim | 2.04 | 10 | 1 | 159.4 | 7.35 | 8.66 |
| 3 | Flufenacetat | Monheim | 2.96 | 200 | 665 | 19.6 | 71 | 23.17 |
| 3 | Met. SAC | Monheim | 2.96 | 10 | 1.30 | 159.4 | 4.92 | 13.20 |
| 6 | Bentazon | Schmallenberg | 7.38 | 23 | 54.91 | 9.5 | 14.09 | 10.08 |
| 9 | Nicosulfuron | Schmallenberg | 5.1 | 29 | 0.001 | 22.8 | 4.46 | 34.91 |
| 12 | Isoproturon | Neustadt | 4.77 | 126 | 101.4 | 7 | 14.52 | 21.37 |
| 14 | Metalaxyl | Neustadt | 4.24 | 86 | 5.13 | 14.6 | 10.10 | 25.30 |

Mainly those studies were selected for further extrapolation modelling, in which the influence of preferential flow is assumed to be low and no major time lag of the substance break through between experimental and inverse modelling results occurred. However, two lysimeter studies in this selection could have been influenced by fast transport processes in soil such as preferential flow (opt. 9 nicosulfuron, op. 14 metalaxyl). They were included to check in how far extrapolations are influenced by these processes. However, the optimised parameters were not based on the preferential flow module.

Only a limited number of weather years were available in the lysimeter reports and annual precipitation including irrigation during the study was at least 800 mm according to the lysimeter test guideline (BBA 1990). Consequently, the weather data of the first completely reported lysimeter year (i.e. year 2) were considered in the additional simulation period.

In order to definitively estimate the time between application and the maximum concentration in the percolate the pesticide was applied only once in the first year according to the information given in the lysimeter study. Consequently, for the additional simulation period also the crop rotation during in first experimental year was used for the extrapolation modelling.

Also in order to analyse the maximum concentration in leachate for repeated applications a second simulation was performed with annual applications over 20 years.

#### 5.5.1.1 Optimisation 1: terbuthylazin, Schmallenberg, 1990-1992

##### 5.5.1.1.1 Results for terbuthylazin

The simulations were based on a $Kf_{oc}$ of 829 L/kg and a $DegT_{50}$ of 64 d.

The results are summarised in Figure 5-3 and Figure 5-4 for the single and the annual application patterns, respectively. The single application shows that the maximum of the peak is expected to occur 10 years after the application. According to the simulation with annual applications a plateau will be reached after 20 years. However, the nominal maximum concentrations simulated with annual applications ($5x10^{-5}$ µg/L) remain far below the trigger of 0.1 µg/L.

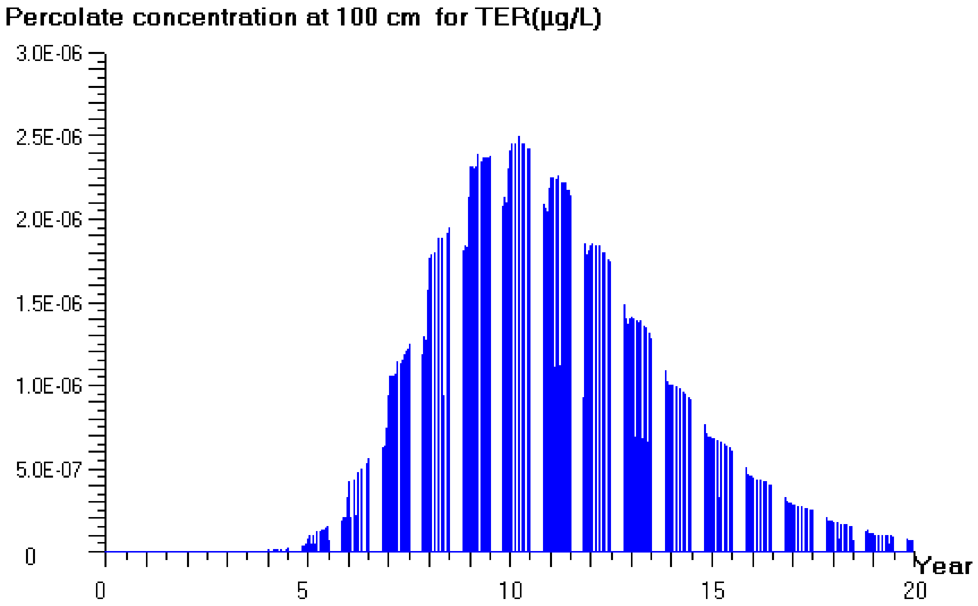


Figure 5-3: Time dependent concentration for terbuthylazin after a single application (optimised parameter setting)

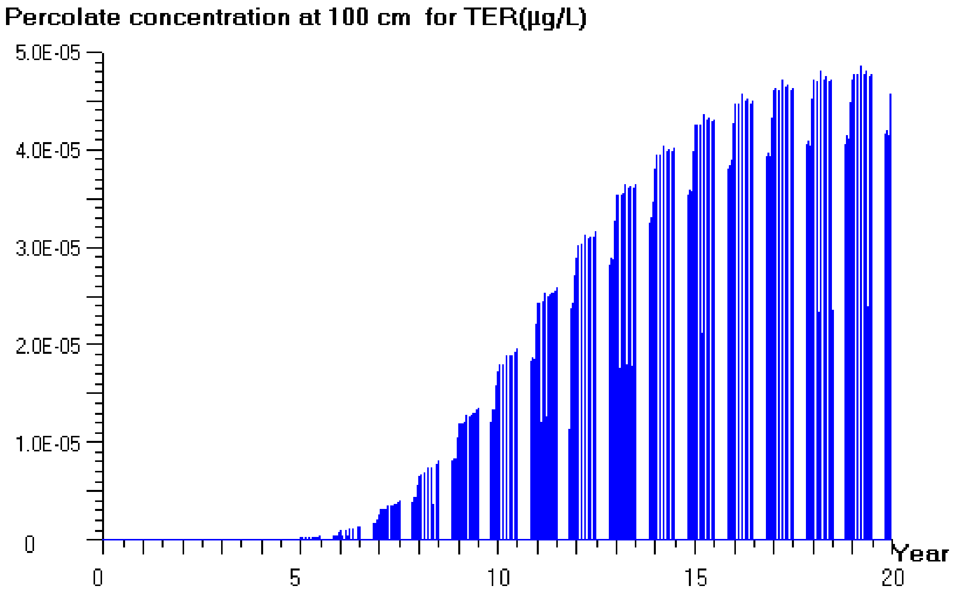


Figure 5-4: Time dependent concentration for terbuthylazin after annual applications (optimised parameter setting)

#### 5.5.1.1.2 Results for the metabolite

A different outcome can be observed for the metabolite GS23158 as shown in Figure 5-5 and Figure 5-6 for the single and the annual application patterns, respectively. The simulations were based on a $Kf_{oc}$ of 5 L/kg and a $DegT_{50}$ of 14 d.

The single application shows that the maximum of the peak (about 0.1 µg/L) is expected to occur 1 year after application. As the concentrations in the diagram are based on daily values they are slightly higher than the respective results of the lysimeter study (maximum average concentrations in the percolate 0.055 µg/L). However, since the experimental percolate concentration are mixed samples over a longer timer period lower concentrations could be expected. According to the simulation with annual applications the plateau with maximum concentrations of 0.2 µg/L will be reached after 5 years.

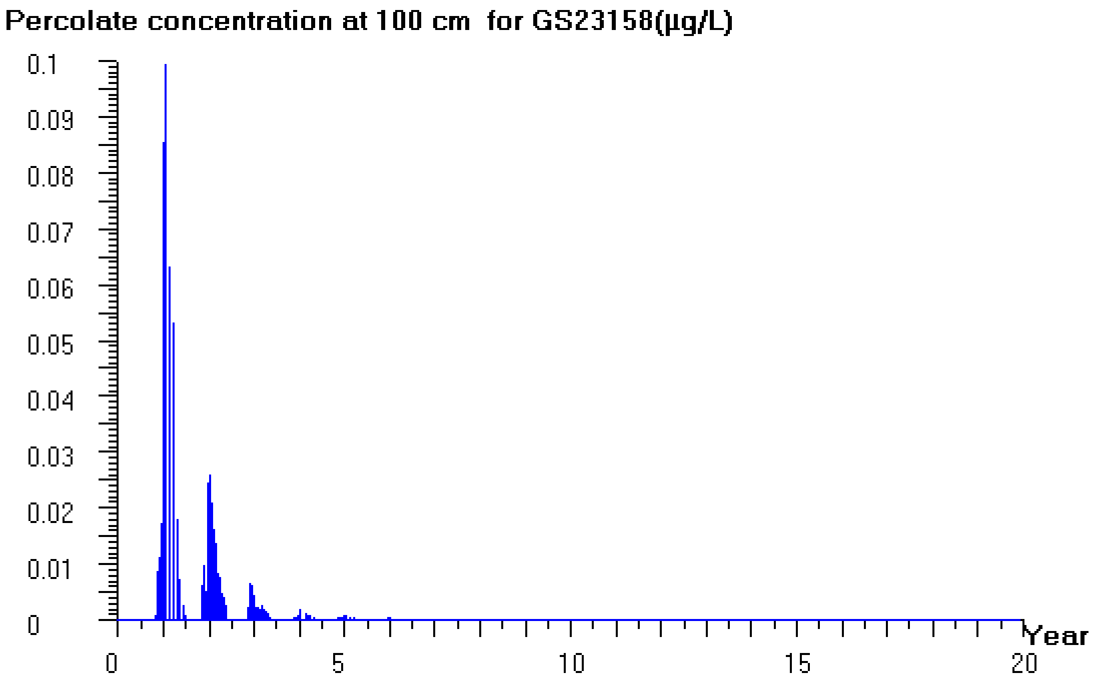


Figure 5-5: Time dependent concentration for GS23158 (terbuthylazin metabolite) after a single application (optimised parameter setting)

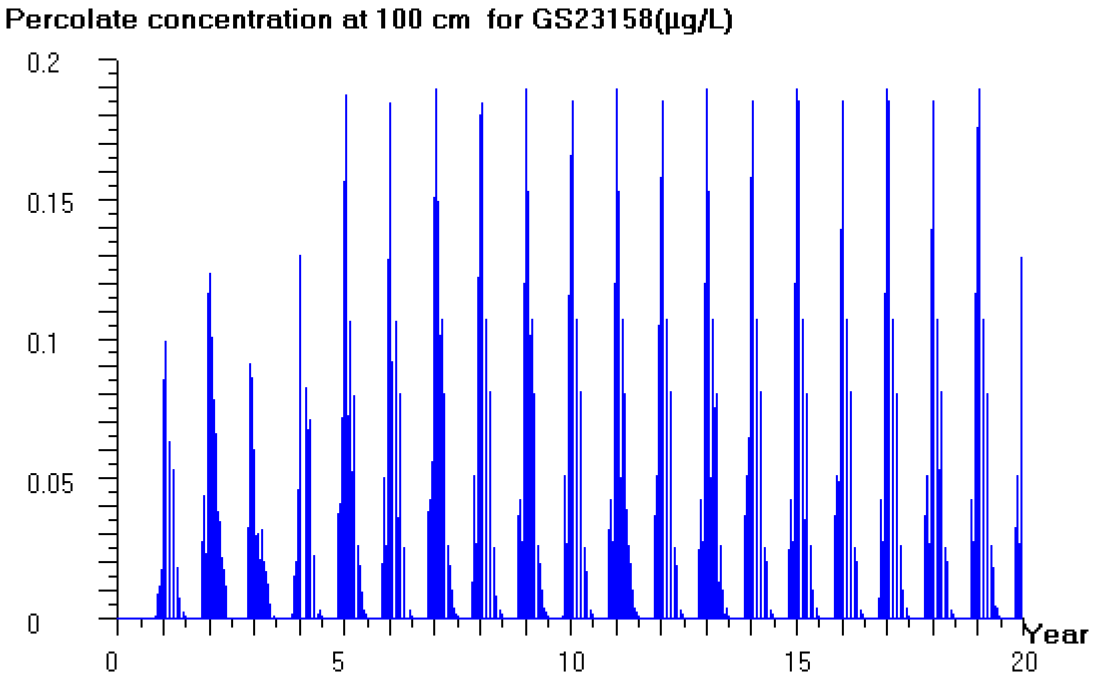


Figure 5-6: Time dependent concentration for GS23158 (terbuthylazin metabolite) after annual applications (optimised parameter setting)

### 5.5.1.2 Optimisation 2: flufenacetat, Monheim, 1993-1995

#### 5.5.1.2.1 Results for flufenacetat

The simulations were based on a $Kf_{oc}$ of 786.4 L/kg and a $DegT_{50}$ of 62.02 d.

The results are summarised in Figure 5-7 and Figure 5-8 for the single and the annual application patterns, respectively. The single application shows that the maximum of the peak is expected to occur 17 years after the application. According to the simulation with annual applications no plateau will be reached after 20 years. However, the nominal concentrations simulated for annual application ($10^{-14}$ µg/L) remain far below the trigger of 0.1 µg/L.

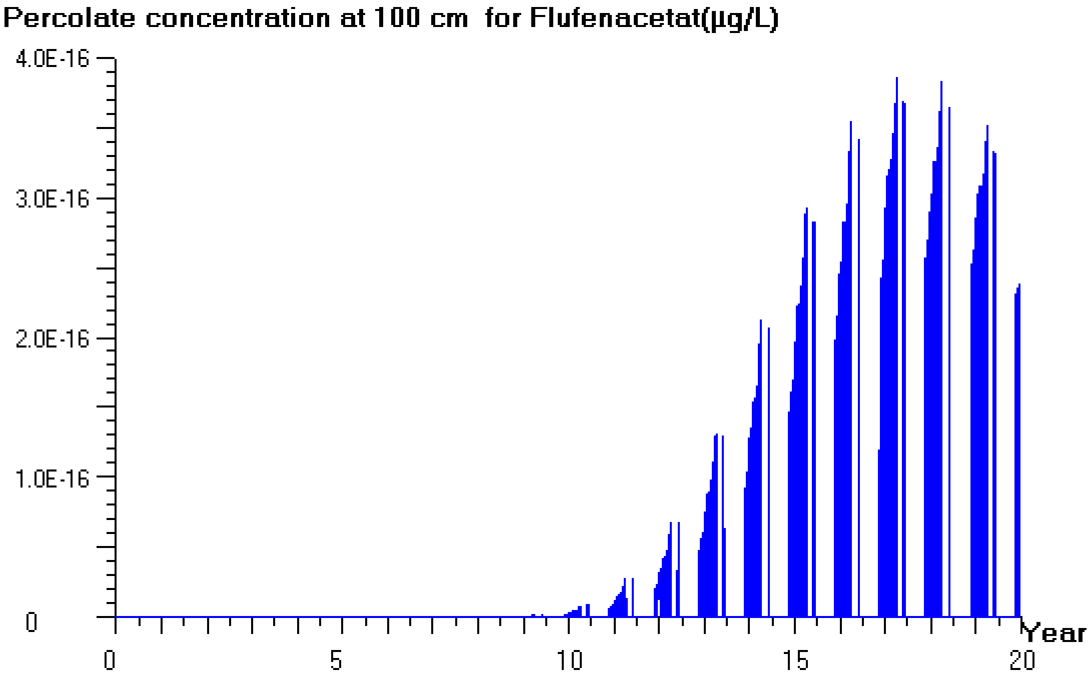


Figure 5-7: Time dependent concentration for flufenacetat after single year applications (optimised parameter setting)

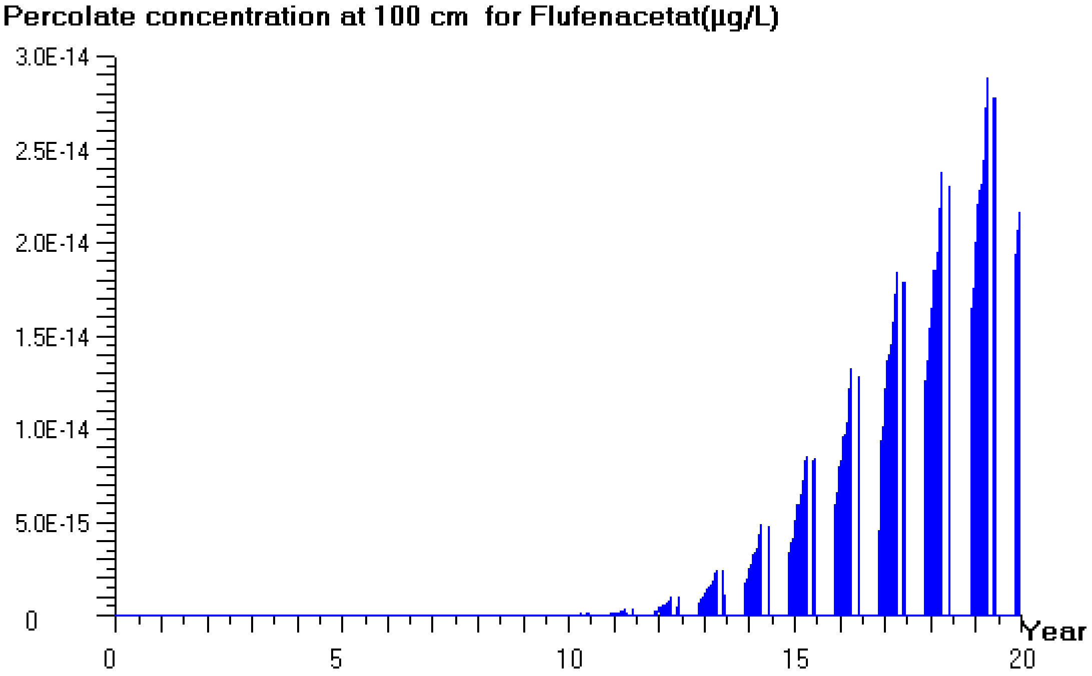


Figure 5-8: Time dependent concentration for flufenacetat after annual applications (optimised parameter setting)

#### 5.5.1.2.2 Results for the metabolite

The simulations were based on a $Kf_{oc}$ of 1 L/kg and a $DegT_{50}$ of 7.35 d.

Compared to the parent compound a different outcome can be observed for the metabolite SAC as shown in Figure 5-9 and Figure 5-10 for applications in the first year and the annual application pattern, respectively. The simulation applications in the first year only showed that the maximum of the peak (about 2.5 µg/L) is expected to occur already 1 year after the application. According to the simulation with annual applications maximum concentrations of about 2.5 µg/L was reached after 3 years. A plateau was not reached in the simulations due to the properties of the metabolite. The occurrence of slightly higher concentrations at the beginning of the simulation compared to the rest of the period was caused by the weather situations in the first year.

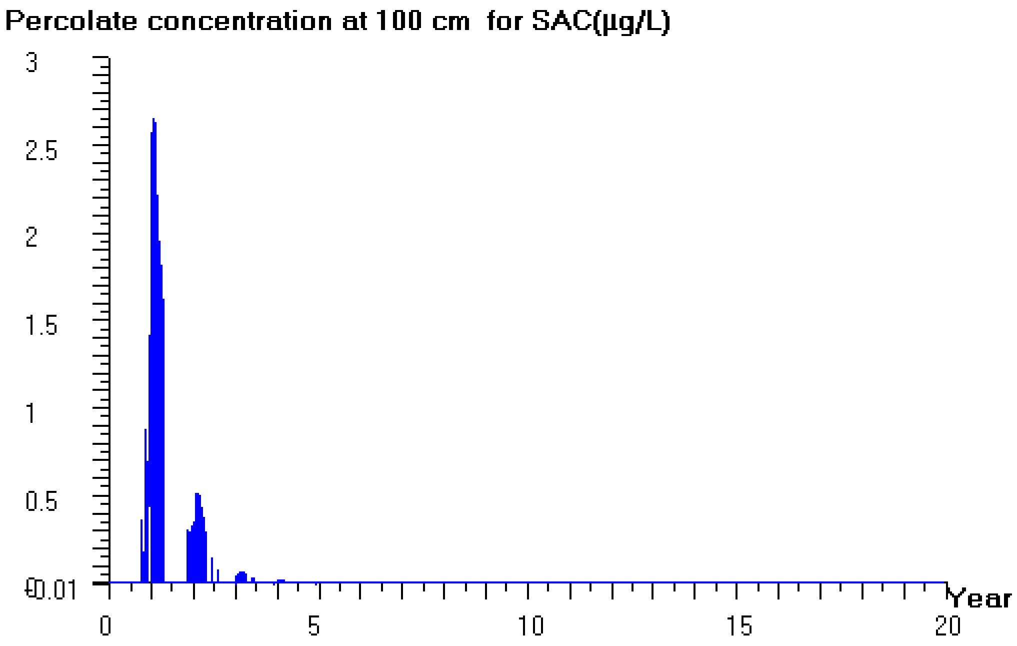


Figure 5-9: Time dependent concentration for SAC (flufenacetat metabolite) after two applications in the first year only (optimised parameter setting)

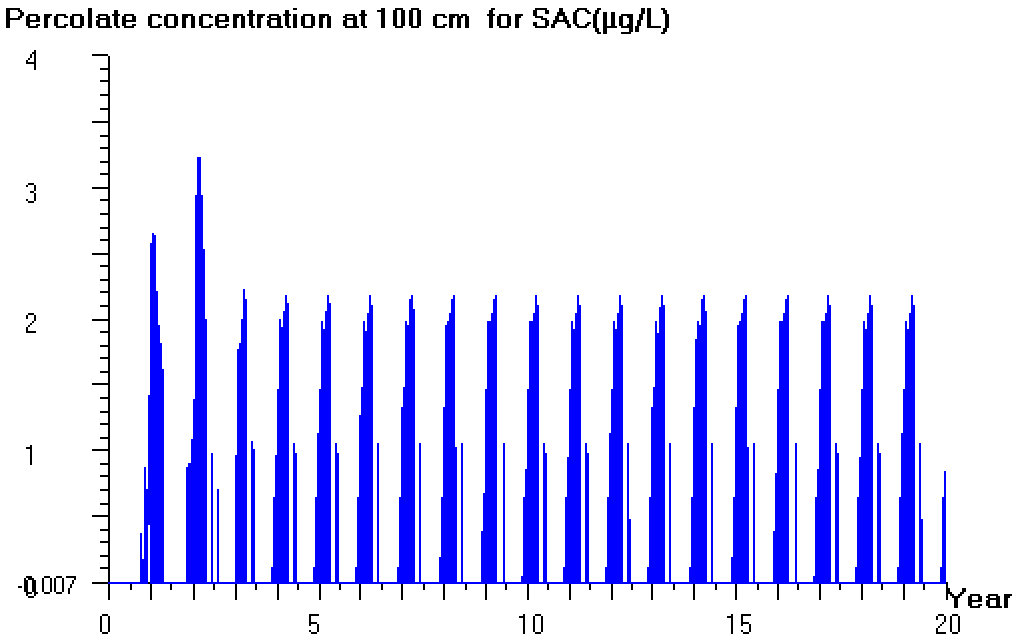


Figure 5-10: Time dependent concentration for SAC (flufenacetat metabolite) after annual applications (optimised parameter setting)

### 5.5.1.3 Optimisation 3: flufenacetat, Monheim, 1993-1996

#### 5.5.1.3.1 Results for flufenacetat

The simulations were based on a $Kf_{oc}$ of 665 L/kg and a $DegT_{50}$ of 71 d.

The results are summarised in Figure 5-11 and in Figure 5-12 for the single year and the annual application patterns, respectively. The single application shows that the maximum of the peak is expected to occur 17 years after the application. According to the simulation with annual applications no plateau will be reached after 20 years. However, the nominal concentrations simulated for annual application ($10^{-11}$ µg/L) remain below far the trigger of 0.1 µg/L.

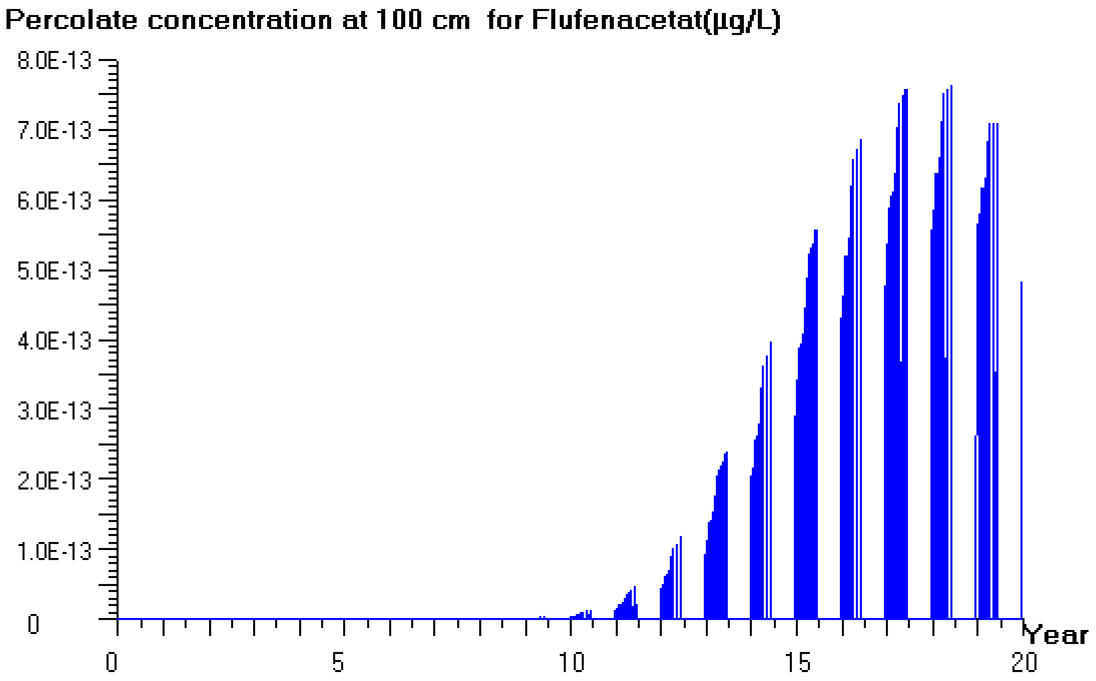


Figure 5-11: Time dependent concentration for flufenacetat after single year applications (optimised parameter setting)

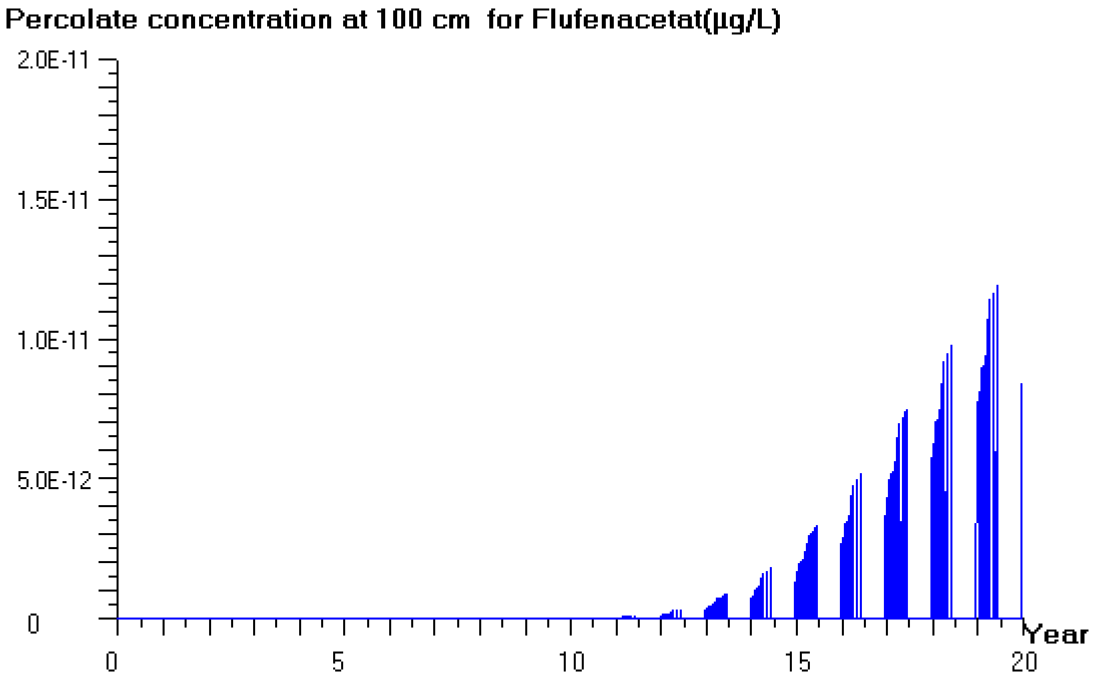


Figure 5-12: Time dependent concentration for flufenacetat after annual applications (optimised parameter setting)

#### 5.5.1.3.2 Results for the metabolite

The simulations were based on a $Kf_{oc}$ of 1.3 L/kg and a $DegT_{50}$ of 4.92 d.

A different outcome can be observed for the metabolite SAC as shown in Figure 5-13 and Figure 5-14 for applications in the first year and the annual application pattern, respectively. The simulation with applications in the first year only showed that the maximum of the peak (about 1 µg/L) is expected to occur already 1 year after the application. According to the simulation with annual applications maximum concentrations of 0.4 µg/L will be reached after 4 years. A plateau was not reached in the simulations due to the properties of the metabolite. The occurrence of slightly higher concentrations at the beginning of the simulation compared to the rest of the period was caused by the weather situations in the first year.

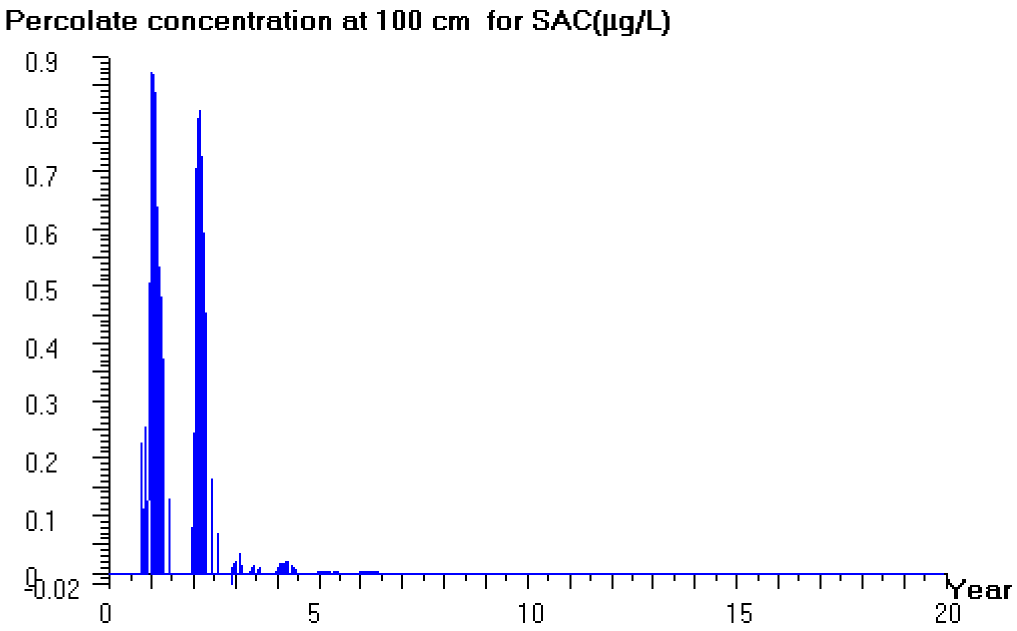


Figure 5-13: Time dependent concentration for SAC (flufenacetat metabolite) after two applications in the first year only (optimised parameter setting)

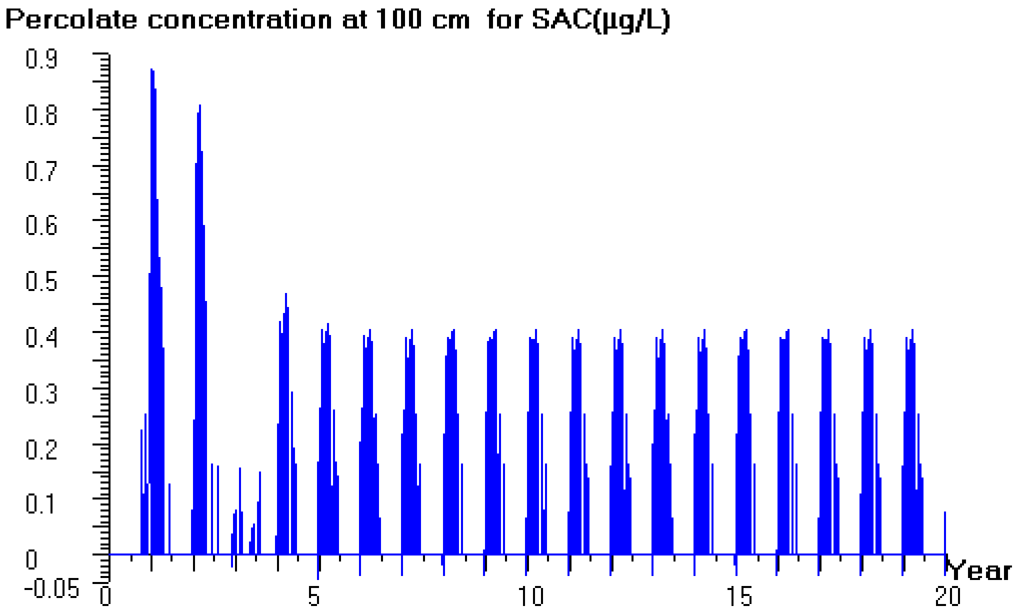


Figure 5-14: Time dependent concentration for SAC (flufenacetat metabolite) after annual applications (optimised parameter setting)

### 5.5.1.4 Optimisation 6: bentazon, Schmallenberg, 1990-1993, 1 Application

The results are summarised in Figure 5-15 and Figure 5-16 for the single and the annual application patterns, respectively. The simulation for a single application shows that the maximum of the peak is expected to occur 1 year after the application (application in November 1st year). Though the calculated concentrations are slightly higher than the respective results of the lysimeter study (maximum concentrations in the percolate 0.06 µg/L) this is not in contradiction with the experiment since the experimental percolate concentration are mixed samples over a longer time period but the diagram is based on daily values.

According to the simulation with annual applications a plateau will be reached after 2 years with maximum daily concentrations of 0.09 µg/L. Due to the fast degradation of bentazon the plateau is not significantly higher than the concentrations caused by a single application.

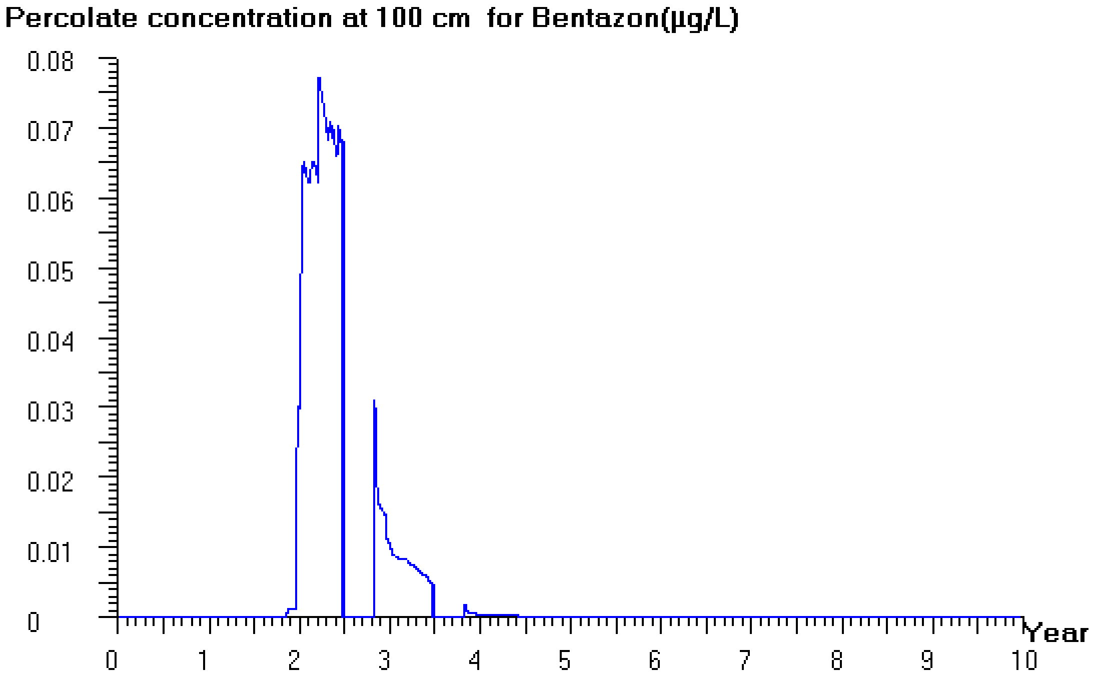


Figure 5-15: Time dependent concentration for bentazon after a single application (optimised parameter setting)

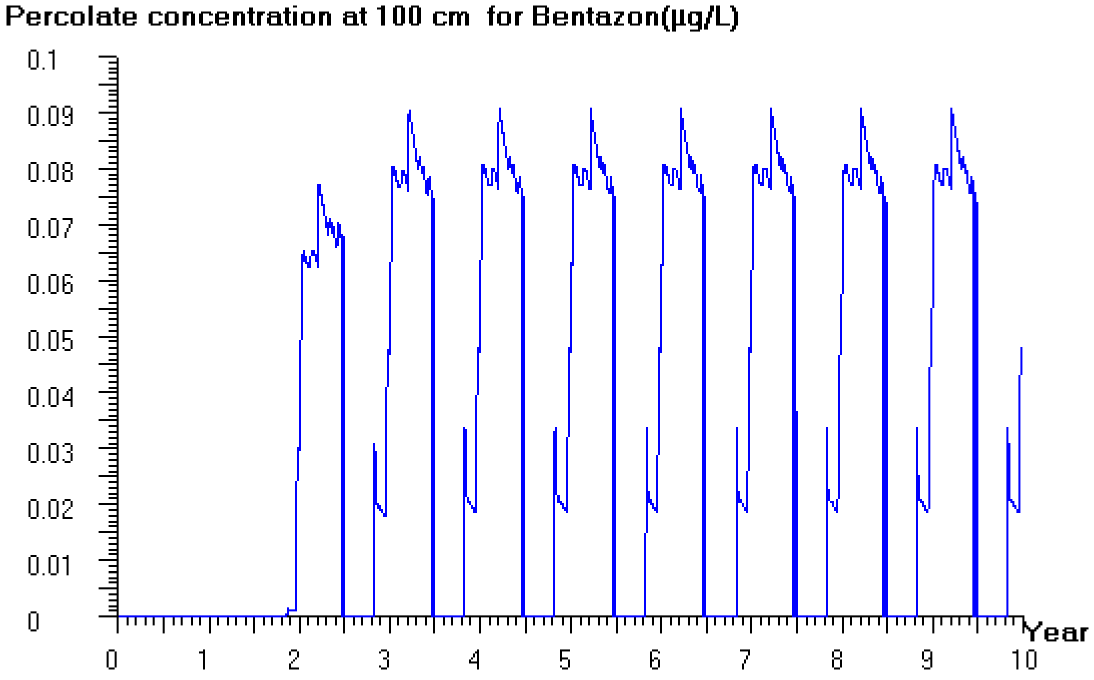


Figure 5-16:Time dependent concentration for bentazon after annual applications (optimised parameter setting)

### 5.5.1.5 Optimisation 9: nicosulfuron, Schmallenberg, 1990-1993, 1 Application

This lysimeter study could have been influenced by fast transport processes in soil such as preferential flow. The simulations were based on a $Kf_{oc}$ of 0.01 L/kg and a $DegT_{50}$ of 4.5 d without using the preferential flow module in PELMO.

The results are summarised in Figure 5-17 and Figure 5-18 for two applications and the annual pattern, respectively. The simulation for two applications show that the maximum of the peak was simulated to occur 1.4 months after the first application (The diagrams show the begin of the PELMO simulation in January, not the actual begin of the study in April/May). The calculated concentrations showed significant differences compared to the results of the lysimeter study because even based on the $Kf_{oc}$ of 0 the model could not correctly simulate the fast breakthrough of the compound.

Due to the fast degradation of nicosulfuron the plateau is not higher than the concentrations caused by single applications.

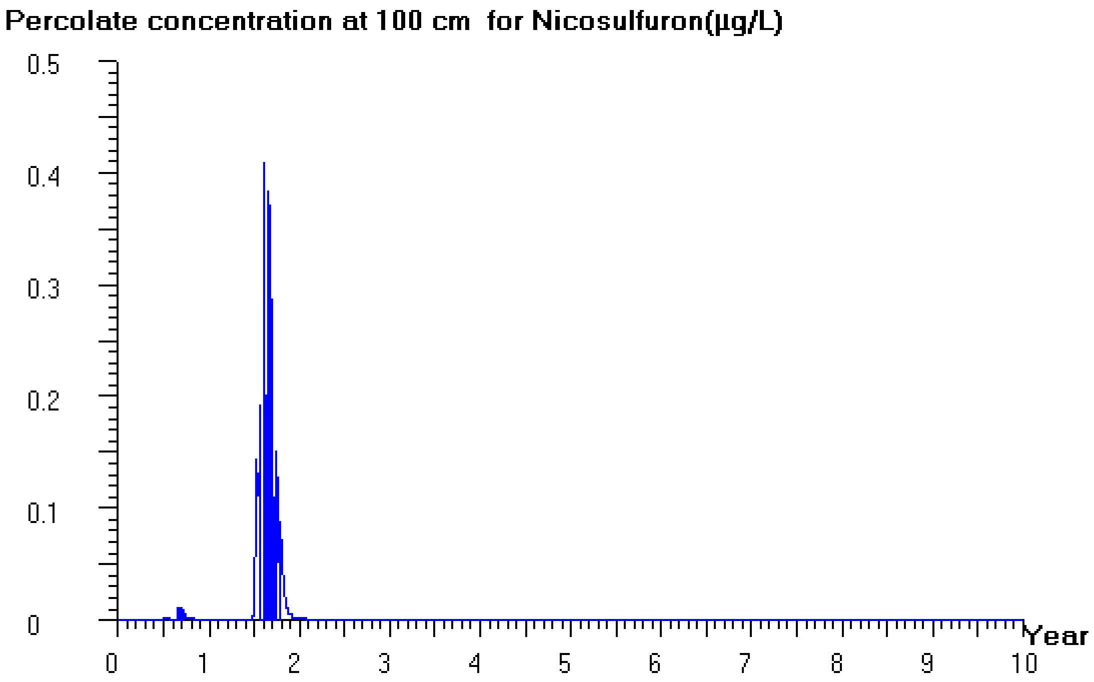


Figure 5-17: Time dependent concentration for nicosulfuron after a two applications (optimised parameter setting)

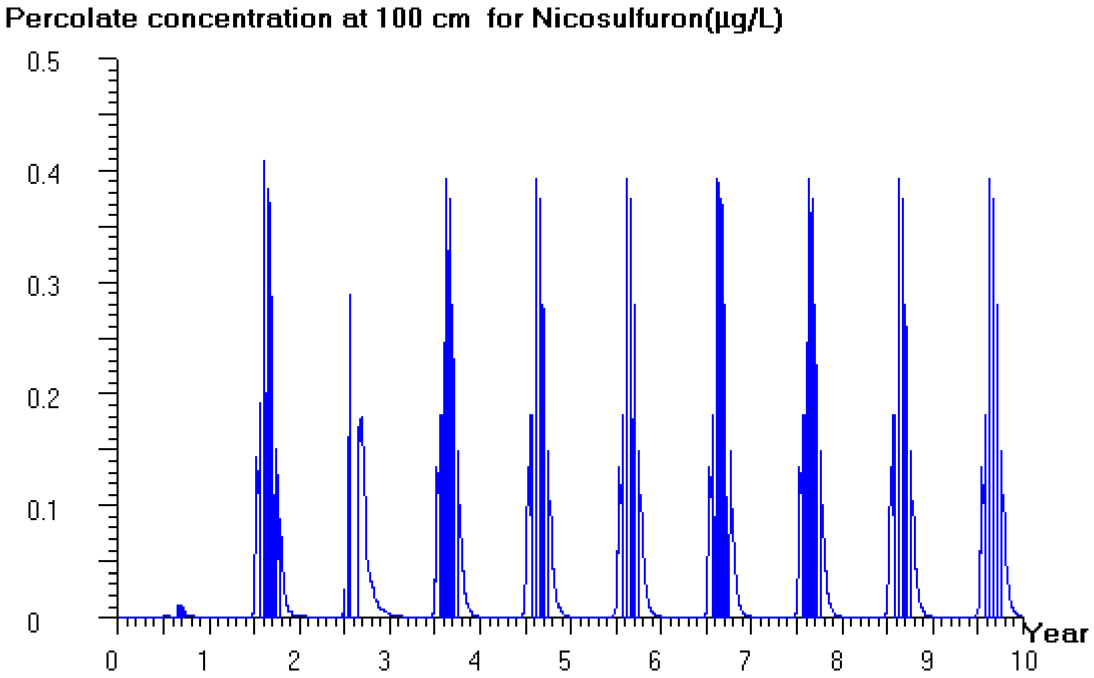


Figure 5-18: Time dependent concentration for nicosulfuron after annual applications (optimised parameter setting)

#### 5.5.1.6 Optimisation 10: diazinon, Neustadt, 1991-1994, 4 Applications

##### 5.5.1.6.1 Results for diazinon

The simulations were based on a $Kf_{oc}$ of 413 L/kg and a $DegT_{50}$ of 7.9 d.

For both situations it is not expected that any residues of diazinon would appear in the percolate at 100 cm depth.

##### 5.5.1.6.2 Results for the metabolite

The simulations were based on a $Kf_{oc}$ of 1 L/kg and a $DegT_{50}$ of 5.1 d.

A different outcome can be observed for the metabolite G27550 as shown in Figure 5-19 and Figure 5-20 for applications in the first year and application every third year, respectively. The simulation with first year applications shows that the maximum of the peak (about 0.6 µg/L) is expected to occur already within the first year after the application. Principally, a similar pattern was observed for the simulation with repeated applications. However, due to the extremely small $Kf_{oc}$ of 0, the periodically repeated identical weather year and the same application dates, a single very sharp peak of more than 1.5 to 2.5 µg/L appeared regularly.

Due to the short half-life no accumulation of concentrations is to be expected for the metabolite.

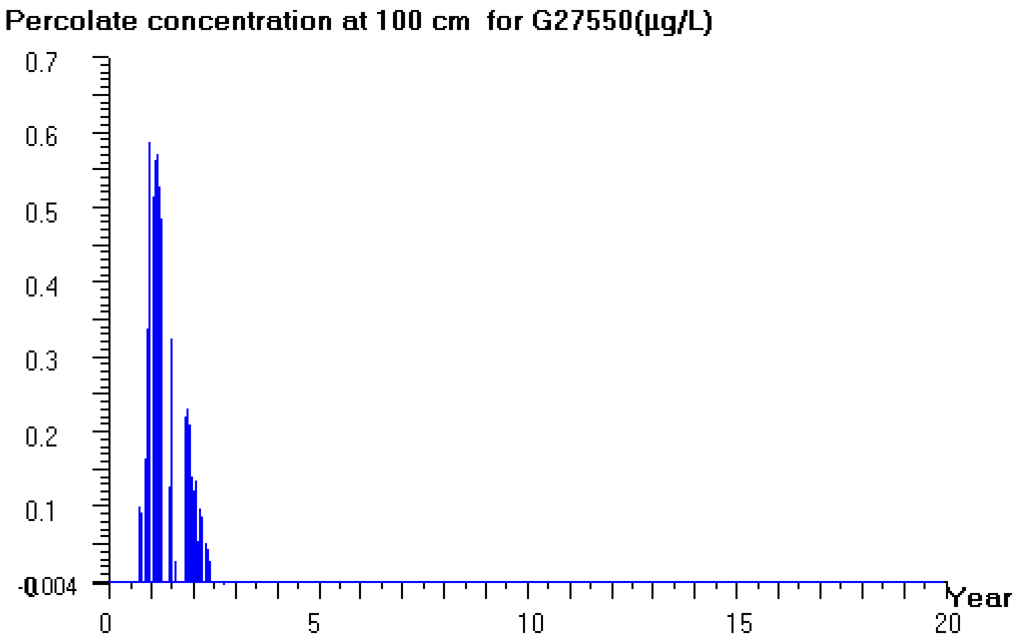


Figure 5-19: Time dependent concentration for G27550 (diazinon metabolite) after eight applications in the first two years (optimised parameter setting)

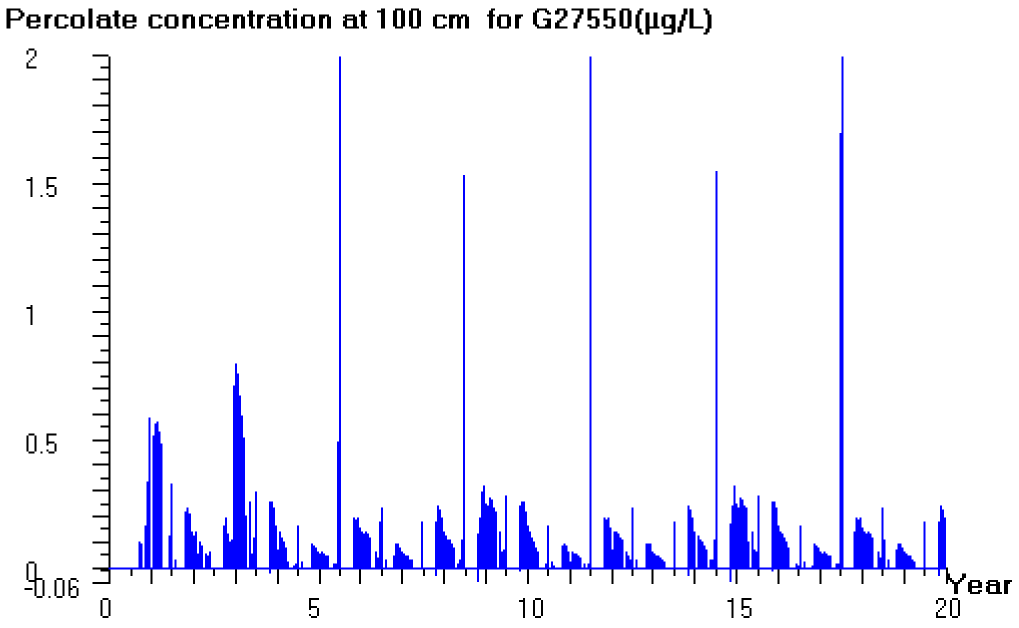


Figure 5-20: Time dependent concentration for G27550 (diazinon metabolite) after annual applications (optimised parameter setting)

#### 5.5.1.7 Optimisation 11: diazinon, Neustadt, 1991-1994, 4 Applications

##### 5.5.1.7.1 Results for diazinon

The simulations were based on a $Kf_{oc}$ of 413 L/kg and a $DegT_{50}$ of 7.9 d.

For both situations it is not expected that any residues of diazinon would appear in the percolate at 100 cm depth.

##### 5.5.1.7.2 Results for the metabolite

The simulations were based on a $Kf_{oc}$ of 2.0 L/kg and a $DegT_{50}$ of 8 d.

A different outcome can be observed for the metabolite G27550 as shown in Figure 5-21 and Figure 5-22 for applications in the first year and applications every year, respectively. The simulation with first year applications shows that the maximum of the peak (about 2 µg/L) is expected to occur already within the first year after the application. A similar pattern was observed for the simulation with repeated applications. A sharp peak was calculated for the fifth year when the periodical weather series was considered. A possible explanation of this phenomenon is the low half-life of the compound together with an ill-timed application date.

However, due to the short half-life no accumulation is to be expected for the metabolite.

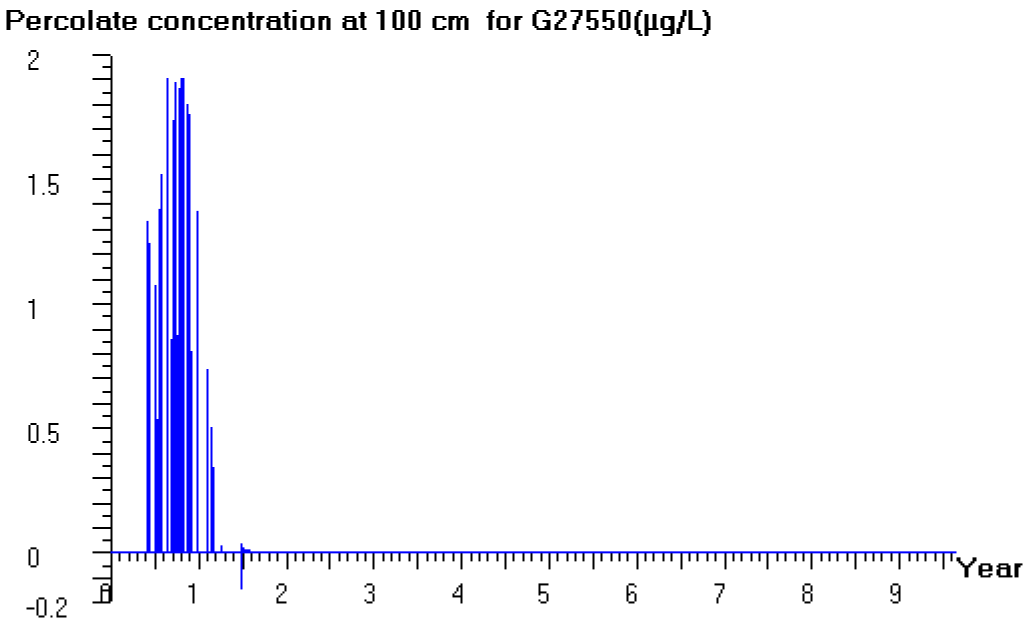


Figure 5-21: Time dependent concentration for G27550 (diazinon metabolite) after four applications in the first year only (optimised parameter setting)

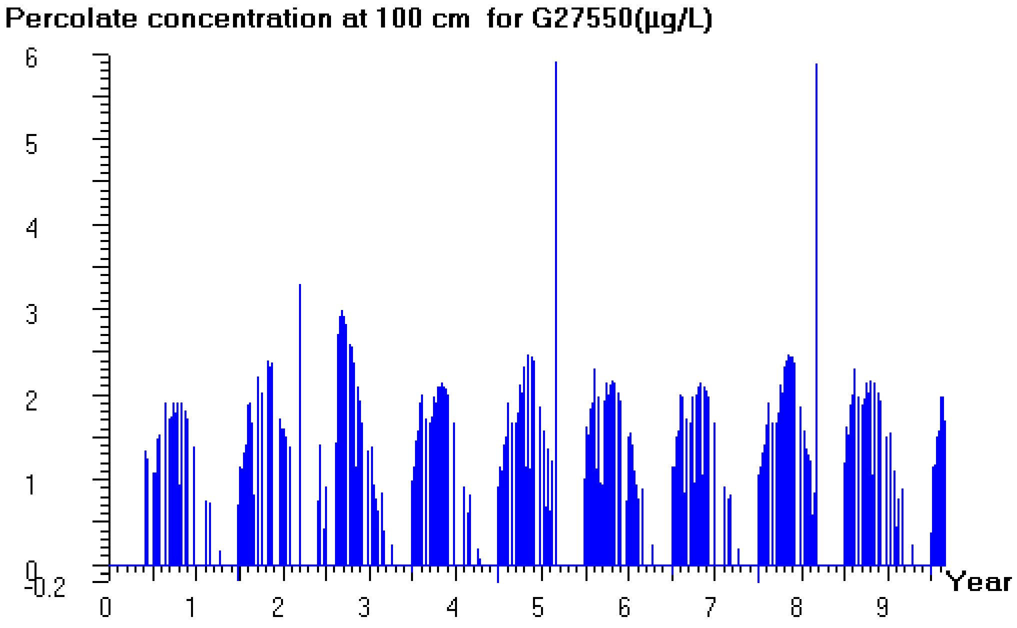


Figure 5-22: Time dependent concentration G27550 (diazinon metabolite) after four applications every year (optimised parameter setting)

#### 5.5.1.8 Optimisation 12: isoproturon, Neustadt, 1989-1992

The simulations were based on a $Kf_{oc}$ of 101.4 L/kg and a $DegT_{50}$ of 14.5 d.

The results are summarised in Figure 5-23 and Figure 5-24 for the variation with two applications and the annual application pattern, respectively. The two application pattern shows that the maximum of the peak is expected to occur 1 year after the application (1st application November year 1). Due to the fast degradation of isoproturon the plateau is not higher than the concentrations observed for the single applications.

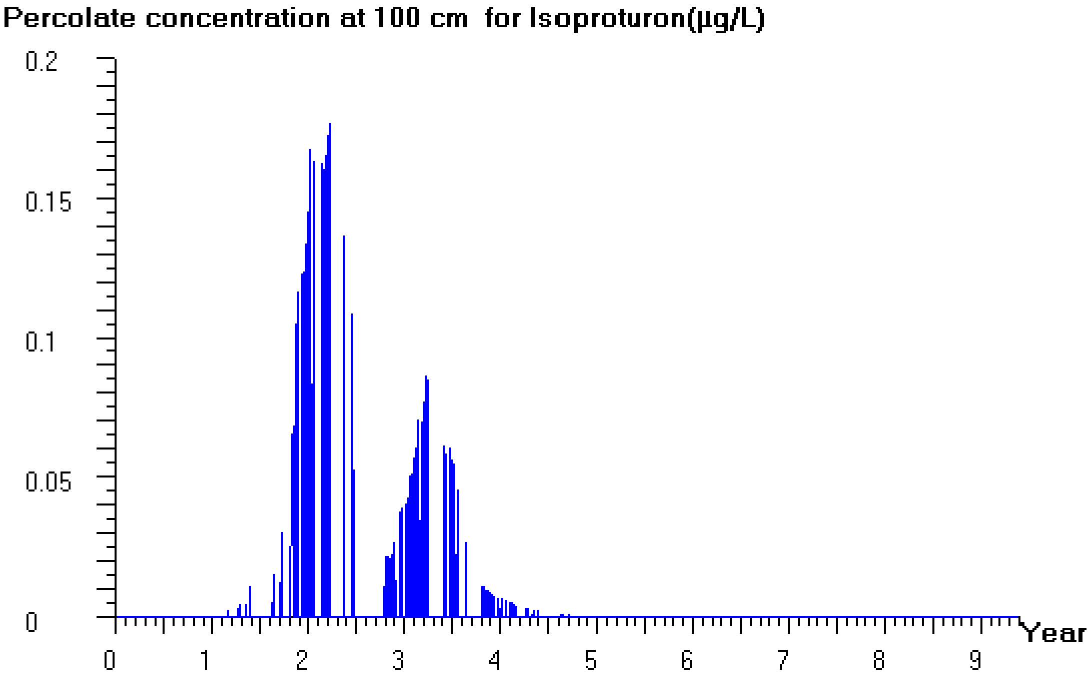


Figure 5-23: Time dependent concentration for isoproturon after two annual applications (optimised parameter setting)

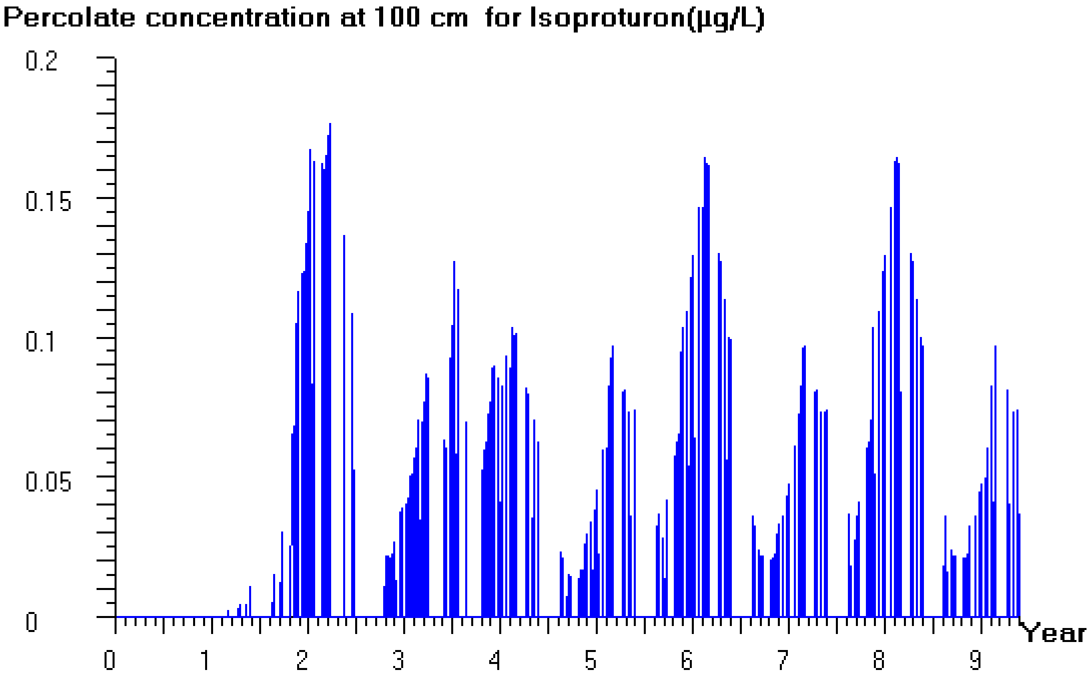


Figure 5-24: Time dependent concentration for isoproturon after annual applications (optimised parameter setting)

#### 5.5.1.9 Optimisation 14: metalaxyl, Neustadt, 1992-1994, 3 Applications

This lysimeter study could have been influenced by fast transport processes in soil such as preferential flow. The simulations were based on a $Kf_{oc}$ of 5.1 L/kg and a $DegT_{50}$ of 10.1 d without using the preferential flow option in PELMO.

The results are summarised in Figure 5-25 and Figure 5-26 for the applications in the first year only and the biennial application pattern, respectively. The single year applications show that the maximum of the peak is expected to occur about 6 months after the application (1st application on 29th June).

According to the simulation with annual applications a plateau will be reached already after 3 years with higher maximum daily concentrations of 0.4 µg/L. Due to the fast degradation of metalaxyl the plateau is not significantly higher than the concentrations caused by single applications. The difference compared to the applications in the first year only is caused by the weather pattern rather than accumulation in soil.

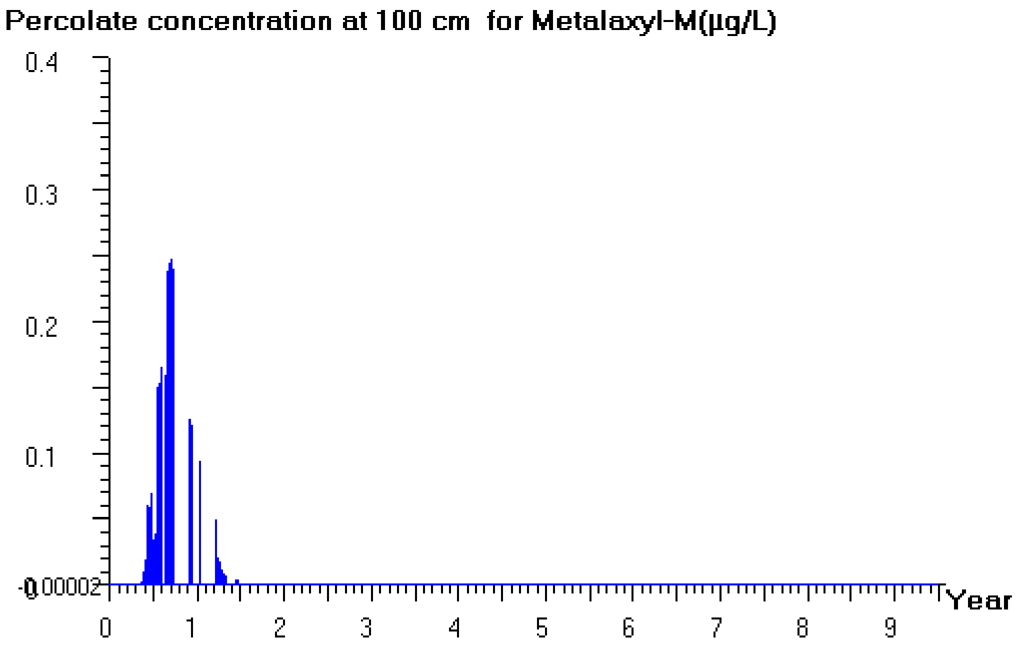


Figure 5-25: Time dependent concentration for metalaxyl after a three applications in the first year (optimised parameter setting)

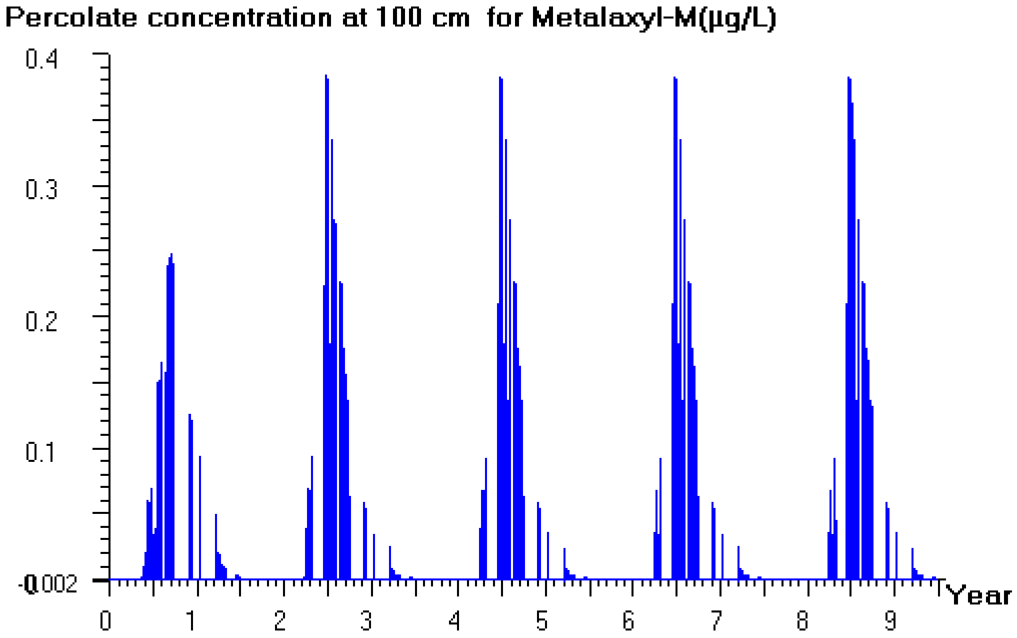


Figure 5-26: Time dependent concentration for metalaxyl after biennial applications (optimised parameter setting)

### 5.5.2 Simulations using the standard FOCUS Hamburg scenario

Independent of on the quality of the parameter estimation by inverse modelling additional simulations were performed using the sorption and degradation parameters obtained in the optimisations (see Table 5-4). All simulations were performed with FOCUS PELMO 5.5.3. For these simulations the same scenario was used as for the simulations presented in the previous chapter (i.e. the standard FOCUS Hamburg scenario over 26 years, 80th temporal percentile). The results are presented in the last column of Table 5-6. The other simulation results in the table refer to simulations using the initial tier 1 parameters and to respective lysimeter results (copied from the previous chapter).

The comparison in Table 5-6 shows a heterogenic outcome:

- In most of the comparisons (13) the optimised parameters led to simulations below respective simulations with tier 1 parameter setting. This is in line with the results of the previous chapter where it was concluded that standard FOCUS PELMO simulations based on tier 1 parameter setting result in higher concentrations than lysimeter studies. Also, it is reasonable that FOCUS PELMO simulations based on inverse modelling show the same trend as lysimeter studies themselves.
- In 3 situations (flufenacetat opt. 2 and opt.3, isoproturon opt. 13 included preferential flow option) the concentrations with initial and optimised parameter setting were both zero. The respective lysimeter studies performed with flufenacetat didn't show any occurrence of the active substance as well. In contrast, isoproturon was determined in the leachate of the respective study. However, the authors of the lysimeter study assumed preferential flow as a possible process in the study.
- If simulations with optimised parameter settings were higher than tier 1 simulations (e.g. thiamethoxam, op. 4, isoxaben opt. 8, isoproturon, opt. 13) the respective lysimeter study was probably influenced by preferential flow but PELMO's preferential flow module was switched off. That is also reasonable as the inverse modelling mimics the behaviour in the lysimeter study which leads to conservative parameters which may end with higher PELMO simulations than with tier 1 parameter setting.
- For a minor number of simulations (e.g. bentazon, opt. 7) FOCUS PELMO simulations based on initial parameter setting and inverse modelling led to similar results. In these simulations, the inverse modelling simply confirms the tier 1 parameter setting.
- In no situation (clothianidin opt 5) higher metabolite concentrations were calculated based on inverse modelling than on tier 1 parameter setting. The inverse modelling optimisation did not suggest any degradation in the experiment. As this was a lysimeter study which could have been influenced by preferential flow, the optimisation of the parent lead to difficulties. Therefore, the results of the metabolite could potentially be misleading.

Based on the results it seems that lysimeter studies, which were performed according to the BBA IV, 4-3 guideline, should not be considered as a standard option for the refinement of tier-1 parameters. As analysed in detail many studies were characterised by early substance findings presumably caused by preferential flow. That does not necessarily mean that lysimeter studies are in general influenced by fast transport processes. This selection of lysimeter studies may be biased as lysimeter studies were considered for the evaluation of inverse modelling in the project especially where significant concentrations were detected in the leachate independent of whether the concentrations were due to early break through or caused by chromatographic flow.

However, if lysimeter studies had been especially selected with hardly any substance leaching, other issues could be expected since only a few or no experimental data points could be used for the optimisation using the inverse modelling procedure.

Finally, if the lysimeter study was influenced by preferential flow then switching on the corresponding preferential flow option in PELMO (or directly using FOCUS MACRO) does not seem a straightforward and meaningful solution for use in registration. Such optimisations may increase the understanding of what happened during the lysimeter experiment but FOCUS PELMO simulations based on these optimisations will necessarily lead to less conservative simulations than the lysimeter study results themselves.

Table 5-6: comparison of Tier 1 simulations with calculations based on inverse modelling (no plant uptake)

| No | Substance | $Kf_{oc}$ | | | DegT$_{50}$ (d) | | | | Results (all based on FOCUS Hamburg scenario, 80th temporal percentile) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | EU | D | Inv Mod | EU | D$_{lab}$ | D$_{field}$ | Inv Mod | Tier 1 EU° | Tier 1 D Lab° | Tier 1 D Field° | Inverse Modelling parameters | Lysimeter |
| 1 | Terbuthylazin | 232 | 232 | 829 | 22.4 | 75.6 | 44.5/11.2 | 64 | 0.001 | 0.772 | 0.000/ 0.032 | 0.000 | <0.01 |
| 1 | MT13 GS 23158 | 187 | 187 | 5.1 | 452.6 | 452.6 | - | 1.33 | 25.925 | 20.951 | - | 0.033 | 0.02 |
| 2 | Flufenacetat | 200 | 200 | 786.4 | 19.6 | 19.6 | 22.3 | 62 | 0.000 | 0.000 | 0.000 | 0.000 | 0.03 |
| 2 | FOE 5043-Sulfonic Acid | 10 | 10 | 1 | 21.7 | - | 21.7 | 7.35 | 5.208 | 50.299 | 8.652 | 2.291 | 1.5. |
| 3 | Flufenacetat | 200 | 200 | 665 | 19.6 | 19.6 | 22.3 | 71 | 0.000 | 0.000 | 0.000 | 0.000 | 0.03 |
| 3 | FOE 5043-Sulfonic Acid | 10 | 10 | 1.30 | 21.7 | - | 21.7 | 4.92 | 5.208 | 50.299 | 8.652 | 1.150 | 0.54 |
| 4 | Thiamethoxam | 58 | 58 | 0.001 | 32.7 | 118.1 | 32.7 | 6.31 | 0.415 | 14.071 | 0.414 | 0.566 | 0.095 |
| 4 | Thiamethoxam* | 58 | 58 | 146 | 32.7 | 118.1 | 32.7 | 1.6 | 0.415 | 14.071 | 0.414 | 0.000 | 0.095 |
| 4 | Clothianidin* | 133 | 133 | 142 | 103.6 | 103.6 | - | 2.9 | 0.513 | 1.770 | - | 0.000 | 0.27 |
| 5 | Thiamethoxam | 58 | 58 | 7.7 | 32.7 | 118.1 | 32.7 | 7.92 | 0.415 | 14.071 | 0.414 | 0.337 | 0.095 |
| 5 | Thiamethoxam* | 58 | 58 | 546 | 32.7 | 118.1 | 32.7 | 10.98 | 0.415 | 14.071 | 0.414 | 0.000 | 0.095 |
| 5 | Clothianidin | 133 | 133 | 283 | 103.6 | 103.6 | - | 198042 | 0.513 | 1.770 | - | 20.529 | 0.27 |
| 6 | Bentazon | 23 | 23 | 54.91 | 9.2 | 19.4 | 9.2 | 23.12 | 0.185 | 5.605 | 0.185 | 0.072 | 0.08 |
| 7 | Bentazon | 23 | 23 | 38.23 | 9.2 | 19.4 | 9.2 | 14.09 | 0.185 | 5.605 | 0.185 | 0.263 | 0.08 |
| 8 | Isoxaben | 351 | 351 | 43.57 | 94.4 | 301 | 307 / 40.3 | 10.0 | 0.058 | 4.457 | 4.666 / 0.000 | 0.175 | 0.05 |

| No | Substance | $Kf_{oc}$ | | | $DegT_{50}$ (d) | | | | Results (all based on FOCUS Hamburg scenario, 80th temporal percentile) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | EU | D | Inv Mod | EU | $D_{lab}$ | $D_{field}$ | Inv Mod | Tier 1 EU° | Tier 1 D Lab° | Tier 1 D Field° | Inverse Modelling parameters | Lysimeter |
| 8 | Isoxaben* | 351 | 351 | 269 | 94.4 | 301 | 307 / 40.3 | 50 | 0.058 | 4.457 | 4.666 / 0.000 | 0.007 | 0.05 |
| 8 | Hydroxy-Isoxaben | 37 | 37 | 53.8 | 58.9 | 92.7 | 58.9 | 5.8 | 15.060 | 25.638 | 17.326/ 13.886 | 0.057 | 0.07 |
| 9 | Nicosulfuron | 29 | 29 | 0.001 | 22.8 | 22.8 | - | 4.46 | 0.222 | 0.222 | - | 0.011 | 0.17 |
| 9 | Nicosulfuron | 29 | 29 | 6.76 | 22.8 | 22.8 | - | 7.78 | 0.222 | 0.222 | - | 0.036 | 0.17 |
| 10 | Diazinon Met G27550 | 6 | 6 | 1.0 | 55.7 | 55.7 | - | 5.09 | 86.583 | 88.144 | - | 1.495 | 0.29 |
| 11 | Diazinon Met G27550 | 6 | 6 | 1.95 | 55.7 | 55.7 | - | 8.01 | 86.583 | 88.144 | - | 4.270 | 1.02 |
| 12 | Isoproturon | 126 | 126 | 101 | 7 | 7 | - | 14.52 | 0 | 0 | - | 0.038 | 0.089 |
| 12 | desmethyl-isoproturon | 147 | 147 | 88.4 | 21.7 | 21.7 | - | 10.34 | 0 | 0 | - | 0.020 | 0.022 |
| 13 | Isoproturon | 126 | 126 | 24.97 | 7 | 7 | - | 2.13 | 0 | 0 | - | 0.053 | 0.272 |
| 13 | Isoproturon* | 126 | 126 | 139.1 | 7 | 7 | - | 3.97 | 0 | 0 | - | 0.000 | 0.272 |
| 14 | Metalxyl | 86 | 86 | 5.13 | 14.6 | 14.6 | 19.9 | 10.10 | 0 | 0 | - | 0.293 | 0.05 |
| 15 | Metalxyl | 86 | 86 | 0.001 | 14.6 | 14.6 | 19.9 | 5.71 | 0 | 0 | - | 0.065 | 0.05 |

* considering preferential flow module in PELMO

° 80th temporal percentile

## 5.5.3 Combined simulations with lysimeter and FOCUS conditions

In order to improve the understanding about the influence of the various scenario parameters on the predicted concentrations in the percolate (e.g. weather and soil), which is necessary for the extrapolation of lysimeter results, further simulations were performed:

- Combination of the lysimeter soil (and lysimeter application pattern) with standard (FOCUS Hamburg) scenario weather pattern.
- Combination of the lysimeter weather with standard (FOCUS Hamburg) soil and application pattern

All simulations were performed with FOCUS PELMO 5.5.3. The results are presented in the following section using the same studies as in the previous chapter (Table 5-5).

As the FOCUS scenarios are based on weather series over 26 years only repeated annual applications were considered for the comparison.

### 5.5.3.1 Optimisation 1: terbuthylazin, Schmallenberg, 1990-1992

#### 5.5.3.1.1 Results for terbuthylazin

The simulations were based on a $Kf_{oc}$ of 829 L/kg and a $DegT_{50}$ of 64 d.

The results are summarised in Figure 5-27 and Figure 5-28 for the combination FOCUS Hamburg climate and FOCUS Hamburg soil, respectively. When simulating FOCUS Hamburg climate the maximum of the peak is expected to occur 14 years after the application. According to the simulation with FOCUS Hamburg soil a plateau will be reached after 20 years. However, the nominal concentrations simulated ($5\ 10^{-5}$ µg/L) remain far below the trigger of 0.1 µg/L.

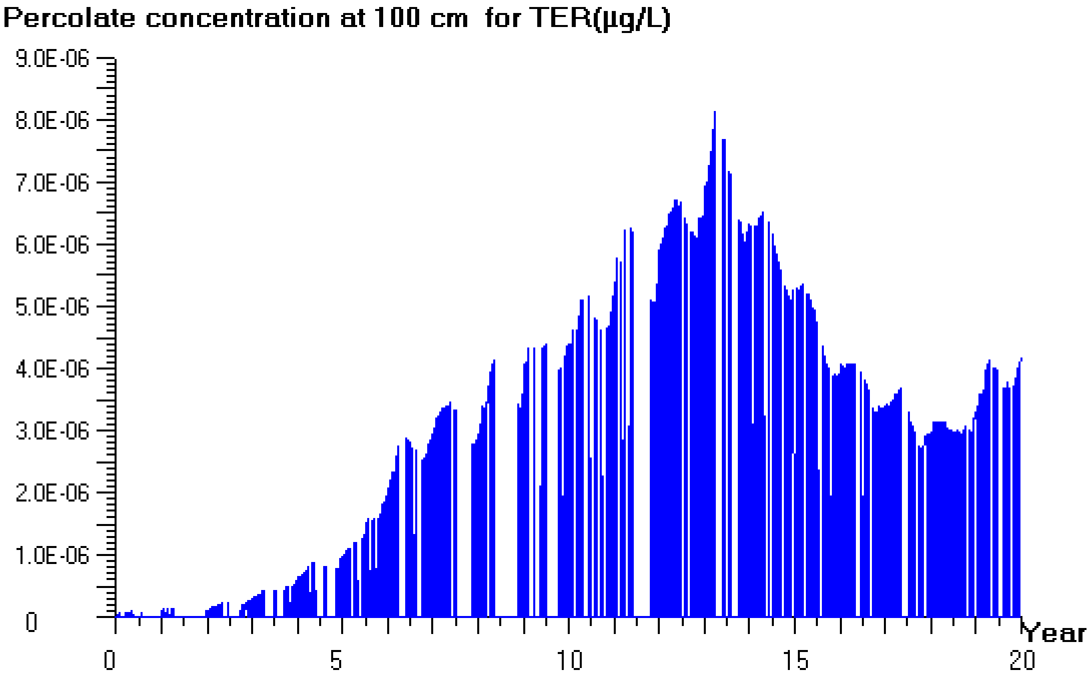


Figure 5-27: Time dependent concentration for terbuthylazin considering FOCUS Hamburg climate and lysimeter soil (optimised parameter setting)

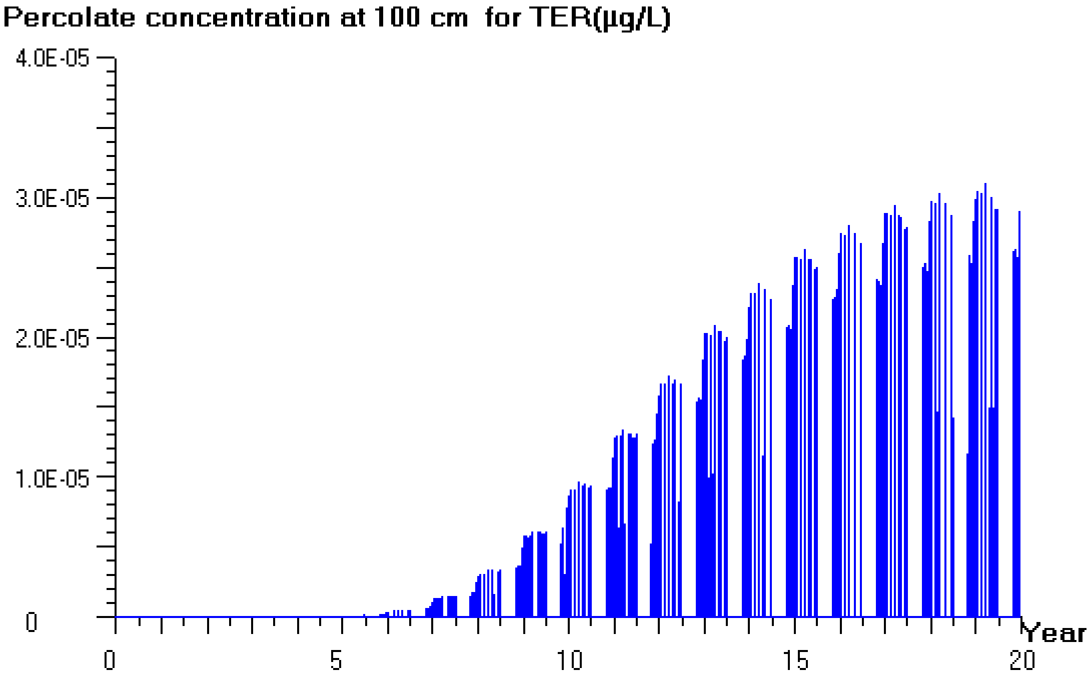


Figure 5-28: Time dependent concentration for terbuthylazin considering FOCUS Hamburg soil and lysimeter weather (optimised parameter setting)

#### 5.5.3.1.2 Results for the metabolite

A different outcome can be observed for the metabolite GS23158 as shown in Figure 5-29 and Figure 5-30 for the combination FOCUS Hamburg climate and FOCUS Hamburg soil, respectively. The simulations were based on a $Kf_{oc}$ of 5 L/kg and a $DegT_{50}$ of 14 d.

When simulating FOCUS Hamburg climate the maximum of the peak is expected to occur 4 years after the application. According to the simulation with FOCUS Hamburg soil a plateau will be reached after 5 years with maximum concentrations of about 0.18 µg/L.

The reason for the slightly higher concentrations when using the FOCUS Hamburg soil (Figure 5-30) is most probably the weather conditions in Schmallenberg compared to the FOCUS Hamburg weather.

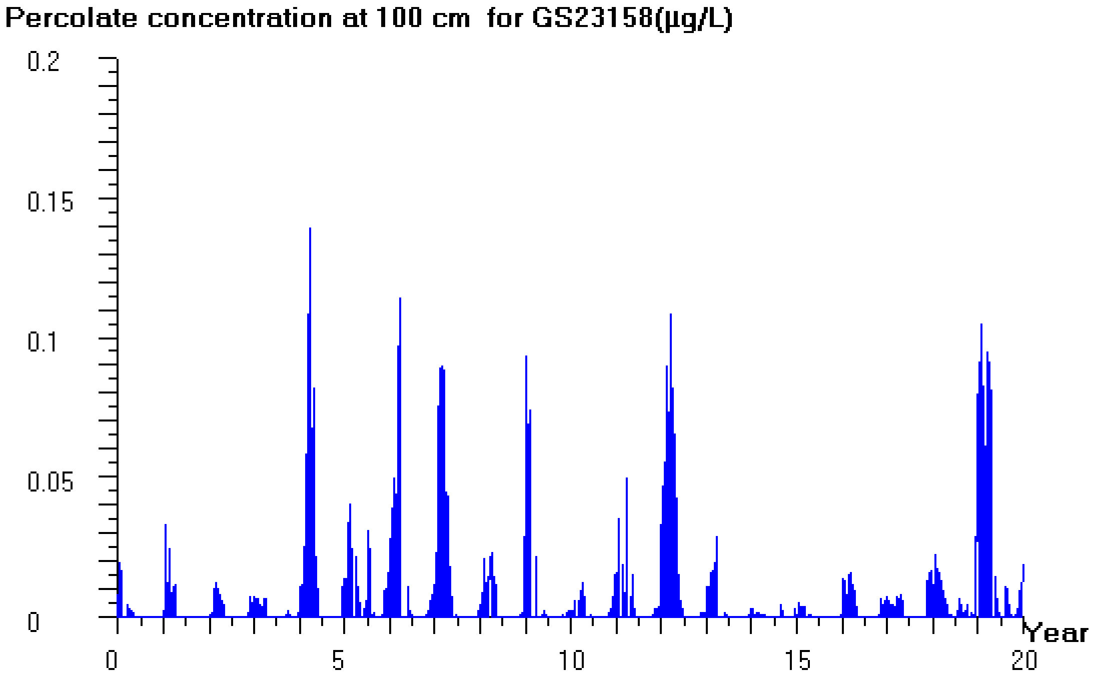


Figure 5-29: Time dependent concentration for GS 23158 (terbuthylazin metabolite) considering FOCUS Hamburg climate and lysimeter soil (optimised parameter setting)

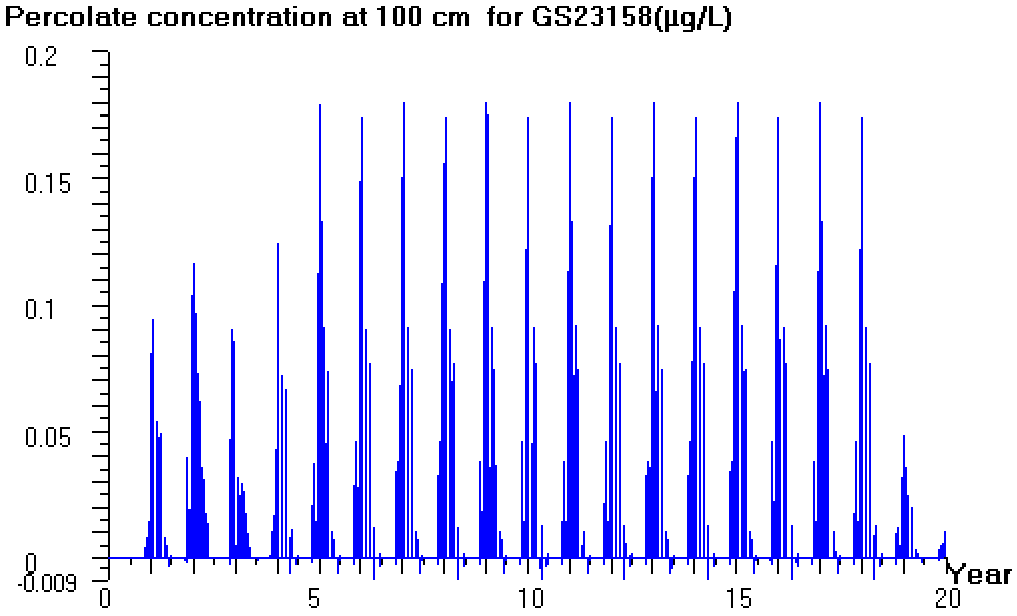


Figure 5-30: Time dependent concentration for GS 23158 (terbuthylazin metabolite) considering FOCUS Hamburg soil and lysimeter weather (optimised parameter setting)

### 5.5.3.2 Optimisation 2: flufenacetat, Monheim, 1993-1995

#### 5.5.3.2.1 Results for flufenacetat

The simulations were based on a $Kf_{oc}$ of 786.4 L/kg and a $DegT_{50}$ of 62.02 d.

The results are summarised in Figure 5-31 and Figure 5-32 for the combination FOCUS Hamburg climate and FOCUS Hamburg soil, respectively. When simulating FOCUS Hamburg climate the maximum of the peak is expected to occur 19 years after the application. According to the simulation with FOCUS Hamburg soil a plateau will be reached after 19 years. However, the nominal concentrations simulated ($4 \times 10^{-13}$ µg/L) remain far below the trigger of 0.1 µg/L.

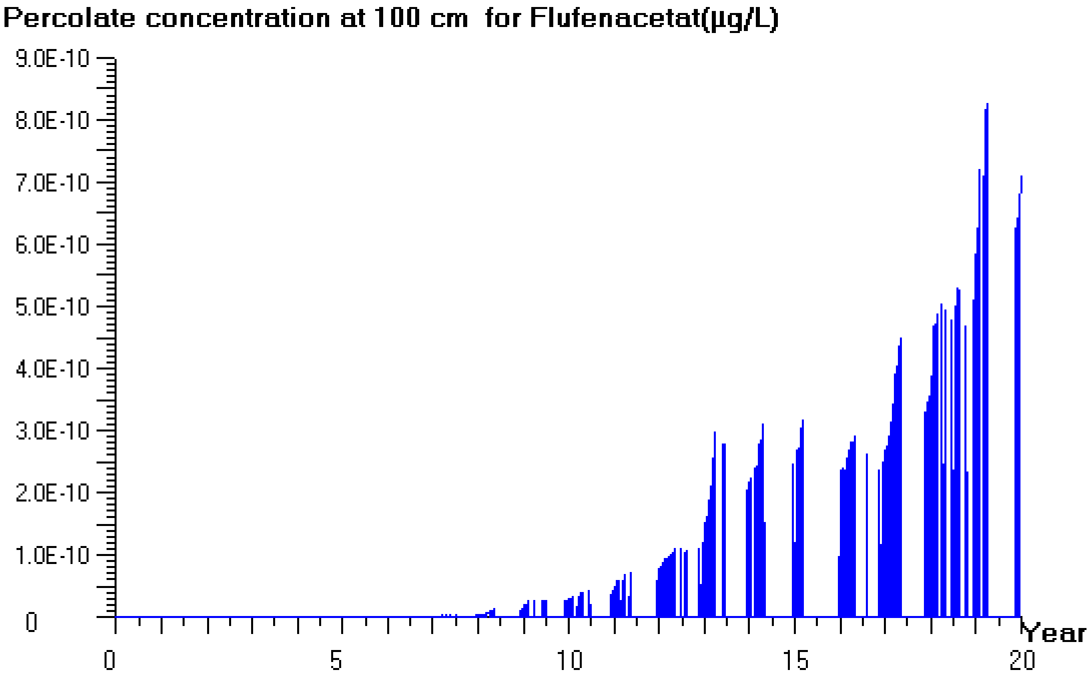


Figure 5-31: Time dependent concentration for flufenacetat considering FOCUS Hamburg climate and lysimeter soil (optimised parameter setting)

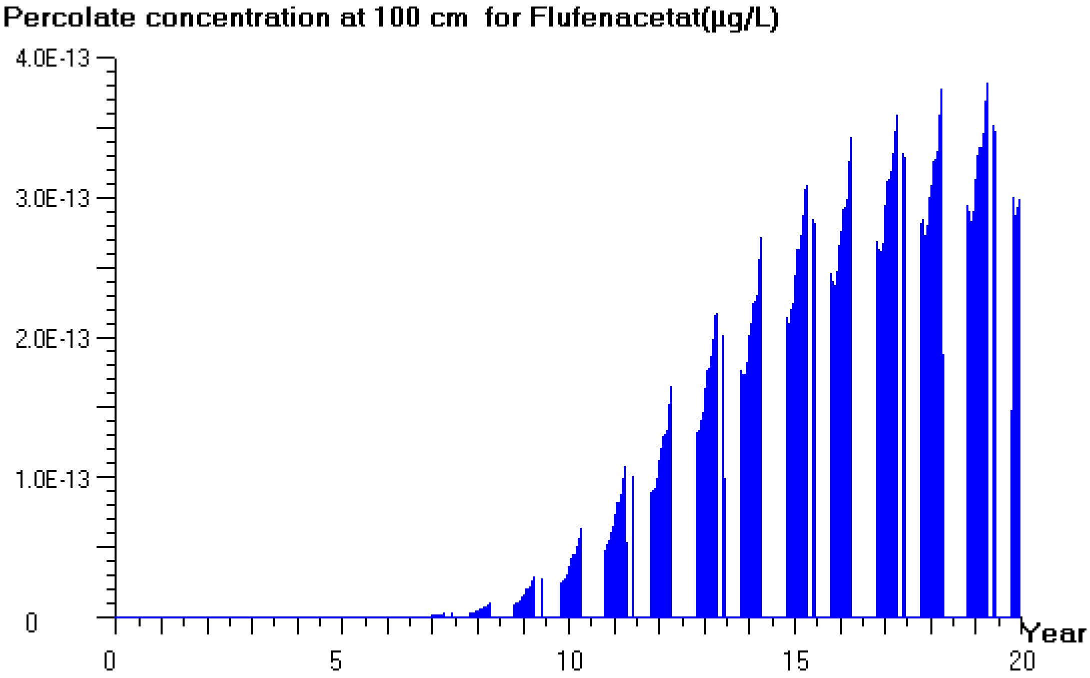


Figure 5-32: Time dependent concentration for flufenacetat considering FOCUS Hamburg soil and lysimeter weather (optimised parameter setting)

#### 5.5.3.2.2 Results for the metabolite

A different outcome can be observed for the metabolite SAC as shown in Figure 5-33 and Figure 5-34 for the combination FOCUS Hamburg climate and FOCUS Hamburg soil, respectively. The simulations were based on a $Kf_{oc}$ of 1 L/kg and a $DegT_{50}$ of 7.35 d.

When simulating FOCUS Hamburg climate the maximum of the peak is expected to occur 5 years after the application with maximum concentrations of 3.7 µg/L. According to the simulation with FOCUS Hamburg soil steady state concentrations will be reached after 4 years with maximum concentrations of about 1.5 µg/L. Due to the properties of the compound (fast degradation) no plateau was reached. The occurrence of slightly higher concentrations at the beginning of the simulation compared to the rest of the period was caused by the weather situations in the first year.

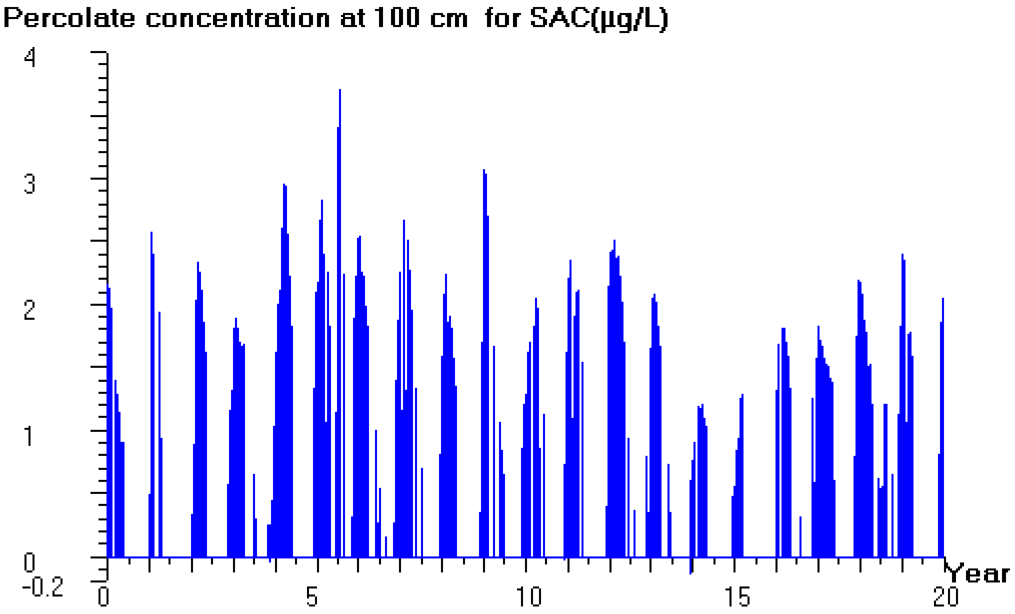


Figure 5-33:Time dependent concentration for SAC (Flufenacetat metabolite) considering FOCUS Hamburg climate and lysimeter soil (optimised parameter setting)

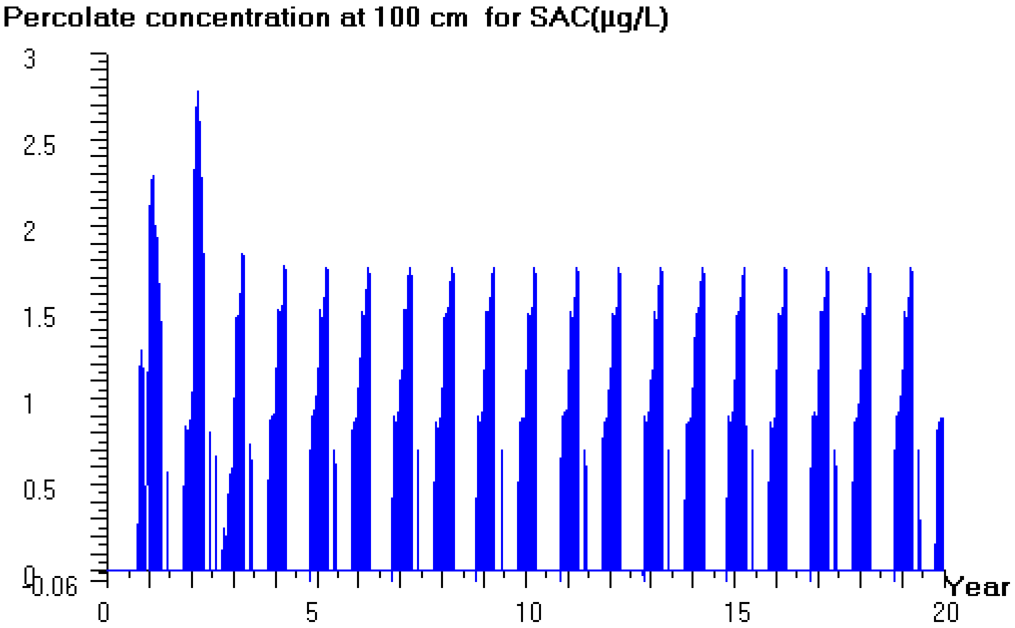


Figure 5-34: Time dependent concentration for SAC (Flufenacetat metabolite) considering FOCUS Hamburg soil and lysimeter weather (optimised parameter setting)

### 5.5.3.3 Optimisation 3: flufenacetat, Monheim, 1993-1996

#### 5.5.3.3.1 Results for flufenacetat

The simulations were based on a $Kf_{oc}$ of 665 L/kg and a $DegT_{50}$ of 71 d.

The results are summarised in Figure 5-35 and Figure 5-36 for the combination FOCUS Hamburg climate and FOCUS Hamburg soil, respectively. When simulating FOCUS Hamburg climate the maximum of the peak is expected to occur 19 years after the application. According to the simulation with FOCUS Hamburg soil a plateau will be reached after 19 years. However, the nominal concentrations simulated ($5x10^{-11}$ µg/L) remain far below the trigger of 0.1 µg/L.

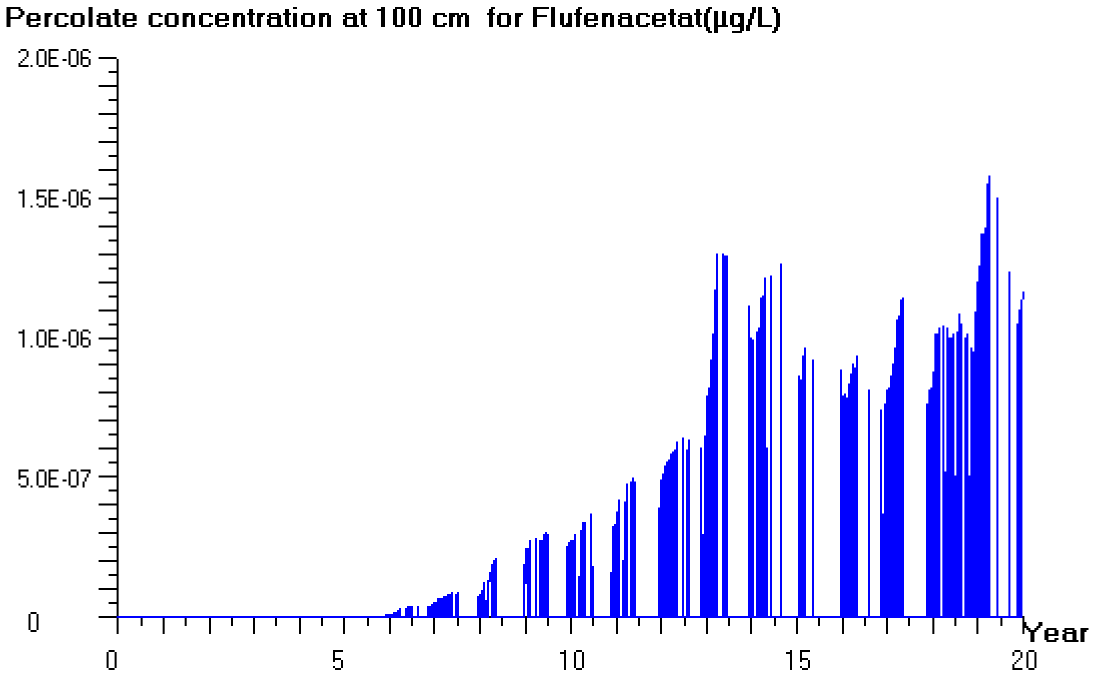


Figure 5-35: Time dependent concentration for flufenacetat considering FOCUS Hamburg climate and lysimeter soil (optimised parameter setting)

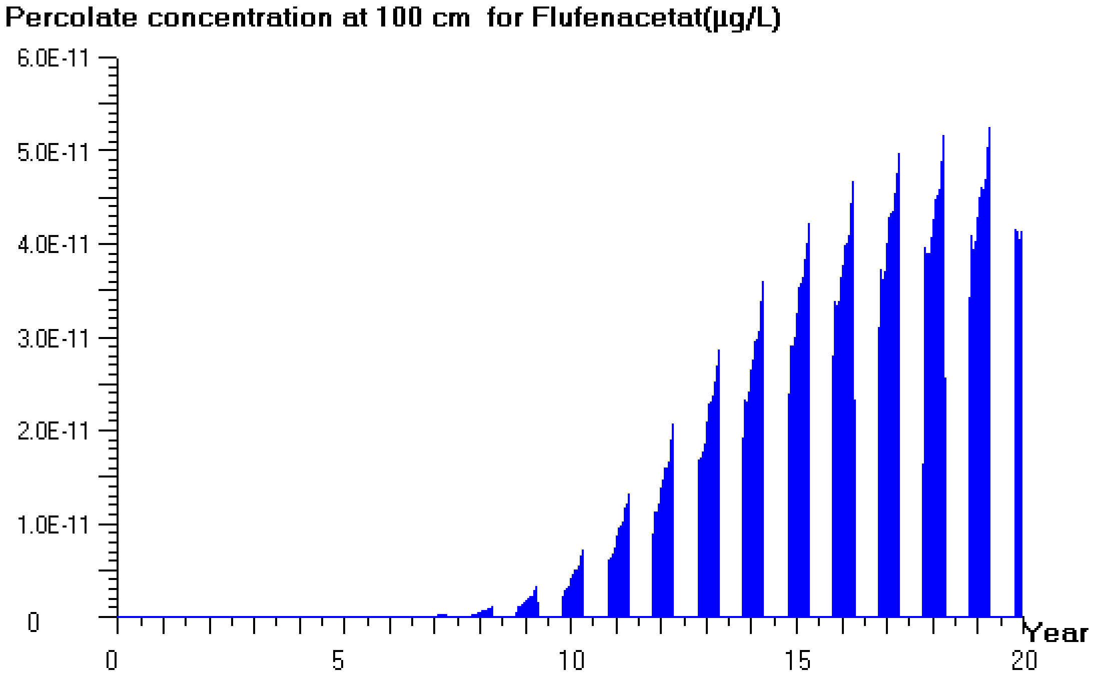


Figure 5-36: Time dependent concentration for flufenacetat considering FOCUS Hamburg soil and lysimeter weather (optimised parameter setting)

#### 5.5.3.3.2 Results for the metabolite

A different outcome can be observed for the metabolite SAC as shown in Figure 5-37 and Figure 5-38 for the combination FOCUS Hamburg climate and FOCUS Hamburg soil, respectively. The simulations were based on a $Kf_{oc}$ of 1.3 L/kg and a $DegT_{50}$ of 4.92 d.

When simulating FOCUS Hamburg climate the maximum of the peak is expected to occur 5 years after the application with maximum concentrations of 2 µg/L. According to the simulation with FOCUS Hamburg soil steady state concentrations will be reached after 4 years with maximum concentrations of about 0.3 µg/L. Due to the properties of the compound no plateau was reached. The occurrence of slightly higher concentrations at the beginning of the simulation compared to the rest of the period was caused by the weather situations in the first year.

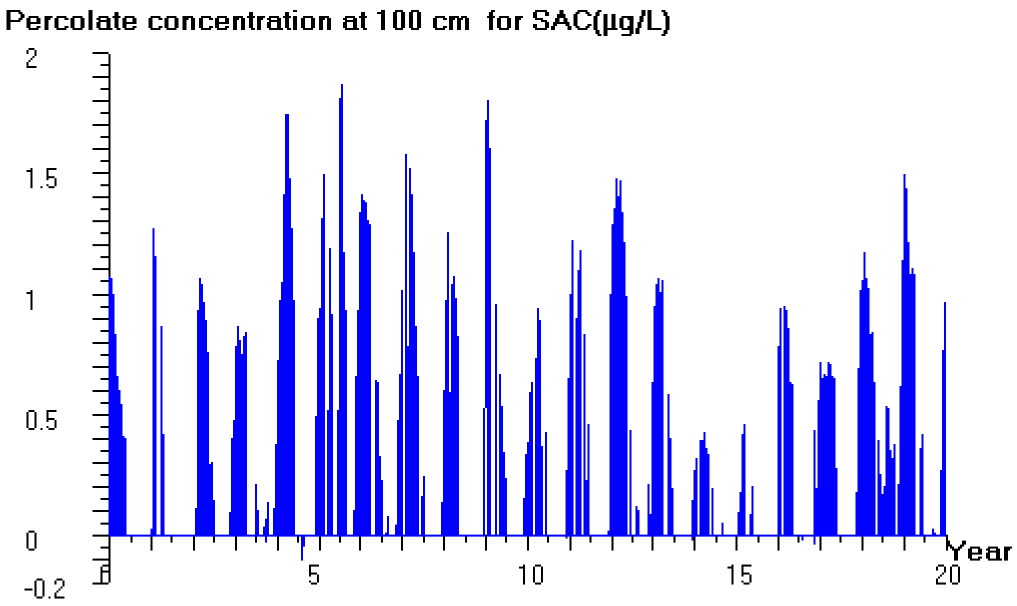


Figure 5-37: Time dependent concentration for SAC (flufenacetat metabolite) considering FOCUS Hamburg climate and lysimeter soil (optimised parameter setting)

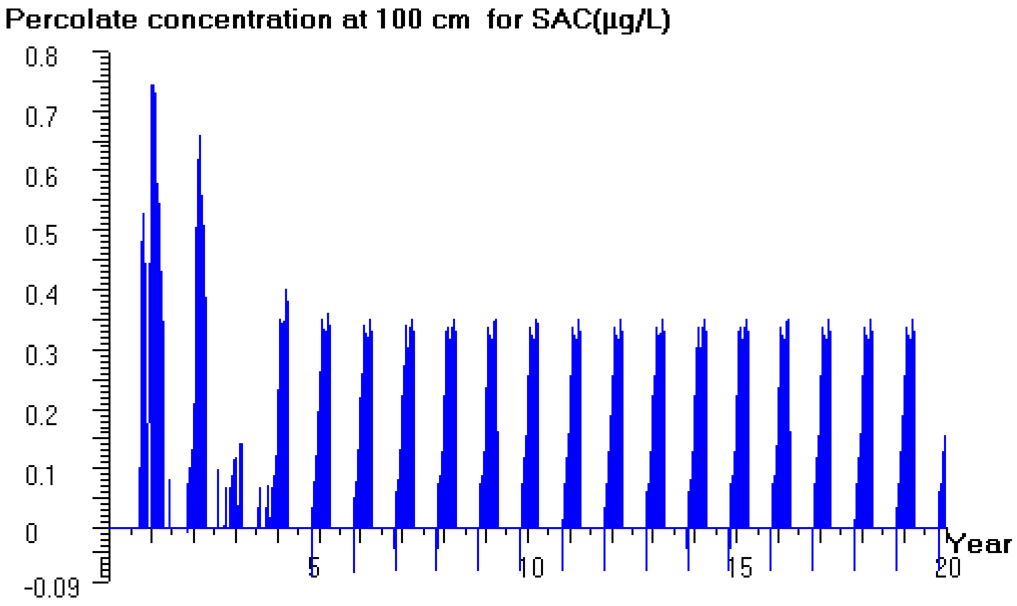


Figure 5-38: Time dependent concentration for SAC (flufenacetat metabolite) considering FOCUS Hamburg soil and lysimeter weather (optimised parameter setting)

#### 5.5.3.4 Optimisation 6: bentazon, Schmallenberg, 1990-1993, 1 Application

The simulations were based on a $Kf_{oc}$ of 38.32 L/kg and a $DegT_{50}$ of 23 d.

The results are summarised in Figure 5-39 and Figure 5-40 for the combination FOCUS Hamburg climate and FOCUS Hamburg soil, respectively. When simulating FOCUS Hamburg climate conditions the maximum of the peak is expected to occur 6 years after the application with maximum concentrations of about 0.18 µg/L. According to the simulation with FOCUS Hamburg soil a plateau will be reached after 3 years with maximum concentrations of 0.055 µg/L. Due to the fast degradation of bentazon the plateau is not significantly higher than the concentrations caused by single applications. The reason for the slightly higher concentrations when using the FOCUS Hamburg soil is most probably the weather conditions in Schmallenberg compared to the FOCUS Hamburg weather. However, it seems reasonable, that changing weather conditions in different years strongly influence the annual leaching behaviour of the active substance bentazon.

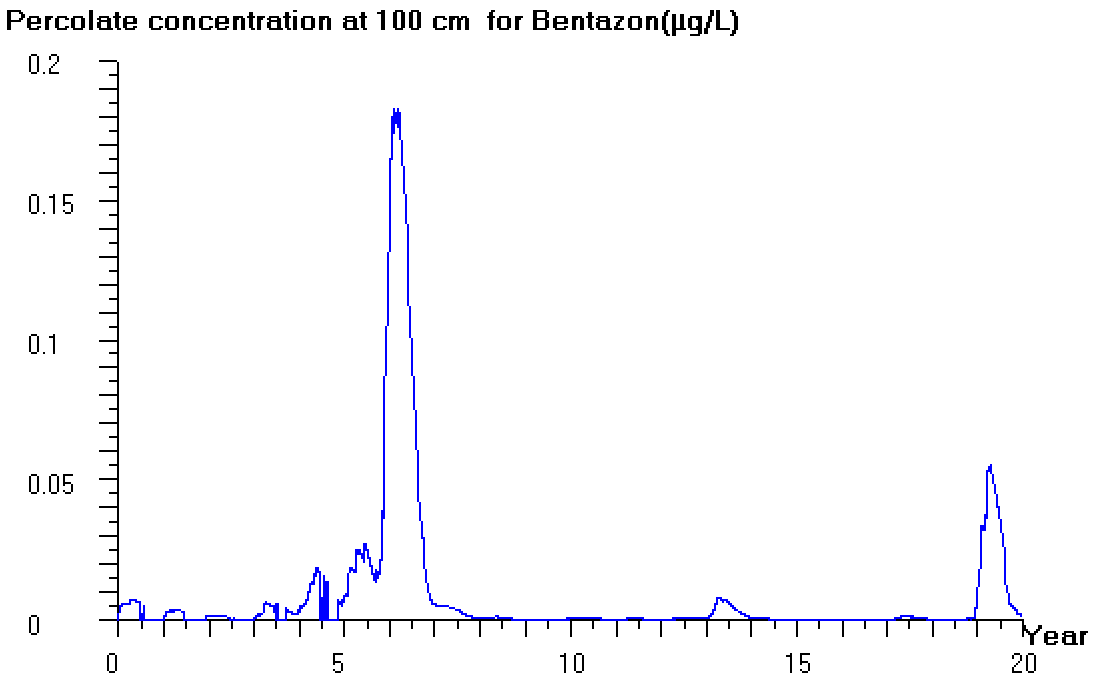


Figure 5-39: Time dependent concentration for bentazon considering FOCUS Hamburg climate and lysimeter soil (optimised parameter setting)

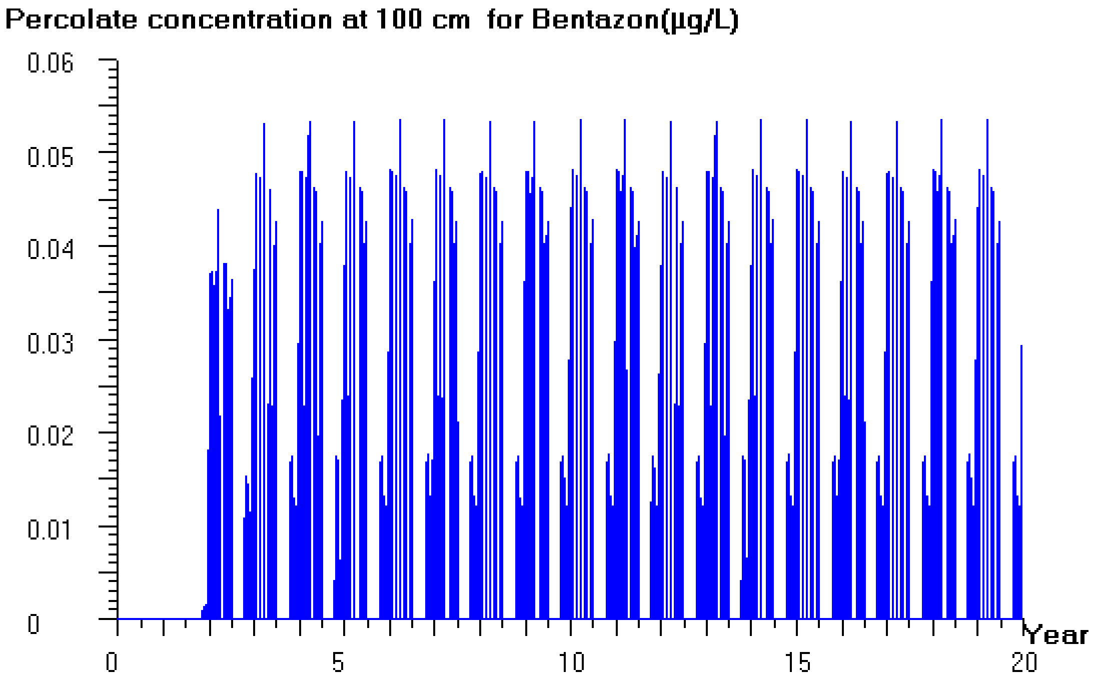


Figure 5-40: Time dependent concentration for bentazon considering FOCUS Hamburg soil and lysimeter weather (optimised parameter setting)

#### 5.5.3.5 Optimisation 9: nicosulfuron, Schmallenberg, 1990-1993, 1 Application

The simulations were based on a $Kf_{oc}$ of 0.01 L/kg and a $DegT_{50}$ of 4.5 d.

The results are summarised in Figure 5-41 and Figure 5-42 for the combination FOCUS Hamburg climate and FOCUS Hamburg soil, respectively. When simulating FOCUS Hamburg climate the maximum of the peak is expected to occur 6 years after the application with an exceptionally high maximum of 2 µg/L. This peak is probably caused by an unfavoured combination of weather conditions and time of application. According to the simulation with FOCUS Hamburg soil steady state concentrations of 0.18 µg/L will be reached after 4 years. Due to the fast degradation of nicosulfuron no plateau was reached.

The reason for the regularly higher concentrations when considering the FOCUS Hamburg soil is most probably the weather conditions in Schmallenberg (higher rainfall) compared to the FOCUS Hamburg weather. Similar as in the previous simulation with bentazon changing weather conditions in different years can also strongly influence the annual leaching behaviour of the active substance nicosulfuron.

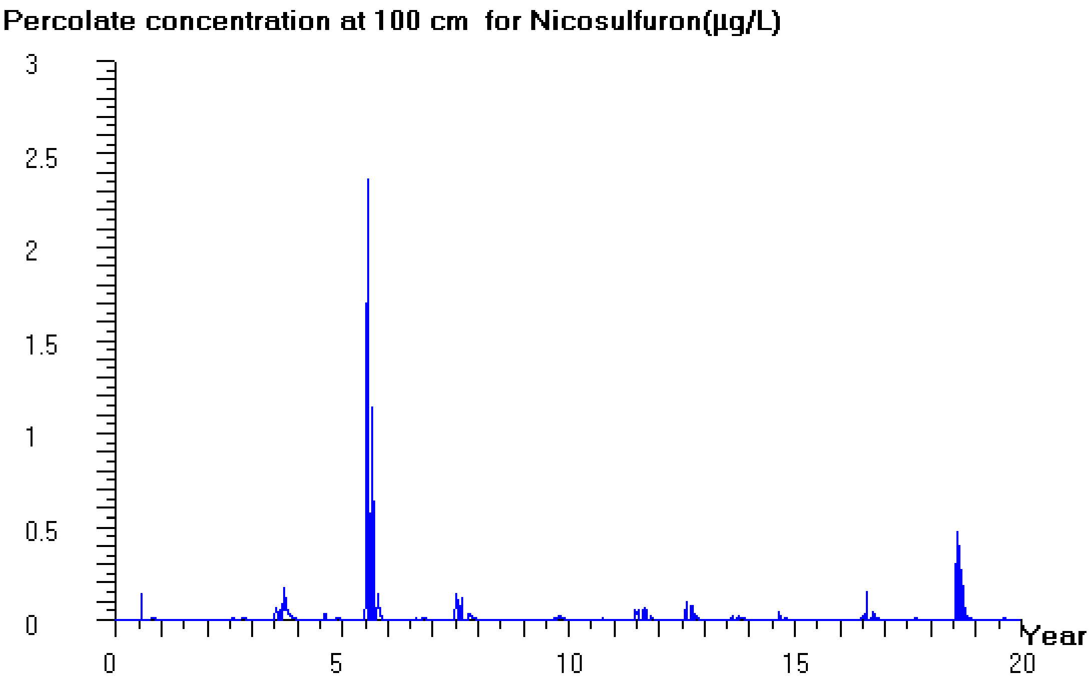


Figure 5-41: Time dependent concentration for nicosulfuron considering FOCUS Hamburg climate and lysimeter soil (optimised parameter setting)

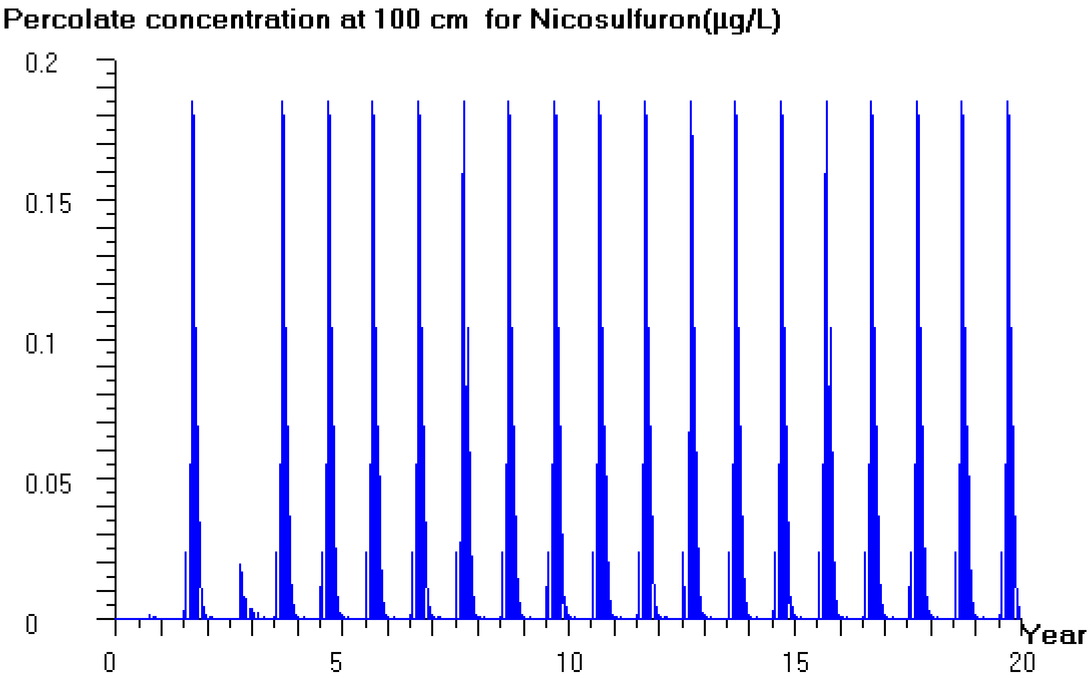


Figure 5-42: Time dependent concentration for nicosulfuron considering FOCUS Hamburg soil and lysimeter weather (optimised parameter setting)

### 5.5.3.6 Optimisation 10: diazinon, Neustadt, 1991-1994, 4 applications

#### 5.5.3.6.1 Results for diazinon

The simulations were based on a $Kf_{oc}$ of 413 L/kg and a $DegT_{50}$ of 7.9 d.

Independent on the combination no percolate was simulated in the leachate. This is because of the short half-life in combination with the high $Kf_{oc}$ value of 413 L/kg

#### 5.5.3.6.2 Results for the metabolite

A different outcome can be observed for the metabolite G27550 as shown in Figure 5-43 and Figure 5-44 for the combination FOCUS Hamburg climate and FOCUS Hamburg soil, respectively. The simulations were based on a $Kf_{oc}$ of 1 and a $DegT_{50}$ of 5.1.

When simulating FOCUS Hamburg climate the maximum of the peak is expected to occur 5 years after the application with maximum concentrations of 4 µg/L. According to the simulation with FOCUS Hamburg soil steady state concentrations will be reached after 5 years with maximum concentrations of about 0.2 µg/L. Due to the properties of the compound no plateau was formed. The occurrence of slightly higher concentrations at the beginning of the simulation compared to the rest of the period was caused by the weather situations in year 3.

The significant difference between the simulations is caused by the greater vulnerability of the soil to leaching (less organic carbon content) in the lysimeter study compared to the FOCUS Hamburg scenario soil. Additionally, the influence of the higher rainfall in the FOCUS Hamburg climate as compared to the Neustadt lysimeter site may have caused these differences.

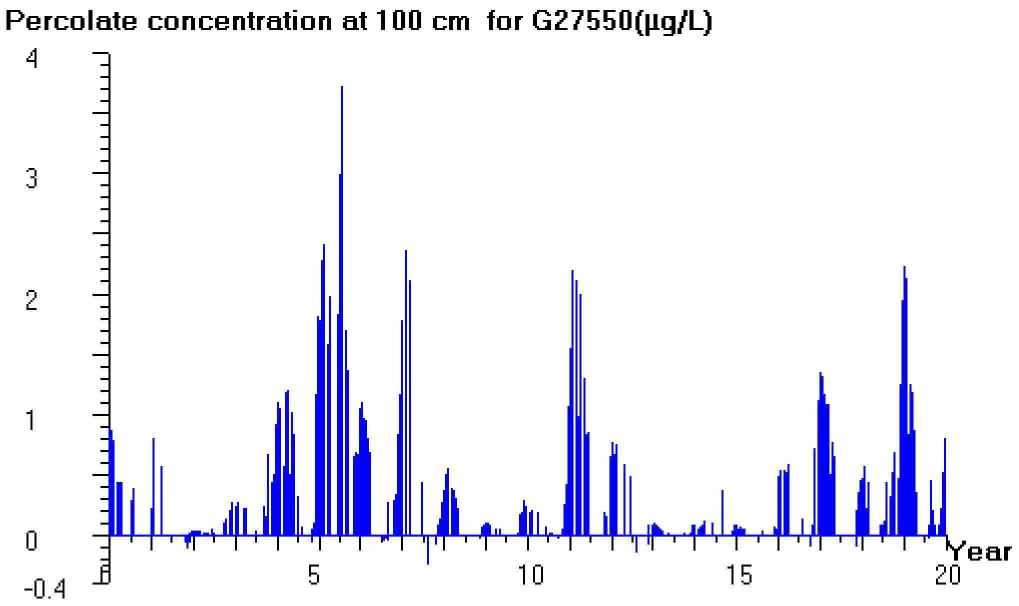


Figure 5-43: Time dependent concentration for G27550 considering FOCUS Hamburg climate and lysimeter soil (optimised parameter setting)

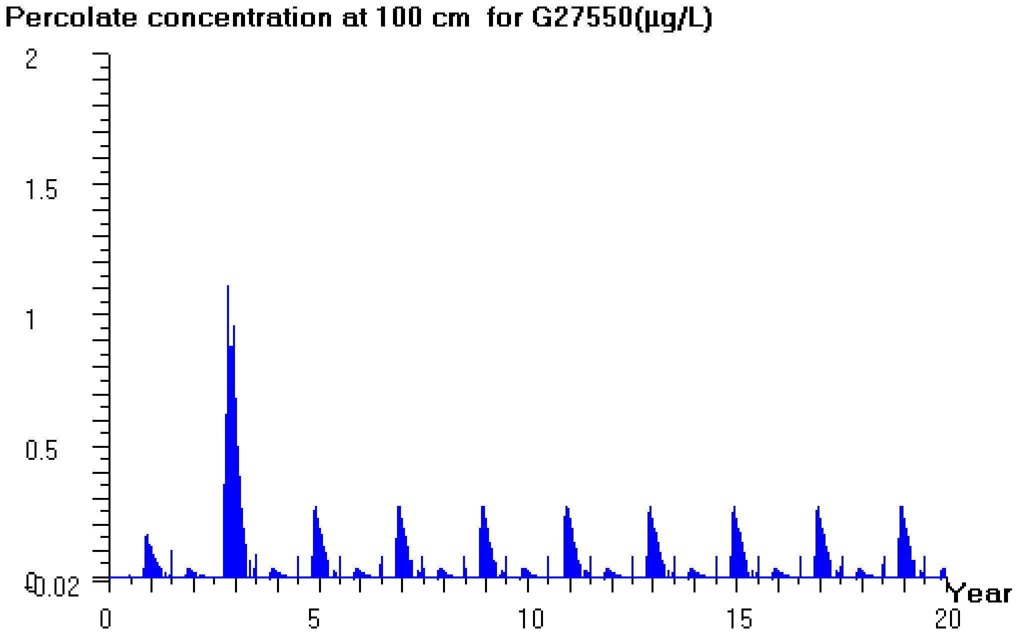


Figure 5-44: Time dependent concentration for G27550 considering FOCUS Hamburg soil and lysimeter weather (optimised parameter setting)

### 5.5.3.7 Optimisation 11: diazinon, Neustadt, 1991-1994, 4 applications

#### 5.5.3.7.1 Results for diazinon

The simulations were based on a $Kf_{oc}$ of 413 L/kg and a $DegT_{50}$ of 7.9 d.

Independent of the combination no substance was simulated in the leachate. This is because of the short half-life in combination with the high $Kf_{oc}$ value of 413 L/kg.

#### 5.5.3.7.2 Results for the metabolite

A different outcome can be observed for the metabolite G27550 as shown in Figure 5-45 and Figure 5-46 for the combination FOCUS Hamburg climate and FOCUS Hamburg soil, respectively. The simulations were based on a $Kf_{oc}$ of 1.95 and a $DegT_{50}$ of 8.

When simulating FOCUS Hamburg climate the maximum of the peak is expected to occur 5 years after the application with maximum concentrations of 15 µg/L. According to the simulation with FOCUS Hamburg soil steady state concentrations will be reached after 4 years with maximum concentrations of about 2 µg/L. Due to the properties of the compound no plateau was formed, but nearly constant leachate concentration every year have been calculated by using the same weather conditions after the third year. The occurrence of slightly higher concentrations at the beginning of the simulation compared to the rest of the period was caused by the different weather situations in year 3.

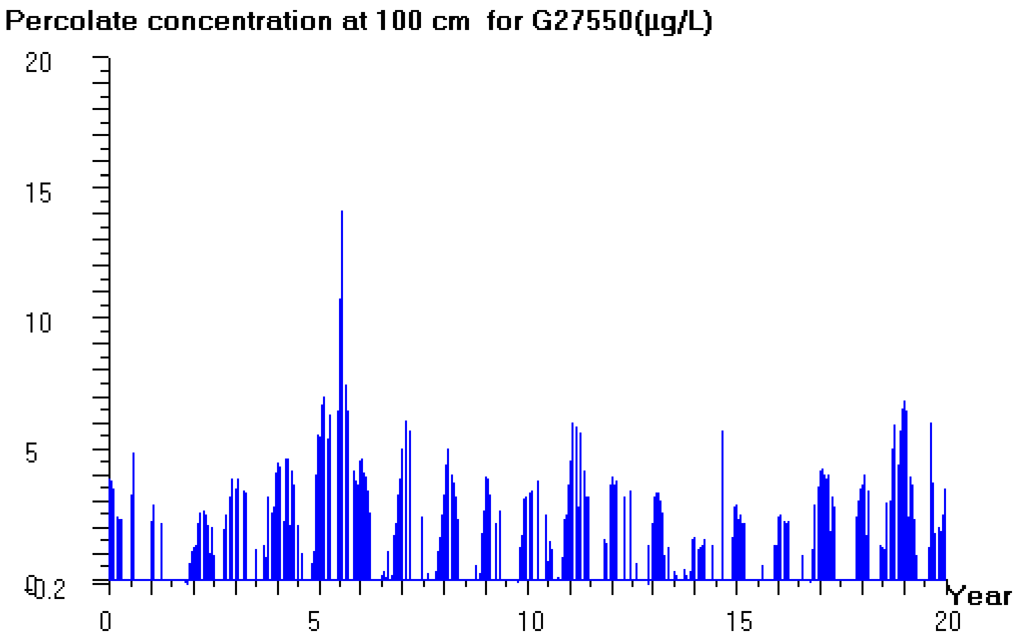


Figure 5-45: Time dependent concentration for G27550 considering FOCUS Hamburg climate and lysimeter soil (optimised parameter setting)

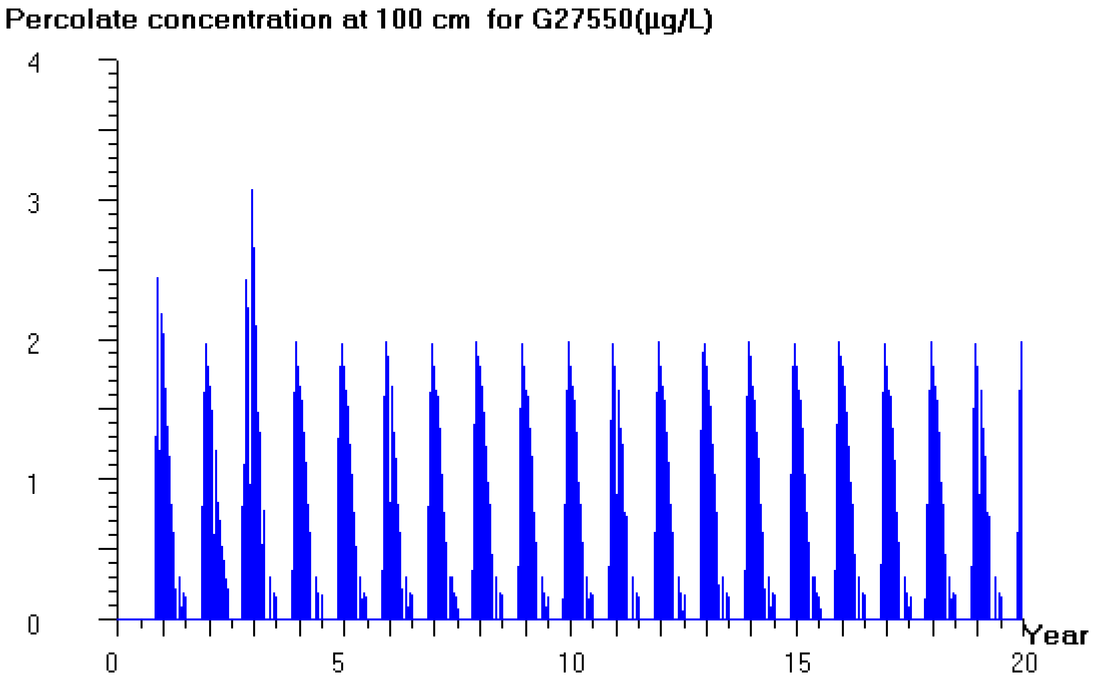


Figure 5-46: Time dependent concentration for G27550 considering FOCUS Hamburg soil and lysimeter weather (optimised parameter setting)

#### 5.5.3.8 Optimisation 12: isoproturon, Neustadt, 1989-1992

The simulations were based on a $Kf_{oc}$ of 101.4 L/kg and a $DegT_{50}$ of 14.5 d.

The results are summarised in Figure 5-47 and Figure 5-48 for the combination FOCUS Hamburg climate and FOCUS Hamburg soil, respectively. When simulating FOCUS Hamburg climate the maximum of the peak is expected to occur 14 years after the application with maximum concentrations of about 8.5 µg/L. According to the simulation with FOCUS steady state concentrations will be reached after 6 years with maximum concentrations of 0.001 µg/L.

The significant differences between the simulations with few magnitudes of order are caused by the greater vulnerability of the soil to leaching (less organic carbon content) in the lysimeter study compared to the FOCUS Hamburg scenario soil. Additionally, the influence of the higher rainfall in the FOCUS Hamburg climate as compared to the Neustadt lysimeter site may have caused these differences.

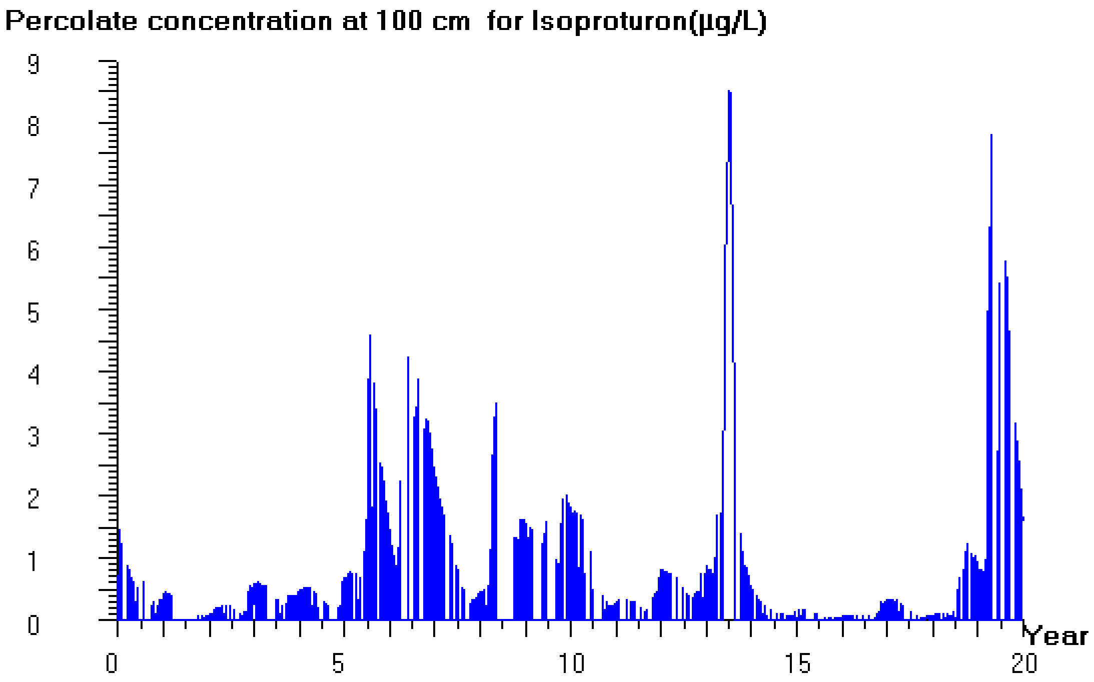


Figure 5-47: Time dependent concentration for isoproturon considering FOCUS Hamburg climate and lysimeter soil (optimised parameter setting)

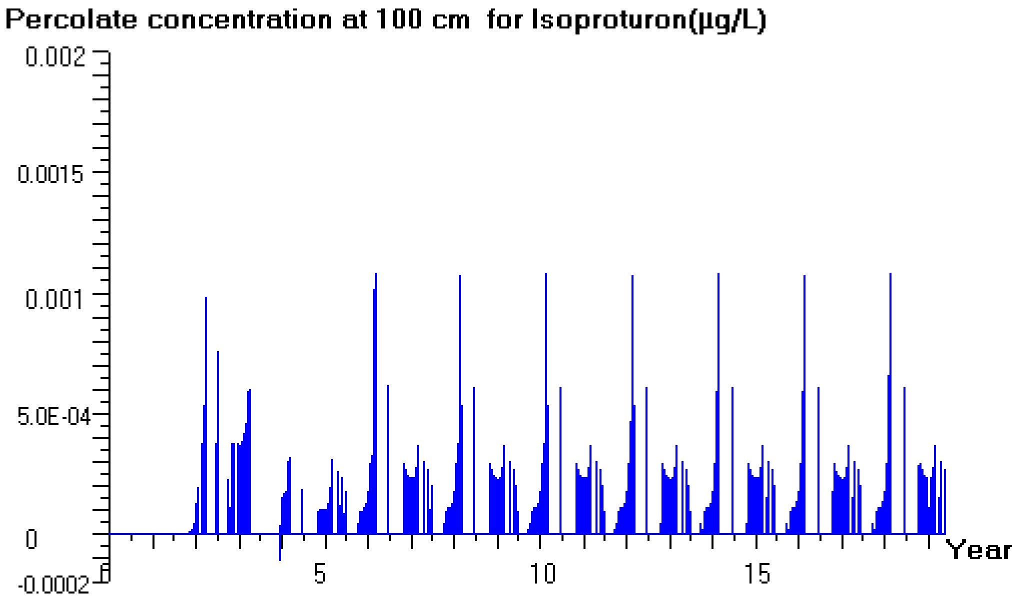


Figure 5-48: Time dependent concentration for isoproturon considering FOCUS Hamburg soil and lysimeter weather (optimised parameter setting)

#### 5.5.3.9 Optimisation 14: metalaxyl, Neustadt, 1992-1994, 3 Applications

The simulations were based on a $Kf_{oc}$ of 5.1 L/kg and a $DegT_{50}$ of 10.1 d.

The results are summarised in Figure 5-49 and Figure 5-50 for the combination FOCUS Hamburg climate and FOCUS Hamburg soil, respectively. When simulating FOCUS Hamburg climate the maximum of the peak is expected to occur 39 years after the application with maximum concentrations of about 1.7 µg/L. According to the simulation with FOCUS steady state concentrations will be reached after 3 years with maximum concentrations of 0.3 µg/L.

The significant differences between the simulations are caused by the greater vulnerability of the soil to leaching (less organic carbon content) in the lysimeter study compared to the FOCUS Hamburg scenario soil. Additionally, the influence of the higher rainfall in the FOCUS Hamburg climate as compared to the Neustadt lysimeter site may have caused these differences.

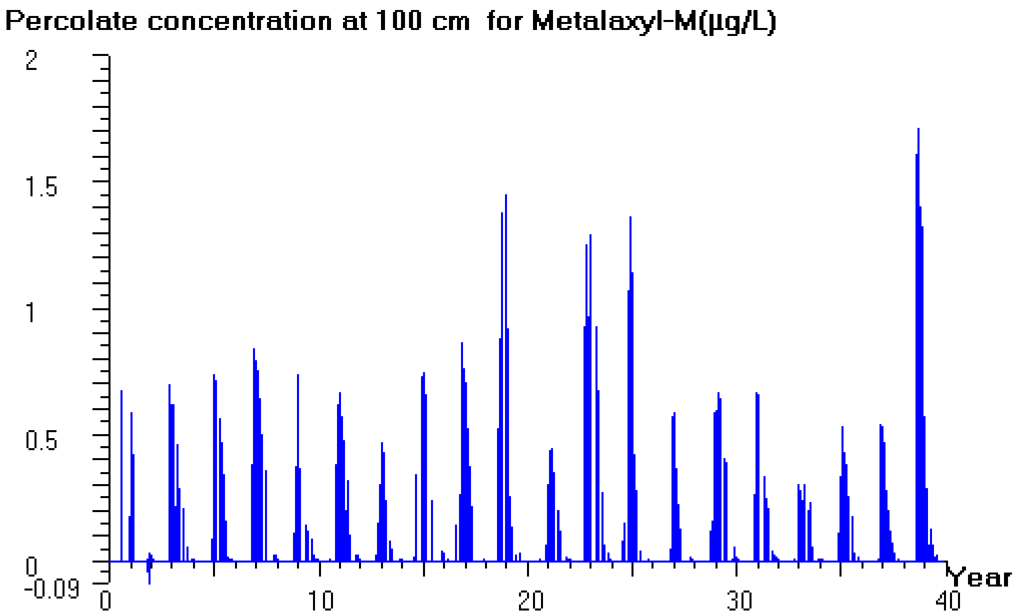


Figure 5-49: Time dependent concentration for metalaxyl considering FOCUS Hamburg climate and lysimeter soil (optimised parameter setting)

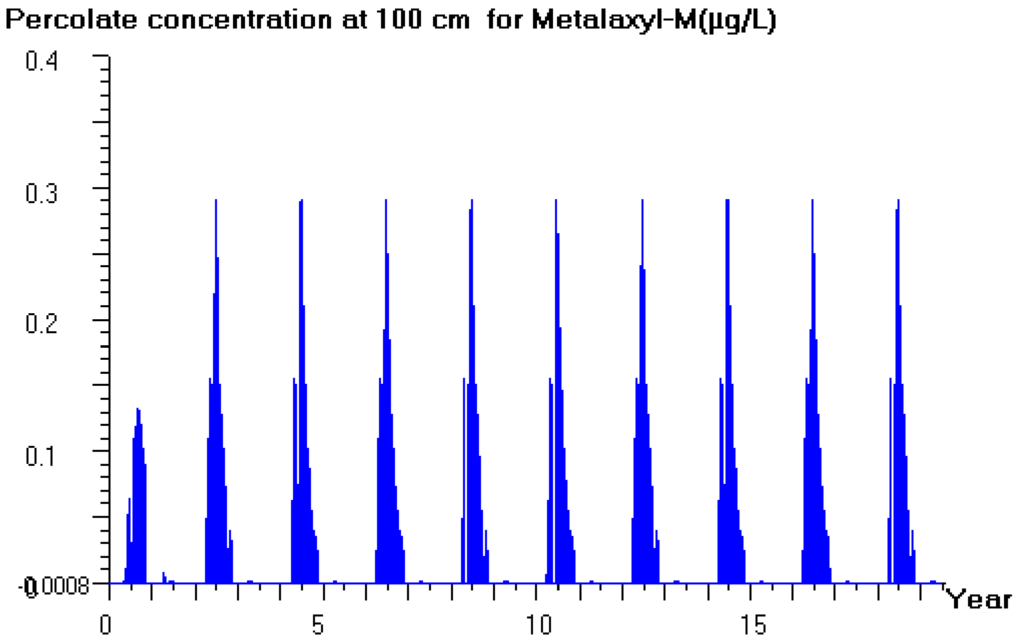


Figure 5-50: Time dependent concentration for metalaxyl considering FOCUS Hamburg soil and lysimeter weather (optimised parameter setting)

### 5.5.4 Comparison of the different combinations based on optimised parameters

Table 5-7 shows the main outcome of the results for the different extrapolations based on the inverse modelling optimisations. All simulation results refer to annual applications over 20 years. The experimental concentrations refer either to applications in one year only (single applications) or in several years (repeated applications).

Furthermore, the simulations with FOCUS climate describe the 80th percentile of long term annual concentrations whereas the simulation using the lysimeter climate are mainly based on the weather conditions in the second year which was repeated. That may lead to the situation that higher concentrations are detected in the lysimeter study (related to the first year) than long term concentrations in the simulation (driven by the second year).

The following conclusions can be nevertheless drawn from the results:

The maximum concentration for a certain combination of lysimeter site and lysimeter soil depends mainly on the lysimeter study with the following general tendencies (see also Table 5-7):

- If the lysimeter study was performed in Schmallenberg (Nordrhein-Westfalen) the combination of FOCUS Hamburg soil and lysimeter weather condition leads to a higher leachate concentration than the combination of FOCUS Hamburg climate and lysimeter soil conditions. This provides evidence that the Schmallenberg climate has in general higher rainfall than the FOCUS Hamburg climate but the soil conditions are more or less identical. This is not surprising since the FOCUS Hamburg scenario soil was parameterised based on the Borstel soil which is also used for the lysimeter studies performed in Schmallenberg.
- If the lysimeter study was performed in Neustadt (Rheinland-Pfalz) or Monheim the combination FOCUS Hamburg soil and lysimeter weather condition leads to lower leachate concentration than the combination FOCUS Hamburg climate and lysimeter soil conditions. This provides evidence that the FOCUS Hamburg climate has higher effective rainfall than the lysimeter climate and the lysimeter soils in Neustadt have less organic carbon than the FOCUS Hamburg soil conditions with respect to leaching (as shown also by the average organic carbon contents in the top metre of the soils at FOCUS Hamburg, Neustadt and Monheim with 0.78%, 0.49% and 0.60%, respectively).

For other comparisons (e.g. taking into account prolonged simulations with pure lysimeter conditions or pure FOCUS simulations) these rules are still valid but with some “random noise” due to unfavourable weather conditions during the study.

The effect of repeated annual versus single applications from PELMO computer simulations with prolonged lysimeter conditions showed no clear tendency (6 cases with no effect, 6 cases with higher concentrations than the respective single concentration, on average 70%, range 15% to 270%). That may lead to the conclusion that single applications in lysimeter studies are not sufficiently conservative. However, optimised input parameters of the related substances were all characterised by low sorption and fast degradation. That means that a significant plateau for most substances, which have been investigated here, cannot be expected even if these compounds are applied repeatedly over a longer study time. Instead the increased concentrations were caused by the already mentioned “random noise” due to a higher probability of unfavourable weather conditions for prolonged studies.

However, summarising all observations the following conclusions can be drawn:

- The model system “lysimeter study” responds sensitively to real soil and weather conditions in the experimental study. Small fluctuations with regard to these conditions may end with measurable effects on the concentrations in the leachate.
- The FOCUS scenario conditions cannot be considered as more conservative than the conditions during lysimeter studies according to BBA (1990). This is because the guideline mentions ranges (e.g. rainfall above 800 mm, organic carbon not above 1.5 %) rather than fixed values (as in the FOCUS scenarios).

Table 5-7: Results of the different combinations for prolonged simulations with optimised parameters based on the results of the inverse modelling and annual applications over 20 years (µg/L)

| No | Substance | Lysimeter site | Lysimeter<br>maximum measured annual concentration | Lysimeter climate<br>Lysimeter soil/crop(1)<br>Single app. | Lysimeter climate<br>Lysimeter soil/crop(1)<br>Annual app. | Lysimeter climate<br>FOCUS soil/crop(1) | FOCUS climate<br>Lysimeter soil/crop(2) | FOCUS climate (3)<br>FOCUS soil/crop(2) |
|---|---|---|---|---|---|---|---|---|
| 1 | Terbuthylazin | Schmallenberg | <0.01 (single app) | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 1 | Metabolite G23158 | Schmallenberg | 0.02 (single app) | 0.023 | 0.062 | 0.065° | 0.025 | 0.033 |
| 2 | Flufenacetat | Monheim | 0.03 (single app) | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 2 | Metabolite SAC | Monheim | 1.5 (single app) | 1.684 | 2.136 | 1.523 | 1.835 | 2.291 |
| 3 | Flufenacetat | Monheim | 0.03 (repeated app) | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 3 | Metabolite SAC | Monheim | 0.54 (repeated app) | 0.620 | 0.620 | 0.509 | 0.938 | 1.150 |
| 6 | Bentazon | Schmallenberg | 0.08 (repeated app) | 0.036 | 0.047 | 0.026° | 0.007 | 0.072 |
| 9 | Nicosulfuron | Schmallenberg | 0.17 (repeated app) | 0.071 | 0.071 | 0.039° | 0.018 | 0.011 |
| 10 | Metabolite 27550 of diazinon | Neustadt | 0.29 (repeated app) | 0.331 | 0.382 | 0.531 | 0.718+ | 1.495 |
| 11 | Metabolite 27550 of diazinon | Neustadt | 1.02 (single app) | 1.042 | 2.066 | 1.819 | 3.337+ | 4.270 |
| 13 | Isoproturon | Neustadt | 0.089 (single app) | 0.098 | 0.098 | 0.000 | 0.872+ | 0.053 |
| 14 | Metalaxyl | Neustadt | 0.05 (single app) | 0.067 | 0.125 | 0.131 | 0.298+ | 0.293 |

(1) maximum annual concentrations in µg/L (2) 80th percentile of annual/biennial concentrations (3) no plant uptake

+ Lysimeter soil significant less OC than FOCUS soil, application pattern slightly different ° lysimeter climate more vulnerable

The following conclusions could be drawn based on the analysis of the different combinations of simulations:

- The effect of repeated annual versus single applications from PELMO computer simulations with prolonged lysimeter conditions showed no clear tendency (6 cases with no effect, 6 cases with higher concentrations than the respective single concentration, on average 70%, range 15% to 270%). As optimised input parameters of the related substances were all characterised by low sorption and fast degradation a significant plateau is not expected to be formed even if these compounds are applied repeatedly over a longer study time. Instead, it is more likely that the increased concentrations were simply caused by the higher probability of unfavourable weather conditions for prolonged studies.
- It was previously concluded that simulations with lysimeter weather conditions lead to lower leachate concentrations than simulations with FOCUS Hamburg weather if the lysimeter study was performed at locations with smaller annual precipitation than in the FOCUS Hamburg scenario (Neustadt, Monheim). Based on this result, it can also be concluded that the irrigation requirements in the guideline for lysimeter studies (BBA 1990) are not able to account for differences between the climate at the site and the FOCUS scenario.
- The soil (in particular the organic carbon content) used for studies in Schmallenberg is quite comparable to the FOCUS Hamburg scenario since the respective soil from the location “Borstel” in northern Germany was also used for the parameterisation of the FOCUS Hamburg scenario. Differences between respective simulations are therefore related to different crop parameterisation.
- In contrast, the organic carbon contents of the lysimeter soils from the other two locations (Neustadt, Monheim), where lysimeter studies have also been conducted in Germany, are characterised by lower organic carbon content than in the FOCUS Hamburg scenario. As expected higher concentrations were often simulated with PELMO when using the lysimeter soil instead of the FOCUS scenario soil.
- According to the PELMO simulations the overall effect of these differences in lysimeter and FOCUS Hamburg scenario conditions on the annual concentrations could be on average described by a factor of 2 (see the differences in Table 5-7, columns 5 to 9).
- There is no clear trend that PELMO simulations with optimised parameter setting and the standard FOCUS Hamburg scenario (climate and soil, 80th percentile) result in higher concentrations than lysimeter results. In contrast, it seems that concentrations are calculated similarly as for the experimental study (FOCUS<lysimeter: 2 cases, FOCUS=lysimeter: 5 cases, FOCUS>lysimeter: 7 cases).
- It must be assumed from the comparison, that small fluctuation with regard to soil and weather conditions may end with measurable effects on the concentrations in the leachate.

## 5.6 Summary and Conclusions

For many years lysimeter studies were considered in German pesticide regulation as a higher tier study for the assessment of leaching potential. The presupposition of this approach is, that conservative conditions for leaching: a sandy soil with low organic carbon content and approximately 800 mm precipitation per year are representative as “realistic worst case” for German national conditions. In the past the representativeness of lysimeter studies was often controversially discussed and questioned with regard to their suitability as a direct trigger for decisions ("endpoint study"). Major concerns are related to the relatively short study time of normally two or three years in combination with single applications at the beginning of the experiment. This is often not in line with results of leaching models which predict significant leaching only after long time periods of repeated applications.

The specifications of the FOCUS Hamburg scenario are to a large extent based on the conditions for lysimeter studies according to BBA Part 4.3 (BBA 1990) and the German authorities are still accepting lysimeter studies as endpoint studies. Therefore, the suitability of lysimeter studies as a "process study" in this analysis mainly concentrated on the major concerns with regard to the short study time in combination with single applications at the beginning of the experiment.

This evaluation was conducted based on inverse modelling using the software tool “inversePELMO” which combines the simulation model PELMO with the optimisation tool “PEST” (Klein 2011). The idea was to obtain key parameters for risk assessment such as $Kf_{oc}$ (Freundlich sorption constant related to organic carbon) and $DegT_{50}$ (degradation time to 50%) directly from lysimeter studies. The aim of such a study is to get a deeper look into the processes that led to a certain lysimeter result. According to FOCUS (2009/2014) inverse modelling is recommended to be used to improve the standard modelling at tier 1 by considering additional information from higher tier studies.

For the evaluation studies performed between 1989 and 1999 at in total 4 different lysimeter sites were considered none of which were outside of Germany. It was assumed that this limitation would generally lead to comparable conditions as in the FOCUS Hamburg scenario. The lysimeter sites were located in Neustadt (Rhineland-Palatinate), Schmallenberg, Monheim (both North Rhine-Westphalia) and Hamburg.

Furthermore, only lysimeter studies were included which showed some leaching of the active compound or at least of one metabolite.

- In five lysimeter cores only parent residues were available (no metabolites).
- In two lysimeter cores only metabolite residues were detected.
- In eight lysimeter cores parent and metabolite residues were available.

In total degradation rates and adsorption values of eight different parent compounds and six metabolites were analysed by inverse modelling (some of the substances were considered in several optimisations). Unfortunately, key input data was not available from most lysimeter studies to perform inverse modelling with high quality. The issues were

- weather information not sufficient (only monthly values available)
- irrigation sometimes recorded on a monthly basis

- data on potential evapotranspiration not reported
- not all samples analysed (only radioactivity reported )

Some deficiencies could be explained by the fact that the lysimeter guideline (BBA 1990) does not consider the needs of inverse modelling optimisations. Especially, the lack of data on daily potential evapotranspiration led to fitting outside the expected range for the respective parameters.

Before the substance parameters were optimised the hydrology in soil was fitted based on initial soil moisture and crop specific Kc-factors. These factors are used to transpose the generic potential evaporation data to crop specific values. As long as the visual representation and the FOCUS chi² test of the cumulative leachate showed satisfactorily agreement with the experimental data an optimisation of the percolate was not rejected just because parameters deviated from normal parameterisation.

When optimising the parameters $Kf_{oc}$ and $DegT_{50}$ the cumulative substance amounts fluxes determined in the percolate were considered. In some situations the soil residues in the soil core after the study were used for the optimisation when the substance was never detected in the leachate. That was done to check whether still meaningful results can be obtained. However, based on these results it can be concluded that respective inverse modelling should not be performed since percolate concentrations are essential for an adequate optimisation of the results.

For a significant number of optimisations the standard FOCUS PELMO model could not adequately describe the substance transport in the lysimeter. Considering the total water storage capacity of the cores these studies were characterised by very early breakthrough of substances. It was concluded that these studies were partly influenced by preferential flow. Though this process is mostly happening in heavy soils preferential flow has been reported also in sandy soils. For example, an extensive study of 14C-Benazolin-ethyl in a parallel field and lysimeter study (Jene et al. 1998) was conducted. This study demonstrated that the solute transport exhibited through the upper part of the soil profile was dominated by matrix flow, whereas preferential flow occurred in the lower part. The authors additionally found that the travel time and the transformation behaviour of the reactive chemical were different in pathways which were only a few centimetres apart. It was assumed by Jene et al. (1998) that the collection and transport of the lysimeter cores may have induced disturbances of the soil structure which led to the formation of macro-pores within the soil core. Cracks may also exist between the lysimeter wall and the soil core.

In order to check the effect of longer study periods "prolonged" simulations were performed for some lysimeter studies previously considered for inverse modelling optimisation. These “prolonged" simulations should answer the question whether the length of a certain study was sufficient and the experimental study was not stopped before the bulk of the chemicals reached the bottom of the soil core. Another aspect of these prolonged simulations was to investigate the effect of multiple applications on long-term concentrations in the percolate. Mainly those studies were selected for further extrapolation modelling, in which the influence of preferential flow is assumed to be low and no major time lag of the substance break through between experimental and inverse modelling results occurred. However, two lysimeter studies in this selection could have still been influenced by fast transport processes in soil such as preferential flow. They were included in the analysis to check in how far extrapolation results are influenced by these processes. The optimised parameters for these two studies were not based on the preferential flow module. Simulations were performed using the optimised sorption and degradation parameters in combination with periodical climate as observed during the study. As only a limited number of weather years were available and as annual precipitation including irrigation during the study was at least 800 mm (lysimeter guideline BBA 1990) the first complete weather file (i.e. year 2) was always considered for the additional “prolonged” simulation period. In order to definitively estimate the time between application and the maximum concentration in the percolate pesticide was applied only in the first year according to the information given in the lysimeter study. Consequently, for the additional simulation period the crop rotation in the first experimental year was used. Furthermore, in order to analyse the maximum concentration in leachate for repeated applications an additional simulation was performed with annual applications.

Unfortunately this analysis could not answer all open questions with regards to minimum study duration and multiple application patterns. However some general observations were

- For substances with low sorption constants (optimisation 6, section 5.5.1.4) the experimental period according to BBA (1990) seems to be sufficient as it covers the maximum annual concentrations within the experimental period. Additionally, for this substance type the effect of multiple applications can be considered negligible.
- For substance with high sorption constants (optimisation 1, section 5.5.1.1) the maximum concentrations would not be observed during the standard study period according to BBA (1990). Additionally, the effect of multiple applications seems to be significant for this substance type. The maximum concentrations as well as the time the peaks occurred are strongly dependent on the pattern.
- No correlation could be found for substances in the medium sorption range between the sorption constant and the necessary study duration because the actual weather conditions and the differences in the lysimeter soils led to too much variability.
- The degradation rate should mainly influence the percolate difference for single and multiple applications. This was shown for two substances where significant differences were simulated for both situations (see section 5.5.1.1.1 and 5.5.1.1.2). However, due to the combination of half-life and sorption in soil only concentrations far below the trigger of 0.1 µg/L were simulated. Nevertheless the simulations demonstrate that multiple applications have a significant impact on the percolate concentrations for substances with $DegT_{50}$ above 60 days.

However, all these conclusions were only based on a limited number of studies and finally apply only for these studies. Prolonged simulations can be a meaningful addition tool to describe the lysimeter experiment over a longer period of time. When considering only these few studies standard FOCUS PELMO simulations based on optimised parameters led to concentrations below the respective simulations with standard Tier 1 input parameters. However, in a single exceptional situation the optimised parameters resulted in concentrations above the regulatory relevant trigger but not in the experimental studies.

Although the experimental data set was limited further simulations were performed in order to improve the understanding about the influence of the soil and weather conditions on the predicted concentrations in the percolate which is necessary for the extrapolation of lysimeter results. The following additional simulations were performed:

- Combination of the lysimeter soil (and application pattern) with standard (FOCUS Hamburg) scenario weather pattern.
- Combination of the lysimeter weather with standard (FOCUS Hamburg) soil and application pattern.

Based on the results of this evaluation it can be concluded that the maximum concentration for a certain combination depends mainly on the lysimeter study with the following trends:

- If the lysimeter study was performed in Schmallenberg (North Rhine Westphalia) the combination of FOCUS Hamburg soil and lysimeter weather condition leads to a higher leachate concentration than the combination of FOCUS Hamburg climate and lysimeter soil conditions. This provides evidence that the Schmallenberg climate has in general higher rainfall than the FOCUS Hamburg climate but the soil conditions are more or less identical. This is not surprising since the FOCUS Hamburg scenario soil was parameterised based on the Borstel soil which is also used for the lysimeter studies performed in Schmallenberg
- If the lysimeter study was performed in Neustadt (Rhineland-Palatinate) or Monheim (Nordrhein-Westfalen) the combination FOCUS Hamburg soil and lysimeter weather condition leads to lower leachate concentration than the combination FOCUS Hamburg climate and lysimeter soil conditions. This provides evidence that the FOCUS Hamburg climate has higher effective rainfall than the lysimeter climate whereas the lysimeter soils in Neustadt/Monheim lead to more substance transport since they are characterised by less organic carbon than the FOCUS Hamburg soil conditions (as shown also by the average organic carbon contents in the top metre of the soils at FOCUS Hamburg, Neustadt and Monheim with 0.78%, 0.49% and 0.60%, respectively).

For other comparisons (e.g. taking into account prolonged simulations with pure lysimeter conditions or pure FOCUS simulations) these rules hold still to some extent but with exceptions caused either by unfavourable weather conditions during the study or because of differences in the endpoints (maximum versus 80th percentile concentrations). As explained previously several questions with regard to the use of lysimeter studies either as "endpoint study" or "process study" were addressed. However, most of these open issues could not be adequately addressed due to various limitations of the existing studies. Nevertheless some conclusions could be drawn based on the analyses:

- The effect of repeated annual versus single applications from PELMO computer simulations with prolonged lysimeter conditions showed no clear tendency (6 cases with no effect, 6 cases with higher concentrations than the respective single concentration, on average 70%, range 15% to 270%). As optimised input parameters of the related substances were all characterised by low sorption and fast degradation a significant plateau is not expected to be formed even if these compounds are applied repeatedly over a longer study time. Instead, it is more likely that the increased concentrations were simply caused by the higher probability of unfavourable weather conditions for prolonged studies.
- For the compounds that did not occur in the leachate during the experimental studies in the prolonged simulations small concentrations far below the trigger were simulated with prolonged study time (not measurable).

- It was previously concluded that simulations with lysimeter weather conditions lead to lower leachate concentrations than simulations with FOCUS Hamburg weather if the lysimeter study was performed at locations with smaller annual precipitation than in the FOCUS Hamburg scenario (Neustadt, Monheim). Based on this result, it can also be concluded that the irrigation requirements in the guideline for lysimeter studies (BBA 1990) are not able to account for differences between the climate at the site and the FOCUS scenario.
- The soil (in particular the organic carbon content) used for studies in Schmallenberg is quite comparable to the FOCUS Hamburg scenario since the respective soil from the location “Borstel” in northern Germany was also used for the parameterisation of the FOCUS Hamburg scenario. Differences between respective simulations are therefore related to different crop parameterisation.
- In contrast, the organic carbon contents of the lysimeter soils from the other two locations (Neustadt, Monheim), where lysimeter studies have also been conducted in Germany, are characterised by lower organic carbon content than in the FOCUS Hamburg scenario. As expected higher concentrations were often simulated with PELMO when using the lysimeter soil instead of the FOCUS scenario soil.
- Finally, the study period of future lysimeter studies should depend on the properties of the substance and could be based on tier 1 simulations.

With regard to the general use of inverse modelling as a higher tier option in national groundwater risk assessment the following conclusions can be drawn:

- Given the selection of lysimeter studies used in this evaluation and considering the significant number of optimisations where the standard FOCUS PELMO model could not adequately describe the substance transport in the lysimeter, The use of inverse modelling cannot be recommended as a standard tool/approach for the refinement of tier 1 simulations,
- For a couple of studies inverse modelling showed evidence that the lysimeter study was influenced by preferential flow. In combination with expert judgement this technique could therefore be used to identify respective experiments.
- If a lysimeter study was obviously influenced by preferential flow the results of such an experiment are probably additionally conservative and are not directly comparable with Tier 1 simulations. It is recommended that in these situations the respective studies are further checked whether they could be nevertheless used for regulatory purposes.
- Simple considerations of the FOCUS chi$^2$ error (FOCUS 2006) as quality criteria for invers modelling as it is used by inversePELMO as a criteria doesn't seems to be appropriate since the individual experimental results could be more affected by higher variability than respective results from standard degradation studies. That was especially the case when substances were never detected in the percolate and optimisations were based only on soil residues after the study.
- Instead of focusing on FOCUS chi$^2$ error maximum acceptable deviations from existing tier 1 data on sorption and degradation should be defined which are considered acceptable to be used as higher tier information from inverse modelling. They should be defined in view of the distribution of existing laboratory data on degradation and

sorption. A possible procedure could be to check whether the optimised parameters meet the range between the 10th and 90th percentile of the distribution of these standard studies. If optimised parameters are clearly beyond these ranges their use in the risk assessment should be rejected.

## 5.7 References

BBA (1990): Richtlinie Teil IV 4-3. Lysimeteruntersuchungen zur Verlagerung von Pflanzenschutzmitteln in den Untergrund, Abteilung für Pflanzenschutzmittel und Anwendungstechnik der Biologischen Bundesanstalt Braunschweig.

FOCUS (2006): Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration. Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference Sanco/10058/2005 version 2.0, 434 pp

FOCUS (2009/2014): Assessing Potential for Movement of Active Substances and their Metabolites to Ground Water in the EU. The Final Report of the FOCUS Groundwater Work Group of FOCUS. – Sanco/13144/2010, version 3, 10 October 2014.

Jene, B., Fent G., and Kubiak, R. (1998): Untersuchung zum Vergleich von Ergebnissen aus Feldversuchen, Lysimetern und Simulationsrechnungen im Hinblick auf das Abbau- und Verlagerungsverhalten von 14C-Benazolin-ethyl in einem Sandboden (Report). Staatliche Lehr- und Forschungsanstalt für Landwirtschaft, Weinbau und Gartenbau Fachbereich Ökologie, D-67435 Neustadt/Wstr., Germany.

Klein, M. (2011): Erarbeitung eines Tools zur routinemäßigen Durchführung von Simulationsrechnungen zur inversen Modellierung. Report. FKZ 360 03 050, Umweltbundesamt.

# 6 Recommendations

## 6.1 Part A I:

The protection level of the tiered approach for the groundwater risk assessment in Germany has been investigated in this project.

According to the analysis with 104 substances the national approach for the selection of modelling endpoints differs in 37% (38 substances, 8 active compounds and 30 metabolites) from the EU procedure (29% because of different sorption constants, 13% because of different half-lives). However, 6 of these 30 transformation products were not considered further since they were formed already by parent compounds characterised by different national and EU parameter selection.

Looking at all aspects of the detailed analysis the result indicate, that both methodologies, the national criteria as described in Holdt et al. (2011) as well as the EU methodology for lower tier groundwater modelling ensure for the majority of cases a safe and conservative estimation of the groundwater risk assessment especially when uncertainties correlated with analytical determinations and model haziness below 0.01 µg/L are ignored (national methodology: 81.7%, EU methodology: 74%). Uncertainties with regard to a safe prediction of leachate concentrations by modelling have not been identified for parent compounds but remain especially for a number of degradation products.

The additional impact analysis where the results were compared with regulatory limits confirmed the direct comparisons and it was concluded that the impact of these situations was only minor: Independent on the selection methodology (EU or national) only 3% false negative results were found for parent compounds. The respective result for transformation product was 7% and 5.6% for EU and national methodology, respectively.

It was further confirmed that both methodologies (EU and national endpoint selection) ensure in general a safe and conservative estimation of the groundwater risk assessment also for substances where no correlation between the sorption constant and the organic carbon content can be found. It was concluded that basically no different outcome was found independent which methodology was finally applied. However, when comparing the two selection approaches (EU and German) the EU methodology showed less false-positive comparisons.

According to the analysis with 104 substances the degree of harmonisation between national and EU methodology is about 63% (37% of compounds with different modelling endpoints).

Considering the fact that both methodologies are not able to guarantee 100% safe predictions and considering also that the overall differences between both methodologies are not significant (national methodology: 81.7%, EU methodology: 74% more conservative than lysimeter) and even identical when comparing the calculation against the trigger (EU and national methodology: 3% false negative results for parent compounds) it is recommended to check further options for the harmonisation of the national input parameter selection with the European methodology.

## 6.2 Part A II

Inverse modelling studies were conducted using the software tool “inversePELMO” which combines the simulation model PELMO with the optimisation tool “PEST” (Klein 2011b). The idea was to obtain key parameters for risk assessment such as $Kf_{oc}$ (Freundlich sorption constant related to organic carbon) and $DegT_{50}$ (degradation time to 50%) directly from lysimeter studies.

The analysis showed that for some substances different breakthrough times have been identified between modelling and experimental results which provides reasons to assume, that some of the investigated lysimeter experiments were partly influenced by preferential flow. Though this process is mostly happening in heavy soils preferential flow has been reported also in sandy soils.

It seems necessary to develop objective criteria for the decision whether an inverse modelling study lead to acceptable results.

- Simple considerations of recommended FOCUS $chi^2$ as a criteria doesn't seems to be appropriate since individual experimental results could be more affected by higher variability than respective results from standard degradation study. This is surely the case for soil residues after the study.
- Instead maximum acceptable deviations from existing tier 1 data on sorption and degradation should be defined which are considered acceptable to be used as higher tier information from inverse modelling studies. They should be defined in view of the distribution of existing laboratory data on degradation and sorption. A pragmatic approach could be to use the range of existing data as criterion or alternatively the 10th and 90th percentile of the distribution

Further recommendations:

- If there is evidence that the study period of the lysimeter study was not sufficient (based on the results of prolonged simulations as performed in this project) the respective study should not be used as "endpoint study". At least, the study could be used as "process study" which means that it could be used to obtain higher tier input data followed by "prolonged" computer simulations.
- If there was evidence that a lysimeter study was influenced by preferential flow inverse modelling in combination with expert judgement could be used to identify these studies.
- If a lysimeter study was obviously influenced by preferential flow the results of such an experiment are probably additionally conservative and are not directly comparable with Tier 1 simulations. It is recommended that in these situations the respective studies are further checked whether they could be nevertheless used for regulatory purposes.
- Optimised parameters outside the defined range of laboratory input parameters (e.g. below minimum or above maximum laboratory value) should not be considered as higher tier input data from modelling studies.

Finally, the study period of future lysimeter studies should be adapted dependent on substance properties. For the assessment of the necessary duration tier 1 simulation could be used.

# 7 Appendices

## 7.1 Appendix 1: Description of the data base

The database for collecting all relevant PELMO input parameters was developed using Microsoft Visual Basic. In the following some information about the principal structure is given before the database is described in more detail in the following chapter.

The principal structure considered for the data base is presented in the following figure. Aggregated information for each compound is presented in five tabs. Additionally, specific information can be loaded about sorption or degradation studies (laboratory or field). The addition information on individual sorption studies can be directly loaded from the form showing the aggregated data.

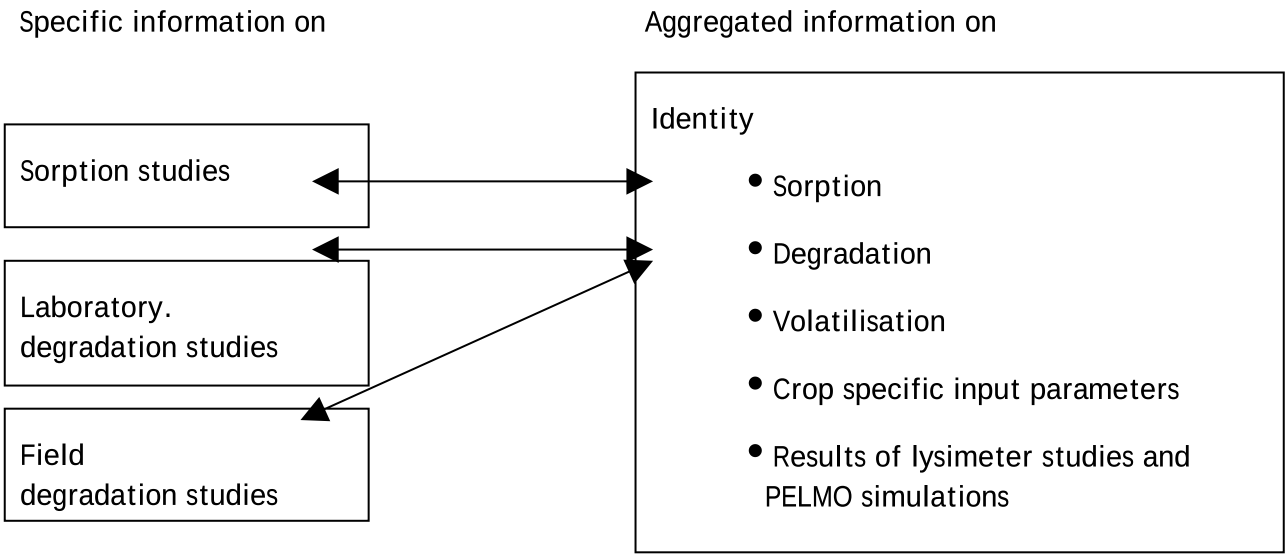
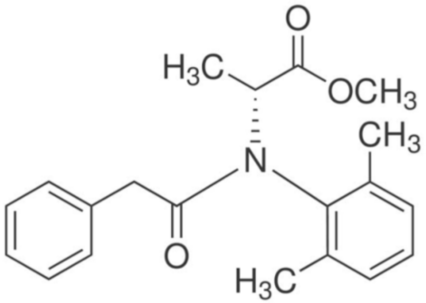
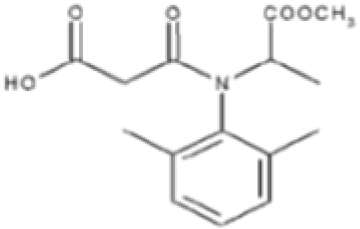
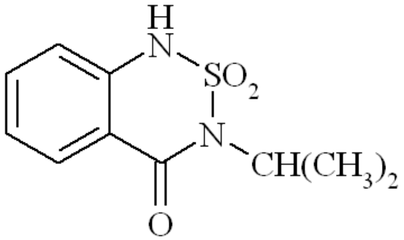


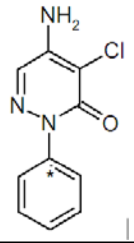
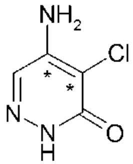
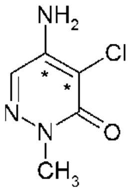
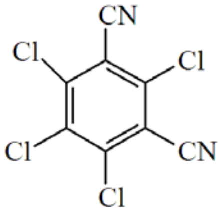
Figure 7-1: Principal structure of the data base

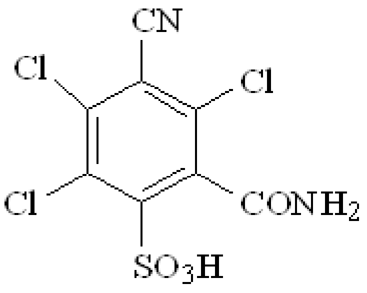
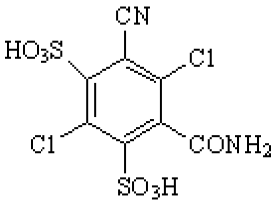
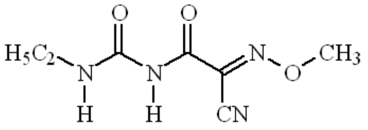
***<u>The rest of this appendix was separated as it may have contained confidential information.</u>***

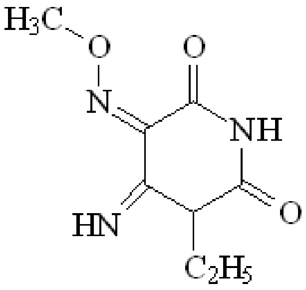
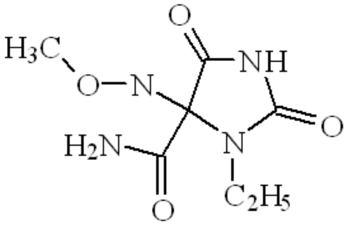
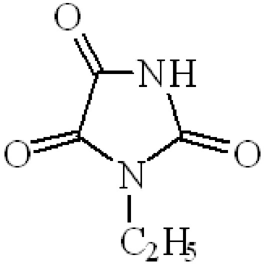
## 7.2 Appendix 2: Content of the data base

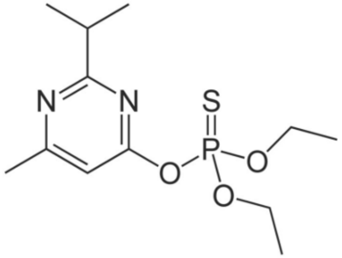
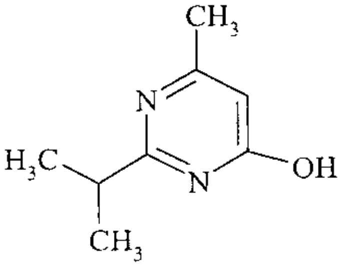
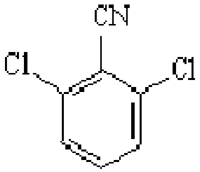
Table 7-1: Principal properties of the compounds available in the database

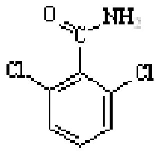
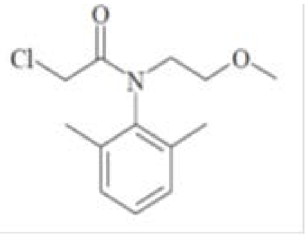
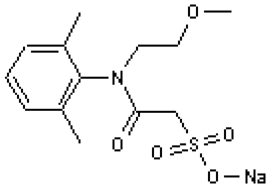
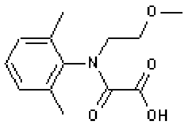
| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 58 | Benalaxyl-M | A | 71626-11-4 | Methyl-N-phenylacetyl-N-2,6-xylyl-DL-alaninate | C20H23NO3 | 325.4 |  |
| 59 | M1 (or M7) | M | | Methyl-N-malonyl-N-2,6-xylyl-alaninate | C15H19NO5 | 293.32 |  |
| 42 | Bentazon | A | 25057-89-0 | 3-isopropyl-(1H)-2,1,3-benzothiadiazin-4-(3H)-one-2,2-dioxide | C10H12N2O3S | 240.3 |  |

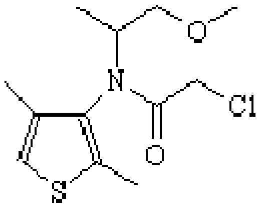
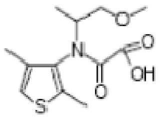
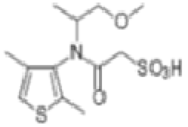
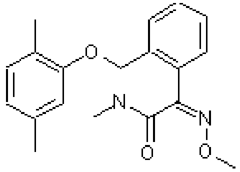
| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 1 | Chloridazon | A | 1698-60-8 | 5-Amino-4-chloro-2-phenylpyridazin-3(2H)-one | C10H8ClN3O | 221.6 |  |
| 2 | Metabolite B | M |  | 5-amino-4-chloropyridazin-3(2H)-one |  | 145.55 |  |
| 3 | Metabolite B1 | M |  | 5-amino-4-chloro-2-methylpyridazine-3-one |  | 159.6 |  |
| 43 | Chlorthalonil | A | 1897-45-6 | Tetrachlorisophthalonitril | C8Cl4N2 | 265.9 |  |

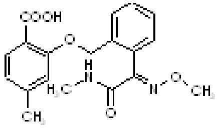
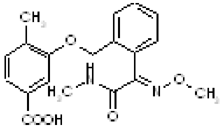
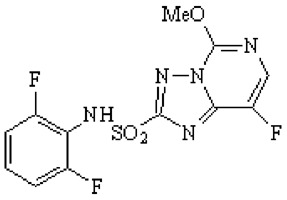
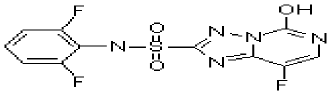
| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 44 | R417888 | M | | 2-amido-3,5,6-trichloro-4-cyanobenzene sulphonic acid | C8H3Cl3N2O4S | 329.6 |  |
| 45 | R419492 | M | | 4-amido2,5-dichloro-6-cyanobenzene-1,3-disulphonic acid | C8H4Cl2N2O7S2 | 375.2 |  |
| 46 | R 611965 (M5, SDS 46851) | M | | 3-carbamyl-2,4,5-trichlorobenzoic acid | | 267.49 | |
| 78 | Cymoxanil | P | | | C7H10N4O3 | 198.18 |  |

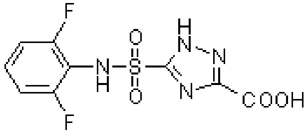
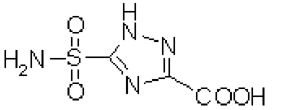
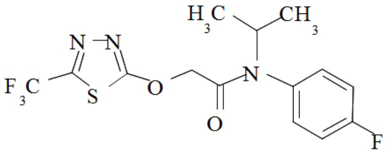
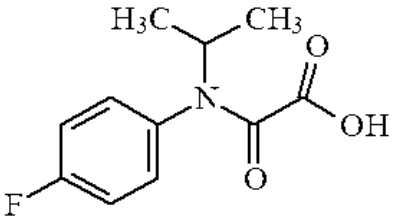
| No. | Name | Type<br>* | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 79 | IN-U3204 | M | 71342-66-0 | 1-ethyldihydro-6-imino-2,3,5(3H)-pyrmidinetrione-5-(O-methyloxime) |  | 198.2 |  |
| 80 | IN-KQ960 | M |  | 3-ethyl-4-(methoxyimino)-2,5-dioxo-4-imidazolidinecarboxamide |  | 216.2 |  |
| 81 | IN-T4226 | M | 57012-86-9 | Ethylimidazolidinetrion |  | 142 |  |

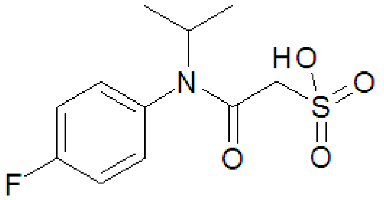
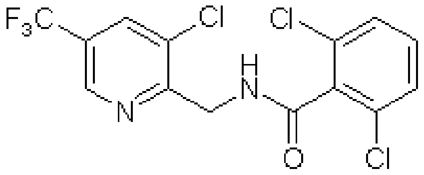
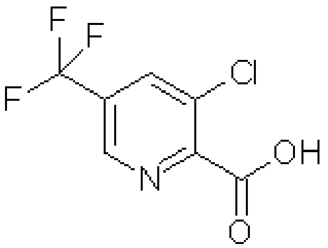
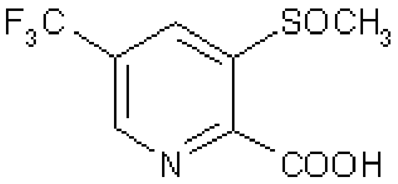
| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 60 | Diazinon | A | 333-41-5 | O,O-Diethyl O-[4-methyl-6-(propan-2-yl)pyrimidin-2-yl] phosphorothioate | C12H21N2O3PS | 304.35 |  |
| 61 | G27550 | M |  | 2-isopropyl-4-methyl-6-hydroxypyrimidine | C8H11N2O | 151 |  |
| 62 | Dichlobenil | A | 1194-65-6 | 2,6-Dichlorobenzonitrile | C7H3Cl2N | 172 |  |

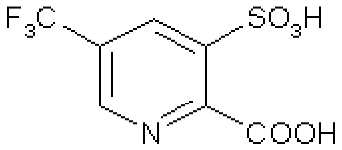
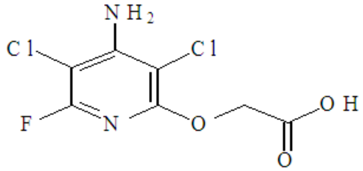
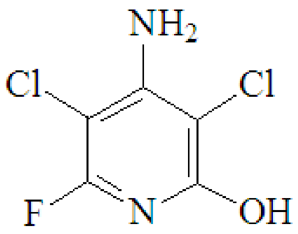
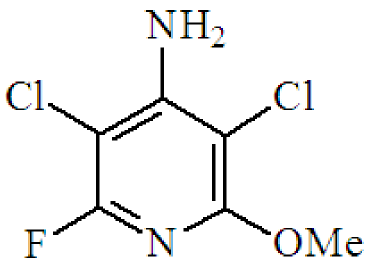
| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 63 | BAM | M | 2008-58-4 | 2,6-Dichlorobenzamide | C7H5Cl2NO | 190.03 |  |
| 50 | Dimethachlor | A | 50563-36-5 | 2-chloro-N-(2-methoxyethyl)acetat-2´,6´-xylidene | C13H18ClNO2 | 255.8 |  |
| 51 | CGA 354742 | M | | [(2,6-dimethyl-phenyl)-(2-methoxyethyl)-carbamyl]-methansulfonsäure, Na-Salz | C13H18NNaO5S | 323 |  |
| 52 | CGA 50266 | M | | N-(2,6-dimethyl-phenyl)-N-(2-methoxy-ethyl)-oxalaminsäure) | C13H17NO4 | 251 |  |

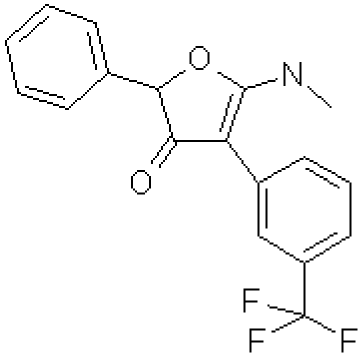
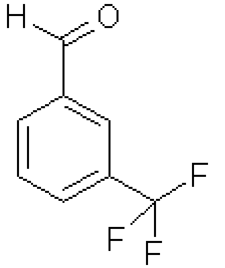
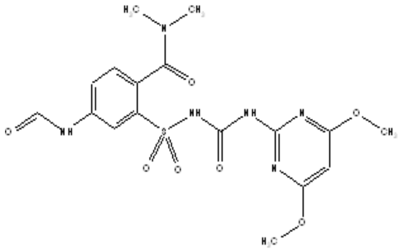
| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 64 | Dimethenamid-P | A | 163515-14-8 | S-2-chloro-N-(2,4-dimethyl-3-thienyl)-N-(2-methoxy-1-methylethyl)-acetamide | C12H18ClNO2S | 275.79 |  |
| 65 | M23 | M |  | Oxalamide, N-(2,4-dimethyl-3-thienyl)-N-(2-methoxy-1-methylethyl)oxamic acid | C12H17NO4S | 271.34 |  |
| 66 | M27 | M |  | Sulfonate,2-[N-(2,4-dimethyl-3-thienyl)-N-(2-methoxy-1-methylethyl)amino |  | 320.41 |  |
| 67 | Dimoxystrobin | A | 149961-52-4 | N-Methyl (E)-methoxyimino-2-[2-((2,5-dimethylphenoxy)methyl)phenyl]-acetamide | C19H22N2O3 | 326.39 |  |

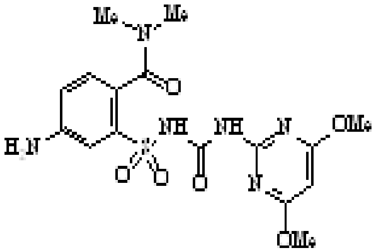
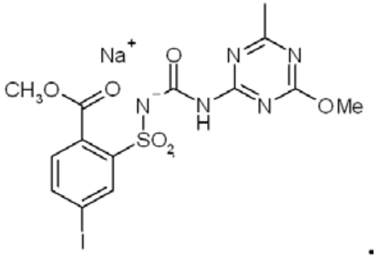
| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 68 | 505M8 | M | | | C19H20N2O5 | 356.4 |  |
| 69 | 505M9 | M | | | C19H20N2O5 | 356.4 |  |
| 88 | Florasulam | P | 145701-23-1 | 2´, 6´, 8´-Trifluor-5-methoxy-[1,2,4]-triazolo[1,5-c]pyrimidin-2-sulfonanilid | C12H8F3N5O3S | 359.3 |  |
| 89 | 5-OH-XDE-570 | M | | N-(2,6difluorophenyl)-8-fluoro-5-hydroxyl(1,2,4)triazolo(1,5c)pyrimidine-2-sulphonamide | C11H5F3N5O3S | 345.26 |  |

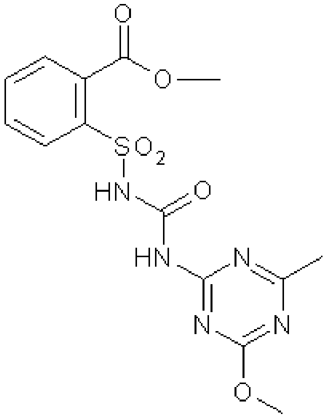
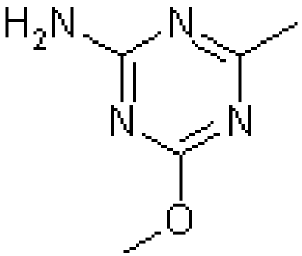
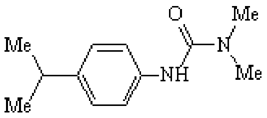
| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 90 | DFP-ASTCA | M | | N-(2,6-difluorophenyl)-5-aminosulphonyl-1H-1,2,4)triazole-3-carboxylic acid | C9H6F2N4O4S | 274.25 |  |
| 91 | ASTCA | M | | 5-(aminosulphonyl)-1H-1,2,4-triazole-3-caroxylic acid | C3H4N2O4S | 162.17 |  |
| 4 | Flufenacetat | A | 142459-58-3 | N-(4-Fluor-phenyl)-N-isopropyl-2-(5-trifluormethyl-[1,3,4]thiadiazol-2-yloxy)-acetamid | C14H13F4N3O2S | 363.34 |  |
| 5 | FOE 5043-Oxalat | M | | M1 | | 225.2 |  |

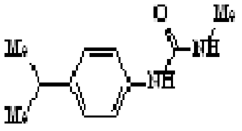
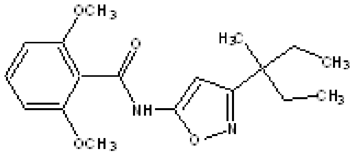
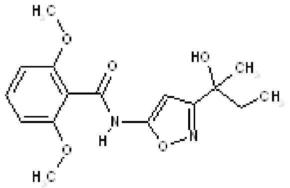
| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 6 | FOE 5043-Sulfonic Acid | M | | M2 | | 275.3 |  |
| 101 | Fluopicolide | P | | 2,6-dichloro-N-{[3-chloro-5-(trifluoromethyl)-2-pyridinyl]methyl}benzamide | C14H11Cl3F3N2O | 383.59 |  |
| 102 | M-02 = PCA = AE C657188 (UMET/2) | M | | 3-chloro-5trifluoromethylpyridine-2-carboxylic acid | | 225.56 |  |
| 103 | M-05 = AE 1344122 = P1 (=RPA433497) | M | | 3-methylsulfinyl-5-trifluoro-methylpyridine-2-carboxylic acid | | 253 |  |

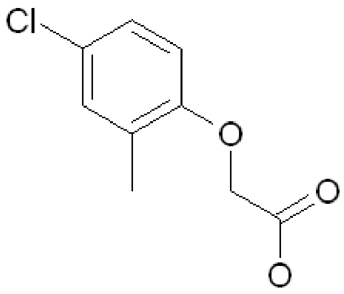
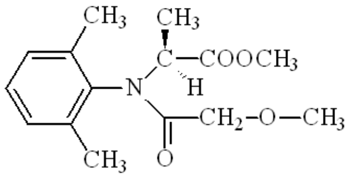
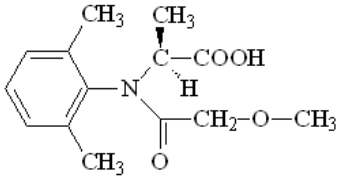
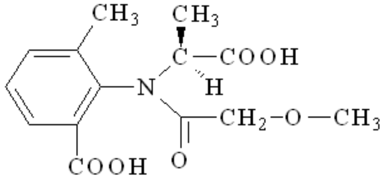
| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 104 | M-10 = AE 1344123 = P4 (=RPA 433965) | M | | 3-sulfo-5-trifluoromethyl pyridine-2-carboxylic acid | | 271.17 |  |
| 7 | Fluroxypyr | A | 69377-81-7 | 4-amino-3,5-dichloro-6-fluoro-2-pyridyloxyacetic acid | C7H5Cl2FN2O3 | 255 |  |
| 8 | Pyridinol | M | | 4-Amino-3,5-dichloro-6-fluoro-pyridin-2-ol | | 197 |  |
| 9 | Methoxypyridine | M | | 4-Amino-3,5-dichloro-6-fluoro- methoxypyridine | | 211 |  |

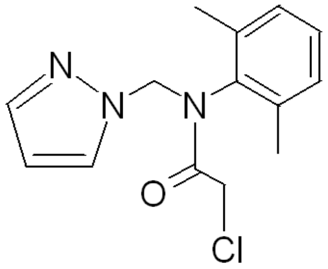
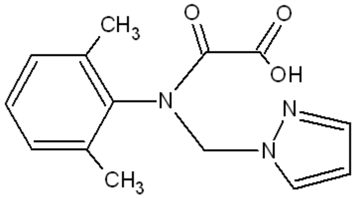
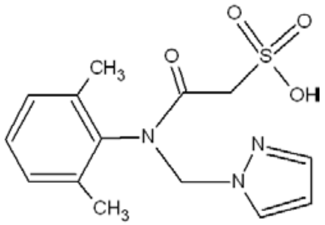
| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 70 | Flurtamone | A | 96525-23-4 | (RS)-5-Methylamino-2-phenyl-4-(a,a,a-trifluoro-m-tolyl)furan-3(2H)-one |  | 333.31 |  |
| 71 | TFMBA | M | 454-92-2 | Trifluoromethylbenzoic acid |  | 190.1 |  |
| 99 | Foramsulfuron | P | 173159-57-4 | 1-(4,6-dimethoxypyrimidin-2-yl)-3-(2-dimethyl-carbamoyl-5-formamidophenylsulfonyl)harnstoff | C17H20N6O7S | 452.45 |  |

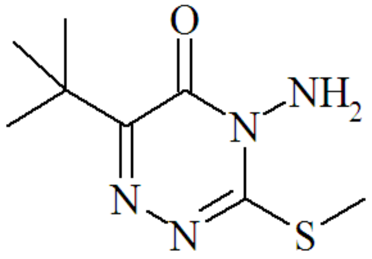
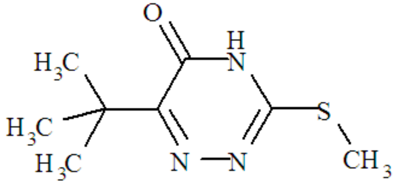
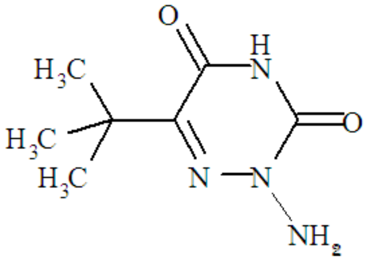
| No. | Name | Type<br>* | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 100 | AE F130619 | M |  |  | C16H20N6O6S | 424 |  |
| 85 | Iodosulfuron | P | 144550-36-7 | Methyl-4-iodo-2-[3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-ureidosulfonyl]benzoate, sodium salt |  | 529.28 |  |

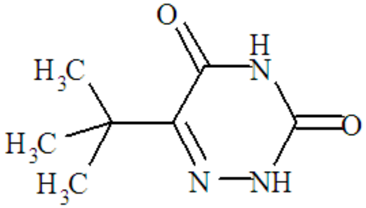
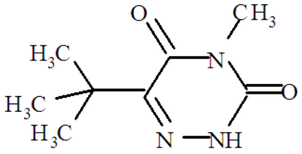
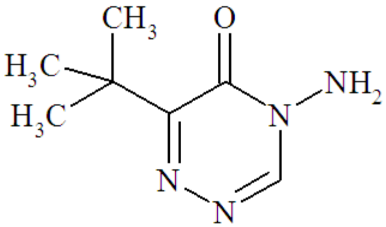
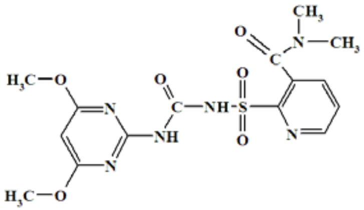
| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 86 | AE F075736 (= Metsulfuron-Methyl) | M |  | 2-[3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)ureidosulfonyl] benzoate | C13H13N5O6S | 381.3 |  |
| 87 | AE F059411 (M 1, IN-A4098, Triazine-Amine) | M |  | 2-amino-4-methoxy-6-methyl-1,3,5-triazine | C5H8N4O | 140.15 |  |
| 72 | Isoproturon | A | 34123-59-6 | 3-(4-Isopropylmethylphenyl)-1,1-dimethylurea | C12H18N2O | 206.3 |  |

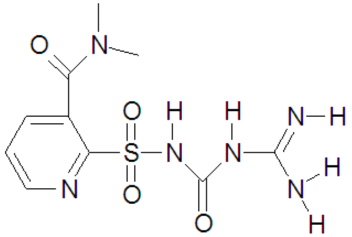
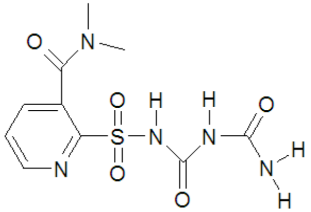
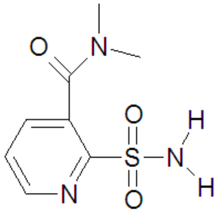
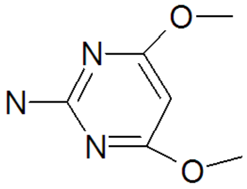
| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 73 | Desmethylisoproturon | M | 34123-57-4 | N-(4-isopropylphenyl)-N'-methylurea | C11H16N2O | 192.26 |  |
| 53 | Isoxaben | A | 82-558-50-7 | N-[3-(1-ethyl-1-methylpropyl)isoxazol-5-yl]-2,6-dimethoxybenzamide | C18H24N2O4 | 332.4 |  |
| 54 | Hydroxy-Isoxaben | M |  |  | C16H18N2O5 | 320.35 |  |

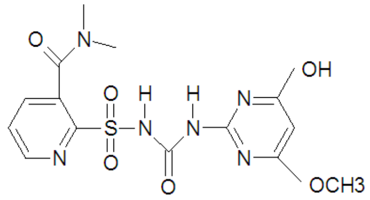
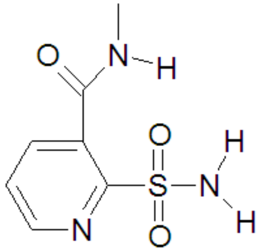
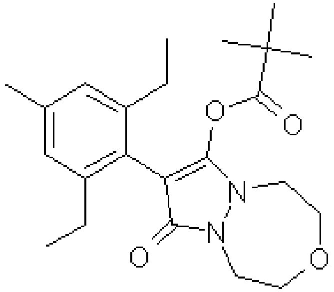
| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 77 | MCPA | P | 94-74-6 | 4-Chlor-o-tolyloxyessigsäure | C9H9ClO3 | 200.3 |  |
| 74 | Metalaxyl-M | P | 70630-17-0 | Methyl-(R )-2-{[(2,6-dimethylphenyl)methoxyacetyl]amino}propionate | C15H21NO4 | 279.3 |  |
| 75 | CGA 62826 (=RS-Form) = NOA 409045 (=R-Form) | M |  | NOA 409045 (=R-Form) =NOA436575 (=S-Form) |  | 265.3 |  |
| 76 | CGA 108906 | M |  |  |  | 265.3 |  |

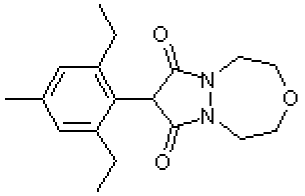
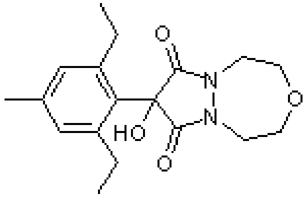
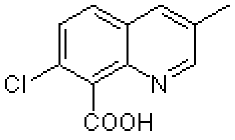
| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 82 | Metazachlor | P | 67129-08-2 | 2-Chlor-N-(pyrazol-1-yimethyl)acet-2',6'-xylidid | C14 H16 Cl N3 O | 277.8 |  |
| 83 | BH 479-4 | M |  | N-(2,6-dimethylphenyl)-N-(1H-pyrazol-1-ylmethyl)oxalamide |  | 273.29 |  |
| 84 | BH 479-8 | M |  | N-(2,6-dimethylphenyl)-N-(1H-pyrazol-1-ylmethyl)aminocarbonylmethylsulfonic acid |  | 323.37 |  |

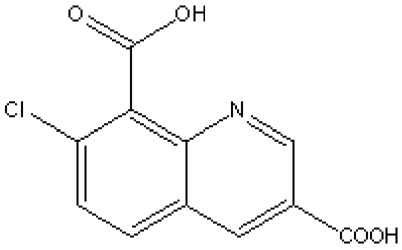
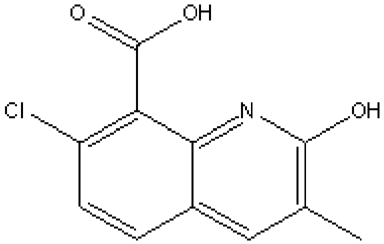
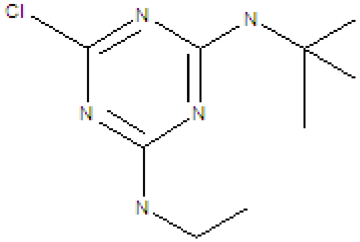
| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 10 | Metribuzin | A | 21087-64-9 | 4-Amino-6-tert-butyl-3-methylthio-1,2,4-triazin-5(4H)-one (ISO) | C8H14N4OS | 214.3 |  |
| 11 | DA Desaminometribuzin | M |  |  | C8H13ON3S | 171 |  |
| 12 | DK Diketometribuzin M02 | M |  |  | C7H11O2N3 | 184 |  |

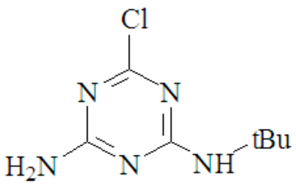
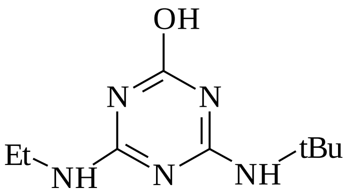
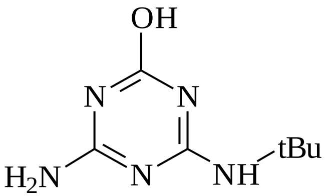
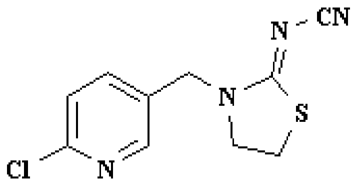
| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 13 | DADK Desamino-diketometribuzin M03 | M |  |  | C7H11O2N3 | 169 |  |
| 14 | Metabolit M17/ 4-methyl-DADK -metribuzin | M |  |  | C8H13O2N3 | 183 |  |
| 15 | U1 Desmethylthio-metribuzin | M |  |  | C7H12ON3 | 154 |  |
| 16 | Nicosulfuron | A | 111991-09-4 | 2-(4,6-dimethoxypyrimidin-2-ylcarbamoylsulfamoyl)-N,N-dimethylnicotinamide | C15H18N6O6S | 410.14 |  |

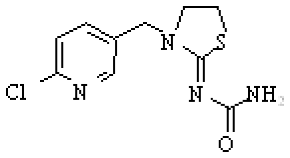
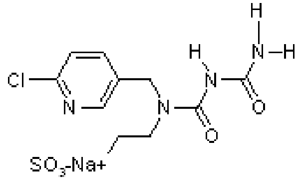
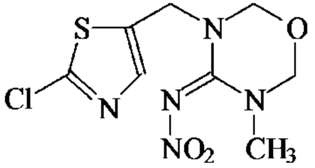
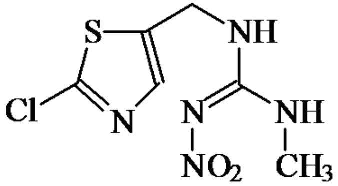
| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 17 | AUSN | M | | 2-(3-amidinoureidosulfonyl)-N,N-imethylnicotinamide (IN-HYY21) | | 314.36 |  |
| 18 | UCSN | M | | N,N-dimethyl-2-ureidocarbonyl-sulfamoylnicotinamide (IN-GDC42) | | 315.3 |  |
| 19 | ASDM | M | | N,N-dimethyl-2-sulfamoyl-nicotinamide (IN-V9367) | | 229.2 |  |
| 20 | ADMP | M | | IN-J0290 | | 155.16 |  |

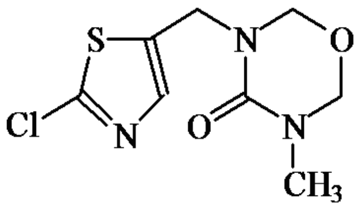
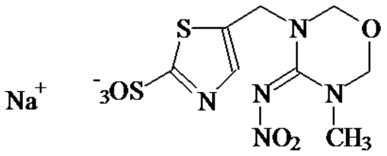
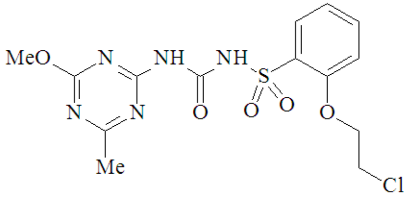
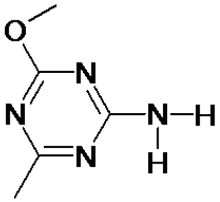
| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 21 | HMUD | M |  | HMUD (IN-37740) 2-(4-hydroxy-6-methoxypyrimidin-2-ylcarbamoylsulfamoyal)-N,N-dimethylnicotinamide |  | 336.4 |  |
| 22 | MU-466 | M |  | MU-466 |  | 215.23 |  |
| 92 | Pinoxaden | P | 243973-20-8 | 8-(2,6-diethyl-p-tolyl)-1,2,4,5-tetrahydro-7-oxo-7H-pyrazolo[1,2-d][1,4,5]oxadiazepin-9-yl-2,2-dimethylpropionate | C23H32N2O4 | 400.5 |  |

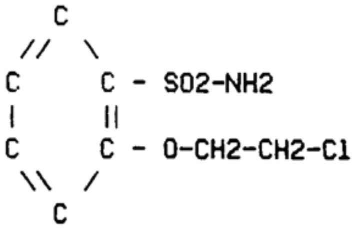
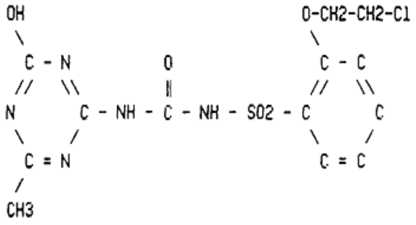
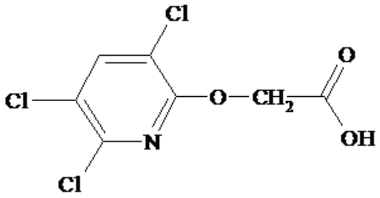
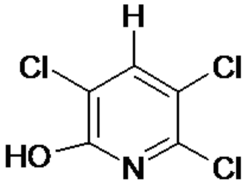
| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 93 | NOA407854 | M | | | C18H24N2O3 | 314.36 |  |
| 94 | NOA447204 | M | | | C18H24N2O4 | 332.37 |  |
| 55 | Quinmerac | A | 90717-03-6 | 7-chloro-3-methylquinoline-8-carboxylic acid | C11H8ClNO2 | 221.64 |  |

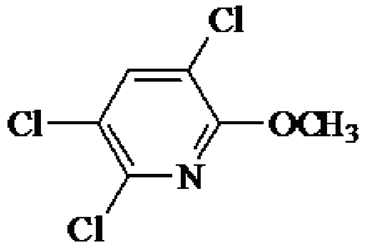
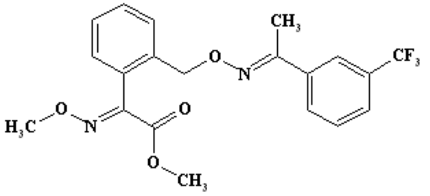
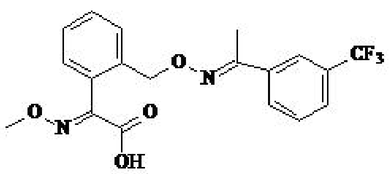
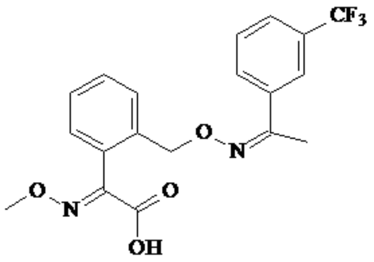
| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 56 | BH 518-2 | M |  | 7-chloro-3-methylquinoline-8-carboxylic acid | C11H6O4NCl | 251.5 |  |
| 57 | BH 518-5 | M |  | 7-chloro-2-hydroxy-3-methylquinoline-8-carboxylic acid | C11H8O3NCl | 237.5 |  |
| 23 | Terbuthylazin | A | 5915-41-3 | N2-tert-butyl-6-chloro-N4-ethyl-1,3,5-triazine-2,4-diamine | C9H16Cl N5 | 229.71 |  |

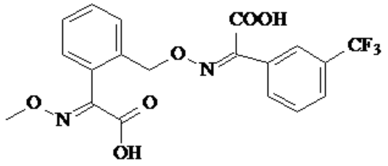
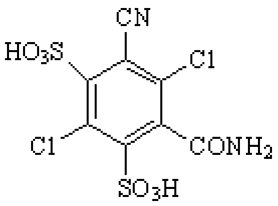
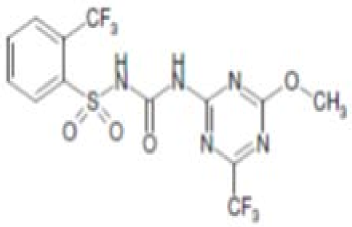
| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 24 | MT1 GS 26379 | M | | Des-ethyl-Terbuthylazin | | 201.67 |  |
| 25 | MT13 GS 23158 | M | | Hydroxy-Terbuthylazin | | 211.28 |  |
| 26 | MT14 / GS 28620 | M | | Des-ethyl-Hydroxy-Terbuthyl-azin | | 183.22 |  |
| 47 | Thiacloprid | A | 111988-49-9 | N-{3-[(6Chloro-3-pydridinyl)methyl]-1,3-thiazolan-2-ylinden}cyanamide | C10H9ClN4S | 252.7 |  |

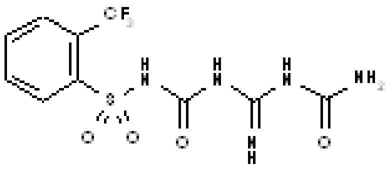
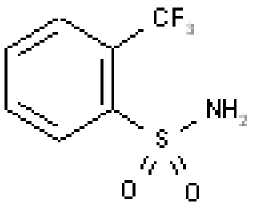
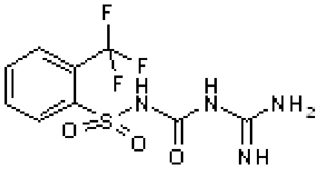
| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 48 | M02, YRC 2254-amid | M | | (Z)-[3-[(6-chloro-3-pyridinyl)methyl]-2-thiazolidinylidene[urea) | C10H11ClN4OS | 270.7 |  |
| 49 | M30, YRC-sulfonsäure, Na-Salz | M | | 2[1-(6-chloropyridine-3-ylmethyl)-3-carbamoyl-ureido] | C10H11ClN4NaO5S | 358.7 |  |
| 27 | Thiamethoxam | A | 153719-23-4 | 3-(2-chloro-thiazol-5-ylmethyl)-5-methyl-[1,3,5]oxadiazinon-4-ylidene-N-nitroamine | C8H10ClN5O3S | 291.72 |  |
| 28 | Clothianidin CGA 322704 | M | | N-(2-chloro-thiazol-5-yl-methyl)-N'-methyl-N''-nitro-guanidine | C6H8ClN5O2S | 249.7 |  |

| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 29 | CGA 355190 | M |  | 1-(2-chloro-thiazol-5-ylmethyl)-3-methyl-urea | C8H10ClN3O2S | 247.1 |  |
| 30 | NOA 459602 | M |  | 5-(5-methyl-4-nitroimino-[1,3,5]oxadiazinan-3-ylmethyl)-thiazole-2-sulfonic acid | C8H10O6N5S2 | 337.3 |  |
| 31 | Triasulfuron | A |  | 1-[2-(2-Chloroethoxy)phenylsulfonyl]-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea | C14H16ClN5O5S | 401.8 |  |
| 32 | CGA 150829 | M |  |  | C5H8N4O | 140.15 |  |

| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 33 | CGA 161149 | M | | | | ? |  |
| 34 | CGA 195660 | M | | | | ? |  |
| 35 | Triclopyr (Säure) | A | 55335-06-3 | 3,5,6-trichloro-2-pyridyloxyacetic acid | $C_7H_4Cl_3NO_3$ | 256.5 |  |
| 36 | TCP (3,5,6-Trichlor-2-pyridinol) | M | | | | 198.4 |  |

| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 37 | TMP (3,5,6-Trichlor-2-methoxy-pyridin | M | | | | 212.5 |  |
| 38 | Trifloxystrobin | A | 141517-21-7 | (E,E)-Methoxyimino-{2-[1-(3-trifluoromethyl-phenyl)-ethylidene-amino-oxymethyl]-phenyl}-acetic acid methyl ester | C20H19F3N2O4 | 408.37 |  |
| 39 | CGA 321113 | M | | (E,E)-Methoxyimino-{2-[1-(-3-trifluoro methyl-phenyl)-ethylideneamino-oxymethyl]-phenyl}-acetic acid | C19H17F3N2O4 | 394.3 |  |
| 40 | CGA 373466 (ZE) | M | | (Z,E)-Methoxyimino-{2-[1-(3-trifluoro methyl-phenyl)-ethylideneamino-oxymethyl]-phenyl}-acetic acid | C19H17F3N2O4 | 394.3 |  |

| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 41 | NOA 413161 | M | | (E,Z)-{2-[carboxy-(3-trifluoromethyl-phenyl)-methyleneaminooxy-methyl]-phenly}-methoxy-iminoacetic acid | C19H15F3N2O6 | 424.3 |  |
| 45 | R419492 | M | | 4-amido2,5-dichloro-6-cyanobenzene-1,3-disulphonic acid | C8H4Cl2N2O7S2 | 375.2 |  |
| 95 | Tritosulfuron | P | 142469-14-5 | 1-[4-methoxy-6-(trifluoromethyl)-1,3,5-triazin-2-yl]-3-[2-(trifluoromethyl)benzenesulfonyl]urea | C13H9F6N5O4S | 445.3 |  |

| No. | Name | Type * | CAS No. | IUPAC Name | Elemental formula | Molecular mass (g/mol) | Chemical structure |
|---|---|---|---|---|---|---|---|
| 96 | BH 635-4 (635M01) | M |  |  | C10H10F3N5O4S | 353.3 |  |
| 97 | BH 635-2 (635M02) | M |  |  | C7H6F3NO2S | 225.2 |  |
| 98 | BH 635-3 (635M03) | M |  |  | C9H9F3N4O3S | 310.27 |  |

* A = active compound M = metabolite

## 7.3 Appendix 3: Information on sorption for the compounds in the data base

Table 7-2: Selected endpoints for sorption according to national and EU methodology

| Number | Name | Diss[1] | Correlation | | | | | EU | | D | | | 1/n | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Kf with | | | | $Kf_{oc}$ with | $Kf_{oc}$ | | $Kf_{oc}$ | | Kf | | |
| | | | OC | pH | CEC | Clay | pH | value | Further Info. | value | Further Info. | Hamburg horizon 1-3: | EU | D |
| 1 | Chloridazon | N | Y | N | -[2] | -[2] | N | 138 | worst case | 138 | worst case values for $Kf_{oc}$ and 1/n | - | 0.914 | 0.914 |
| 2 | Metabolite B | N | Y | N | -[2] | -[2] | N | 49 | ar. mean | 49 | $Kf_{oc}$ ar mean | - | 0.834 | 0.834 |
| 3 | Metabolite B1 | N | Y | N | -[2] | -[2] | N | 92 | ar. mean | 92 | $Kf_{oc}$ ar mean | - | 0.867 | 0.867 |
| 4 | Flufenacetat | N | N | N | - | Y | N | 200 | ar. mean | 200 | no correlation with soil parameters but cv<100% | - | 0.886 | 0.886 |
| 5 | FOE 5043-Oxalat | N | Y | N | -[2] | -[2] | N | 11 | ar. mean | 11 | $Kf_{oc}$ ar mean | - | 0.91 | 0.91 |
| 6 | FOE 5043-Sulfonic Acid | N | Y | N | -[2] | -[2] | N | 10 | ar. mean | 10 | $Kf_{oc}$ ar mean | - | 0.9 | 0.9 |
| 7 | Fluroxypyr | N | Y | N | -[2] | -[2] | Y | 62 | ar. mean | 62 | worst case Kfoc | - | 0.912 | 0.912 |
| 8 | Pyridinol | N | N | N | N | N | N | 780 | ar. mean | - | Kf ar. mean | 13.32 | 0.766 | 0.766 |
| 9 | Methoxypyridine | N | Y | N | -[2] | -[2] | N | 364 | ar. mean | 364 | $Kf_{oc}$ ar mean | | 0.789 | 0.789 |
| 10 | Metribuzin | N | N | N | N | N | N | 36 | ar. mean | - | no correlation with soil parameters | 0.12 | 0.91 | 0.91 |

| Number | Name | Diss[1] | Correlation | | | | | EU | | D | | | 1/n | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Kf with | | | | $Kf_{oc}$ with | $Kf_{oc}$ | | $Kf_{oc}$ | | Kf | | |
| | | | OC | pH | CEC | Clay | pH | value | Further Info. | value | Further Info. | Hamburg horizon 1-3: | EU | D |
| | | | | | | | | | | | 10th percentile (Kf cv>100%, $Kf_{oc}$ >60%) | | | |
| 11 | DA Desaminometribuzin | N | N | N | N | N | N | 50 | ar. mean | | arithmetic mean of Kf ($Kf_{oc}$ >60%, Kf cv< 100%) | 0.67 | 0.918 | 0.918 |
| 12 | DK Diketometribuzin M02 | N | Y | N | N | N | N | 50 | ar. mean | 50 | ar mean | | 0.954 | 0.954 |
| 13 | DADK Desamino-diketometribuzin M03 | N | Y | N | N | N | N | 32 | ar. mean | 32 | ar mean | | 0.941 | 0.941 |
| 14 | Metabolit M17/ 4-methyl-DADK -metribuzin | N | Y | N | N | N | N | 27 | ar. mean | 27 | ar. mean | | 0.912 | 0.912 |
| 15 | U1 Desmethylthio-metribuzin | N | Y | N | N | N | N | 14 | ar. mean | 14 | ar. mean | | 0.993 | 0.993 |
| 16 | Nicosulfuron | N | Y | N | N | N | N | 29 | ar. mean | 29 | ar. mean | | 0.922 | 0.922 |
| 17 | AUSN | N | N | N | Y | Y | N | 46 | ar. mean | - | corr with CEC and clay | 0.29 - 0.13 - 0 - 0 - 0 based on CEC | 0.998 | 0.998 |
| 18 | UCSN | N | N | N | Y | N | N | 8 | ar. mean | - | corr with CEC | 0.06 - 0.04 - 0 - 0 - 0 | 1.058 | 1.058 |

| Number | Name | Diss[1] | Correlation | | | | | EU | | D | | | 1/n | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Kf with | | | | $Kf_{oc}$ with | $Kf_{oc}$ | | $Kf_{oc}$ | | Kf | | |
| | | | OC | pH | CEC | Clay | pH | value | Further Info. | value | Further Info. | Hamburg horizon 1-3: | EU | D |
| 19 | ASDM | N | N | N | Y | Y | N | 9 | ar. mean | - | corr with CEC and clay | 0.06 - 0.03 - 0 - 0 - 0 | 0.999 | 0.999 |
| 20 | ADMP | N | Y | N | N | N | Y | 277 | ar. mean | 277 | ar. mean | | 0.83 | 0.83 |
| 21 | HMUD | N | N | N | N | N | N | 5 | ar. mean | | isotherm not analysed, ar. mean Kf-values | 0.11 | 1 | 1 |
| 22 | MU-466 | N | Y | N | N | N | Y | 8 | ar. mean | 8 | isotherm not analysed | - | 1 | 1 |
| 23 | Terbuthylazin | N | Y | N | Y | N | N | 232 | ar. mean | 232 | | - | 0.927 | 0.927 |
| 24 | MT1 GS 26379 | N | Y | N | N | N | N | 78 | ar. mean | 78 | | - | 0.894 | 0.894 |
| 25 | MT13 GS 23158 | N | Y | N | Y | N | N | 187 | ar. mean | 187 | ar mean, n=7 | - | 0.907 | 0.907 |
| 26 | MT14 GS 28620 | N | N | N | N | N | N | 195 | ar. mean | - | ar mean Kf (n=12) Kf cv <100% | 2.93 | 0.923 | 0.923 |
| 27 | Thiamethoxam | N | Y | N | Y | N | N | 58 | ar. mean | 58 | | | 0.867 | 0.867 |
| 28 | Clothianidin | N | Y | N | Y | N | N | 135 | ar. mean | 135 | ar. mean | - | 0.862 | 0.862 |
| 29 | CGA 355190 | N | Y | N | N | N | N | 93 | ar. mean | 93 | ar mean (cv <60%) | - | 0.819 | 0.819 |

| Number | Name | Diss[1] | Correlation | | | | | EU | | D | | | 1/n | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Kf with | | | | $Kf_{oc}$ with | $Kf_{oc}$ | | $Kf_{oc}$ | | Kf | | |
| | | | OC | pH | CEC | Clay | pH | value | Further Info. | value | Further Info. | Hamburg horizon 1-3: | EU | D |
| 30 | NOA 459602 | N | Y | N | N | N | N | 24 | ar. mean | 24 | ar. mean, 1/n default | | 1 | 1 |
| 31 | Triasulfuron | N | Y | N | N | N | N | 41 | ar. mean | 41 | ar. mean | | 1.037 | 1.037 |
| 32 | CGA 150829 | N | N | N | N | N | N | 142 | ar. mean | - | no correlation with other parameters CV<100%, ar mean Kf | 1.29 | 0.89 | 0.89 |
| 33 | CGA 161149 | N | Y | N | N | N | N | 118 | ar. mean | 118 | ar. mean | | 0.894 | 0.894 |
| 34 | CGA 195660 | N | N | N | N | N | N | 33 | ar. mean | | no correlation with other parameters CV<100%, ar mean Kf | 0.34 | 1.002 | 1.002 |
| 35 | Triclopyr (Säure) | Y | N | N | N | N | N | 1000 (pH 1)<br>25 (pH 14) | ar. mean | 1000 (pH 1)<br>25 (pH 14) | sorption dependent on pH with two $Kf_{oc}$ -values | | 0.628 | 0.628 |
| 36 | TCP (3,5,6-Trichlor-2-pyridinol) | N | Y | N | N | N | N | 91 | ar. mean | 91 | ar mean | | 0.913 | 0.913 |
| 37 | TMP (3,5,6-Trichlor-2-methoxy-pyridin | -[2] | -[2] | -[2] | -[2] | -[2] | -[2] | 0 | | 0 | no data | | 1 | 1 |

| Number | Name | Diss[1] | Correlation | | | | | EU | | D | | | 1/n | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Kf with | | | | $Kf_{oc}$ with | $Kf_{oc}$ | | $Kf_{oc}$ | | Kf | | |
| | | | OC | pH | CEC | Clay | pH | value | Further Info. | value | Further Info. | Hamburg horizon 1-3: | EU | D |
| 38 | Trifloxystrobin | N | Y | N | N | N | N | 2379 | ar. mean | 2379 | ar mean | | 0.96 | 0.96 |
| 39 | CGA 321113 | Y | Y | N | N | N | N | 121 | ar. mean | 121 | ar mean | | 0.9 | 1 |
| 40 | CGA 373466 (ZE) | | Y | N | N | N | N | 88 | ar. mean | 88 | | | 0.894 | 0.894 |
| 41 | NOA 413161 | -[2] | -[2] | -[2] | -[2] | -[2] | -[2] | 4.2 | Single value | 4.2 | single value: Koc = 4.2<br>(Kd = 0.042 und 1/n = 1) | - | 1 | 1 |
| 42 | Bentazon | N | Y | N | N | N | N | 23 | ar. mean | 23 | ar. mean | - | 0.864 | 0.864 |
| 43 | Chlorthalonil | N | N | N | N | N | N | 850 | median, EU agreed endpoint | - | AM of Kf values, no correlation with other parameters and cv 73% (> 100%), | 14.38 | 0.85 | 0.85 |
| 44 | R417888 | Y (acid) | N | N | N | N | N | 10 | AM, EU agreed endpoint | 9 | ar. Mean all soils with %oc ≥ 0.3% (n=5) | - | 0.99 | 0.98 |
| 45 | R419492 | Y (acid) | -[2] | -[2] | -[2] | -[2] | -[2] | 0 | No data | 0 | no data | - | 1 | 1 |

| Number | Name | Diss[1] | Correlation | | | | | EU | | D | | | 1/n | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Kf with | | | | Kf$_{oc}$ with | Kf$_{oc}$ | | Kf$_{oc}$ | | Kf | | |
| | | | OC | pH | CEC | Clay | pH | value | Further Info. | value | Further Info. | Hamburg horizon 1-3: | EU | D |
| 46 | R611965 (SDS- 46851) | Y (acid) | -[2] | -[2] | -[2] | -[2] | -[2] | 77 | Single value, EU agreed endpoint | 77 | Single value | - | 1.07 | 1.07 |
| 47 | Thiacloprid | N | Y | N | N | N | N | 624 | ar. mean | 624 | ar. mean | | 0.867 | 0.867 |
| 48 | M02, YRC 2254-amid | N | Y | N | N | N | N | 319 | ar. mean | 319 | ar. mean | | 0.834 | 0.834 |
| 49 | M30, YRC-sulfonsäure, Na-Salz | N | Y | N | N | N | N | 21 | ar. mean | 21 | ar. mean | | 0.931 | 0.931 |
| 50 | Dimethachlor | N | Y | N | N | N | N | 72 | ar. mean (n=10) | 72 | ar. mean (n=10) | | 0.89 | 0.89 |
| 51 | CGA 354742, Sulfonsäure-Derivate | N | Y | N | N | N | N | 4 | ar mean (n=3) | 4 | ar mean (n=3) 1/n default | | 1.0 | 1.0 |
| 52 | CGA 50266 | - | - | - | - | - | N | 0 | no sorption | 0 | no sorption, WSDB: | | 1.0 | 1.0 |
| 53 | Isoxaben | N | N | N | N | N | N | 351 | ar mean (n=5) | 351 | ar mean (n=5) | | 0.932 | 0.932 |
| 54 | Hydroxy-Isoxaben | N | Y | N | N | N | N | 37 | ar mean (n=5) Freundlich of 1 used | 37 | ar mean (n=5) Freundlich of 1 used | | 1.076 | 1.076 |

| Number | Name | Diss[1] | Correlation | | | | | EU | | D | | | 1/n | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Kf with | | | | $Kf_{oc}$ with | $Kf_{oc}$ | | $Kf_{oc}$ | | Kf | | |
| | | | OC | pH | CEC | Clay | pH | value | Further Info. | value | Further Info. | Hamburg horizon 1-3: | EU | D |
| 55 | Quinmerac | N | Y | N | N | N | Y | 42 | ar mean (n=24) | 42 | Selection n = 24 ($Kf_{oc}$, Kf), but 1/n = 1 default for n = 4 (Kf) instead of 0,9 | | 0.848 | 0.848 |
| 56 | BH 518-2 | N | N | N | N | N | N | 88 | ar mean (n=4) Freundlich 1/n 1.0 used | | ar mean of Kf-values (n=4)<br>($Kf_{oc}$ cv>60, Kf<100) | 1.06 | 0.9 | 0.9 |
| 57 | BH 518-5 | N | Y | N | Y | N | N | 73 | ar mean (n=4) | 73 | ar mean (n=4) | | 0.805 | 0.805 |
| 58 | Benalaxyl-M | N | N | N | N | N | N | 6063 | ar mean (n=4) | | ar mean of Kf-values (n=4) | 66.4 | 0.975 | 0.975 |
| 59 | M1 (or M7) | N | N | N | N | N | N | 495 | ar mean (n=3) | | ar mean of Kf-values (n=3) | 13.19 0 | 0.857 | 0.857 |
| 60 | Diazinon | N | Y | N | N | N | N | 413 | worst case (n=3) | 413 | worst case (n=3) | - | 0.8202 | 0.8202 |
| 61 | G27550 | N | N | N | N | N | N | 6 | ar mean (n=3) | 6 | | - | 0.86 | 0.86 |

| Number | Name | Diss[1] | Correlation | | | | | EU | | D | | | 1/n | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Kf with | | | | $Kf_{oc}$ with | $Kf_{oc}$ | | $Kf_{oc}$ | | Kf | | |
| | | | OC | pH | CEC | Clay | pH | value | Further Info. | value | Further Info. | Hamburg horizon 1-3: | EU | D |
| 62 | Dichlobenil | N | Y | N | N | N | N | 248 | ar mean (n=4) | 248 | ar mean (n=4) | - | 0.8 | 0.8 |
| 63 | BAM | N | Y | N | N | N | N | 41 | ar mean (n=5) | 41 | ar mean (n=5) | - | 0.916 | 0.916 |
| 64 | Dimethenamid-P | N | N | N | N | N | N | 227 | ar mean (n=10) | - | Kf 10th percentile (CV: 102%) n=10 | 1.37 | 0.995 | 0.995 |
| 65 | M23 | N | N | N | N | N | N | 8 | ar mean (n=6) 1/n default | - | AM of Kd values | 0.15 | 1 | 1 |
| 66 | M27 | N | N | N | N | N | N | 7 | ar mean (n=6) | - | Kf 10th percentile (CV: 107%) n=6; 1/n default | 0.01 | 1 | 1.0 |
| 67 | Dimoxystrobin | N | Y | N | N | N | N | 315 | ar mean (n=7) | 315 | ar mean (n=7) | | 0.918 | 0.918 |
| 68 | 505M8 | N | N | N | N | N | N | 34 | ar mean (n=7) | | Kf ar mean (CV: 77%) n=7 | 0.35 | 0.985 | 0.985 |
| 69 | 505M9 | N | N | N | N | N | N | 43 | ar mean (n=8) | | Kf ar mean (CV: 90%) n=8 | 0.63 | 0.869 | 0.869 |

| Number | Name | Diss[1] | Correlation | | | | | EU | | D | | | 1/n | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Kf with | | | | $Kf_{oc}$ with | $Kf_{oc}$ | | $Kf_{oc}$ | | Kf | | |
| | | | OC | pH | CEC | Clay | pH | value | Further Info. | value | Further Info. | Hamburg horizon 1-3: | EU | D |
| 70 | Flurtamone | N | Y | N | N | N | N | 275 | ar mean (n=4) | 275 | ar mean (n=4) | | 0.98 | 0.98 |
| 71 | TFMBA | N | N | N | N | N | N | 32 | ar mean (n=4) | | Kf ar mean (CV: 93%) n=4 | 0.82 | 0.669 | 0.669 |
| 72 | Isoproturon | N | Y | N | N | N | N | 126 | ar mean (n=4) | 126 | ar mean (n=4) | | 0.882 | 0.882 |
| 73 | Desmethylisoproturon | N | Y | N | N | N | N | 147 | ar mean (n=4) | 147 | ar mean (n=4) | | 0.8 | 0.8 |
| 74 | Metalaxyl-M | N | Y | N | Not relevant | Not relevant | N | 86 | ar mean (n=20) | 86 | ar mean (n=20) | - | 0.91 | 0.91 |
| 75 | CGA 62826 (=RS-Form) = NOA 409045 (=R-Form) | | Y | N | Not relevant | Not relevant | N | 16 | ar mean (n = 16) | 16 | ar mean (n = 16) | - | 0.919 | 0.919 |
| 76 | CGA 108906 | | - | - | - | - | - | 0 | No data | 0 | No data | - | 1 | 1.0 |
| 77 | MCPA | Y | Y | Y | N | N | Y | 74 | ar mean (n=8) | 157/pH5<br>38/pH7.8 | pH-dependent $K_{foc}$-values, pKa=3.73, use pH-Tool in FOCUS PELMO | | 0.681 | 0.681 |

| Number | Name | Diss[1] | Correlation | | | | | EU | | D | | | 1/n | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Kf with | | | | Kf$_{oc}$ with | Kf$_{oc}$ | | Kf$_{oc}$ | | Kf | | |
| | | | OC | pH | CEC | Clay | pH | value | Further Info. | value | Further Info. | Hamburg horizon 1-3: | EU | D |
| 78 | Cymoxanil | Y | N | N | N | N | N | 37 | ar mean (n=8) | - | No correlation with soil parameters CV<100%, ar. mean Kf | 0.57 | 0.842 | 0.842 |
| 79 | IN-U3204 | | - | - | - | - | - | 26 | HPLC Method | 26 | HPLC Method worst case Koc and default 1/n | - | 1 | 1 |
| 80 | IN-KQ960 | | - | - | - | - | - | 19 | HPLC Method | 19 | HPLC Method worst case Koc and default 1/n | - | 1 | 1 |
| 81 | IN-T4226 | | - | - | - | - | - | 8.5 | HPLC Method | 8.5 | HPLC Method worst case Koc and default 1/n | - | 1 | 1 |
| 82 | Metazachlor | N | - | - | - | - | - | 124 | ar mean | 124 | | | 0.865 | 0.865 |
| 83 | BH 479-4 | | - | - | - | - | - | 25 | ar mean | 25 | | | 0.9 | 0.9 |
| 84 | BH 479-8 | | - | - | - | - | - | 15 | ar mean | 15 | | | 0.891 | 0.891 |
| 85 | Iodosulfuron | Y | Y | N | N | N | N | 47 | ar mean | 47 | - | - | 0.871 | 0.871 |

| Number | Name | Diss[1] | Correlation | | | | | EU | | D | | | 1/n | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Kf with | | | | $Kf_{oc}$ with | $Kf_{oc}$ | | $Kf_{oc}$ | | Kf | | |
| | | | OC | pH | CEC | Clay | pH | value | Further Info. | value | Further Info. | Hamburg horizon 1-3: | EU | D |
| 86 | AE F075736 (= Metsulfuron-Methyl) | Y | N | N | N | N | N | 31 | ar mean | - | 10th percentile of Kf values | 0.07 | 0.956 | 0.956 |
| 87 | AE F059411 | N | N | N | N | N | N | 72 | ar mean | - | 10th percentile of Kf values | 0.23 | 0.868 | 0.868 |
| 88 | Florasulam | N | N | N | N | N | N | 73 | ar mean | | ar mean of Kf (CV: 88%) | 0.82 | 0.925 | 0.925 |
| 89 | 5-OH-XDE-570 | N | N | N | N | N | N | 24 | ar. mean | 24 | ar. mean of $Kf_{oc}$ | | 0.952 | 0.952 |
| 90 | DFP-ASTCA | N | N | N | N | N | N | 53 | ar. mean | 53 | Freundlich not determined | | 1 | 1 |
| 91 | ASTCA | N | N | N | N | N | N | 83 | ar. mean | 83 | Freundlich not determined | | 1 | 1 |
| 92 | Pinoxaden | N | Y | N | Y | N | N | 357 | ar. mean | 357 | ar. mean | | 0.999 | 0.999 |
| 93 | NOA407854 | N | N | N | N | N | N | 16 | ar. mean | | ar. mean Kf (cv 65%) | 0.23 | 0.942 | 0.942 |
| 94 | NOA447204 | N | Y | N | Y | N | N | 34 | ar. mean | 34 | ar. mean | | 1 | 1 |
| 95 | Tritosulfuron | N | Y | N | N | N | N | 6 | ar. mean | 6 | $Kf_{oc}$ ar. mean (n=16 | | 0.977 | 0.977 |

| Number | Name | Diss[1] | Correlation | | | | | EU | | D | | | 1/n | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Kf with | | | | Kf$_{oc}$ with | Kf$_{oc}$ | | Kf$_{oc}$ | | Kf | | |
| | | | OC | pH | CEC | Clay | pH | value | Further Info. | value | Further Info. | Hamburg horizon 1-3: | EU | D |
| 96 | BH 635-4 (635M01) | N | N | N | N | N | N | 86 | ar. mean | 86 | ar. mean | | 0.923 | 0.923 |
| 97 | BH 635-2 (635M02) | N | N | N | Y | N | N | 46 | ar. mean | 46 | ar. mean | | 0.931 | 0.931 |
| 98 | BH 635-3 (635M03) | N | Y | N | Y | N | N | 30 | ar. mean | 30 | ar. mean | | 0.912 | 0.912 |
| 99 | Foramsulfuron | N | N | N | Y | N | N | 79 | ar. mean | 79 | ar. mean | | 0.874 | 0.874 |
| 100 | AE F130619 | N | N | N | N | N | N | 73 | ar. mean | | ar. mean | 1.51 | 0.925 | 0.925 |
| 101 | Fluopicolide | N | Y | N | N | N | N | 321 | ar. mean | 321 | ar. mean | | 0.903 | 0.903 |
| 102 | M-02 = PCA = AE C657188 (UMET/2) | N | N | N | N | N | N | 6 | ar. mean | | no correlation with Kf$_{oc}$, ar. mean Kf used (cv=50%) | 0.08 | 0.774 | 0.774 |
| 103 | M-05 = AE 1344122 = P1 (=RPA433497) | N | N | N | N | N | N | 26 | ar. mean | | no correlation with Kf$_{oc}$, ar. mean Kf used (cv=49%) | 0.35 | 0.918 | 0.918 |
| 104 | M-10 = AE 1344123 = P4 (=RPA 433965) | N | N | N | N | N | N | 6 | ar. mean | | ar. mean | 0.08 | 1 | 1 |

1 Diss: Dissociating compound 2: no data

## 7.4 Appendix 4: Information on degradation for the compounds in the data base

Table 7-3: Selected endpoints for degradation according to national and EU methodology

| Number | Name | $DegT_{50}$ (normalised lab data) (d) | | | DT 50 (normalised field data) (d) | | | Input data (d) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Geo. mean | 10th/90th percentile | pH dependency | Geo. mean | 10th/90th percentile | pH dependency | f.f.(parent →metabolite | EU | D lab | D field |
| 1 | Chloridazon | 43.2 | - | - | 19 | - | - | | 19 | 43.2 | 19 |
| 2 | Metabolite B | 108 | - | - | - | - | - | 100 | 108 | 108 | - |
| 3 | Metabolite B1 | 144.6 | - | - | - | - | - | 100 | 144.6 | 144.6 | - |
| 4 | Flufenacetat | 19.6 | - | - | 22.3 | - | - | | 19.6 | 19.6 | 22.3 |
| 5 | FOE 5043-Oxalat | 6.6 | - | - | - | - | - | 26 | 6.6 | 6.6 | - |
| 6 | FOE 5043-Sulfonic Acid | 159.4 | - | - | 21.7 | - | 0 | 47 | 21.7 | - | 21.7 |
| 7 | Fluroxypyr | 13.5 | - | - | - | - | - | | 13.5 | 13.5 | - |
| 8 | Pyridinol | - | 19.5 | 77.4 (pH 6.4-5.5<br>12.6 (pH 7.0-7.7) | - | - | - | 29 | 19.5 | 77.4 (Hamburg)<br>12.6 (Kremsmünster) | - |

| Number | Name | $\text{DegT}_{50}$ (normalised lab data) (d) | | | DT 50 (normalised field data) (d) | | | Input data (d) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Geo. mean | 10th/90th percentile | pH dependency | Geo. mean | 10th/90th percentile | pH dependency | f.f.(parent →metabolite | EU | D lab | D field |
| 9 | Methoxypyridine | 179.5 | 49.9/ 954.3 | - | - | - | - | 20 | 179.5 | 954.3 | - |
| 10 | Metribuzin | 10.7 | - | - | - | - | - | | 10.7 | 10.7 | - |
| 11 | DA Desaminometribuzin | 3 | - | - | - | - | - | 9.8 | 3 | 3 | - |
| 12 | DK Diketometribuzin M02 | 5.4 | - | - | - | - | - | 19.7 | 5.4 | 5.4 | - |
| 13 | DADK Desamino-diketometribuzin M03 | 14.1 | - | - | - | - | - | 100 | 14.1 | 14.1 | - |
| 14 | Metabolit M17/ 4-methyl-DADK - metribuzin | 59.9 | - | - | - | - | - | 100 | 59.9 | 59.9 | - |
| 15 | U1 Desmethylthio-metribuzin | 0.2 | - | - | - | - | - | 100 | 0.2 | 0.2 | - |
| 16 | Nicosulfuron | 22.8 | - | - | - | - | - | | 22.8 | 22.8 | - |
| 17 | AUSN | 187.9 | - | - | - | - | - | 100 | 187.9 | 187.9 | - |

| Number | Name | DegT$_{50}$ (normalised lab data) (d) | | | DT 50 (normalised field data) (d) | | | Input data (d) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Geo. mean | 10th/90th percentile | pH dependency | Geo. mean | 10th/90th percentile | pH dependency | f.f.$_{(parent}$ $_{\rightarrow metabolite}$ | EU | D lab | D field |
| 18 | UCSN | 274.9 | - | - | - | - | - | 100 | 274.9 | 274.9 | - |
| 19 | ASDM | 230.8 | - | 319 (pH 6.4-5.5<br>136 (pH 7.0-7.7) | - | - | - | 90 | 230.8 | 319 (Hamburg<br>136 (Kremsmünster) | - |
| 20 | ADMP | 6.3 | - | - | - | - | - | 88 | 6.3 | 6.3 | - |
| 21 | HMUD | 7 | - | - | - | - | - | 65 | 7 | 7 | - |
| 22 | MU-466 | 76.5 | - | - | - | - | - | 100 | 76.5 | 76.5 | - |
| 23 | Terbuthylazin | 75.6 | - | - | - | 44.5 / 11.2 | - | | 22.4 | 75.6 | 44.5 / 11.2 |
| 24 | MT1 GS 26379 | 48.6 | - | - | - | 111.7 12.1 | - | 53.6 | 26.8 | 48.6 | 111.7 12.1 |
| 25 | MT13 GS 23158 | 452.6 | - | - | - | - | - | 19.5 | 452.6 | 452.6 | - |
| 26 | MT14 GS 28620 | 106.6 | - | - | - | - | - | 28% (from MT1), 100% (from MT13) | 106.6 | 106.6 | - |

| Number | Name | DegT$_{50}$ (normalised lab data) (d) | | | DT 50 (normalised field data) (d) | | | Input data (d) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Geo. mean | 10th/90th percentile | pH dependency | Geo. mean | 10th/90th percentile | pH dependency | f.f.(parent →metabolite | EU | D lab | D field |
| 27 | Thiamethoxam | 118.1 | - | - | 32.7 | - | - | | 32.7 | 118.1 | 32.7 |
| 28 | Clothianidin CGA 322704 | 103.6 | - | - | - | - | - | 53 | 103.6 | 103.6 | - |
| 29 | CGA 355190 | 31 | - | - | - | - | - | 100 | 31 | 31 | - |
| 30 | NOA 459602 | 51 | 96.5/19.1 | - | - | - | - | 18 | 51 | 96.5/19.1 | - |
| 31 | Triasulfuron | 77.8 | - | - | 13.6 | - | - | | 13.6 | 77.8 | 13.6 |
| 32 | CGA 150829 | 220.7 | - | - | - | - | - | 100 | 220.7 | 220.7 | - |
| 33 | CGA 161149 | 1000 | - | - | - | - | - | 100 | 1000 | 1000 | - |
| 34 | CGA 195660 | 1000 | - | - | - | - | - | 100 | 1000 | 1000 | - |
| 35 | Triclopyr (Säure) | 27.3 | - | - | - | - | - | | 27.3 | 27.3 | - |
| 36 | TCP (3,5,6-Trichlor-2-pyridinol) | 21.9 | - | - | - | - | - | 100 | 21.9 | 21.9 | - |
| 37 | TMP (3,5,6-Trichlor-2-methoxy-pyridin | 181 | 600. / 4 80 | - | - | - | - | 100 | 181 | 600. / 4 80 | - |

| Number | Name | $\text{DegT}_{50}$ (normalised lab data) (d) | | | DT 50 (normalised field data) (d) | | | Input data (d) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Geo. mean | 10th/90th percentile | pH dependency | Geo. mean | 10th/90th percentile | pH dependency | f.f.$_{(\text{parent} \rightarrow \text{metabolite})}$ | EU | D lab | D field |
| 38 | Trifloxystrobin | 0.6 | - | - | 5.2 | - | - | | 0.6 | 0.6 | 5.2 |
| 39 | CGA 321113 | 154.9 | - | - | 41.9 | - | - | 100 | 41.9 | 154.9 | 41.9 |
| 40 | CGA 373466 (ZE) | 36.1 | - | - | - | - | - | 100 | 36.1 | 36.1 | - |
| 41 | NOA 413161 | 219.6 | - | - | - | - | - | 100 | 219.6 | 219.6 | - |
| 42 | Bentazon | 19.4 | - | - | 9.2 | - | - | | 9.2 | 19.4 | 9.2 |
| 43 | Chlorthalonil | 5.8 | 1.1 / 21.2 | - | - | - | - | | 5.8 | 1.1 / 21.2 | - |
| 44 | R417888 | 101.9 | - | - | - | - | - | 100 | 101.9 | 101.9 | - |
| 45 | R419492 | 1000 | - | - | - | - | - | 100 | 1000 | 1000 | - |
| 46 | R611965 (SDS-46851) | 103 | - | - | - | - | - | 100 | 103 | 103 | - |
| 47 | Thiacloprid | 1.4 | - | - | - | - | - | | 1.4 | 1.4 | - |
| 48 | M02, YRC 2254-amid | 52.5 | - | - | - | - | - | 100 | 52.5 | 52.5 | - |

| Number | Name | DegT50 (normalised lab data) (d) | | | DT 50 (normalised field data) (d) | | | Input data (d) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Geo. mean | 10th/90th percentile | pH dependency | Geo. mean | 10th/90th percentile | pH dependency | f.f.(parent →metabolite | EU | D lab | D field |
| 49 | M30, YRC-sulfonsäure, Na-Salz | 31.2 | - | - | - | - | - | 100 | 31.2 | 31.2 | - |
| 50 | Dimethachlor | 4.5 | - | - | - | - | - | | 4.5 | 4.5 | - |
| 51 | CGA 354742, Sulfonsäure-Derivate | 14.9 | - | - | - | - | - | 33 | 14.9 | 14.9 | - |
| 52 | CGA 50266, Oxalsäure-Derivate | 12.9 | - | - | - | - | - | 37 | 12.9 | 12.9 | - |
| 53 | Isoxaben | 301 | - | - | 94.4 | 307 / 40.3 | - | | 94.4 | 301 | 307 / 40.3 |
| 54 | Hydroxy-Isoxaben | 92.7 | - | - | - | - | - | 100 | 58.9 | 92.7 | 58.9 |
| 55 | Quinmerac | 18.9 | - | - | 9.8 | - | - | | 9.8 | 18.9 | 9.8 |
| 56 | BH 518-2 | 23.9 | - | - | - | - | - | 49 | 23.9 | 23.9 | - |
| 57 | BH 518-5 | 71.5 | - | - | - | - | - | 23 | 71.5 | 71.5 | - |
| 58 | Benalaxyl-M | 95 | - | - | - | - | - | | 95 | 95 | - |
| 59 | M1 (or M7) | 98.9* | - | - | - | - | - | 100 | 98.9 | 98.9 | - |

| Number | Name | DegT$_{50}$ (normalised lab data) (d) | | | DT 50 (normalised field data) (d) | | | Input data (d) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Geo. mean | 10th/90th percentile | pH dependency | Geo. mean | 10th/90th percentile | pH dependency | f.f.(parent →metabolite | EU | D lab | D field |
| 60 | Diazinon | 7.9 | - | 12.8 (acid)<br>5.7 (neutral/basic) | - | - | - | | 7.9 | 12.8 (Hamburg)<br>5.7 (Kremsmünster) | - |
| 61 | G27550 | 55.7 | - | - | - | - | - | 100 | 55.7 | 55.7 | - |
| 62 | Dichlobenil | 26.3* | - | - | 72* | - | - | | 26.3 | 26.3 | 72 |
| 63 | BAM | 2666* | - | - | 119.3 | - | - | 86.2 | 119.3 | 2666 | 119.3 |
| 64 | Dimethenamid-P | 18.1 | 53.2 / 10.3 | - | - | - | - | | 18.1 | 53.2 / 10.3 | - |
| 65 | M23 | 28.7 | - | - | - | - | - | 14.2 | 28.7 | 28.7 | - |
| 66 | M27 | 44.4 | - | - | - | - | - | 12.45 | 44.4 | 44.4 | - |
| 67 | Dimoxystrobin | 197.6 | | - | 73.1 | - | - | | 73.1 | 197.6 | 73.1 |
| 68 | 505M8 | 25.3 | - | - | - | - | - | 50 | 25.3 | 25.3 | - |
| 69 | 505M9 | 34.4 | - | - | - | - | - | 50 | 34.4 | 34.4 | - |
| 70 | Flurtamone | 124.6 | - | - | 16.2 | - | - | | 16.2 | 124.6 | 16.2 |

| Number | Name | DegT$_{50}$ (normalised lab data) (d) | | | DT 50 (normalised field data) (d) | | | Input data (d) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Geo. mean | 10th/90th percentile | pH dependency | Geo. mean | 10th/90th percentile | pH dependency | f.f.(parent →metabolite) | EU | D lab | D field |
| 71 | TFMBA | 13.4 | - | - | - | - | - | 100 | 13.4 | 13.4 | - |
| 72 | Isoproturon | 7 | - | - | - | - | - | | 7 | 7 | - |
| 73 | Desmethylisoproturon | 21.7 | - | - | - | - | - | 100 | 21.7 | 21.7 | - |
| 74 | Metalaxyl-M | 14.6 | - | - | 19.9 | - | - | | 14.6 | 14.6 | 19.9 |
| 75 | CGA 62826 (=RS-Form)<br>= NOA 409045 (=R-Form) | 20.6 | 106.8 / 7.1 | - | 16.5 | - | - | 79 | 16.5 | 106.8 / 7.1 | 16.5 |
| 76 | CGA 108906 | 1000 | - | - | - | - | - | 10 | 1000 | 1000 | - |
| 77 | MCPA | 26.7 | - | - | - | - | - | | 26.7 | 26.7 | - |
| 78 | Cymoxanil | 1.0 | - | 2.2 (acid)<br>0.3 (neutral/basic) | - | - | - | | 1.0 | 2.2 (Hamburg)<br>0.3 (Kremsmünster) | - |
| 79 | IN-U3204 | 0.3 | 0.1/0.7 | - | - | - | - | 35 | 0.3 | 0.1/0.7 | - |
| 80 | IN-KQ960 | 1.6 | 0.5 /8.1 | - | - | - | - | 18 (via IN-U3204) | 1.6 | 0.5 /8.1 | - |

| Number | Name | $DegT_{50}$ (normalised lab data) (d) | | | DT 50 (normalised field data) (d) | | | Input data (d) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Geo. mean | 10th/90th percentile | pH dependency | Geo. mean | 10th/90th percentile | pH dependency | f.f.(parent →metabolite | EU | D lab | D field |
| 81 | IN-T4226 | 0.7 | - | - | - | - | - | 100% (via IN-KQ960), 82% (via IN-U3204) | 0.7 | 0.7 | - |
| 82 | Metazachlor | 10.8 | - | - | 6.9 | - | - | | 6.9 | 10.8 | 6.9 |
| 83 | BH 479-4 | 89.9 | - | - | 56.4 | - | - | 50 | 56.4 | 89.9 | 56.4 |
| 84 | BH 479-8 | 123.2 | - | - | 116.4* | - | - | 50 | 116.4 | 123.2 | - |
| 85 | Iodosulfuron | 2 | - | - | - | - | - | | 2 | 2 | - |
| 86 | AE F075736 (= Metsulfuron-Methyl) | 27.1 | - | - | - | - | - | 84.5 | 27.1 | 27.1 | - |
| 87 | AE F059411 | 110.7 | - | - | - | - | - | 36 (from F075736)<br>1% (from parent) | 110.7 | 110.7 | - |
| 88 | Florasulam | 3.1 | | Y | | No data | Y | | 3.1 | 3.1 | |
| 89 | 5-OH-XDE-570 | 20.9 | | N | | No data | 0 | 84 | 20.9 | 20.9 | |
| 90 | DFP-ASTCA | 12.4 | | N | | no data | 0 | 39 | 12.4 | 12.4 | |

| Number | Name | DegT$_{50}$ (normalised lab data) (d) | | | DT 50 (normalised field data) (d) | | | Input data (d) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Geo. mean | 10th/90th percentile | pH dependency | Geo. mean | 10th/90th percentile | pH dependency | f.f.(parent →metabolite | EU | D lab | D field |
| 91 | ASTCA | 201.6 | | N | | no data | 0 | 75.5 | 201.6 | 201.6 | |
| 92 | Pinoxaden | 3.1 | | N | 0.7 | geo. mean (n=13) | 0 | | 0.7 | 3.1 | 0.7 |
| 93 | NOA407854 | 9.7 | 44.2 / 2.7 | Y | 1.4 | geo mean (no acidic soils in field studies) | Y | 100 | 1.4 | 44.2 / 2.7 | 1.4 |
| 94 | NOA447204 | 45.1 | 45.1 | Y | 17.5 | geo mean (n=17) | Y | 12.4 | 17.5 | 45.1 | 17.5 |
| 95 | Tritosulfuron | 36.1 | 247.4 / 9.5 | Y | 9.7 | geo mean (n=7) | Y | | 9.7 | 247.4 / 9.5 | 9.7 |
| 96 | BH 635-4 (635M01) | 44 | 44 | N | 68.5 | geo mean (n=3) | 0 | 17.1 (from Tritosulfuron) | 44 | 44 | 68.5 |
| 97 | BH 635-2 (635M02) | 30.8 | 30.8 | N | 54.9 | geo mean (n=5) | 0 | 16.5 (from Tritosulfuron)<br>100 (from 635M03) | 30.8 | 30.8 | 54.9 |
| 98 | BH 635-3 (635M03) | 88.2 | 88.2 | N | 126 | worst case of 2 | 0 | 100 (from 635M01) | 88.2 | 88.2 | 126 |

| Number | Name | $DegT_{50}$ (normalised lab data) (d) | | | DT 50 (normalised field data) (d) | | | Input data (d) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Geo. mean | $10^{th}/90^{th}$ percentile | pH dependency | Geo. mean | $10^{th}/90^{th}$ percentile | pH dependency | f.f.(parent →metabolite | EU | D lab | D field |
| 99 | Foramsulfuron | 4.4 | 4.4 | N | | no data | 0 | | 4.4 | 4.4 | |
| 100 | AE F130619 | 0.5 | 0.5 | N | | no data | 0 | 100 | 0.5 | 0.5 | |
| 101 | Fluopicolide | 270.8 | 270.8 | N | 138.8 | geo mean (n=7) | 0 | | 138.8 | 270.8 | 138.8 |
| 102 | M-02 = PCA = AE C657188 (UMET/2) | 2.8 | 2.8 | N | | no data | 0 | 71.2 | 2.8 | 2.8 | |
| 103 | M-05 = AE 1344122 = P1 (=RPA433497) | 43.4 | 147 / 19 | N | | no data | 0 | 20.3 | 43.4 | 147 / 19 | |
| 104 | M-10 = AE 1344123 = P4 (=RPA 433965) | 26.4 | 215 / 4.7 | N | | no data | 0 | 9.5 | 26.4 | 215 / 4.7 | |

* worst case selected (too few studies)

Table 7-4: comparison of FOCUS PELMO Tier 1 (no plant uptake) - simulations with available lysimeter data (concentrations in µg/L)

| Substance | $Kf_{oc}$ | | $DegT_{50}$ (d) | | | Crop | App Date** | Nominal App Rate (g/ha) | Results | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EU | D | EU | $D_{lab}$ | $D_{field}$ | | | | Tier 1 EU° | Tier 1 D Lab° | Tier 1 D Field° | Lysimeter°° | Figure |
| Chloridazon | 138 | 138 | 19 | 43.2 | | Sugar beet | 1 day before emergence | 2960 | 0.023 | 4.496 | 0.023 | 0.009 | Figure 7-2 |
| Metabolite B | 49 | 49 | 108 | 108 | | Sugar beet | 1 day before emergence | 2960 | 199.875 | 221.85 | 199.875 | 40.56 | Figure 7-3 |
| Metabolite B1 | 92 | 92 | 144.6 | 144.6 | | Sugar beet | 1 day before emergence | 2960 | 9.627 | 11.430 | 9.627 | 2.12 | Figure 7-4 |
| Flufenacetat | 200 | 200 | 19.6 | 19.6 | 22.3 | Maize | 1 day before emergence | 480 | 0.000 | 0.000 | 0.000 | 0.03 | Figure 7-5 |
| FOE 5043-Oxalat | 11 | 11 | 6.6 | 6.6 | | Maize | 1 day before emergence | 480 | 0.077 | 0.077 | - | 0.01 | Figure 7-6 |
| FOE 5043-Sulfonic Acid | 10 | 10 | 21.7 | - | 21.7 | Maize | 1 day before emergence | 480 | 5.208 | 50.299 | 8.652 | 0.5/1.5 | Figure 7-7 |
| Fluroxypyr | 62 | 62 | 13.5 | 13.5 | - | Grass | October 8 | 420 | 0.156 | 0.156 | - | 0.015 | Figure 7-8 |
| Pyridinol | 780 | 13.32 (Kf) | 19.5 | 77.4 (Hamburg)<br>12.6 (Kremsmünster) | - | Grass | October 8 | 420 | 0.012 | 0.006 | - | 0.01 | Figure 7-9 |
| Methoxypyridine | 364 | 364 | 179.5 | 954.3 | - | Grass | October 8 | 420 | 0.036 | 1.582 | - | <0.01 | Figure 7-10 |

| Substance | $Kf_{oc}$ | | DegT$_{50}$ (d) | | | Crop | App Date** | Nominal App Rate (g/ha) | Results | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EU | D | EU | $D_{lab}$ | $D_{field}$ | | | | Tier 1 EU° | Tier 1 D Lab° | Tier 1 D Field° | Lysi-meter°° | Figure |
| Metribuzin | 36 | 0.12 (Kf) | 10.7 | 10.7 | - | Potatoes | May 4 | 516 | 0.206 | 0.243 | - | <0.01 | Figure 7-11 |
| DA Desaminometribuzin | 50 | 0.67 (Kf) | 3 | 3 | - | Potatoes | May 4 | 516 | 0.003 | 0.003 | - | <0.01 | Figure 7-12 |
| DK Diketometribuzin M02 | 50 | 50 | 5.4 | 5.4 | - | Potatoes | May 4 | 516 | 0.018 | 0.016 | - | <0.01 | Figure 7-13 |
| DADK Desamino-diketometribuzin M03 | 32 | 32 | 14.1 | 14.1 | - | Potatoes | May 4 | 516 | 0.486 | 0.228 | - | 0.23 | Figure 7-14 |
| Metabolit M17/ 4-methyl-DADK - metribuzin | 27 | 27 | 59.9 | 59.9 | - | Potatoes | May 4 | 516 | 12.186 | 7.785 | - | 0.08 | Figure 7-15 |
| U1 Desmethylthio-metribuzin | 14 | 14 | 0.2 | 0.2 | - | Potatoes | May 4 | 516 | 0.003 | 0.004 | - | 0.095 | Figure 7-16 |
| Nicosulfuron | 29 | 29 | 22.8 | 22.8 | - | Maize | June 20 | 40 (25% c.i.) | 0.222 | 0.222 | - | 0.17 | Figure 7-17 |
| AUSN | 46 | 0.29 - 0.13 - 0 - 0 - 0 (Kf)+ | 187.9 | 187.9 | - | Maize | June 20 | 40 (25% c.i.) | 3.845 | 5.007 | - | 0.89 | Figure 7-18 |
| UCSN | 8 | 0.06 - 0.04 - 0 - 0 - 0 (Kf)+ | 274.9 | 274.9 | - | Maize | June 20 | 40 (25% c.i.) | 2.496 | 1.51 | - | 0.36 | Figure 7-19 |
| ASDM | 9 | 0.06 - 0.03 - 0 - 0 - 0 (Kf)+ | 230.8 | 319 (Hamburg 136 (Krems | - | Maize | June 20 | 40 (25% c.i.) | 5.467 | 5.743 | - | 2.24 | Figure 7-20 |

| Substance | $Kf_{oc}$ | | $DegT_{50}$ (d) | | | Crop | App Date** | Nominal App Rate (g/ha) | Results | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EU | D | EU | $D_{lab}$ | $D_{field}$ | | | | Tier 1 EU° | Tier 1 D Lab° | Tier 1 D Field° | Lysimeter°° | Figure |
| | | | | münster) | | | | | | | | | |
| ADMP | 277 | 277 | 6.3 | 6.3 | - | Maize | June 20 | 40 (25% c.i.) | 0.005 | 0.005 | - | <0.01 | Figure 7-21 |
| HMUD | 5 | 0.11 (Kf) | 7 | 7 | - | Maize | June 20 | 40 (25% c.i.) | 0.238 | 0.168 | - | 0.03 | Figure 7-22 |
| MU-466 | 8 | 8 | 76.5 | 76.5 | - | Maize | June 20 | 40 (25% c.i.) | 3.921 | 3.921 | - | 0.15 | Figure 7-23 |
| Terbuthylazin | 232 | 232 | 22.4 | 75.6 | 44.5 / 11.2 | Maize | May 18 | 1000 | 0.001 | 0.772 | 0.000/ 0.032 | <0.01 | Figure 7-24 |
| MT1 GS 26379 | 78 | 78 | 26.8 | 48.6 | 111.7 12.1 | Maize | May 18 | 1000 | 0.615 | 2.567 | 0.000/ 17.535 | <0.01 | Figure 7-25 |
| MT13 GS 23158 | 187 | 187 | 452.6 | 452.6 | - | Maize | May 18 | 1000 | 25.925 | 20.951 | - | 0.02 | Figure 7-26 |
| MT14 GS 28620 | 195 | 2.93 (Kf) | 106.6 | 106.6 | - | Maize | May 18 | 1000 | 0.000 | 0.000 | - | 0.01 | Figure 7-27 |
| Thiamethoxam | 58 | 58 | 32.7 | 118.1 | 32.7 | Potatoes | June 19, July 6, July 25, Aug 10 | 4*50 | 0.415 | 14.071 | 0.414 | 0.095 | Figure 7-28 |
| Clothianidin CGA 322704 | 133 | 133 | 103.6 | 103.6 | - | Potatoes | June 19, July 6, July 25, Aug 10 | 4*50 | 0.513 | 1.770 | - | 0.27 | Figure 7-29 |
| CGA 355190 | 93 | 93 | 31 | 31 | - | Potatoes | June 19, July 6, July 25, Aug 10 | 4*50 | 0.290 | 1.496 | - | <0.01 | Figure 7-30 |
| NOA 459602 | 24 | 24 | 51 | 96.5/ 19.1 | - | Potatoes | June 19, July 7, July 25, Aug 10 | 4*50 | 4.656 | 7.669 | - | 0.332 | Figure 7-31 |
| Triasulfuron | 41 | 41 | 13.6 | 77.8 | 13.6 | Winter cereals | April 29 | 7.5 | 0.007 | 0.765 | 0.007 | <0.025 | Figure 7-32 |

| Substance | $K_{foc}$ | | DegT$_{50}$ (d) | | | Crop | App Date** | Nominal App Rate (g/ha) | Results | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EU | D | EU | $D_{lab}$ | $D_{field}$ | | | | Tier 1 EU° | Tier 1 D Lab° | Tier 1 D Field° | Lysi-meter°° | Figure |
| CGA 150829 | 142 | 1.29 (Kf) | 220.7 | 220.7 | - | Winter cereals | April 29 | 7.5 | 0.110 | 0.159 | - | <0.025 | Figure 7-33 |
| CGA 161149 | 118 | 118 | 1000 | 1000 | - | Winter cereals | April 29 | 7.5 | 1.124 | 0.946 | - | <0.025 | Figure 7-34 |
| CGA 195660 | 33 | 0.34 (Kf) | 1000 | 1000 | - | Winter cereals | April 29 | 7.5 | 3.002 | 2.442 | - | <0.025 | Figure 7-35 |
| Triclopyr (Säure) | 1000 (pH 1) 25 (pH 14) | 1000 (pH 1) 25 (pH 14) | 27.3 | 27.3 | - | Grass | June 5 | 2000 | 30.692 | 30.692 | | 0.07 | Figure 7-36 |
| TCP (3,5,6-Trichlor-2-pyridinol) | 91 | 91 | 21.9 | 21.9 | - | Grass | June 5 | 2000 | 6.933 | 6.933 | | 0.06 | Figure 7-37 |
| TMP (3,5,6-Trichlor-2-methoxy-pyridin | 0 | 0 | 181 | 600. / 4 80 | - | Grass | June 5 | 2000 | 559.168 | 660.698 | | <0.01 | Figure 7-38 |
| Trifloxystrobin | 2379 | 2379 | 0.6 | 0.6 | 5.2 | Spring Cereals | April 23, May 28 | 2*250 | 0.000 | 0.000 | 0.000 | <0.01 | Figure 7-39 |
| CGA 321113 | 121 | 121 | 41.9 | 154.9 | 41.9 | Spring Cereals | April 23, May 28 | 2*250 | 1.080 | 66.738 | 4.463 | 1.22 | Figure 7-40 |
| CGA 373466 (ZE) | 88 | 88 | 36.1 | 36.1 | - | Spring Cereals | April 23, May 28 | 2*250 | 1.690 | . | 1.878 | 0.24 | Figure 7-41 |
| NOA 413161 | 4.2 | 4.2 | 219.6 | 219.6 | - | Spring Cereals | April 23, May 28 | 2*250 | 322.229 | 268.349 | - | 6.69 | Figure 7-42 |

| Substance | $Kf_{oc}$ | | DegT$_{50}$ (d) | | | Crop | App Date** | Nominal App Rate (g/ha) | Results | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EU | D | EU | D$_{lab}$ | D$_{field}$ | | | | Tier 1 EU° | Tier 1 D Lab° | Tier 1 D Field° | Lysimeter°° | Figure |
| Bentazon | 23 | 23 | 9.2 | 19.4 | 9.2 | Winter cereals | March 17 | 1000 | 0.185 | 5.605 | 0.185 | 0.08 | Figure 7-43 |
| Chlorthalonil | 850 | 14.38 (Kf) | 5.8 | 1.1 / 21.2 | - | Winter cereals | 6 and 22 June | 1170/1370 (50/90% c.i.). | 0.000 | 0.000 / 0.000 | - | n.d. | Figure 7-44 |
| R417888 | 10 | 9 | 101.9 | 101.9 | - | Winter cereals | 6 and 22 June | 1170/1370 | 200.659 | 196.642/ 205.130 | - | 9.3 | Figure 7-45 |
| R419492 | $0^x$ | $0^x$ | 1000 | 1000 | - | Winter cereals | 6 and 22 June | 1170/1370 | 320.369 | 325.051 / 305.202 | - | 4.65 | Figure 7-46 |
| R611965 (SDS- 46851) | 77 | 77 | 103 | 103 | - | Winter cereals | 6 and 22 June | 1170/1370 | 42.023 | 43.840 / 41.514 | - | 1.3 | Figure 7-47 |
| Thiacloprid | 624 | 624 | 1.4 | 1.4 | - | grass | May 17 and 31 | 2*400 | 0.000 | 0.000 | | n.d. | Figure 7-48 |
| M02, YRC 2254-amid | 319 | 319 | 52.5 | 52.5 | - | grass | May 17 and 31 | 2*400 | 0.000 | 0.000 | | n.d. | Figure 7-49 |
| M30, YRC-sulfonsäure, Na-Salz | 21 | 21 | 31.2 | 31.2 | - | grass | May 17 and 31 | 2*400 | 51.299 | 51.299 | | 2.52 | Figure 7-50 |
| Dimethachlor | 72 | 72 | 4.5 | 4.5 | - | OSR | 1 day before emergence | 1500 | 0.000 | | | n.d. | Figure 7-51 |
| CGA 354742, Sulfonsäure-Derivate | 4 | 4 | 14.9 | 14.9 | - | OSR | 1 day before emergence | 1.500 | 51.14 | 51.140 | | 35.1 | Figure 7-52 |

| Substance | $Kf_{oc}$ | | $DegT_{50}$ (d) | | | Crop | App Date** | Nominal App Rate (g/ha) | Results | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EU | D | EU | $D_{lab}$ | $D_{field}$ | | | | Tier 1 EU° | Tier 1 D Lab° | Tier 1 D Field° | Lysi-meter°° | Figure |
| CGA 50266, Oxalsäure-Derivate | 0 | 0 | 12.9 | 12.9 | - | OSR | 1 day before emergence | 1.500 | 48.319 | 48.319 | | 36.2 | Figure 7-53 |
| Isoxaben | 351 | 351 | 94.4 | 301 | 307 / 40.3 | fallow | 21 Oct | 250 | 0.058 | 4.457 | 4.666 / 0.000 | 0.05 | Figure 7-54 |
| Hydroxy-Isoxaben | 37 | 37 | 58.9 | 92.7 | 58.9 | fallow | 21 Oct | 250 | 15.060 | 25.638 | 17.326/ 13.886 | 0.07 | Figure 7-55 |
| Quinmerac | 42 | 42 | 9.8 | 18.9 | 9.8 | Sugar beet | 16 May | 225 | 0.000 | 0.032 | 0.000 | <0.02 | Figure 7-56 |
| BH 518-2 | 88 | 1.06 (Kf) | 23.9 | 23.9 | - | Sugar beet | 16 May | 225 | 0.010 | 0.038 | - | 6.49 | Figure 7-57 |
| BH 518-5 | 73 | 73 | 71.5 | 71.5 | - | Sugar beet | 16 May | 225 | 0.060 | 0.286 | - | <0.01 | Figure 7-58 |
| Benalaxyl-M | 6063 | 66.4 (Kf) | 95 | 95 | - | Tomatoes | 30 May, 13 June,28 June,4 July | 4*240 | 0.000 | 0.000 | 0.000 | n.d. | Figure 7-59 |
| M1 (orM7) | 495 | 13.19 (Kf) | 98.9 | 98.9 | - | Tomatoes | 30 May, 13 June,28 June,4 July | 4*240 | 0.002 | 0.000 | - | 4.9 | Figure 7-60 |
| Diazinon | 413 | 413 | 7.9 | 12.8 (Hamburg)<br>5.7 (Krems | - | Sugar beet | 24 may, 21 June,25 July,19 Aug | 4*240 | 0.000 | 0.000 | - | 0.07 | Figure 7-61 |

| Substance | $Kf_{oc}$ | | $DegT_{50}$ (d) | | | Crop | App Date** | Nominal App Rate (g/ha) | Results | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EU | D | EU | $D_{lab}$ | $D_{field}$ | | | | Tier 1 EU° | Tier 1 D Lab° | Tier 1 D Field° | Lysi-meter°° | Figure |
| | | | | münster) | | | | | | | | | |
| G27550 | 6 | 6 | 55.7 | 55.7 | - | Sugar beet | 24 may, 21 June,25 July,19 Aug | 4*240 | 86.583 | 88.144 | - | 1.02 | Figure 7-62 |
| Dichlobenil | 248 | 248 | 26.3 | 26.3 | 72 | fallow | 16 May | 8100 | 0.000 | 0.000 | 0.613 | <LOQ | Figure 7-63 |
| BAM | 41 | 41 | 119.3 | 2666 | 119.3 | fallow | 16 May | 8100 | 1428. | 3478 | 3457. | 94.1 | Figure 7-64 |
| Dimethenamid-P | 227 | 1.37 (Kf) | 18.1 | 53.2 / 10.3 | - | Maize | 1 day before emergence | 1440 | 0.011 | 0.000/ 2.422 | | n.d. | Figure 7-65 |
| M23 | 8 | 0.15 (Kf) | 28.7 | 28.7 | - | Maize | 1 day before emergence | 1440 | 15.287 | 15.283 / 21.446 | | 1 | Figure 7-66 |
| M27 | 7 | 0.01 (Kf) | 44.4 | 44.4 | - | Maize | 1 day before emergence | 1440 | 29.581 | 34.148 / 43.889 | | 4 | Figure 7-67 |
| Dimoxystrobin | 315 | 315 | 73.1 | 197.6 | 73.1 | Winter cereals | 12. May, 17 June | 2*250 (incl. c.i.) | 0.018 | 1.910 | 0.018 | n.d. | Figure 7-68 |
| 505M8 | 34 | 0.35 (Kf) | 25.3 | 25.3 | - | Winter cereals | 12. May, 17 June | 2*0.25 (incl. c.i.) | 2.207 | 3.244 | - | 2.35 | Figure 7-69 |
| 505M9 | 43 | 0.63 (Kf) | 34.4 | 34.4 | - | Winter cereals | 12. May, 17 June | 2*0.25 (incl. c.i.) | 0.946 | 6.832 | - | 1.99 | Figure 7-70 |
| Flurtamone | 275 | 275 | 16.2 | 124.6 | 16.2 | Winter cereals | 1 day before emergence | 329 | 0.001 | 5.204 | 0.001 | <0.01 | Figure 7-71 |

| Substance | $Kf_{oc}$ | | $DegT_{50}$ (d) | | | Crop | App Date** | Nominal App Rate (g/ha) | Results | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EU | D | EU | $D_{lab}$ | $D_{field}$ | | | | Tier 1 EU° | Tier 1 D Lab° | Tier 1 D Field° | Lysi-meter°° | Figure |
| TFMBA | 32 | 0.82 (Kf) | 13.4 | 13.4 | - | Winter cereals | 1 day before emergence | 329 | 0.000 | 0.031 | - | 0.09 | Figure 7-72 |
| Isoproturon | 126 | 126 | 7 | 7 | - | Winter cereals | 1 day before emergence | 1500 (incl. c.i.) | 0.000 | 0.000 | - | 0.272/0.089 | Figure 7-73 |
| Desmethylisoproturon | 147 | 147 | 21.7 | 21.7 | - | Winter cereals | 1 day before emergence | 1500 (incl. c.i.) | 0.000 | 0.000 | - | 0.051/0.022 | Figure 7-74 |
| Metalaxyl-M | 86 | 86 | 14.6 | 14.6 | 19.9 | Potatoes | 29.June. 14.July. , 27.July. | 100/100/200 (80% c.i.) | 0.000 | 0.000/ 2.884 | 0.004 | 0.05 | Figure 7-75 |
| CGA 62826 | 16 | 16 | 16.5 | 106.8 / 7.1 | 16.5 | Potatoes | 29.June. 14.July. , 27.July. | 100/100/200 (80% c.i.) | 1.018 | 12.400 / 0.106 | 1.132 | 4.12 | Figure 7-76 |
| CGA 108906 | $0^x$ | $0^x$ | 1000 | 1000 | - | Potatoes | 29.June. 14.July. , 27.July. | 100/100/200 (80% c.i.) | 2.778 | 1.424/ 2.884 | 2.772 | 1.11 | Figure 7-77 |
| MCPA | 74 | 157/pH5<br>38/pH7.8 | 26.7 | 26.7 | - | Spring wheat | 31 May | 2000 (90% c.i.) | 0.000 | 0.000 (H) /<br>0.000 (K) | - | n.d. | Figure 7-78 |
| Cymoxanil | 37 | 0.57 (Kf) | 1.0 | 2.2 (Hamburg)<br>0.3 (Kremsmünster) | - | Potatoes | June 30, July 6 and July 14 | 3*0.32 (80% c.i.) | 0.000 | 0.000/ 0.000 | - | <loq | Figure 7-79 |

| Substance | $Kf_{oc}$ | | $DegT_{50}$ (d) | | | Crop | App Date** | Nominal App Rate (g/ha) | Results | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EU | D | EU | $D_{lab}$ | $D_{field}$ | | | | Tier 1 EU° | Tier 1 D Lab° | Tier 1 D Field° | Lysi-meter°° | Figure |
| IN-U3204 | 26 | 26 | 0.3 | 0.1/0.7 | - | Potatoes | June 30, July 6 and July 14 | 3*0.32 (80% c.i.) | 0.000 | 0.000/ 0.000 | - | <loq | Figure 7-80 |
| IN-KQ960 | 19 | 19 | 1.6 | 0.5 /8.1 | - | Potatoes | June 30, July 6 and July 14 | 3*0.32 (80% c.i.) | 0.000 | 0.016/ 0.000 | - | <loq | Figure 7-81 |
| IN-T4226 | 8.5 | 8.5 | 0.7 | 0.7 | - | Potatoes | June 30, July 6 and July 14 | 3*0.32 (80% c.i.) | 0.000 | 0.001/ 0.000 | - | 0.02 | Figure 7-82 |
| Metazachlor | 124 | 124 | 6.9 | 10.8 | 6.9 | OSR | 4 September | 960 (40% c.i.) | 0.000 | 0.000 | 0.000 | n.d. | Figure 7-83 |
| BH 479-4 | 25 | 25 | 56.4 | 89.9 | 56.4 | OSR | 4 September | 960 (40% c.i.) | 35.898 | 57.137 | 45.464 | 21.4 | Figure 7-84 |
| BH 479-8 | 15 | 15 | 116.4 | 123.2 | - | OSR | 4 September | 960 (40% c.i.) | 93.616 | 95.578 | 93.616 | $6.17^{++}$ | Figure 7-85 |
| Iodosulfuron | 47 | 47 | 2 | 2 | - | winter cereals | 24 March | 15 (50% c.i.) | 0.000 | 0.000 | - | $0.007^{++}$ | Figure 7-86 |
| AE F075736 | 31 | 0.07 (Kf) | 27.1 | 27.1 | - | winter cereals | 24 March | 15 (50% c.i.) | 0.041 | 0.216 | - | 0.058 | Figure 7-87 |
| AE F059411 | 72 | 0.23 (Kf) | 110.7 | 110.7 | - | winter cereals | 24 March | 15 (50% c.i.) | 0.043 | 0.212 | - | 0.034 | Figure 7-88 |
| Florasulam | 73 | 0.82 (Kf) | 3.1 | 3.1 | | OSR (BBCH 12-16) | 5 Nov | 4 (25% ci) | 0 | 0 | - | 0.01 | Figure 7-89 |
| 5-OH-XDE-570 | 24 | 24 | 20.9 | 20.9 | | OSR | 5 Nov | 4 (25% ci) | 0.067 | 0.067 | - | 0.07 | Figure 7-90 |
| DFP-ASTCA | 53 | 53 | 12.4 | 12.4 | | OSR | 5 Nov | 4 (25% ci) | 0.016 | 0.016 | - | 0.02 | Figure 7-91 |
| ASTCA | 83 | 83 | 201.6 | 201.6 | | OSR | 5 Nov | 4 (25% ci) | 0.08 | 0.08 | - | 0.06 | Figure 7-92 |

| Substance | $Kf_{oc}$ | | $DegT_{50}$ (d) | | | Crop | App Date** | Nominal App Rate (g/ha) | Results | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EU | D | EU | $D_{lab}$ | $D_{field}$ | | | | Tier 1 EU° | Tier 1 D Lab° | Tier 1 D Field° | Lysi-meter°° | Figure |
| Pinoxaden | 357 | 357 | 0.7 | 3.1 | 0.7 | winter wheat | Oct 17, Apr 05 | 50 (25% 70% ci) | 0 | 0 / 0 | - | - | Figure 7-93 |
| NOA407854 | 16 | 0.23 (Kf) | 1.4 | 44.2 / 2.7 | 1.4 | winter wheat | Oct 17, Apr 05 | 50 (25% 70% ci) | 0 | 3.463 / 0.002 | - | 0.05 | Figure 7-94 |
| NOA447204 | 34 | 34 | 17.5 | 45.1 | 17.5 | winter wheat | Oct 17, Apr 05 | 50 (25% 70% ci) | 0.074 | 0.729 / 0.420 | - | 0.206 | Figure 7-95 |
| Tritosulfuron | 6 | 6 | 9.7 | 247.4 / 9.5 | 9.7 | winter wheat | 28 Apr | 50 (70% ci) | 0.034 | 0.031 / 5.831 | - | 0.04 | Figure 7-96 |
| BH 635-4 (635M01) | 86 | 86 | 44 | 44 | 68.5 | winter wheat | 28 Apr | 50 (70% ci) | 0.018 | 0.018 / 0.025 | - | 1.04 | Figure 7-97 |
| BH 635-2 (635M02) | 46 | 46 | 30.8 | 30.8 | 54.9 | winter wheat | 28 Apr | 50 (70% ci) | 0.07 | 0.07 / 0.033 | - | 0.11 | Figure 7-98 |
| BH 635-3 (635M03) | 30 | 30 | 88.2 | 88.2 | 126 | winter wheat | 28 Apr | 50 (70% ci) | 0.243 | 0.242 / 0.071 | - | 0.57 | Figure 7-99 |
| Foramsulfuron | 79 | 79 | 4.4 | 4.4 | | maize | 17 June, 19 July | 45 (50%, 76% ci) | 0 | 0 | - | 0.005 | Figure 7-100 |
| AE F130619 | 73 | 1.51 (Kf) | 0.5 | 0.5 | | maize | 17 June, 19 July | 45 (50%, 76% ci) | 0 | 0 | - | 0.005 | Figure 7-101 |
| Fluopicolide | 321 | 321 | 138.8 | 270.8 | 138.8 | potatoes | 27 May, 17 June, 20 July, 30 July | 104(50% ci), 107, 108, 107 (80% ci) | 0.136 | 1.718 / 1.718 | 0.136 / 0.139 | 0.009 | Figure 7-102 |
| M-02 = PCA = AE C657188 (UMET/2) | 6 | 0.08 (Kf) | 2.8 | 2.8 | | potatoes | 27 May, 17 June, 20 July, 30 July | 104(50% ci), 107, 108, 107 (80% ci) | 0.018 | 0.119 / 0.119 | 0.063 / 0.063 | n.d. | Figure 7-103 |

| Substance | $Kf_{oc}$ | | $DegT_{50}$ (d) | | | Crop | App Date** | Nominal App Rate (g/ha) | Results | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EU | D | EU | $D_{lab}$ | $D_{field}$ | | | | Tier 1 EU° | Tier 1 D Lab° | Tier 1 D Field° | Lysimeter°° | Figure |
| M-05 = AE 1344122 = P1 (=RPA433497) | 26 | 0.35 (Kf) | 43.4 | 147 / 19 | | potatoes | 27 May, 17 June, 20 July, 30 July | 104(50% ci), 107, 108, 107 (80% ci) | 0.613 | 0.256 / 2.193 | 0.184 / 2.223 | 0.902 | Figure 7-104 |
| M-10 = AE 1344123 = P4 (=RPA 433965) | 6 | 0.08 (Kf) | 26.4 | 215 / 4.7 | | potatoes | 27 May, 17 June, 20 July, 30 July | 104(50% ci), 107, 108, 107 (80% ci) | 0.538 | 0.07 / 1.809 | 0.056 / 1.904 | 0.931 | Figure 7-105 |

* if not expressed differently: Koc °° pKa 3.97 + based on CEC correlation ** Annual simulations ° 90th percentile °°worst case annual concentration in µg/L ++ individual samples

x: no data, default value

Table 7-5: comparison of FOCUS PELMO Tier 1 (PUF = 0.5) - simulations with available lysimeter data (concentrations in µg/L)

| Substance | $Kf_{oc}$ | | DegT$_{50}$ (d) | | | Crop | App Date** | Nominal App Rate (g/ha) | Results | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EU | D | EU | $D_{lab}$ | $D_{field}$ | | | | Tier 1 EU° | Tier 1 D Lab° | Tier 1 D Field° | Lysi-meter°° |
| Chloridazon | 138 | 138 | 19 | 43.2 | 19 | Sugar beet | 1 day before emergence | 2960 | 0.016 | 2.951 | 0.016 | 0.009 |
| Metabolite B | 49 | 49 | 108 | 108 | - | Sugar beet | 1 day before emergence | 2960 | 100.862 | 117.05 | 100.862 | 40.56 |
| Metabolite B1 | 92 | 92 | 144.6 | 144.6 | - | Sugar beet | 1 day before emergence | 2960 | 5.805 | 6.894 | 5.805 | 2.12 |
| Flufenacetat | 200 | 200 | 19.6 | 19.6 | 22.3 | Maize | 1 day before emergence | 480 | 0 | 0 | 0 | 0.03 |
| FOE 5043-Oxalat | 11 | 11 | 6.6 | 6.6 | - | Maize | 1 day before emergence | 480 | 0.058 | 0.058 | | 0.01 |
| FOE 5043-Sulfonic Acid | 10 | 10 | 21.7 | - | 21.7 | Maize | 1 day before emergence | 480 | 2.871 | 23.852 | 5.392 | 0.015 |
| Fluroxypyr | 62 | 62 | 13.5 | 13.5 | - | Grass | October 8 | 420 | 0.139 | 0.139 | | 0.015 |
| Pyridinol | 780 | 13.32 (Kf) | 19.5 | 77.4 (Hamburg)<br>12.6 (Kremsmünster) | - | Grass | October 8 | 420 | 0.011 | 0.006 | | 0.01 |
| Methoxypyridine | 364 | 364 | 179.5 | 954.3 | - | Grass | October 8 | 420 | 0.031 | 1.114 | | <0.01 |
| Metribuzin | 36 | 0.12 (Kf) | 10.7 | 10.7 | - | Potatoes | May 4 | 516 | 0.107 | 0.067 | | <0.01 |
| DA Desaminometribuzin | 50 | 0.67 (Kf) | 3 | 3 | - | Potatoes | May 4 | 516 | 0.002 | 0.001 | | <0.01 |
| DK Diketometribuzin M02 | 50 | 50 | 5.4 | 5.4 | - | Potatoes | May 4 | 516 | 0.009 | 0.004 | | <0.01 |

| Substance | $Kf_{oc}$ | | $DegT_{50}$ (d) | | | Crop | App Date** | Nominal App Rate (g/ha) | Results | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EU | D | EU | $D_{lab}$ | $D_{field}$ | | | | Tier 1 EU° | Tier 1 D Lab° | Tier 1 D Field° | Lysi-meter°° |
| DADK Desamino-diketometribuzin M03 | 32 | 32 | 14.1 | 14.1 | - | Potatoes | May 4 | 516 | 0.245 | 0.074 | | 0.23 |
| Metabolit M17/ 4-methyl-DADK -metribuzin | 27 | 27 | 59.9 | 59.9 | - | Potatoes | May 4 | 516 | 5.742 | 2.75 | | 0.08 |
| U1 Desmethylthio-metribuzin | 14 | 14 | 0.2 | 0.2 | - | Potatoes | May 4 | 516 | 0.002 | 0.001 | | 0.095 |
| Nicosulfuron | 29 | 29 | 22.8 | 22.8 | - | Maize | June 16 | 60 | 0.353 | 0.353 | | 0.17 |
| AUSN | 46 | 0.29 - 0.13 - 0 - 0 - 0 (Kf)+ | 187.9 | 187.9 | - | Maize | June 16 | 60 | 4.009 | 5.44 | | 0.89 |
| UCSN | 8 | 0.06 - 0.04 - 0 - 0 - 0 (Kf)+ | 274.9 | 274.9 | - | Maize | June 16 | 60 | 2.249 | 1.509 | | 0.36 |
| ASDM | 9 | 0.06 - 0.03 - 0 - 0 - 0 (Kf)+ | 230.8 | 319 (Hamburg 136 (Kremsmünster) | - | Maize | June 16 | 60 | 5.865 | 5.982 | | 2.24 |
| ADMP | 277 | 277 | 6.3 | 6.3 | - | Maize | June 16 | 60 | 0.007 | 0.007 | | <0.01 |
| HMUD | 5 | 0.11 (Kf) | 7 | 7 | - | Maize | June 16 | 60 | 0.329 | 0.229 | | 0.03 |
| MU-466 | 8 | 8 | 76.5 | 76.5 | - | Maize | June 16 | 60 | 4.251 | 4.251 | | 0.15 |

| Substance | $Kf_{oc}$ | | $DegT_{50}$ (d) | | | Crop | App Date** | Nominal App Rate (g/ha) | Results | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EU | D | EU | $D_{lab}$ | $D_{field}$ | | | | Tier 1 EU° | Tier 1 D Lab° | Tier 1 D Field° | Lysi-meter°° |
| Terbuthylazin | 232 | 232 | 22.4 | 75.6 | 44.5 /<br>11.2 | Maize | May 18 | 1000 | 0 | 0.569 | 0.025 | <0.01 |
| MT1 GS 26379 | 78 | 78 | 26.8 | 48.6 | 111.7<br>12.1 | Maize | May 18 | 1000 | 0.471 | 1.873 | 11.824 | <0.01 |
| MT13 GS 23158 | 187 | 187 | 452.6 | 452.6 | - | Maize | May 18 | 1000 | 15.882 | 13.098 | | 0.02 |
| MT14 GS 28620 | 195 | 2.93 (Kf) | 106.6 | 106.6 | - | Maize | May 18 | 1000 | 0 | 0 | | 0.01 |
| Thiamethoxam | 58 | 58 | 32.7 | 118.1 | 32.7 | Potatoes | June 19, July 6, July 25, Aug 10 | 4*50 | 0.332 | 9.835 | 0.332 | 0.095 |
| Clothianidin CGA 322704 | 133 | 133 | 103.6 | 103.6 | - | Potatoes | June 19, July 6, July 25, Aug 10 | 4*50 | 0.356 | 1.174 | | 0.27 |
| CGA 355190 | 93 | 93 | 31 | 31 | - | Potatoes | June 19, July 6, July 25, Aug 10 | 4*50 | 0.213 | 1.042 | | <0.01 |
| NOA 459602 | 24 | 24 | 51 | 96.5/19.1 | - | Potatoes | June 19, July 7, July 25, Aug 10 | 4*50 | 3.205 | 4.881 | | 0.332 |
| Triasulfuron | 41 | 41 | 13.6 | 77.8 | 13.6 | Winter cereals | April 29 | 7.5 | 0.005 | 0.416 | 0.005 | <0.025 |
| CGA 150829 | 142 | 1.29 (Kf) | 220.7 | 220.7 | - | Winter cereals | April 29 | 7.5 | 0.066 | 0.084 | | <0.025 |
| CGA 161149 | 118 | 118 | 1000 | 1000 | - | Winter cereals | April 29 | 7.5 | 0.619 | 0.687 | | <0.025 |
| CGA 195660 | 33 | 0.34 (Kf) | 1000 | 1000 | - | Winter cereals | April 29 | 7.5 | 1.422 | 1.13 | | <0.025 |

| Substance | $K_{f oc}$ | | $DegT_{50}$ (d) | | | Crop | App Date** | Nominal App Rate (g/ha) | Results | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EU | D | EU | $D_{lab}$ | $D_{field}$ | | | | Tier 1 EU° | Tier 1 D Lab° | Tier 1 D Field° | Lysi-meter°° |
| Triclopyr (Säure) | 1000 (pH 1) 25 (pH 14) | 1000 (pH 1) 25 (pH 14) | 27.3 | 27.3 | - | Grass | June 5 | 2000 | 20.347 | 20.347 | | 0.07 |
| TCP (3,5,6-Trichlor-2-pyridinol) | 91 | 91 | 21.9 | 21.9 | - | Grass | June 5 | 2000 | 4.187 | 4.187 | | 0.06 |
| TMP (3,5,6-Trichlor-2-methoxy-pyridin | 0 | 0 | 181 | 600. / 4 80 | - | Grass | June 5 | 2000 | 229.627 | 508.832 | | <0.01 |
| Trifloxystrobin | 2379 | 2379 | 0.6 | 0.6 | 5.2 | Spring Cereals | April 23, May 28 | 2*250 | 0 | 0 | 0 | <0.01 |
| CGA 321113 | 121 | 121 | 41.9 | 154.9 | 41.9 | Spring Cereals | April 23, May 28 | 2*250 | 0.782 | 41.575 | 3.406 | 1.22 |
| CGA 373466 (ZE) | 88 | 88 | 36.1 | 36.1 | - | Spring Cereals | April 23, May 28 | 2*250 | 1.222 | | 1.34 | 0.24 |
| NOA 413161 | 4.2 | 4.2 | 219.6 | 219.6 | - | Spring Cereals | April 23, May 28 | 2*250 | 159.747 | 135.202 | | 6.69 |
| Bentazon | 23 | 23 | 9.2 | 19.4 | 9.2 | Winter cereals | March 17 | 1000 | 0.13 | 3.402 | | 0.08 |
| Chlorthalonil | 850 | 14.38 (Kf) | 5.8 | 1.1 / 21.2 | - | Winter cereals | 6 and 22 June | 1170/1370 (50/90% c.i.). | 0 | 0 | | n.d. |
| R417888 | 10 | 9 | 101.9 | 101.9 | - | Winter cereals | 6 and 22 June | 1170/1370 | 112.993 | 98.566 | | 9.3 |

| Substance | $Kf_{oc}$ | | $DegT_{50}$ (d) | | | Crop | App Date** | Nominal App Rate (g/ha) | Results | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EU | D | EU | $D_{lab}$ | $D_{field}$ | | | | Tier 1 EU° | Tier 1 D Lab° | Tier 1 D Field° | Lysi-meter°° |
| R419492 | 0 x | 0 x | 1000 | 1000 | - | Winter cereals | 6 and 22 June | 1170/1370 | 170.372 | 125.486 | | 4.65 |
| R611965 (SDS- 46851) | 77 | 77 | 103 | 103 | - | Winter cereals | 6 and 22 June | 1170/1370 | 25.252 | 25.432 | | 1.3 |
| Thiacloprid | 624 | 624 | 1.4 | 1.4 | - | grass | May 17 and 31 | 2*400 | 0 | 0 | | n.d. |
| M02, YRC 2254-amid | 319 | 319 | 52.5 | 52.5 | - | grass | May 17 and 31 | 2*400 | 0 | 0 | | n.d. |
| M30, YRC-sulfonsäure, Na-Salz | 21 | 21 | 31.2 | 31.2 | - | grass | May 17 and 31 | 2*400 | 36.801 | 36.801 | | 2.52 |
| Dimethachlor | 72 | 72 | 4.5 | 4.5 | - | OSR | 1 day before emergence | 1500 | 0 | 0 | | n.d. |
| CGA 354742, Sulfonsäure-Derivate | 4 | 4 | 14.9 | 14.9 | - | OSR | 1 day before emergence | 1.500 | 36.409 | 36.409 | | 35.1 |
| CGA 50266, Oxalsäure-Derivate | 0 | 0 | 12.9 | 12.9 | - | OSR | 1 day before emergence | 1.500 | 29.069 | 29.069 | | 36.2 |
| Isoxaben | 351 | 351 | 94.4 | 301 | 307 / 40.3 | fallow | 21 Oct | 250 | 0.058 | 4.457 | 4.666 | 0.05 |
| Hydroxy-Isoxaben | 37 | 37 | 58.9 | 92.7 | 58.9 | fallow | 21 Oct | 250 | 15.06 | 25.638 | 17.326 | 0.07 |
| Quinmerac | 42 | 42 | 9.8 | 18.9 | 9.8 | Sugar beet | 16 May | 225 | 0 | 0.016 | 0 | <0.02 |
| BH 518-2 | 88 | 1.06 (Kf) | 23.9 | 23.9 | - | Sugar beet | 16 May | 225 | 0.006 | 0.019 | | 6.49 |
| BH 518-5 | 73 | 73 | 71.5 | 71.5 | - | Sugar beet | 16 May | 225 | 0.026 | 0.127 | | <0.01 |

| Substance | $Kf_{oc}$ | | $DegT_{50}$ (d) | | | Crop | App Date** | Nominal App Rate (g/ha) | Results | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EU | D | EU | $D_{lab}$ | $D_{field}$ | | | | Tier 1 EU° | Tier 1 D Lab° | Tier 1 D Field° | Lysi-meter°° |
| Benalaxyl-M | 6063 | 66.4 (Kf) | 95 | 95 | - | Tomatoes | 30 May, 13 June,28 June,4 July | 4*240 | 0 | 0 | 0 | n.d. |
| M1 (orM7) | 495 | 13.19 (Kf) | 98.9 | 98.9 | - | Tomatoes | 30 May, 13 June,28 June,4 July | 4*240 | 0 | 0 | | 4.9 |
| Diazinon | 413 | 413 | 7.9 | 12.8 (Hamburg)<br>5.7 (Kremsmünster) | - | Sugar beet | 24 may, 21 June,25 July,19 Aug | 4*240 | 0 | 0 | | 0.07 |
| G27550 | 6 | 6 | 55.7 | 55.7 | - | Sugar beet | 24 may, 21 June,25 July,19 Aug | 4*240 | 45.943 | 49.871 | | 1.02 |
| Dichlobenil | 248 | 248 | 26.3 | 26.3 | 72 | fallow | 16 May | 8100 | 0 | 0 | 0.613 | <LOQ |
| BAM | 41 | 41 | 119.3 | 2666 | 119.3 | fallow | 16 May | 8100 | 1428 | 3478 | 3457 | 94.1 |
| Dimethenamid-P | 227 | 1.37 (Kf) | 18.1 | 53.2 / 10.3 | - | Maize | 1 day before emergence | 1440 | 0.009 | 1.832 | | n.d. |
| M23 | 8 | 0.15 (Kf) | 28.7 | 28.7 | - | Maize | 1 day before emergence | 1440 | 7.629 | 11.975 | | 1 |
| M27 | 7 | 0.01 (Kf) | 44.4 | 44.4 | - | Maize | 1 day before emergence | 1440 | 12.167 | 20.854 | | 4 |
| Dimoxystrobin | 315 | 315 | 73.1 | 197.6 | 73.1 | Winter cereals | 12. May, 17 June | 2*250 (incl. c.i.) | 0.013 | 1.261 | 0.013 | n.d. |

| Substance | $K_{foc}$ | | $DegT_{50}$ (d) | | | Crop | App Date** | Nominal App Rate (g/ha) | Results | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EU | D | EU | $D_{lab}$ | $D_{field}$ | | | | Tier 1 EU° | Tier 1 D Lab° | Tier 1 D Field° | Lysi-meter°° |
| 505M8 | 34 | 0.35 (Kf) | 25.3 | 25.3 | - | Winter cereals | 12. May, 17 June | 2*0.25 (incl. c.i.) | 1.579 | 2.243 | | 2.35 |
| 505M9 | 43 | 0.63 (Kf) | 34.4 | 34.4 | - | Winter cereals | 12. May, 17 June | 2*0.25 (incl. c.i.) | 0.665 | 4.16 | | 1.99 |
| Flurtamone | 275 | 275 | 16.2 | 124.6 | 16.2 | Winter cereals | 1 day before emergence | 329 | 0.001 | 3.752 | 0.001 | <0.01 |
| TFMBA | 32 | 0.82 (Kf) | 13.4 | 13.4 | - | Winter cereals | 1 day before emergence | 329 | 0 | 0.02 | | 0.09 |
| Isoproturon | 126 | 126 | 7 | 7 | - | Winter cereals | 1 day before emergence | 1500 (incl. c.i.) | 0 | 0 | | 0.272/0.089 |
| Desmethylisoproturon | 147 | 147 | 21.7 | 21.7 | - | Winter cereals | 1 day before emergence | 1500 (incl. c.i.) | 0 | 0 | | 0.051/0.022 |
| Metalaxyl-M | 86 | 86 | 14.6 | 14.6 | 19.9 | Potatoes | 29.June. 14.July. , 27.July. | 100/100 /200 (80% c.i.) | 0 | 0 | 0.003 | 0.05 |
| CGA 62826 | 16 | 16 | 16.5 | 106.8 / 7.1 | 16.5 | Potatoes | 29.June. 14.July. , 27.July. | 100/100 /200 (80% c.i.) | 0.797 | 7.987 | 0.892 | 4.12 |
| CGA 108906 | 0x | 0x | 1000 | 1000 | - | Potatoes | 29.June. 14.July. , 27.July. | 100/100 /200 (80% c.i.) | 1.574 | 1.562 | 2.255 | 1.11 |

| Substance | $Kf_{oc}$ | | $DegT_{50}$ (d) | | | Crop | App Date** | Nominal App Rate (g/ha) | Results | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EU | D | EU | $D_{lab}$ | $D_{field}$ | | | | Tier 1 EU° | Tier 1 D Lab° | Tier 1 D Field° | Lysi-meter°° |
| MCPA | 74 | 157/pH5<br>38/pH7.8 | 26.7 | 26.7 | - | Spring wheat | 31 May | 2000 (90% c.i.) | 0 | 0 | | n.d. |
| Cymoxanil | 37 | 0.57 (Kf) | 1.0 | 2.2 (Hamburg)<br>0.3 (Kremsmünster) | - | Potatoes | June 30, July 6 and July 14 | 3*0.32 (80% c.i.) | 0 | 0 | | <loq |
| IN-U3204 | 26 | 26 | 0.3 | 0.1/0.7 | - | Potatoes | June 30, July 6 and July 14 | 3*0.32 (80% c.i.) | 0 | 0 | | <loq |
| IN-KQ960 | 19 | 19 | 1.6 | 0.5 /8.1 | - | Potatoes | June 30, July 6 and July 14 | 3*0.32 (80% c.i.) | 0 | 0.012 | | <loq |
| IN-T4226 | 8.5 | 8.5 | 0.7 | 0.7 | - | Potatoes | June 30, July 6 and July 14 | 3*0.32 (80% c.i.) | 0 | 0 | | 0.02 |
| Metazachlor | 124 | 124 | 6.9 | 10.8 | 6.9 | OSR | 4 September | 960 (40% c.i.) | 0 | 0 | 0 | n.d. |
| BH 479-4 | 25 | 25 | 56.4 | 89.9 | 56.4 | OSR | 4 September | 960 (40% c.i.) | 22.088 | 33.138 | 28.08 | 21.4 |
| BH 479-8 | 15 | 15 | 116.4 | 123.2 | - | OSR | 4 September | 960 (40% c.i.) | 55.505 | 56.303 | 55.505 | 6.17++ |
| Iodosulfuron | 47 | 47 | 2 | 2 | - | winter cereals | 24 March | 15 (50% c.i.) | 0 | 0 | | 0.007++ |
| AE F075736 | 31 | 0.07 (Kf) | 27.1 | 27.1 | - | winter cereals | 24 March | 15 (50% c.i.) | 0.027 | 0.098 | | 0.058 |

| Substance | $Kf_{oc}$ | | $DegT_{50}$ (d) | | | Crop | App Date** | Nominal App Rate (g/ha) | Results | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EU | D | EU | $D_{lab}$ | $D_{field}$ | | | | Tier 1 EU° | Tier 1 D Lab° | Tier 1 D Field° | Lysi-meter°° |
| AE F059411 | 72 | 0.23 (Kf) | 110.7 | 110.7 | - | winter cereals | 24 March | 15 (50% c.i.) | 0.025 | 0.085 | | 0.034 |
| Florasulam | 73 | 0.82 (Kf) | 3.1 | 3.1 | | OSR (BBCH 12-16) | 5 Nov | 4 (25% ci) | 0 | 0 | | 0.01 |
| 5-OH-XDE-570 | 24 | 24 | 20.9 | 20.9 | | OSR | 5 Nov | 4 (25% ci) | 0.052 | 0.052 | | 0.07 |
| DFP-ASTCA | 53 | 53 | 12.4 | 12.4 | | OSR | 5 Nov | 4 (25% ci) | 0.012 | 0.012 | | 0.02 |
| ASTCA | 83 | 83 | 201.6 | 201.6 | | OSR | 5 Nov | 4 (25% ci) | 0.049 | 0.049 | | 0.06 |
| Pinoxaden | 357 | 357 | 0.7 | 3.1 | 0.7 | winter wheat | Oct 17, Apr 05 | 50 (25% 70% ci) | 0 | 0 | | - |
| NOA407854 | 16 | 0.23 (Kf) | 1.4 | 44.2 / 2.7 | 1.4 | winter wheat | Oct 17, Apr 05 | 50 (25% 70% ci) | 0 | 2.182 | | 0.05 |
| NOA447204 | 34 | 34 | 17.5 | 45.1 | 17.5 | winter wheat | Oct 17, Apr 05 | 50 (25% 70% ci) | 0.058 | 0.399 | | 0.206 |
| Tritosulfuron | 6 | 6 | 9.7 | 247.4 / 9.5 | 9.7 | winter wheat | 28 Apr | 50 (70% ci) | 0.016 | 2.229 | | 0.04 |
| BH 635-4 (635M01) | 86 | 86 | 44 | 44 | 68.5 | winter wheat | 28 Apr | 50 (70% ci) | 0.01 | 0.010 | | 1.04 |
| BH 635-2 (635M02) | 46 | 46 | 30.8 | 30.8 | 54.9 | winter wheat | 28 Apr | 50 (70% ci) | 0.035 | 0.035 | | 0.11 |
| BH 635-3 (635M03) | 30 | 30 | 88.2 | 88.2 | 126 | winter wheat | 28 Apr | 50 (70% ci) | 0.124 | 0.123 | | 0.57 |

| Substance | $Kf_{oc}$ |  | $DegT_{50}$ (d) |  |  | Crop | App Date** | Nominal App Rate (g/ha) | Results |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | EU | D | EU | $D_{lab}$ | $D_{field}$ |  |  |  | Tier 1 EU° | Tier 1 D Lab° | Tier 1 D Field° | Lysi-meter°° |
| Foramsulfuron | 79 | 79 | 4.4 | 4.4 |  | maize | 17 June, 19 July | 45 (50%, 76% ci) | 0 | 0 |  | 0.005 |
| AE F130619 | 73 | 1.51 (Kf) | 0.5 | 0.5 |  | maize | 17 June, 19 July | 45 (50%, 76% ci) | 0 | 0 |  | 0.005 |
| Fluopicolide | 321 | 321 | 138.8 | 270.8 | 138.8 | potatoes | 27 May, 17 June, 20 July, 30 July | 104(50% ci), 107, 108, 107 (80% ci) | 0.1 | 1.206 | 0.102 | 0.009 |
| M-02 = PCA = AE C657188 (UMET/2) | 6 | 0.08 (Kf) | 2.8 | 2.8 |  | potatoes | 27 May, 17 June, 20 July, 30 July | 104(50% ci), 107, 108, 107 (80% ci) | 0.013 | 0.09 | 0.051 | n.d. |
| M-05 = AE 1344122 = P1 (=RPA433497) | 26 | 0.35 (Kf) | 43.4 | 147 / 19 |  | potatoes | 27 May, 17 June, 20 July, 30 July | 104(50% ci), 107, 108, 107 (80% ci) | 0.435 | 1.373 | 1.373 | 0.902 |
| M-10 = AE 1344123 = P4 (=RPA 433965) | 6 | 0.08 (Kf) | 26.4 | 215 / 4.7 |  | potatoes | 27 May, 17 June, 20 July, 30 July | 104(50% ci), 107, 108, 107 (80% ci) | 0.356 | 0.995 | 1.019 | 0.931 |

* if not expressed differently: Koc °° pKa 3.97 + based on CEC correlation ** Annual simulations ° 90th percentile °°worst case annual concentration in µg/L ++ individual samples

x: no data, default value

Table 7-6: 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 technology

| Input class | $Kf_{oc}$ / Kf | $DegT_{50}$ DE | No | Name | Lysimeter | EU PUF=0 | DE PUF=0 |
|---|---|---|---|---|---|---|---|
| 1 (n=2) | $Kf_{oc}$(AM) | 90th p. | 23 | Terbuthylazin | 0.01 | 0.001 | 0.032 |
| | | | 53 | Isoxaben | 0.05 | 0.058 | 4.666 |
| 2 (n=3) | Kf (AM) | GM | 58 | Benalaxyl-M | 0 | 0 | 0 |
| | | | 78 | Cymoxanil | 0 | 0 | 0 |
| | | | 88 | Florasulam | 0.01 | 0 | 0 |
| 3 (n=1) | Kf (AM) | 90th p. | 10 | Metribuzin | 0.01 | 0.206 | 0.243 |
| 5 (n=2) | Kf (10th p.) | 90th p. | 43 | Chlorthalonil | 0 | 0 | 0 |
| | | | 64 | Dimethenamid-P | 0 | 0.011 | 2.422 |

AM = arithmetic mean
GM = geometric mean
p. = percentile
P = PELMO, L = Lysimeter

Table 7-7: 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 technology

| Input Class | $Kf_{oc}$ / Kf | $DegT_{50}$ DE | No | Substance | Lysimeter (µg/L) | D (µg/L) | EU (µg/L) |
|---|---|---|---|---|---|---|---|
| 1 (n=6) | $Kf_{oc}$(AM) | 90th p. | 9 | Methoxypyridine | 0.01 | 1.582 | 0.036 |
| | | | 24 | MT1 GS 26379 | 0.01 | 17.535 | 0.615 |
| | | | 30 | NOA 459602 | 0.332 | 7.669 | 4.656 |
| | | | 37 | TMP (3,5,6-Trichlor-2-methoxy-pyridin | 0 | 660.698 | 559.168 |
| | | | 79 | IN-U3204 | 0 | 0 | 0 |
| | | | 80 | IN-KQ960 | 0 | 0.016 | 0 |
| 2 (n=9) | Kf (AM) | GM | 21 | HMUD | 0.03 | 0.168 | 0.238 |
| | | | 34 | CGA 195660 | 0.025 | 2.442 | 3.002 |
| | | | 56 | BH 518-2 | 6.49 | 0.038 | 0.01 |
| | | | 59 | M1 (or M7) | 6.49 | 0 | 0.002 |
| | | | 68 | 505M8 | 2.35 | 3.244 | 2.207 |
| | | | 71 | TFMBA | 0.09 | 0.031 | 0 |
| | | | 93 | NOA407854 | 0.05 | 3.463 | 0 |
| | | | 100 | AE F130619 | 0.005 | 0 | 0 |
| | | | 102 | M-02 = PCA = AE C657188 (UMET/2) | 0 | 0.063 | 0.018 |
| 3 (n=4) | Kf (10th p.) | GM | 32 | CGA 150829 | 0.025 | 0.159 | 0.11 |
| | | | 69 | 505M9 | 1.99 | 6.832 | 0.946 |
| | | | 86 | AE F075736 (= Metsulfuron-Methyl) | 0.058 | 0.216 | 0.041 |
| | | | 87 | AE F059411 (M 1, IN-A4098, Triazine-Amine) | 0.034 | 0.212 | 0.043 |
| 4 (n=1) | Kf (AM) | 90th p. | 103 | M-05 = AE 1344122 = P1 (=RPA433497) | 0.902 | 2.193 | 0.613 |
| 6 (n=3) | Kf (CEC) | GM | 17 | AUSN | 0.36 | 5.007 | 3.845 |
| | | | 18 | UCSN | 2.24 | 1.51 | 2.496 |
| | | | 19 | ASDM | 0.03 | 5.743 | 5.467 |
| 7 (n=1) | Kf (pH) | pH | 8 | Pyridinol | 0.01 | 0.006 | 0.012 |

* for parent: $Kf_{oc}$ = AM and $DegT_{50}$ (lab+field) = GM
AM = arithmetic mean
GM = geometric mean
p. = percentile
P = PELMO, L = Lysimeter
pH =average of acid and neutral/basic soils (Kf arithmetic mean, $DegT_{50}$ geometric mean)
CEC = dependent on cation exchange capacity

## 7.5 Appendix 5: Time dependent concentrations supporting the data collection for the validation of the national risk assessment for groundwater

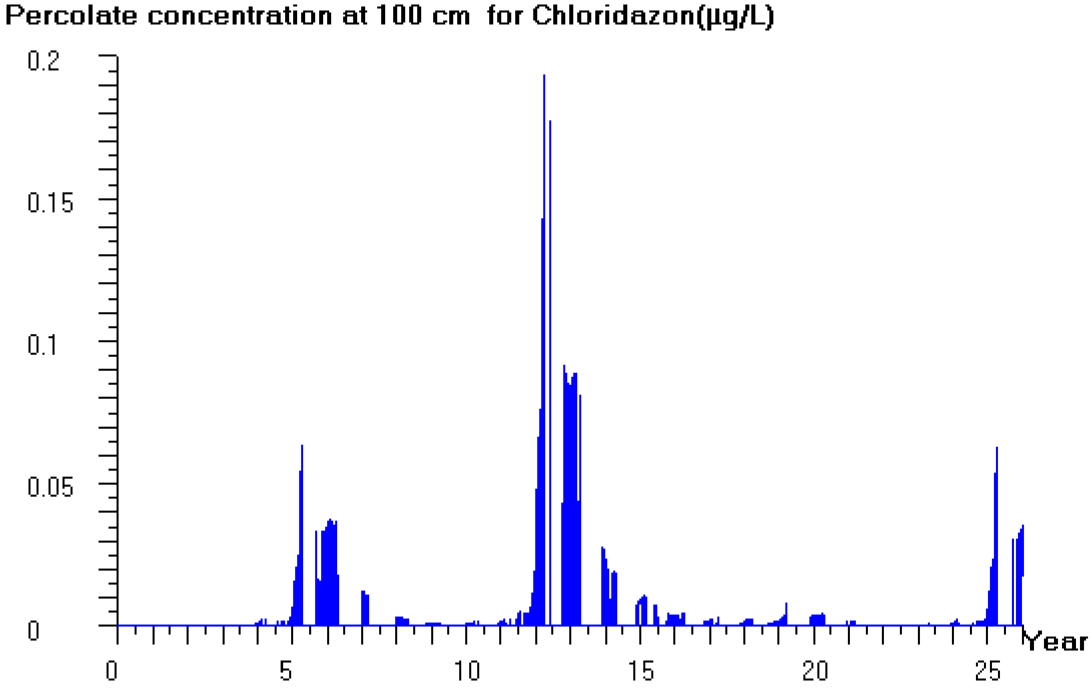


Figure 7-2: Time dependent concentration in the percolate for chloridazon

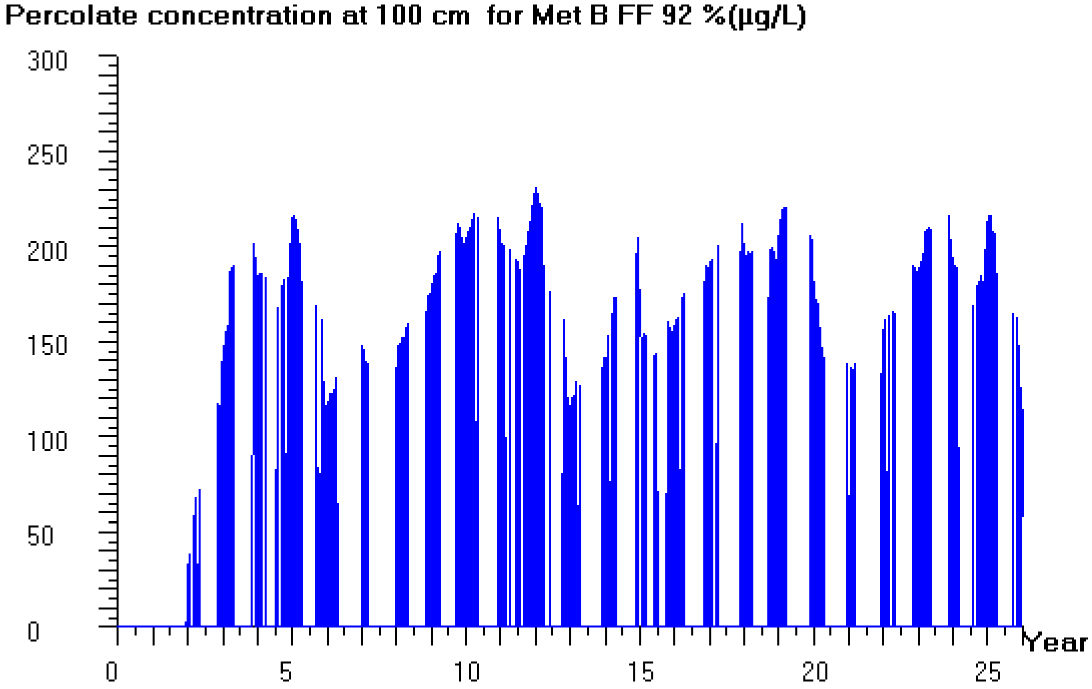


Figure 7-3: Time dependent concentration in the percolate for metabolite B

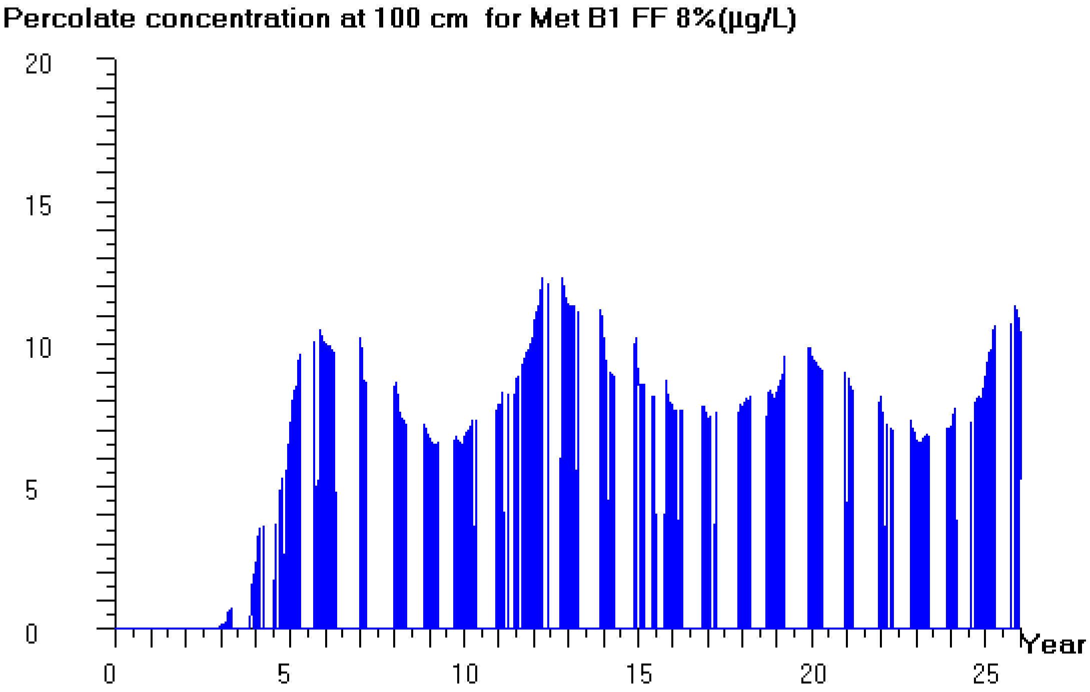


Figure 7-4: Time dependent concentration in the percolate for metabolite B1

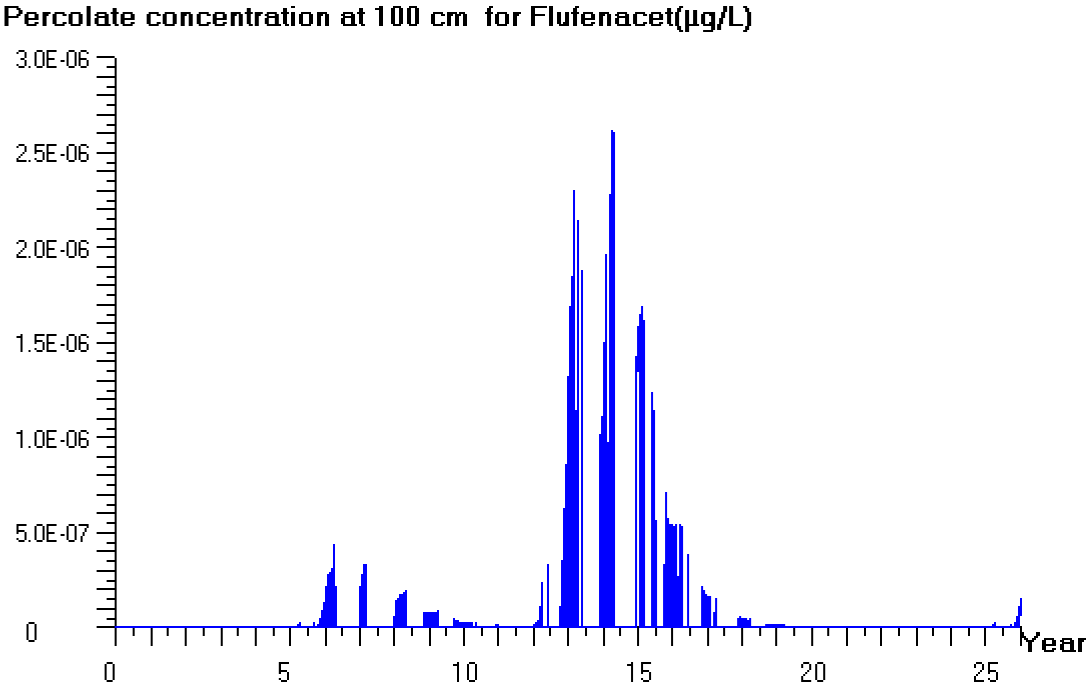


Figure 7-5: Time dependent concentration in the percolate for flufenacetat

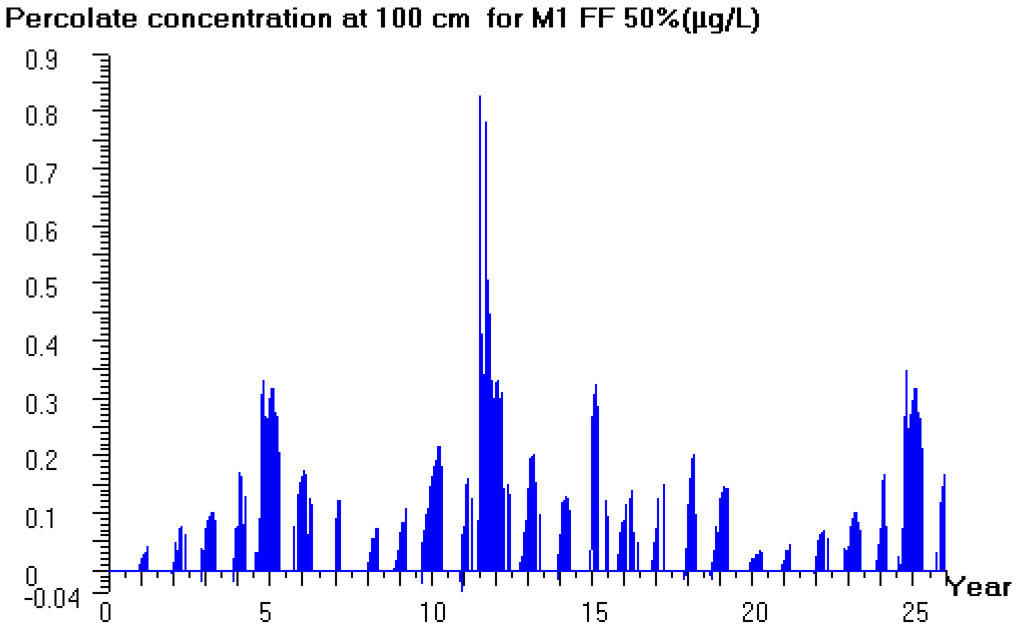


Figure 7-6: Time dependent concentration in the percolate for FOE 5043-oxalat

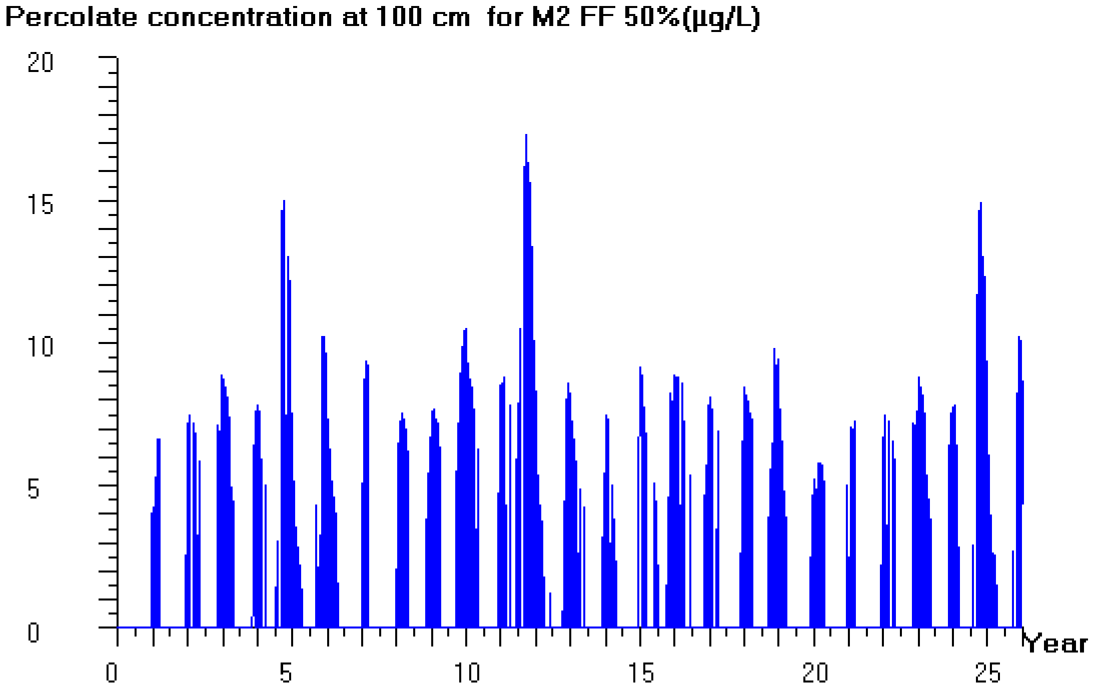


Figure 7-7: Time dependent concentration in the percolate for FOE 5043-sulfonic acid

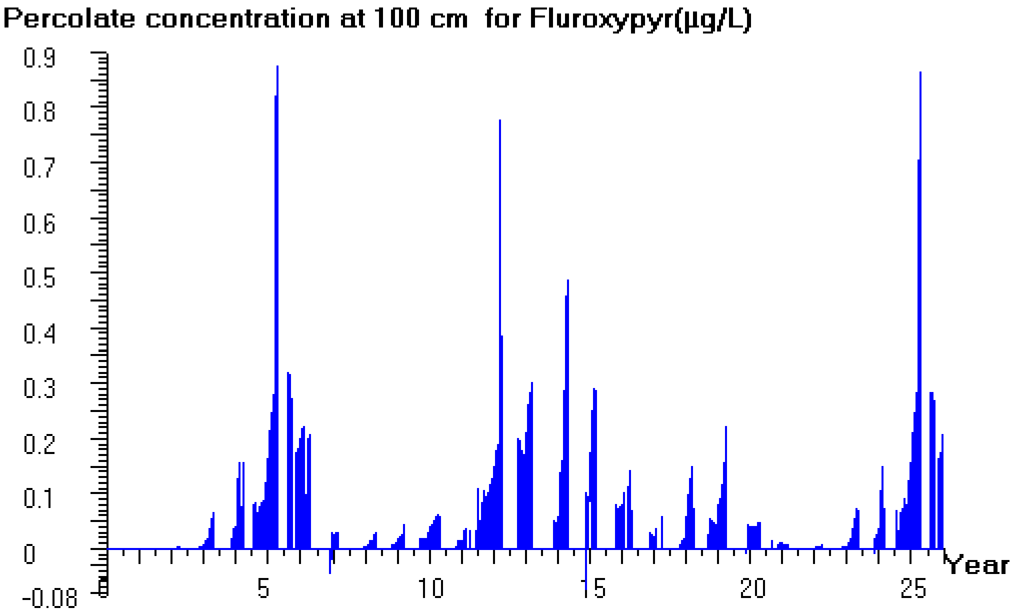


Figure 7-8: Time dependent concentration in the percolate for fluroxypyr

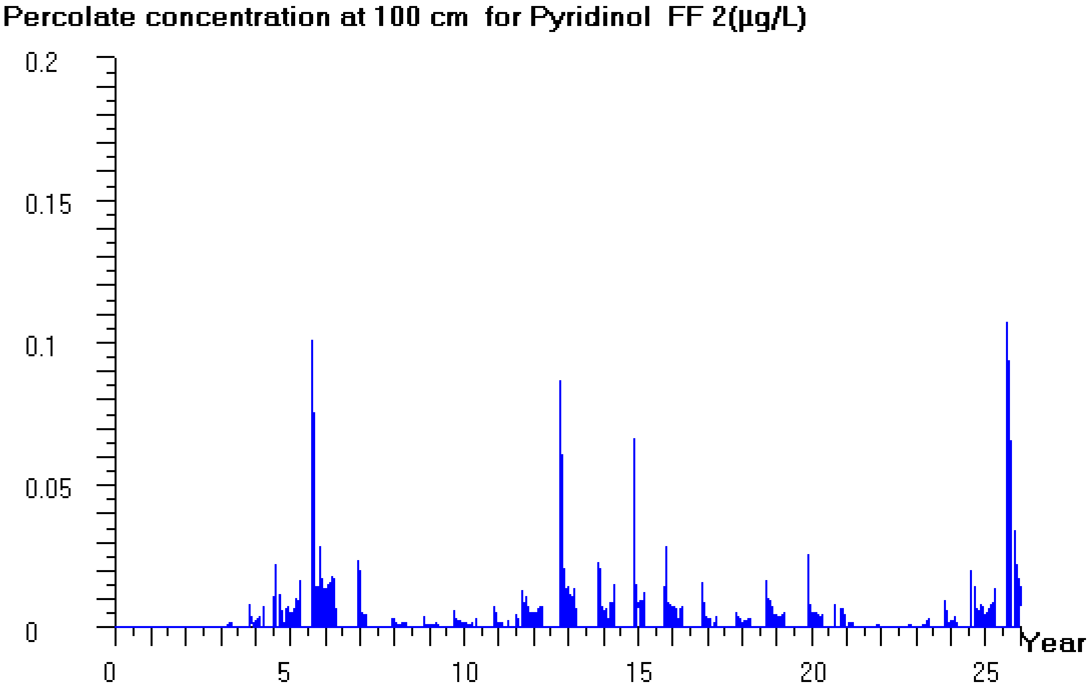


Figure 7-9: Time dependent concentration in the percolate for pyridinol

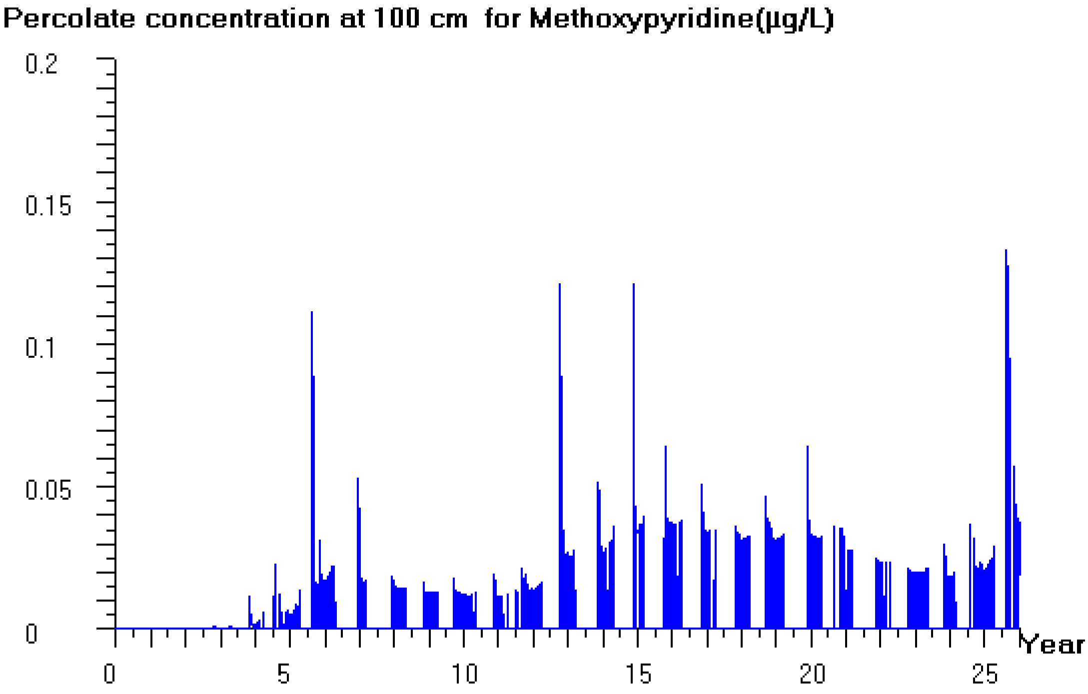


Figure 7-10: Time dependent concentration in the percolate for methoxy pyridine

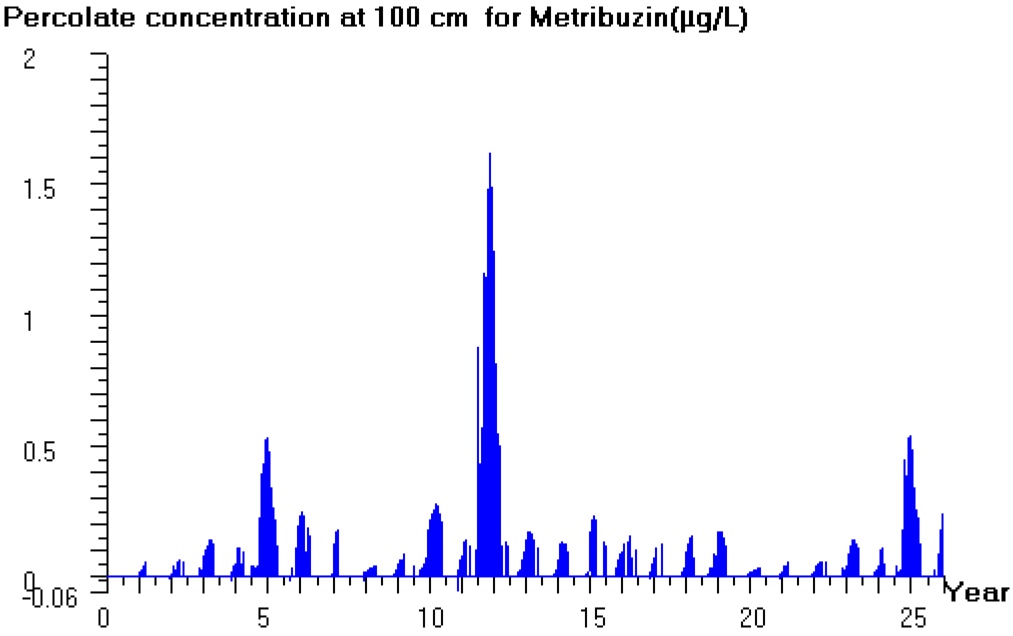


Figure 7-11: Time dependent concentration in the percolate for metribuzin

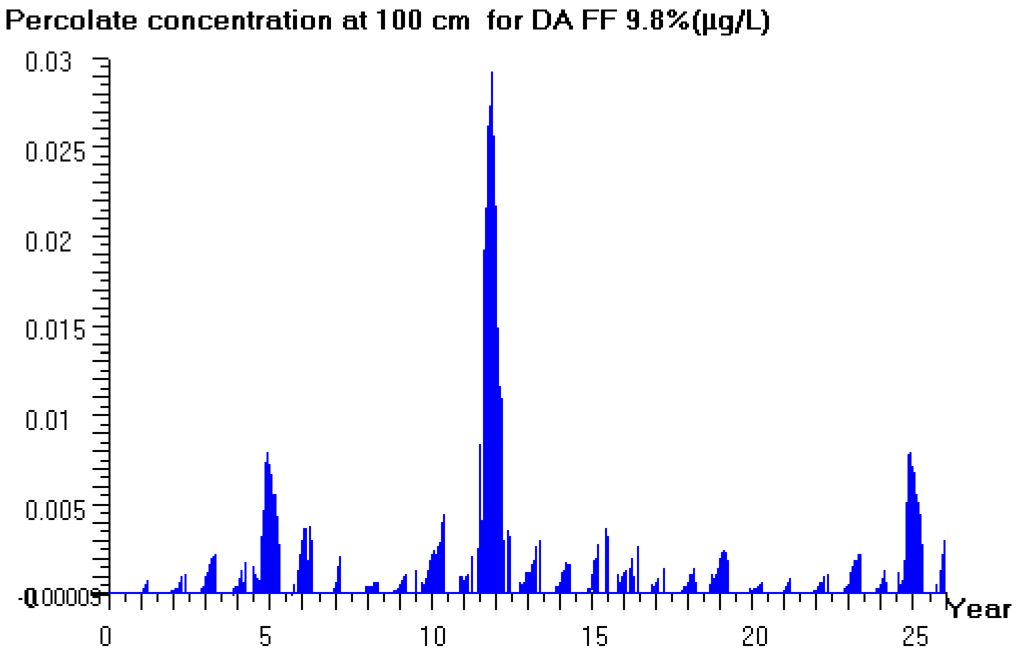


Figure 7-12: Time dependent concentration in the percolate for DA desaminometribuzin

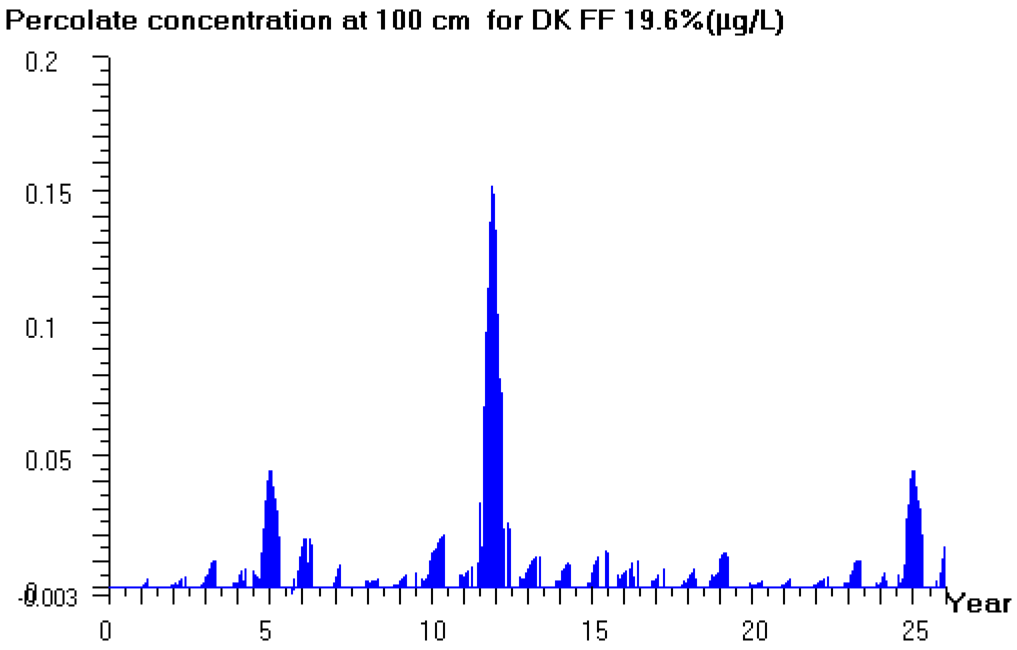


Figure 7-13: Time dependent concentration in the percolate for DK diketometribuzin M02

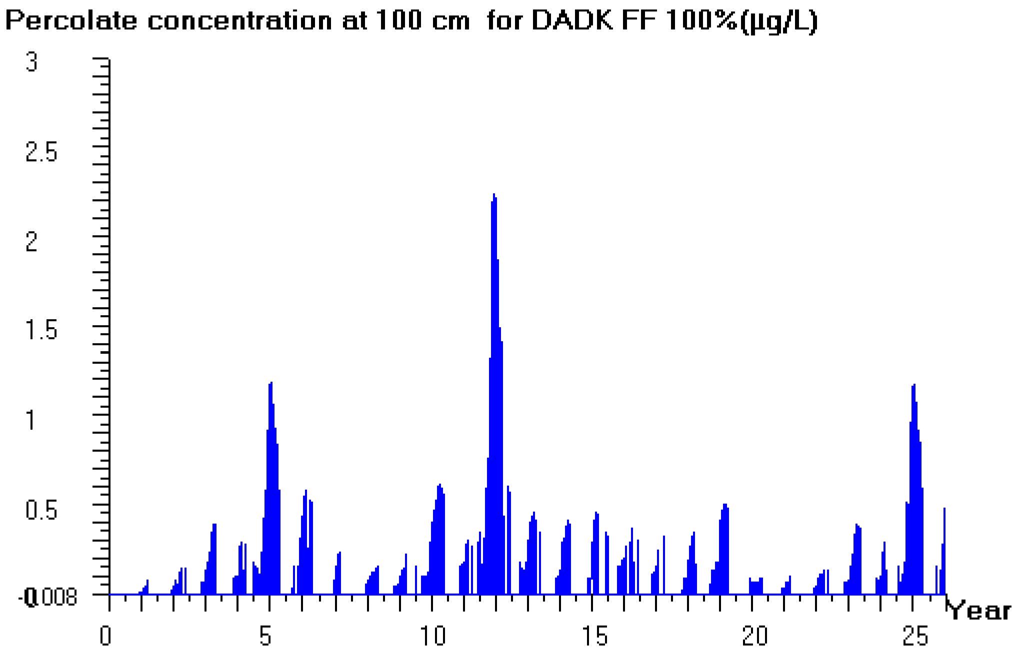


Figure 7-14: Time dependent concentration in the percolate for DADK desamino-diketometribuzin M03

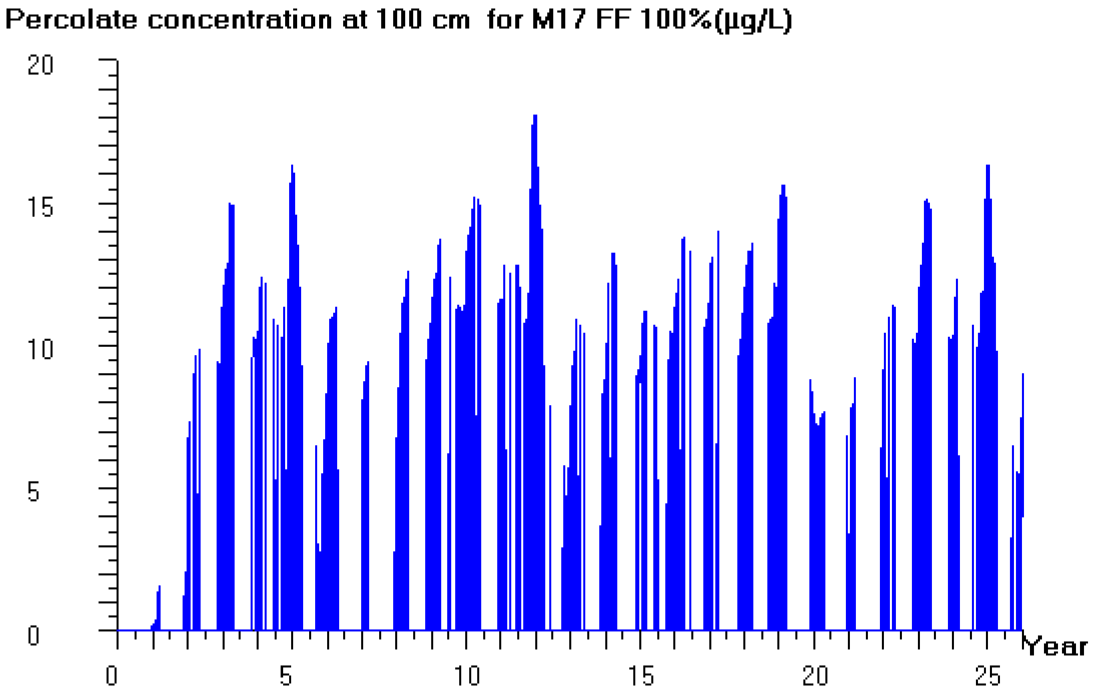


Figure 7-15: Time dependent concentration in the percolate for metabolite M17/ 4-methyl-DADK -metribuzin

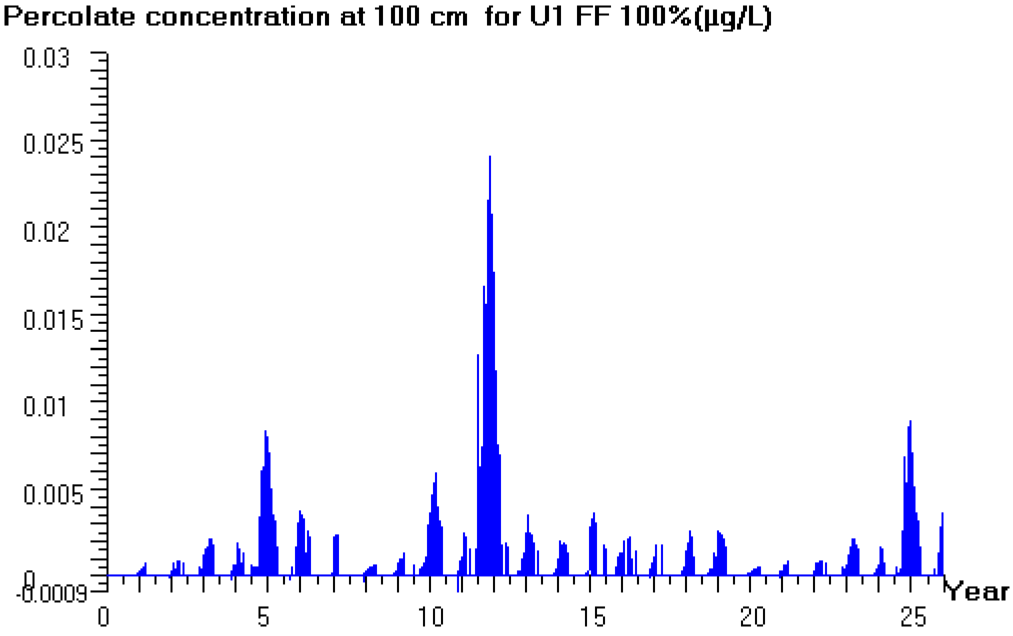


Figure 7-16: Time dependent concentration in the percolate for U1 mesmethylthio-metribuzin

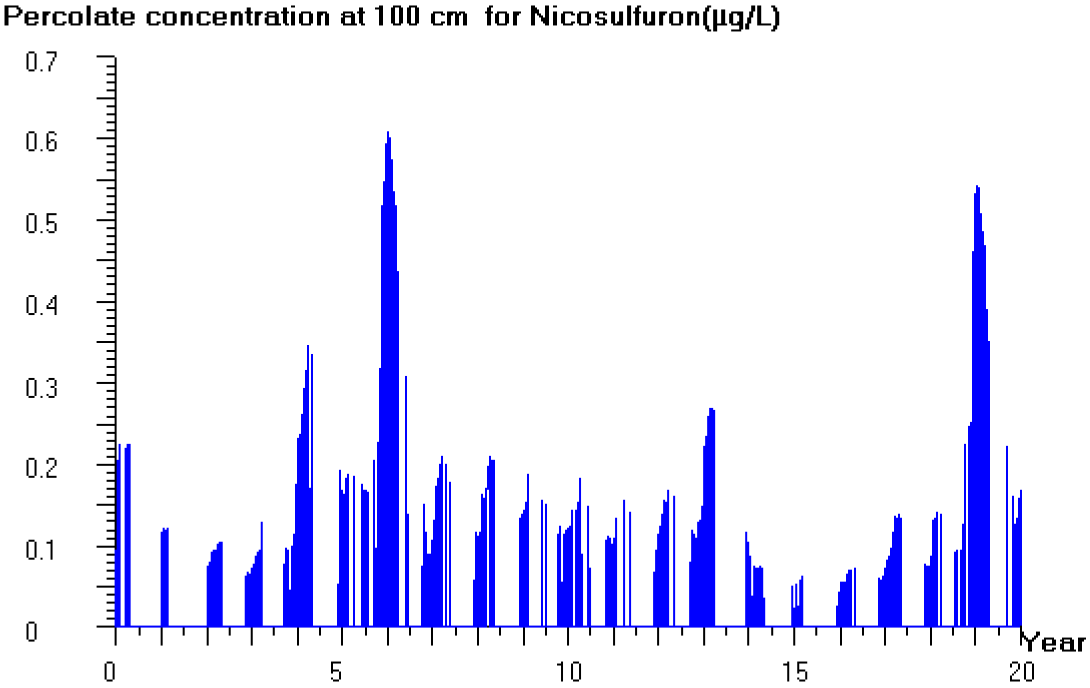


Figure 7-17: Time dependent concentration in the percolate for nicosulfuron

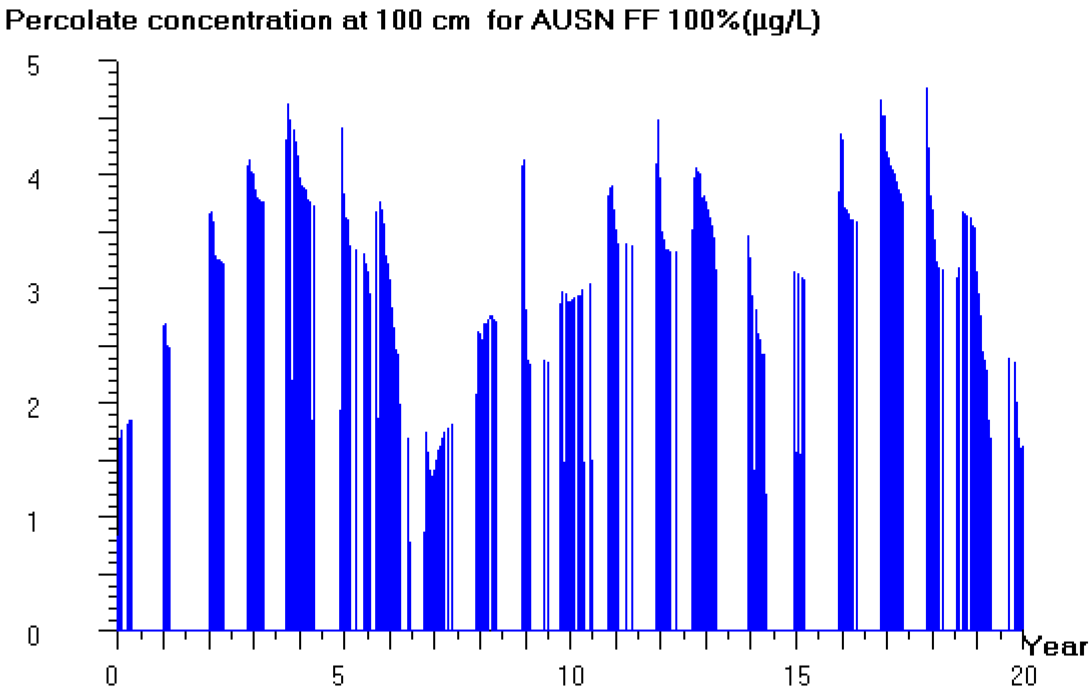


Figure 7-18: Time dependent concentration in the percolate for AUSN

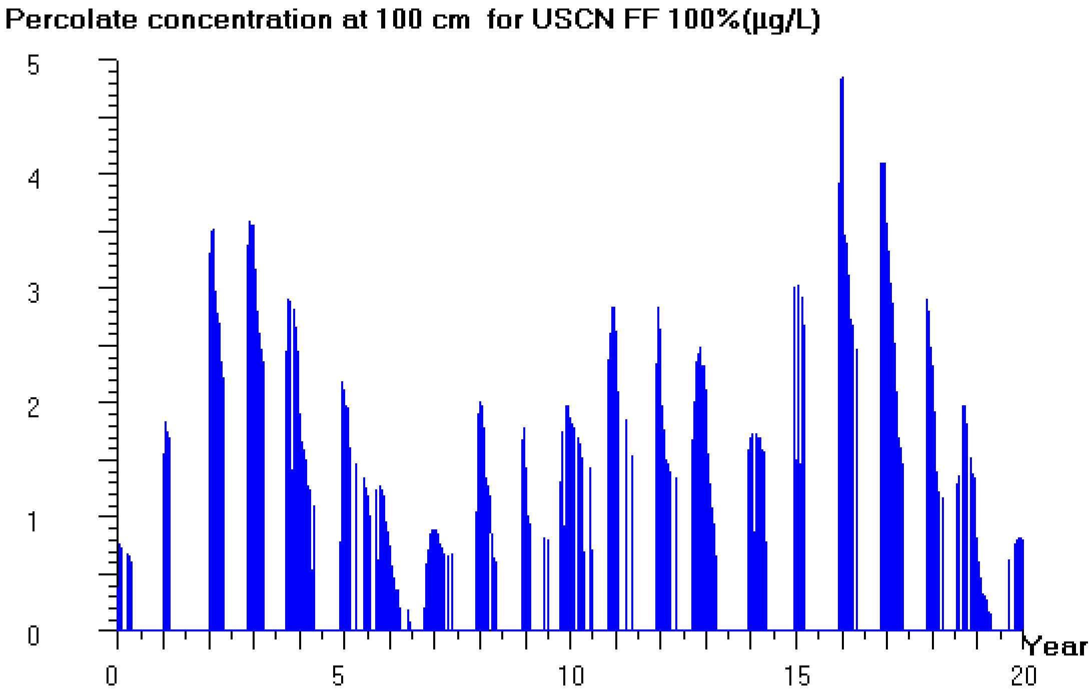


Figure 7-19: Time dependent concentration in the percolate for UCSN

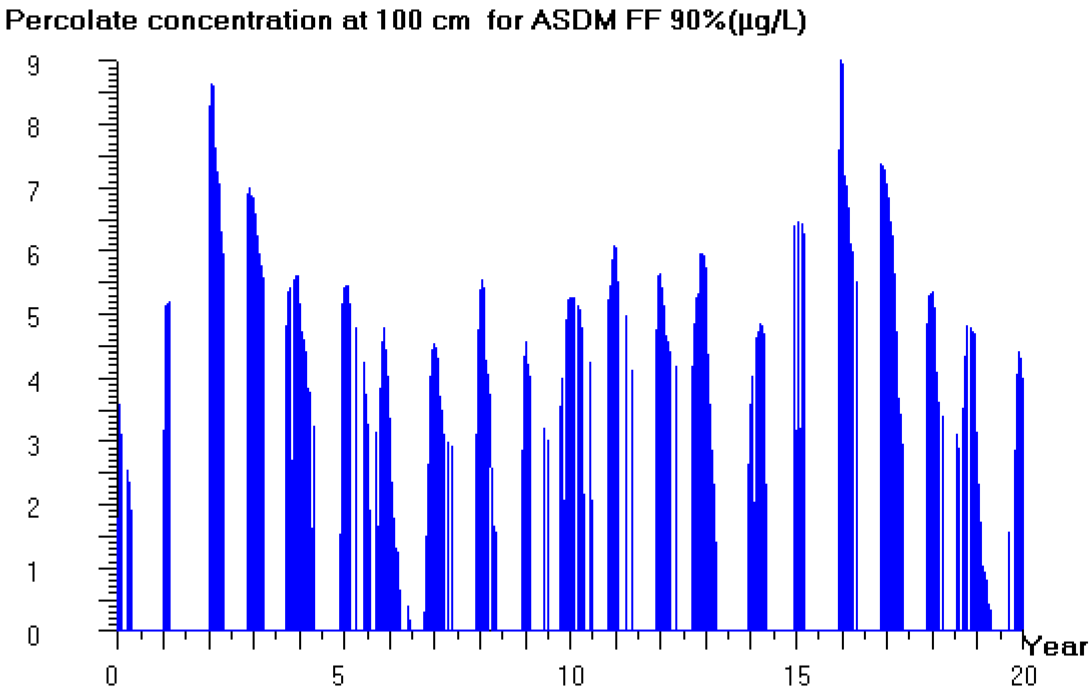


Figure 7-20: Time dependent concentration in the percolate for ASDM

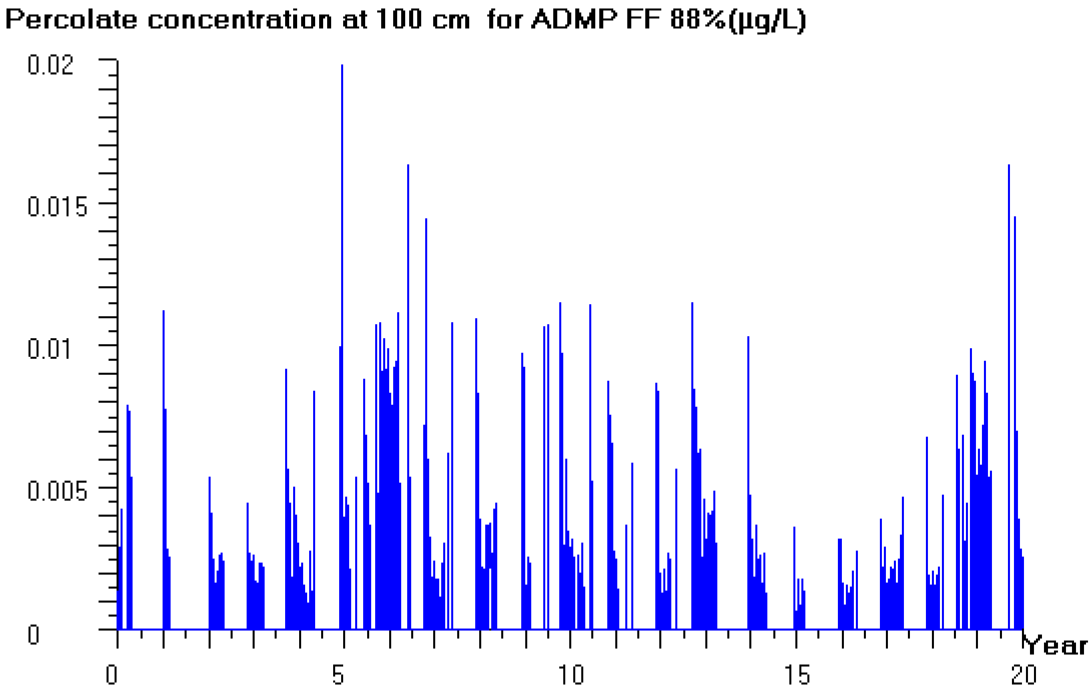


Figure 7-21: Time dependent concentration in the percolate for ADMP

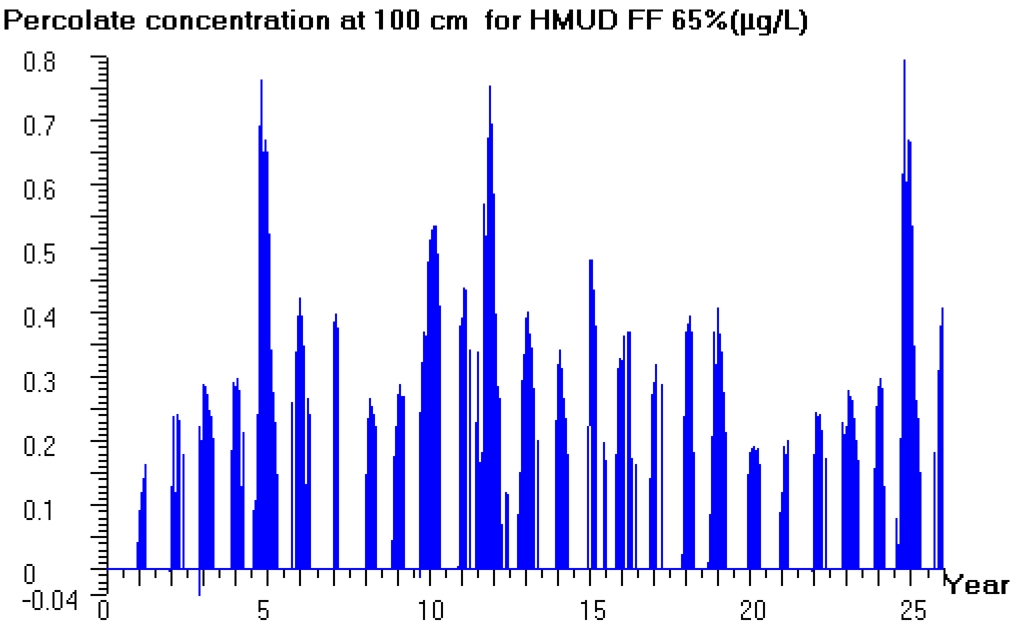


Figure 7-22: Time dependent concentration in the percolate for HMUD

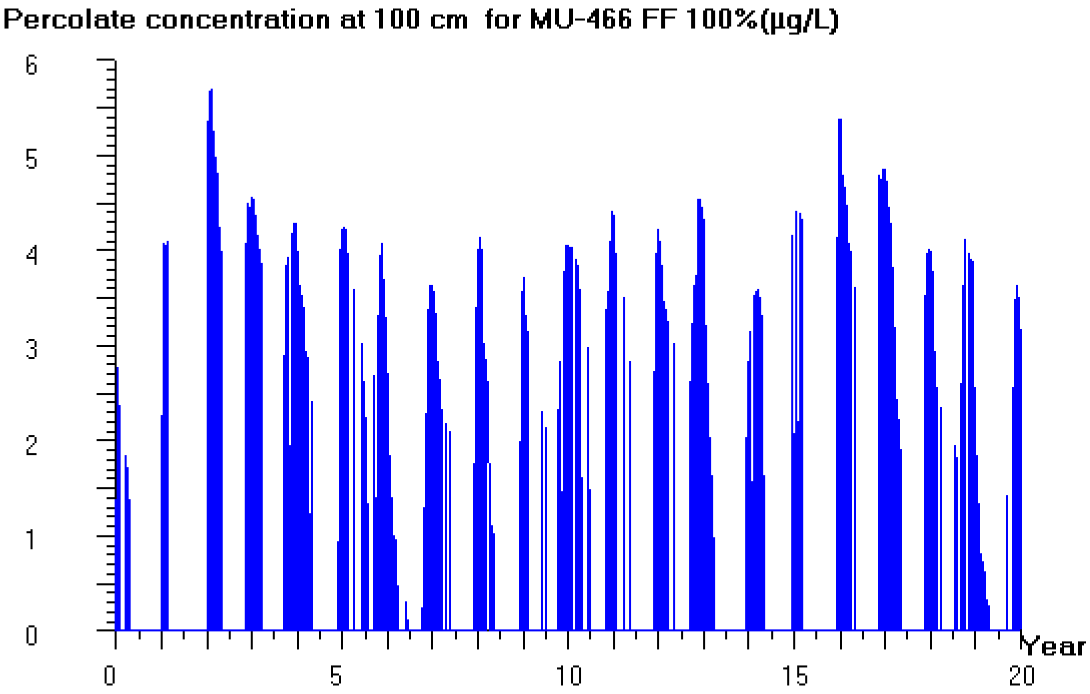


Figure 7-23: Time dependent concentration in the percolate for MU-466

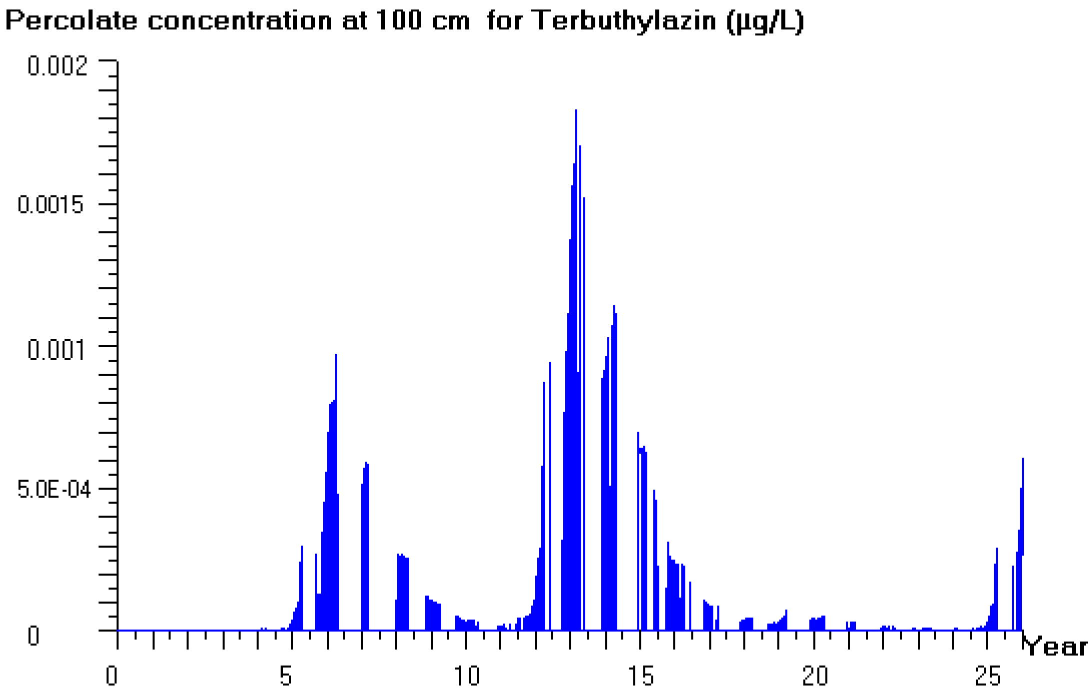


Figure 7-24: Time dependent concentration in the percolate for terbuthylazin

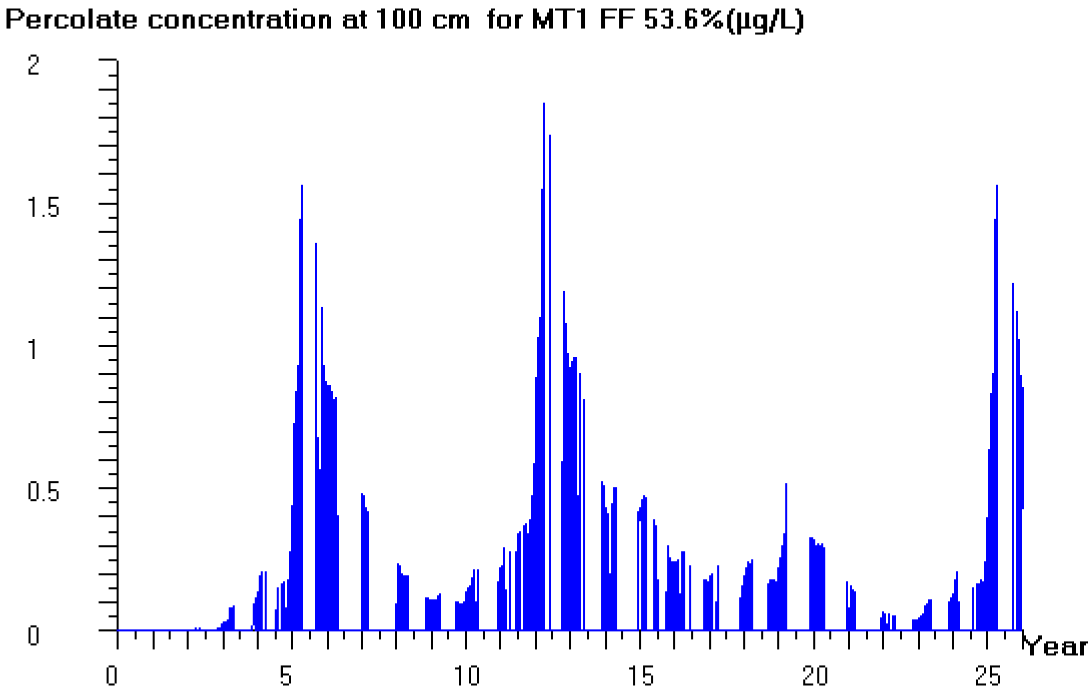


Figure 7-25: Time dependent concentration in the percolate for MT1 GS 26379

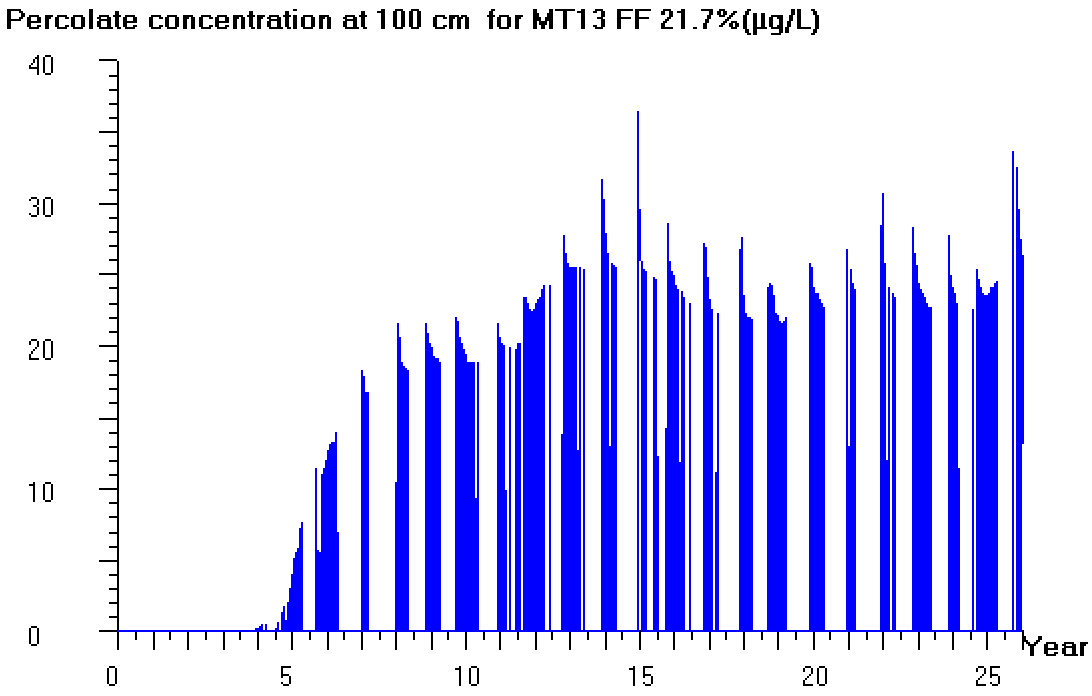


Figure 7-26: Time dependent concentration in the percolate for MT13 GS 23158

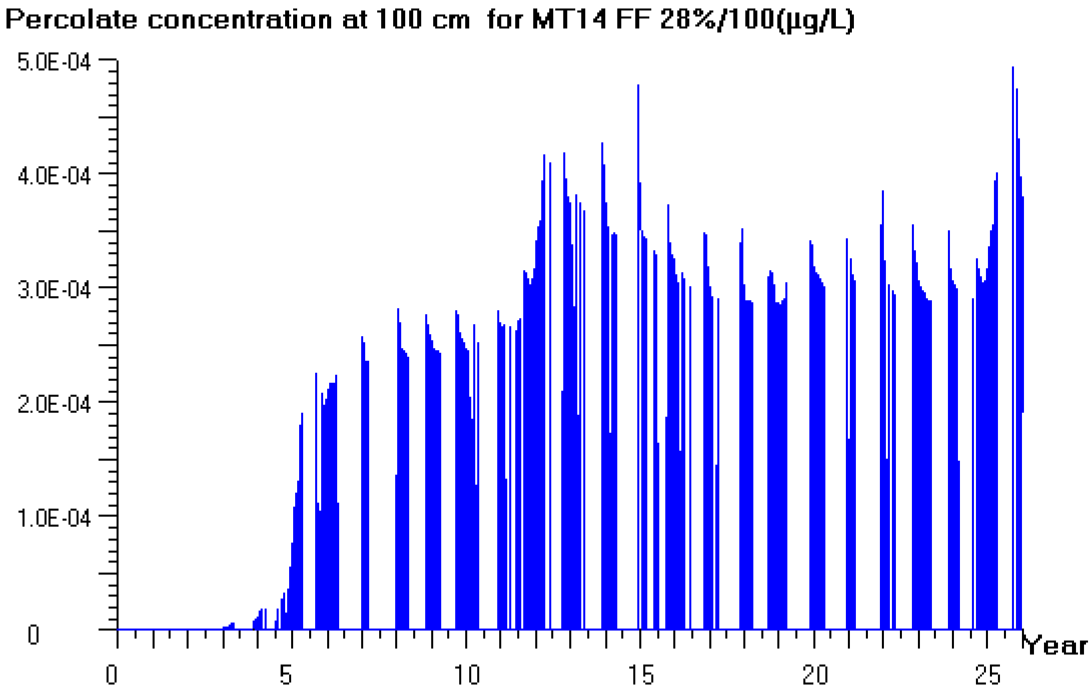


Figure 7-27: Time dependent concentration in the percolate for MT14 GS 28620

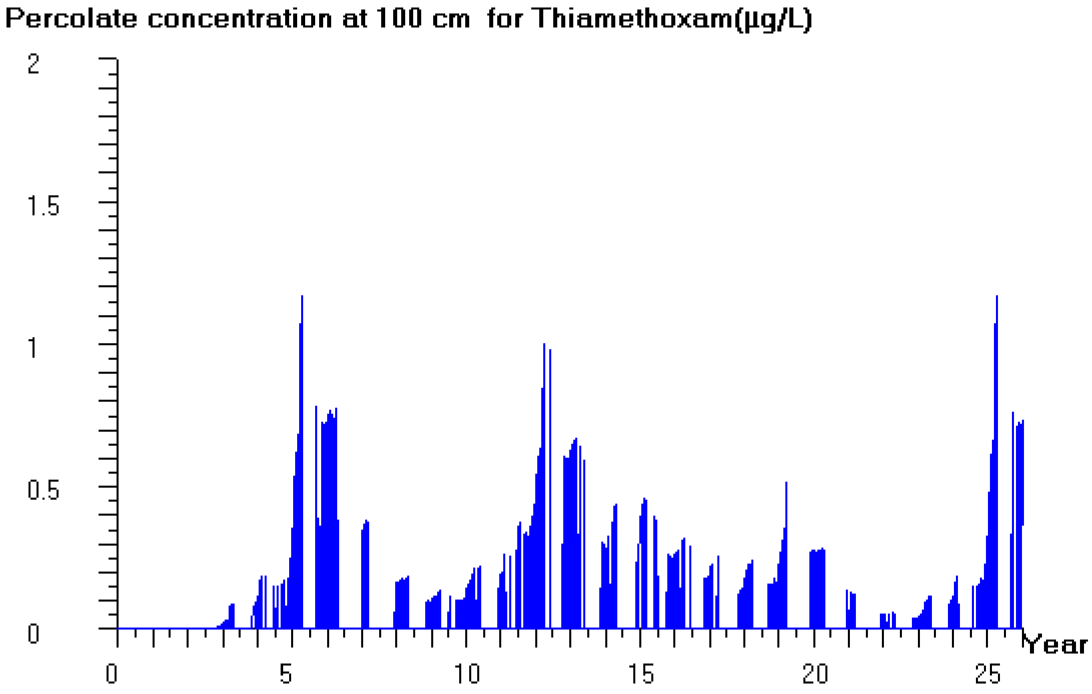


Figure 7-28: Time dependent concentration in the percolate for thiamethoxam

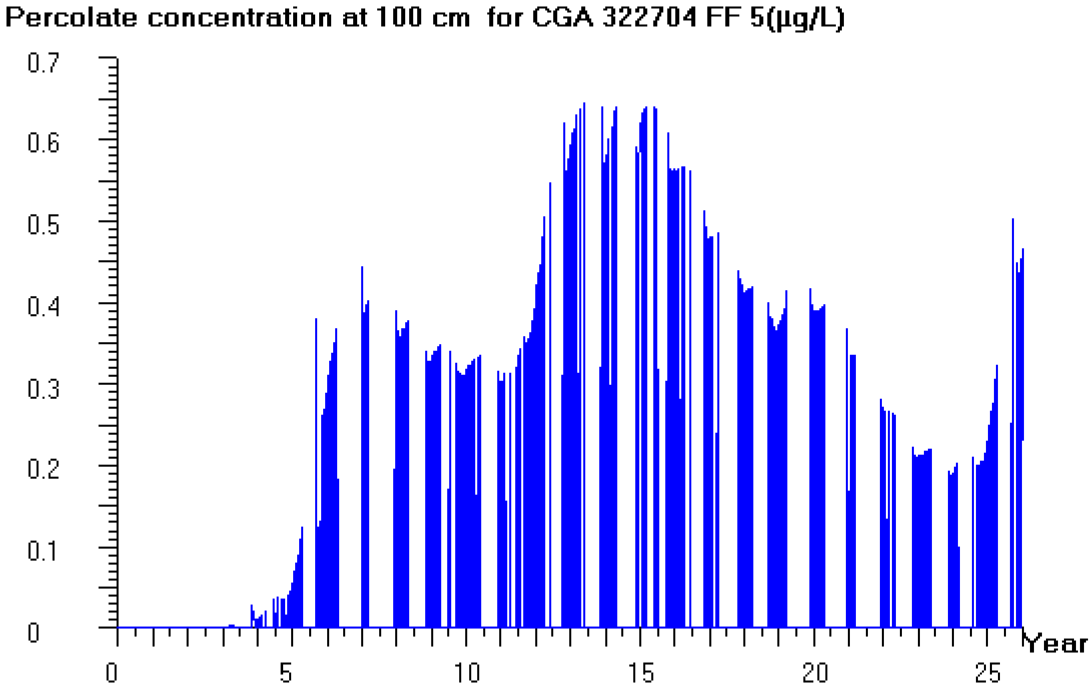


Figure 7-29: Time dependent concentration in the percolate for clothianidin CGA 322704

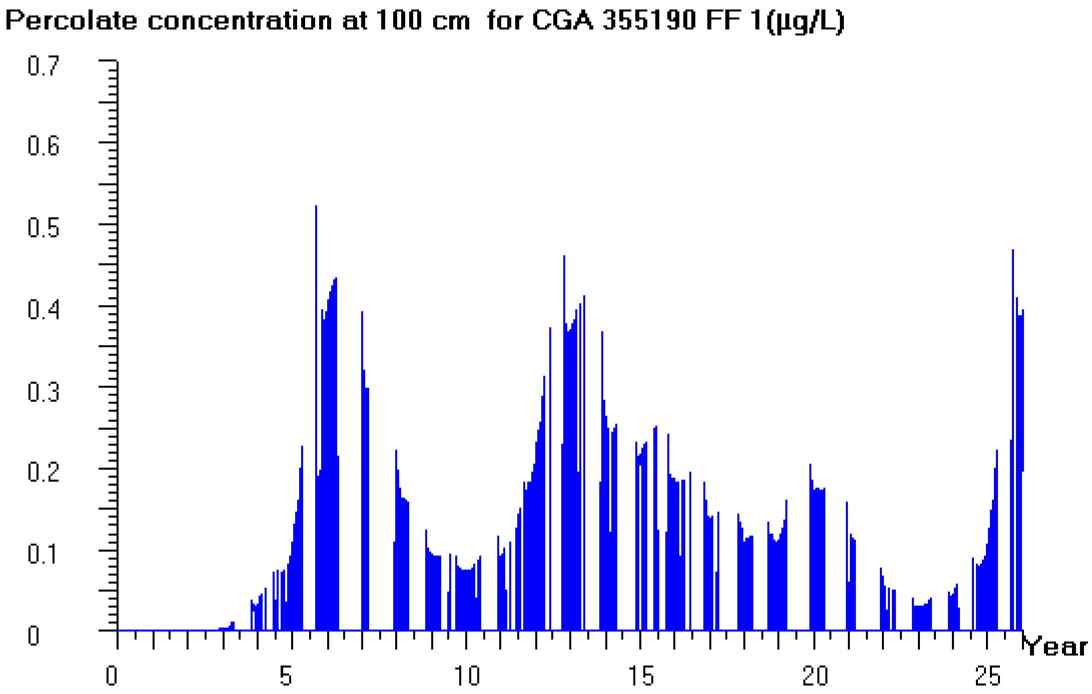


Figure 7-30: Time dependent concentration in the percolate for CGA 355190

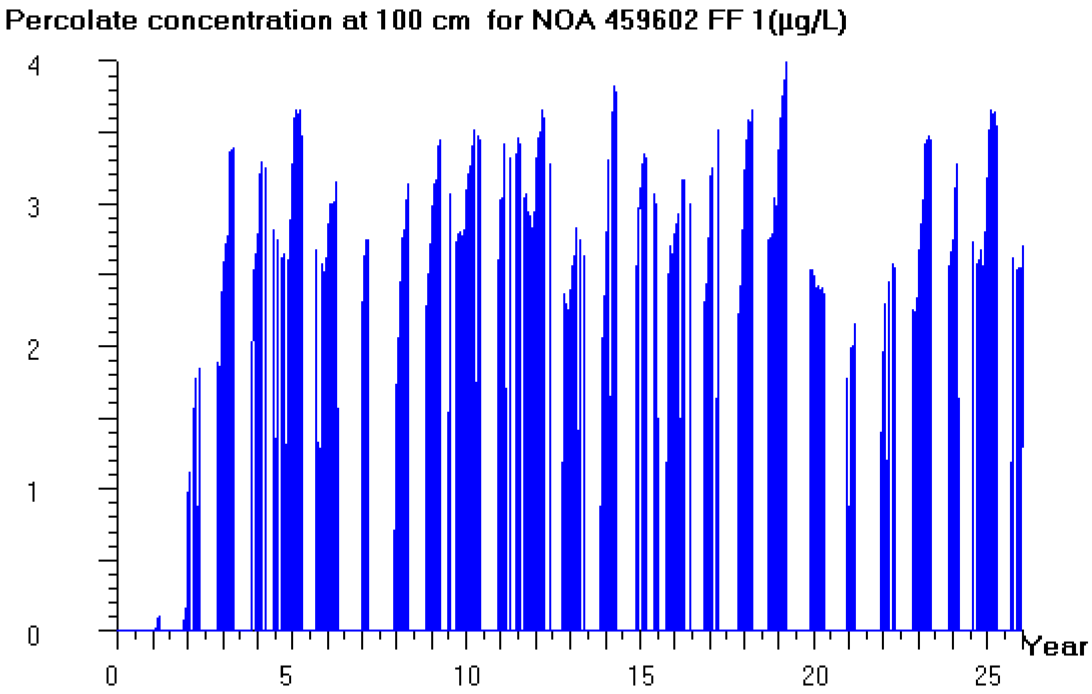


Figure 7-31: Time dependent concentration in the percolate for NOA 459602

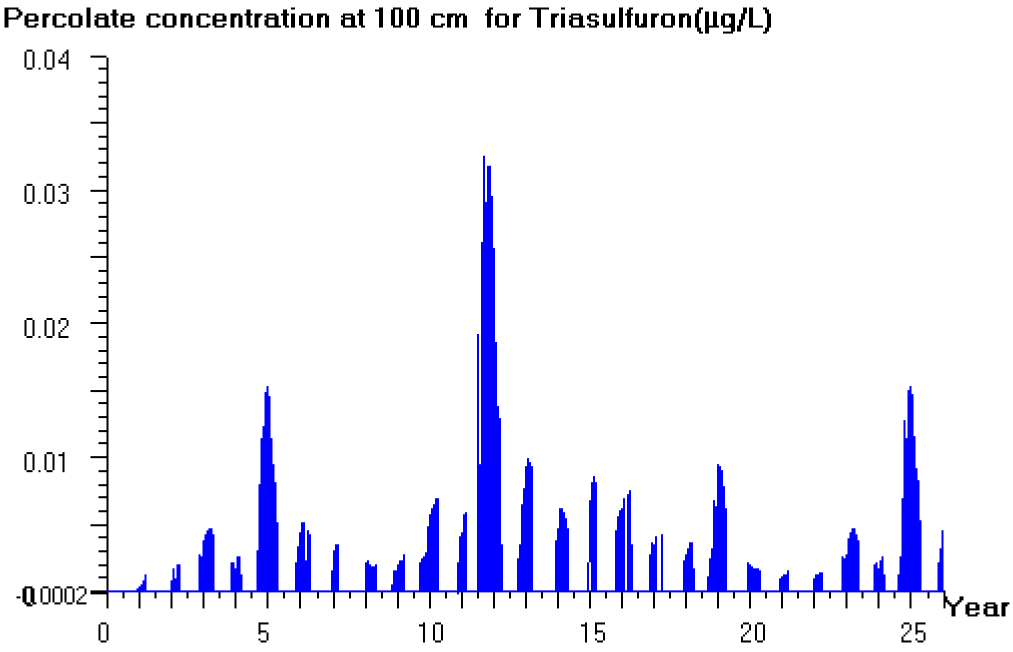


Figure 7-32: Time dependent concentration in the percolate for triasulfuron

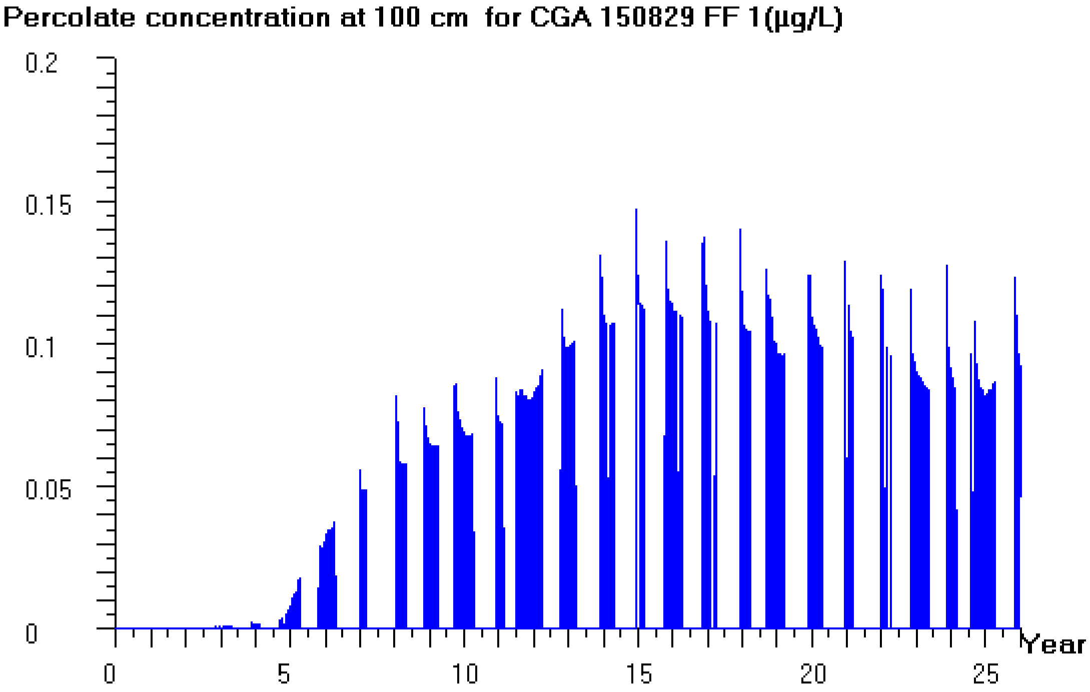


Figure 7-33: Time dependent concentration in the percolate for CGA 150829

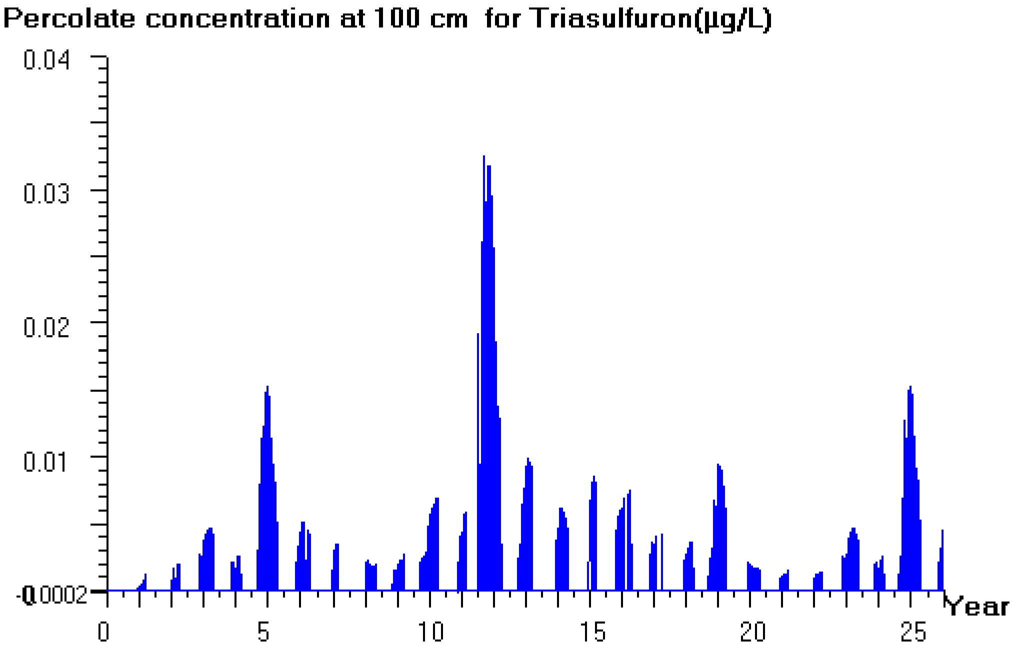


Figure 7-34: Time dependent concentration in the percolate for CGA 161149

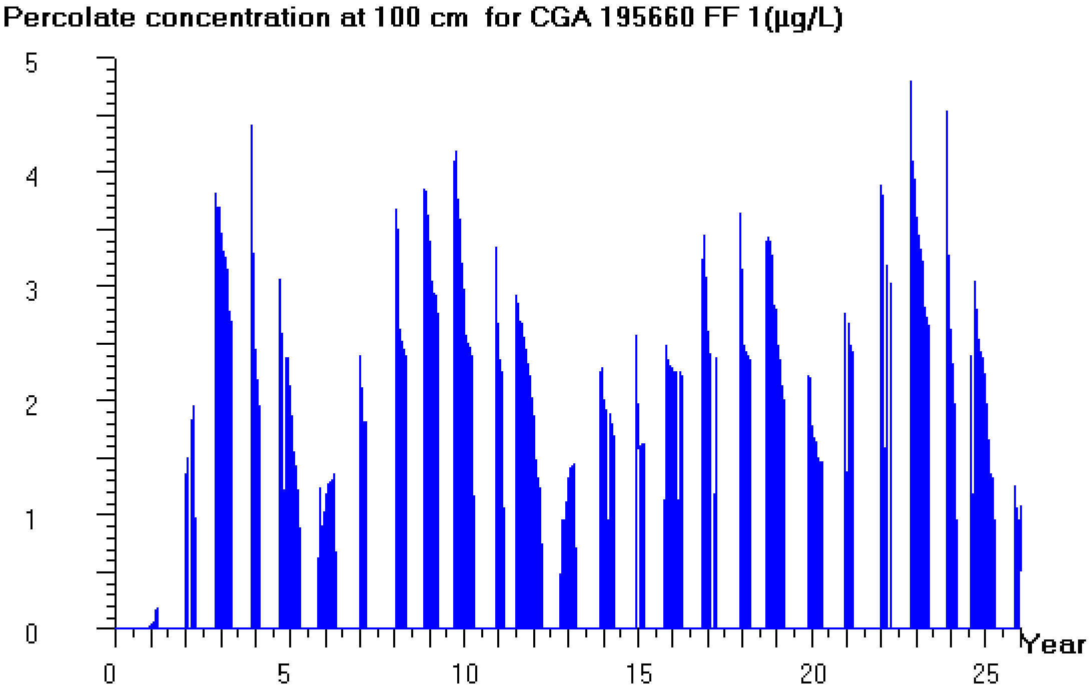


Figure 7-35: Time dependent concentration in the percolate for CGA 195660

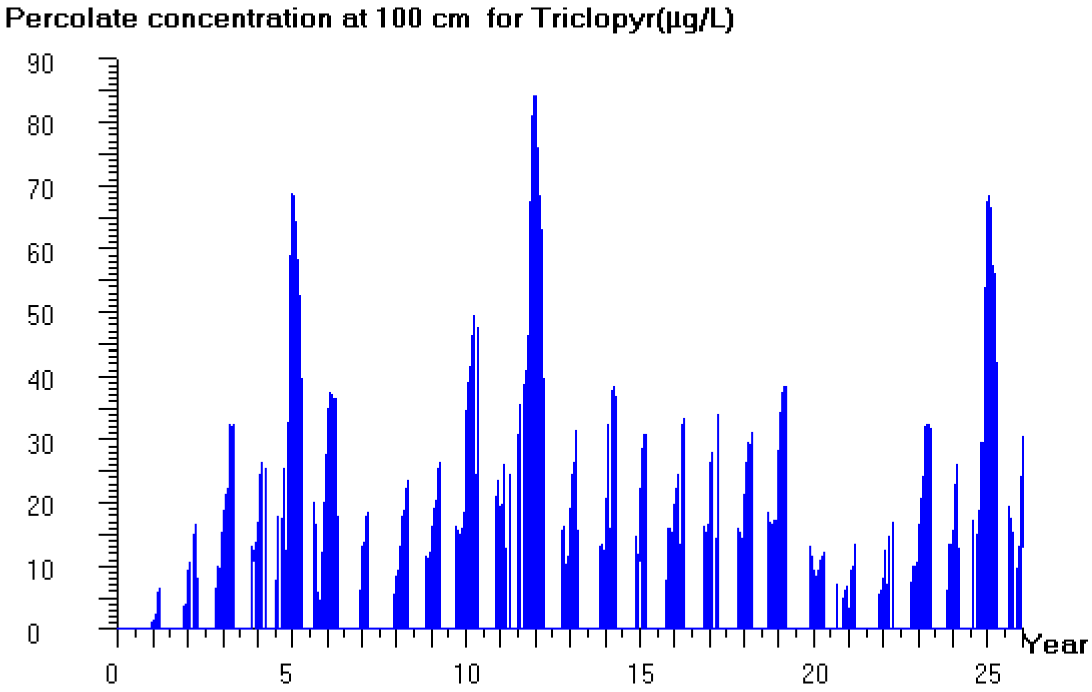


Figure 7-36: Time dependent concentration in the percolate for triclopyr (acid)

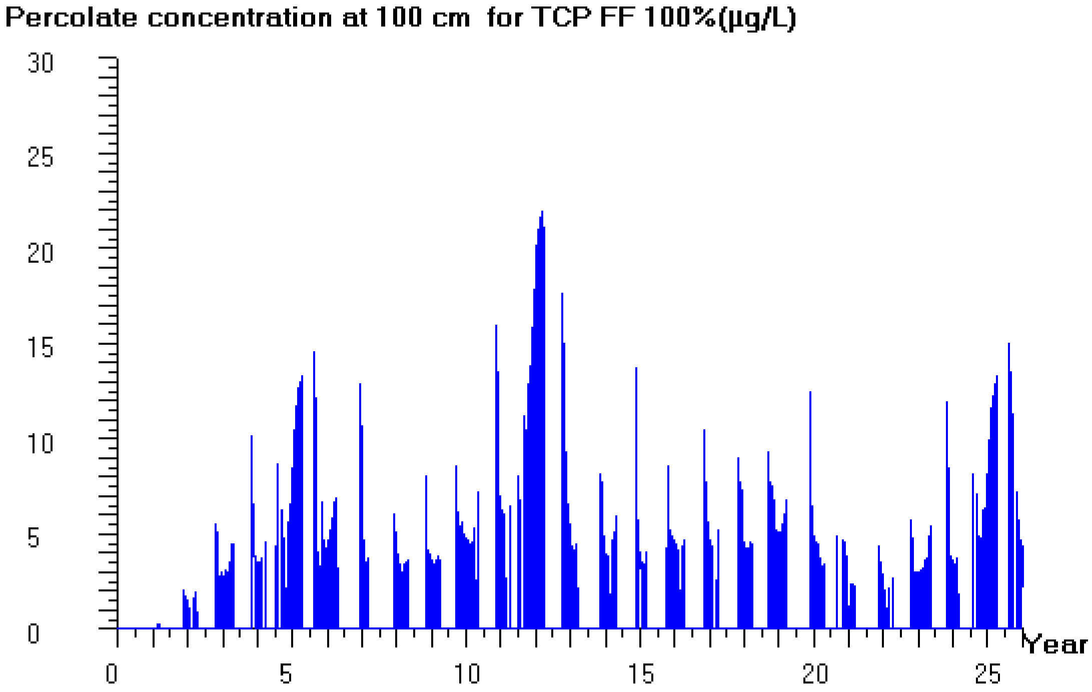


Figure 7-37: Time dependent concentration in the percolate for TCP (3,5,6-trichlor-2-pyridinol)

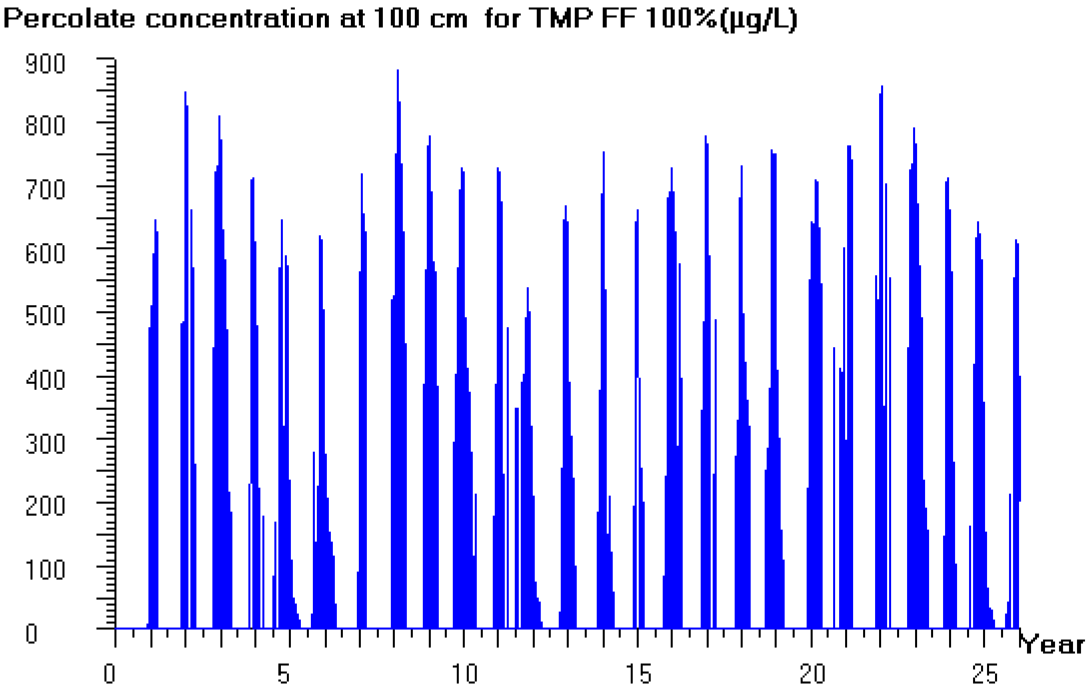


Figure 7-38: Time dependent concentration in the percolate for TMP (3,5,6-trichlor-2-methoxy-pyridin

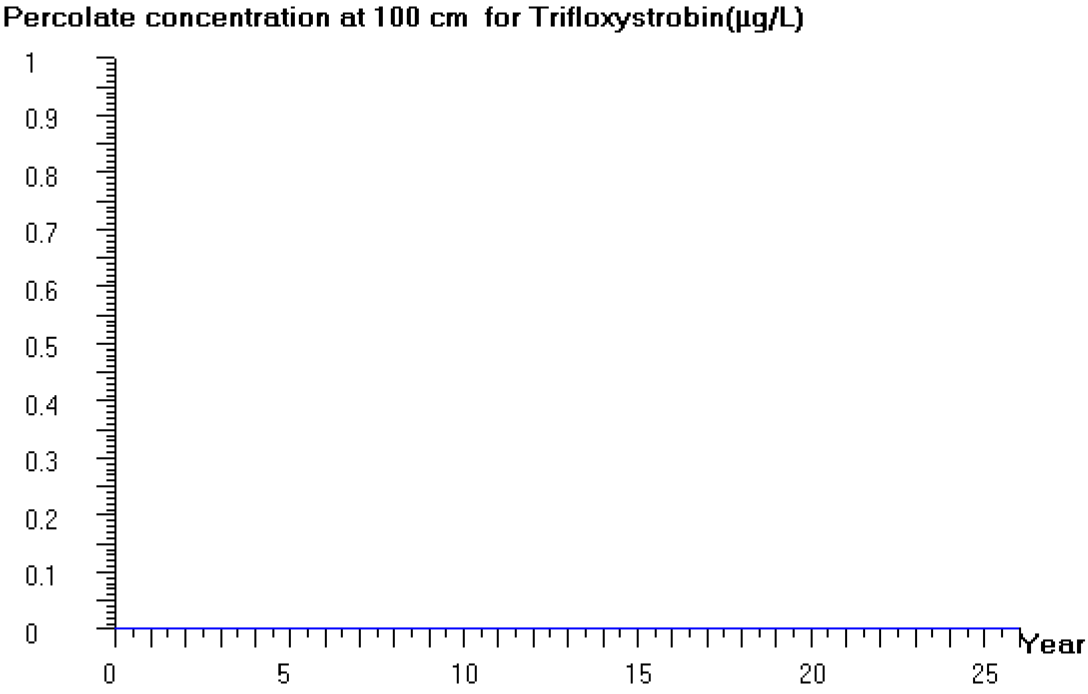


Figure 7-39: Time dependent concentration in the percolate for trifloxystrobin

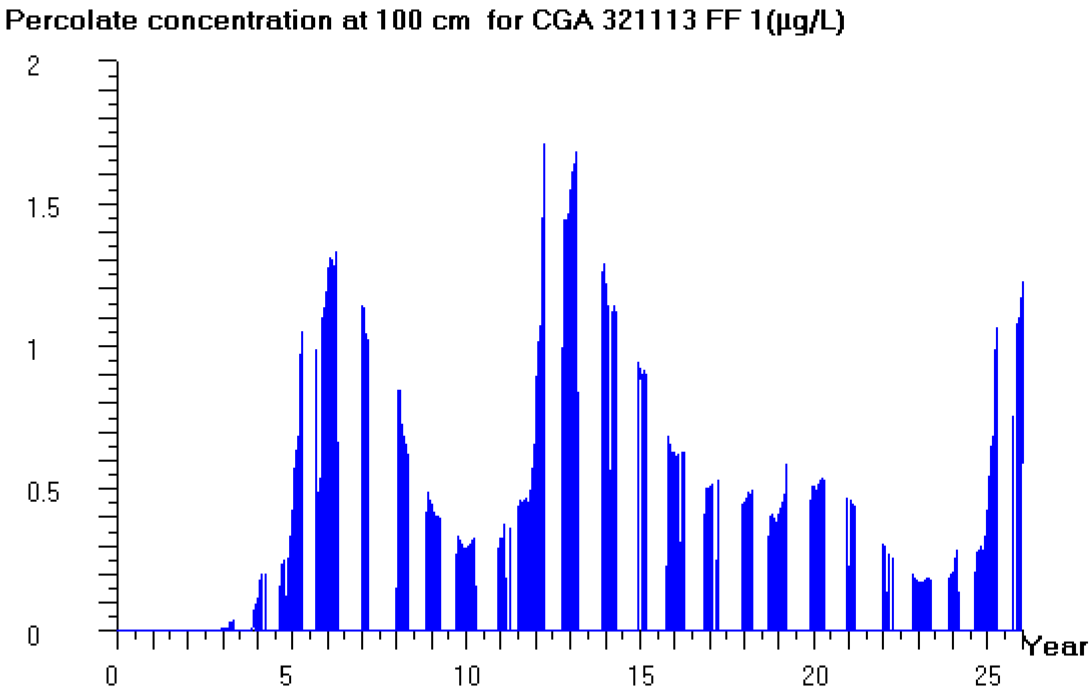


Figure 7-40: Time dependent concentration in the percolate for CGA 321113

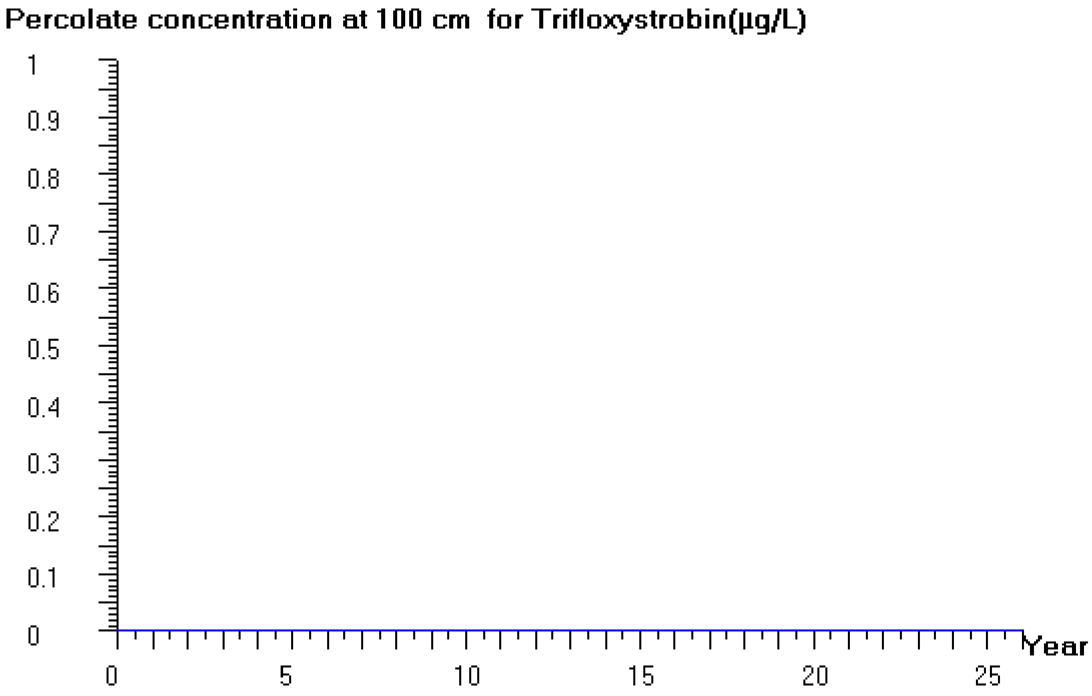


Figure 7-41: Time dependent concentration in the percolate for CGA 373466 (ZE)

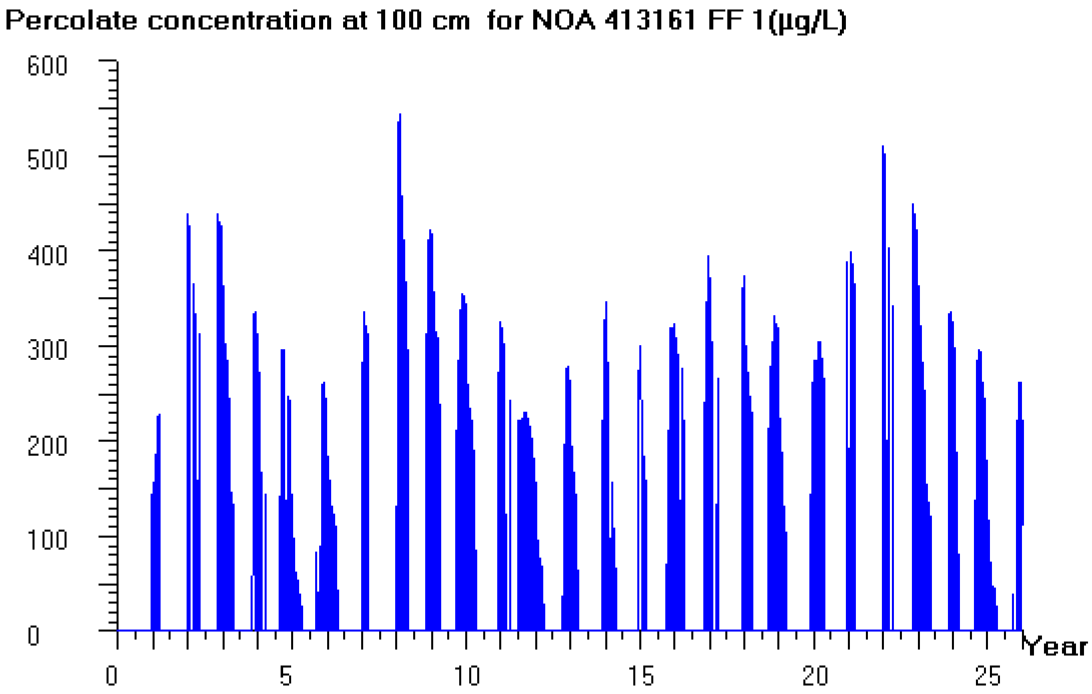


Figure 7-42: Time dependent concentration in the percolate for NOA 413161

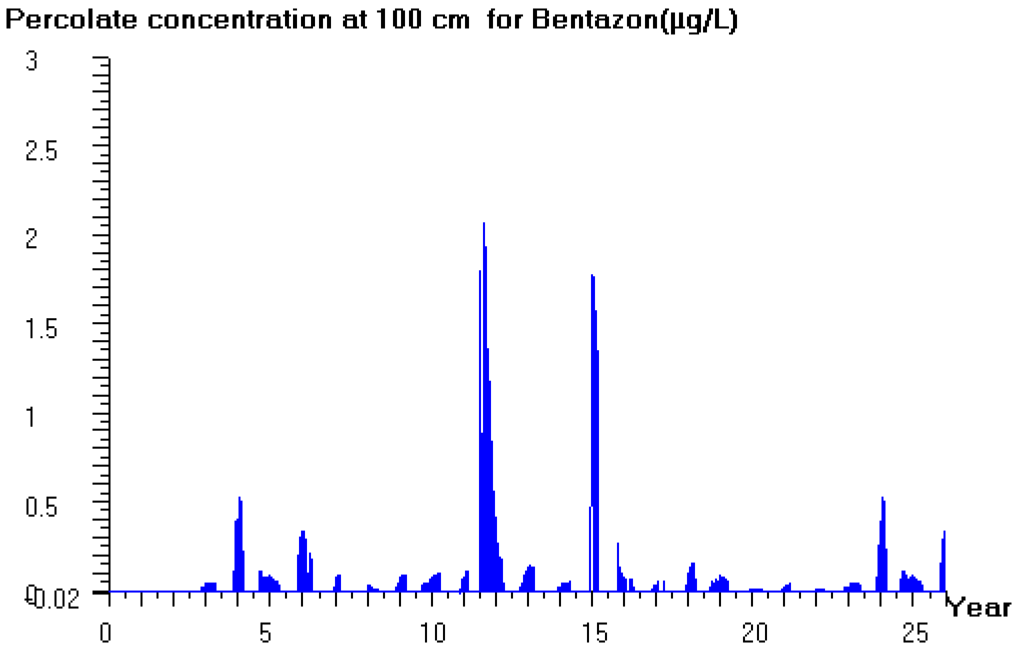


Figure 7-43: Time dependent concentration in the percolate for bentazon

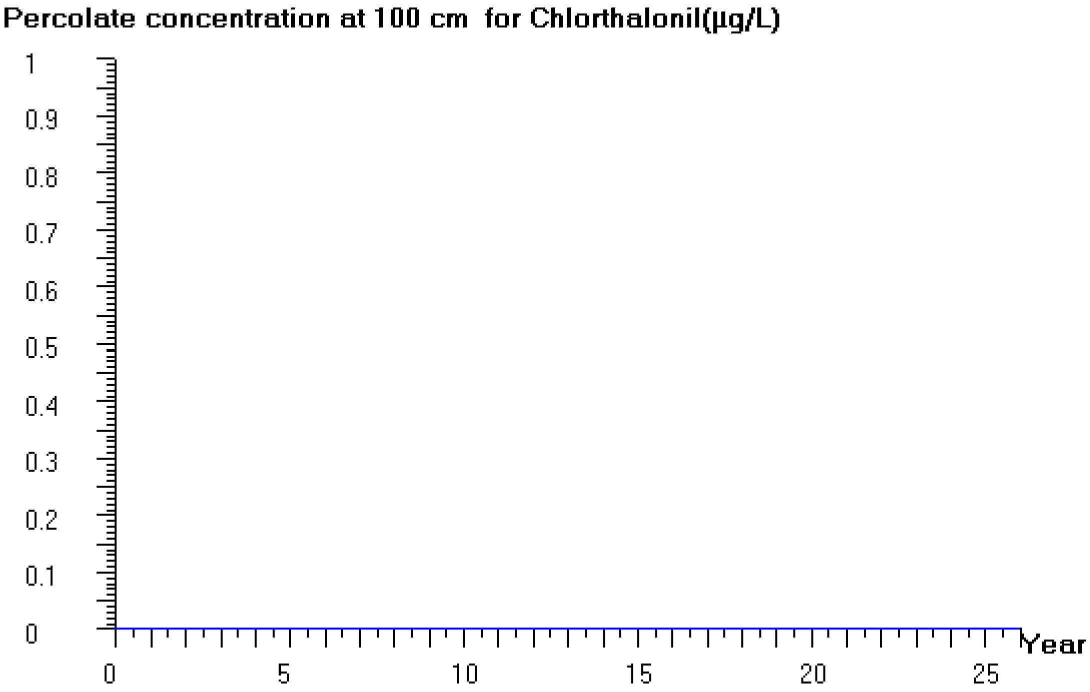


Figure 7-44: Time dependent concentration in the percolate for chlorthalonil

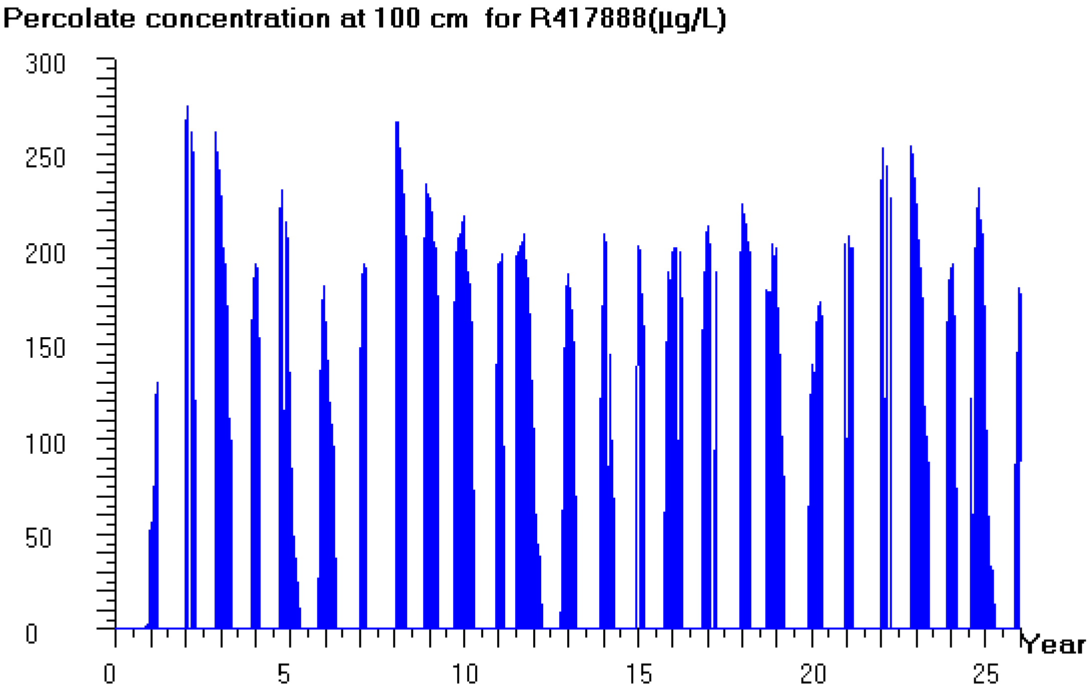


Figure 7-45: Time dependent concentration in the percolate for R417888

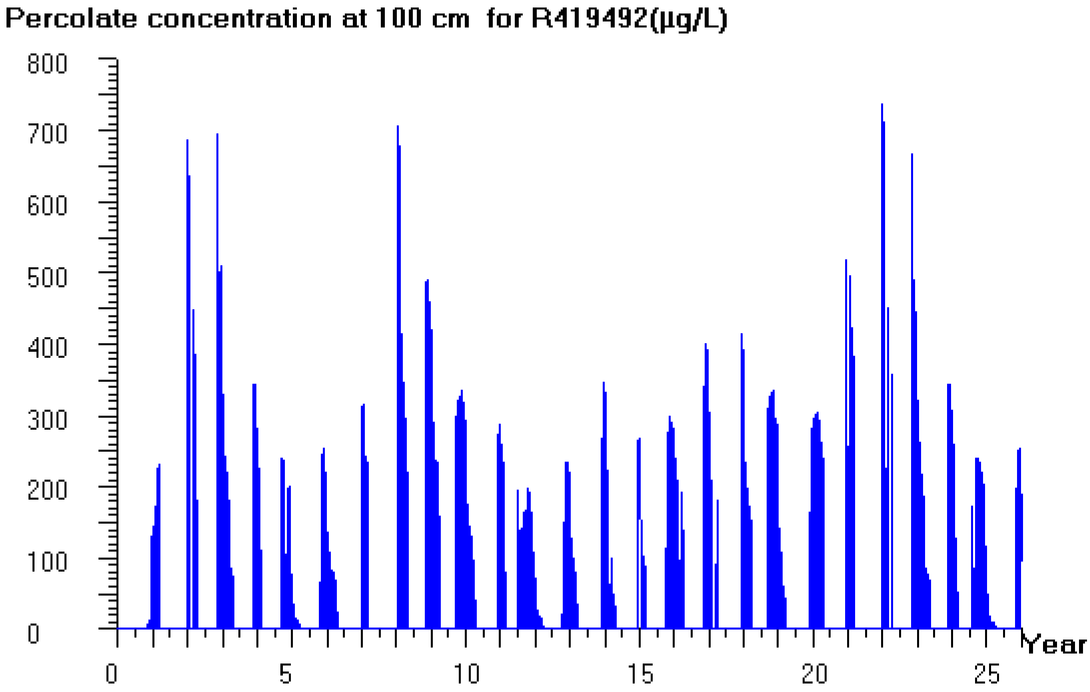


Figure 7-46: Time dependent concentration in the percolate for R419492

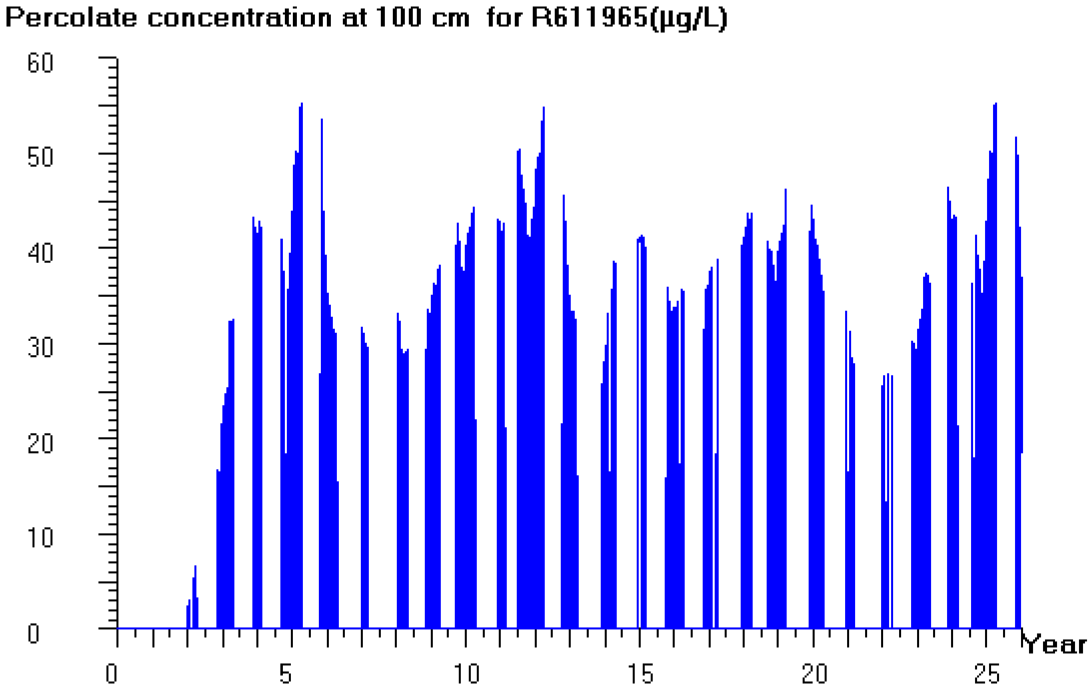


Figure 7-47: Time dependent concentration in the percolate for R611965 (SDS- 46851)

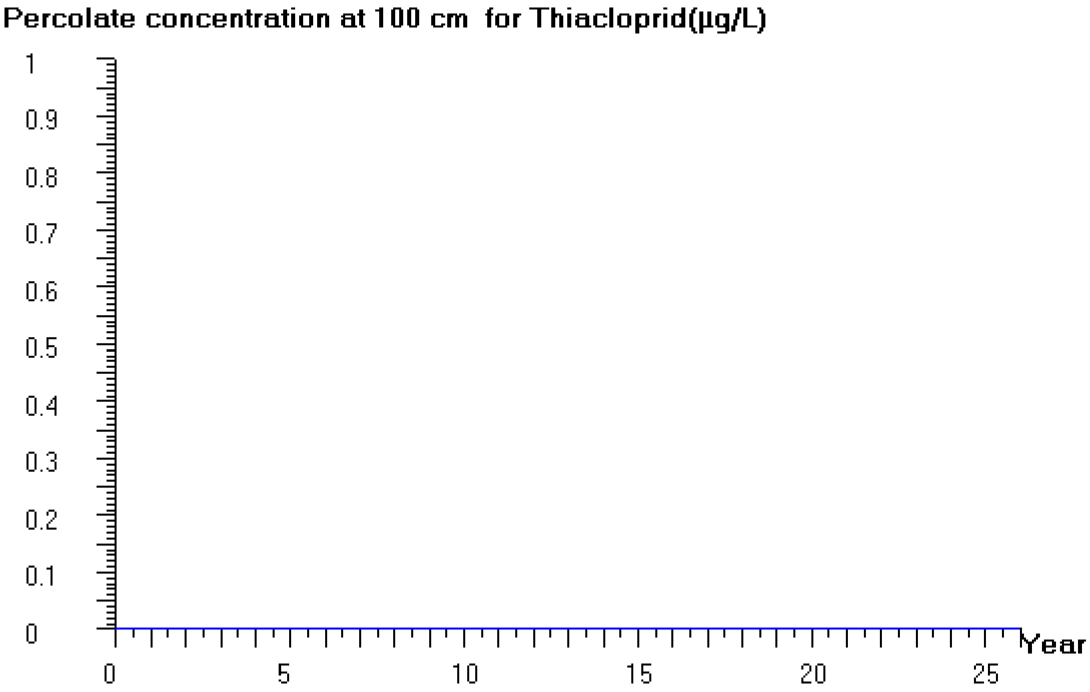


Figure 7-48: Time dependent concentration in the percolate for thiacloprid

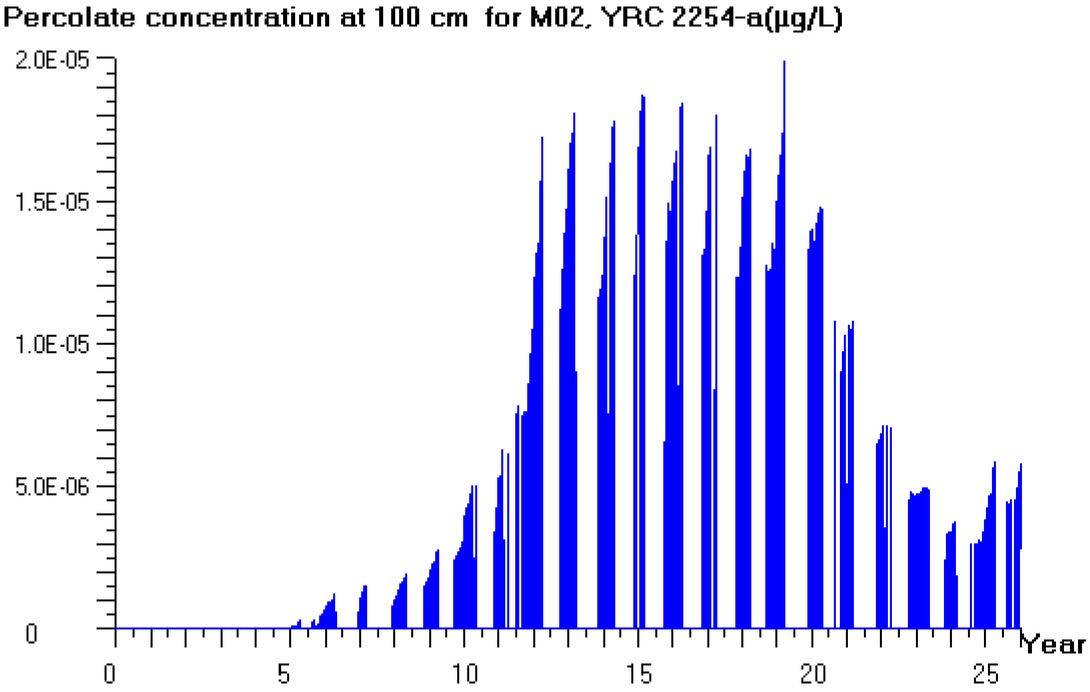


Figure 7-49: Time dependent concentration in the percolate for M02, YRC 2254-amid

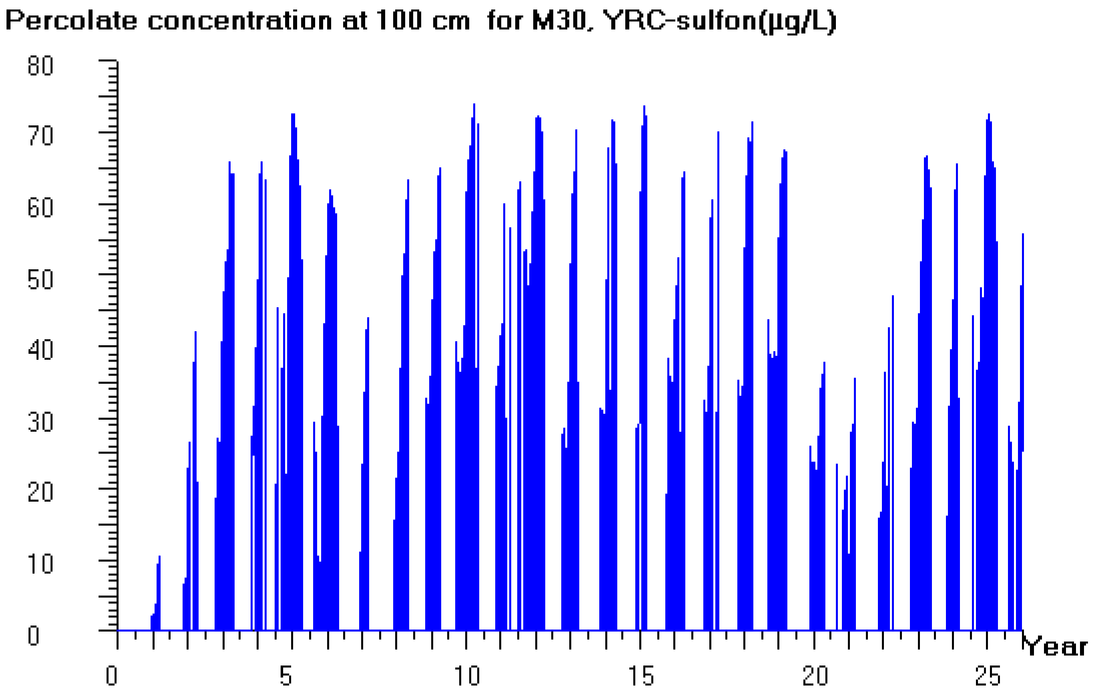


Figure 7-50: Time dependent concentration in the percolate for M30

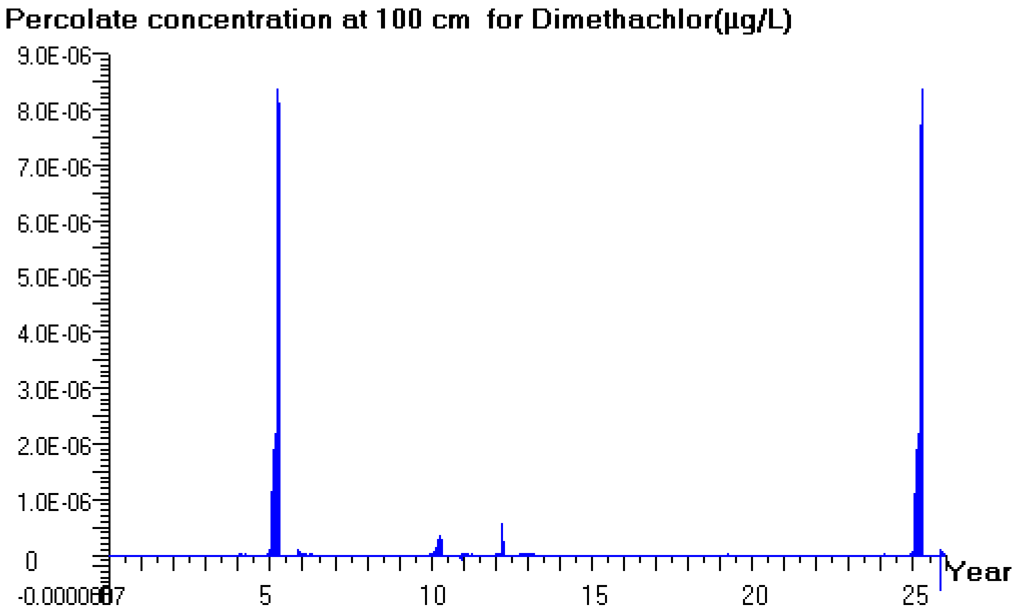


Figure 7-51: Time dependent concentration in the percolate for dimethachlor

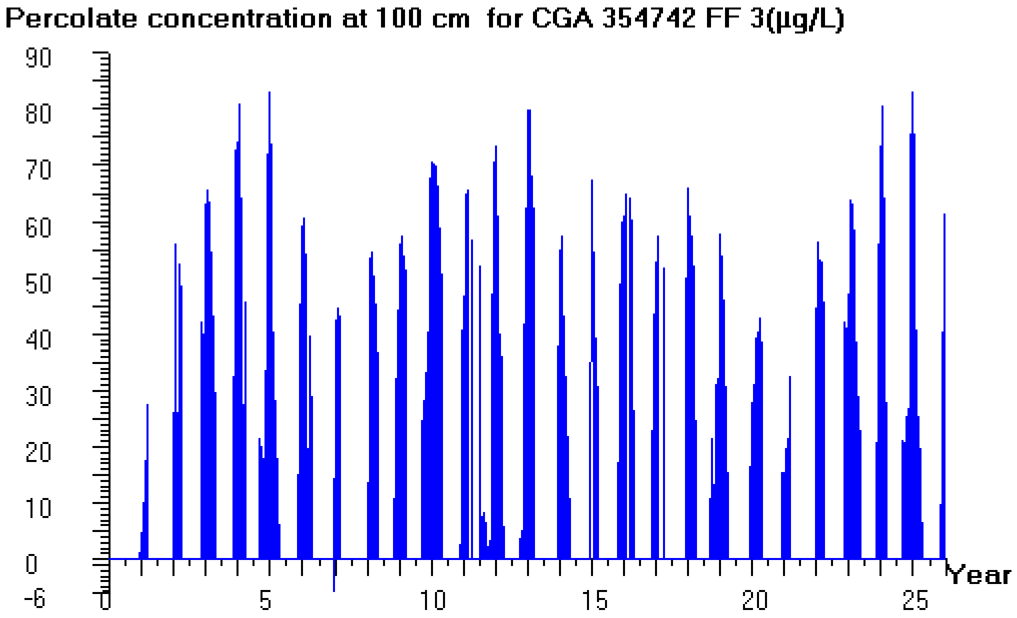


Figure 7-52: Time dependent concentration in the percolate for CGA 354742

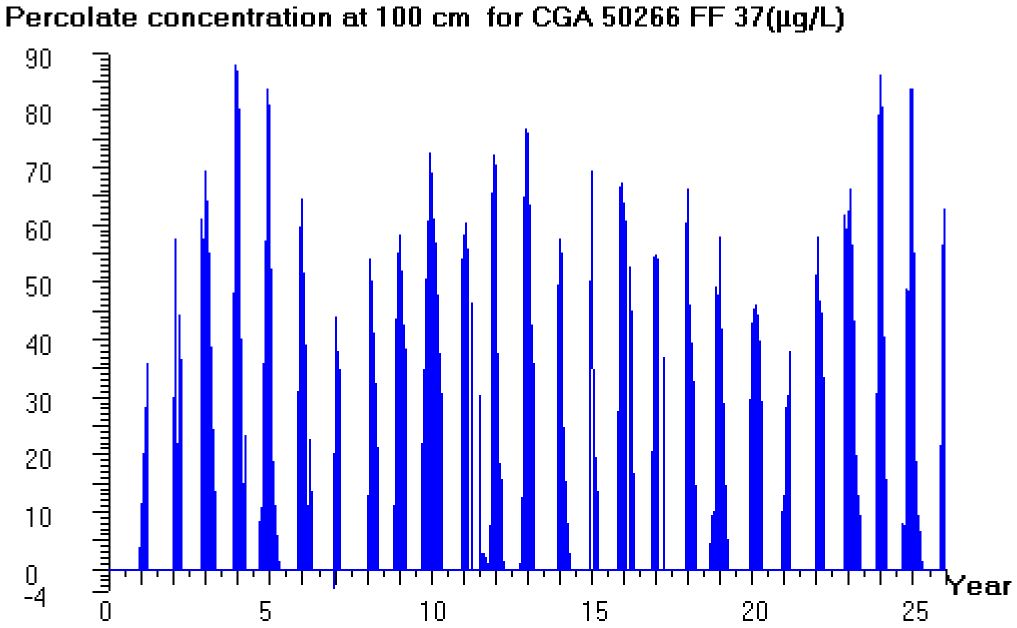


Figure 7-53: Time dependent concentration in the percolate for CGA 50266

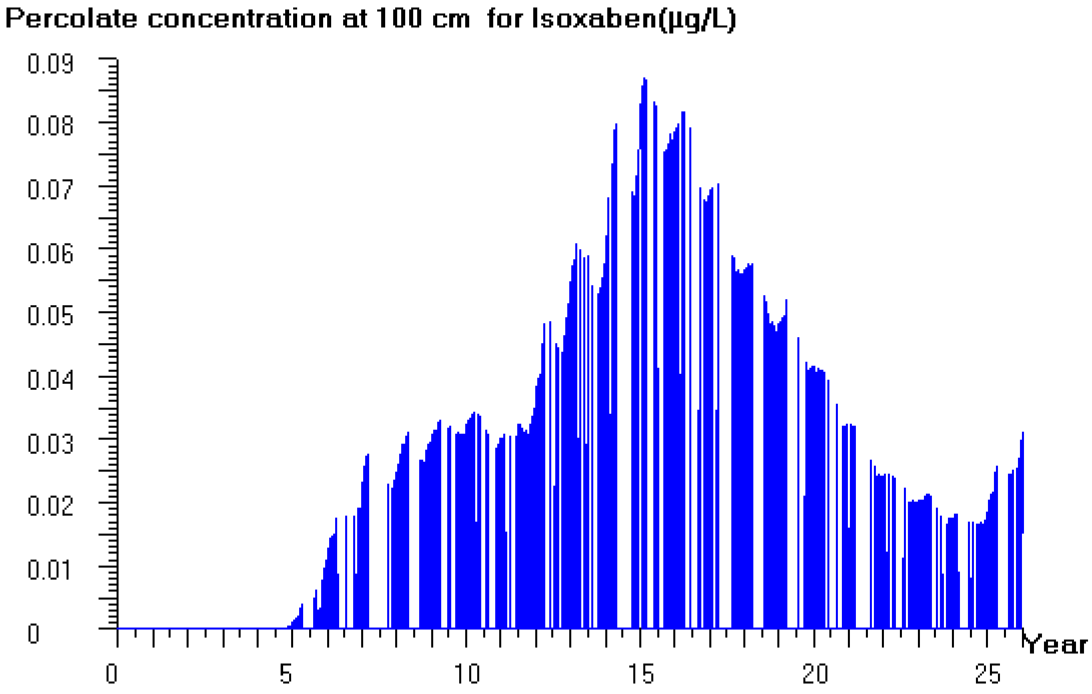


Figure 7-54: Time dependent concentration in the percolate for isoxaben

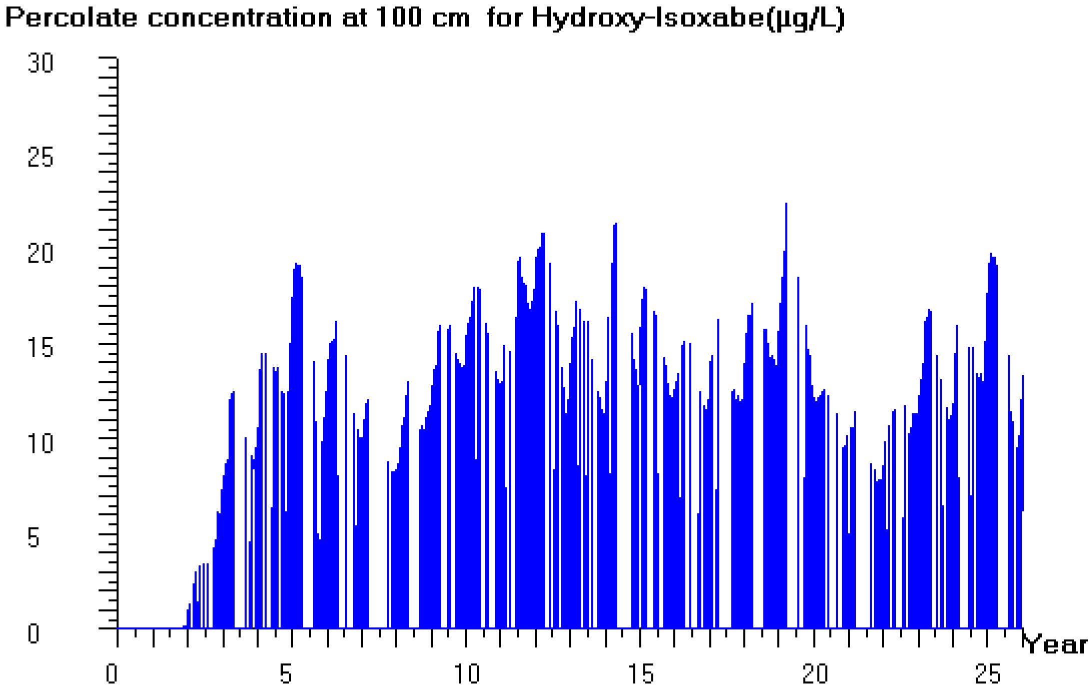


Figure 7-55: Time dependent concentration in the percolate for hydroxy-isoxaben

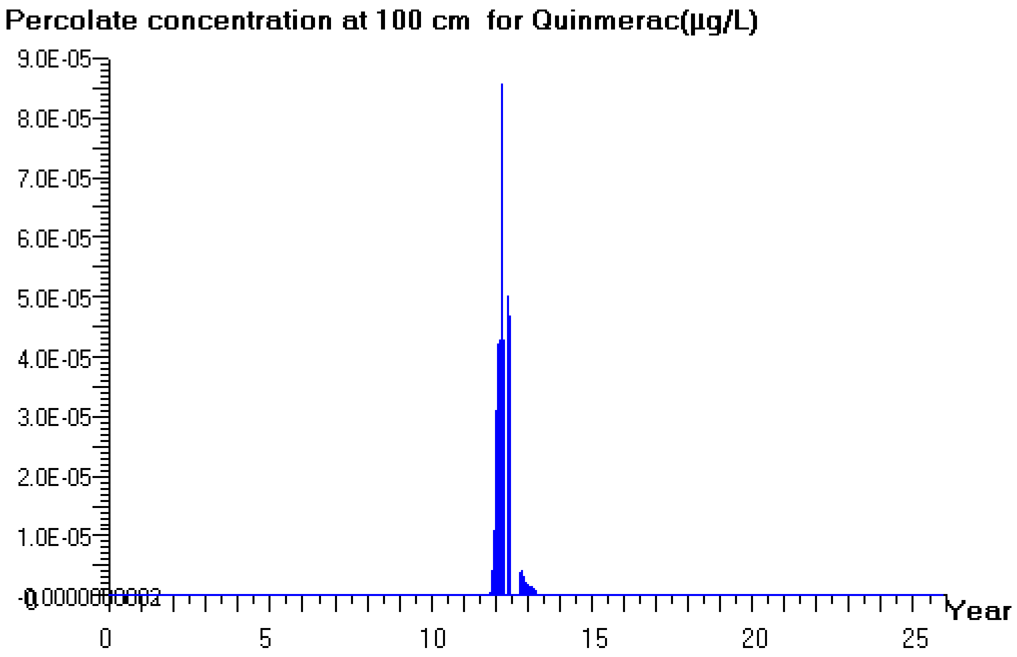


Figure 7-56: Time dependent concentration in the percolate for quinmerac

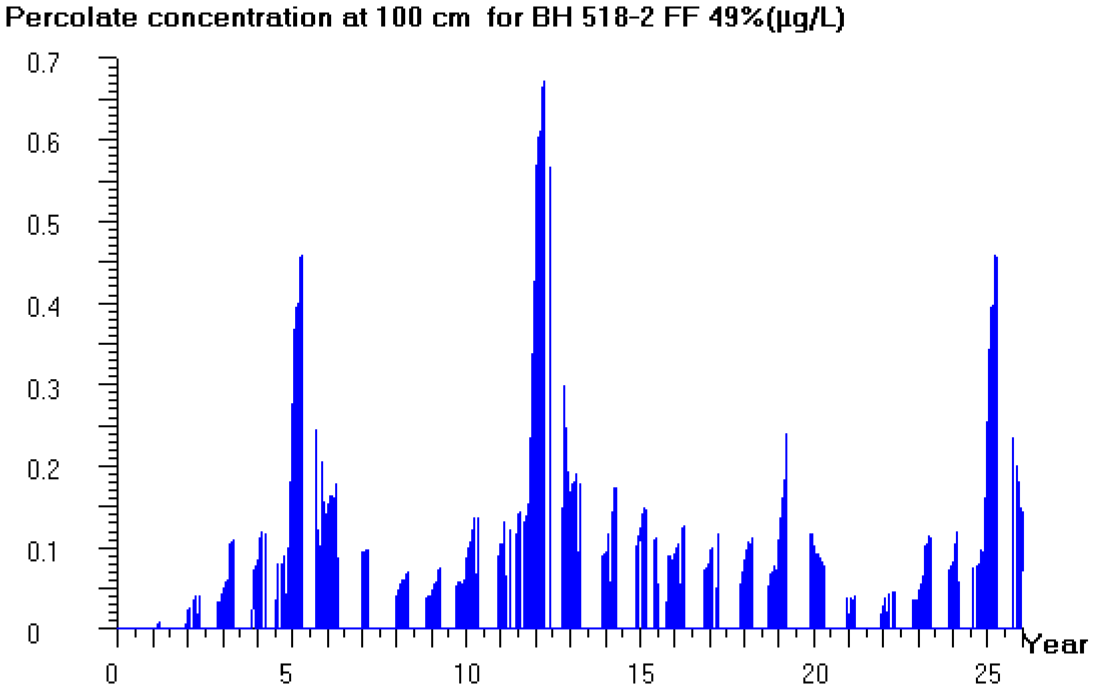


Figure 7-57: Time dependent concentration in the percolate for BH 518-2

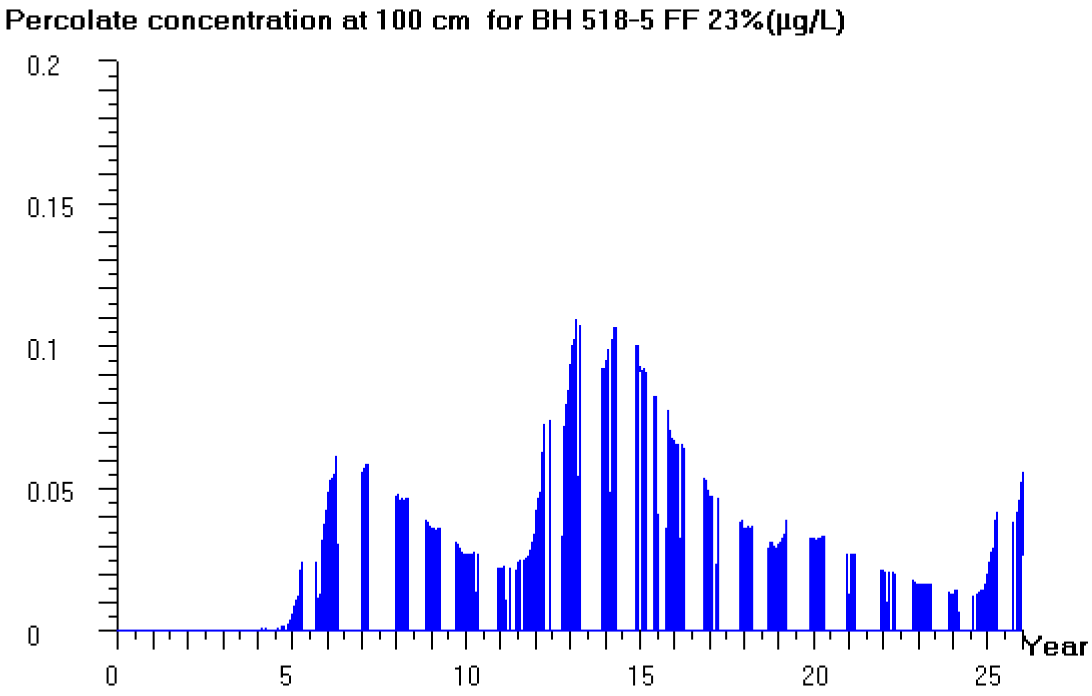


Figure 7-58: Time dependent concentration in the percolate for BH 518-5

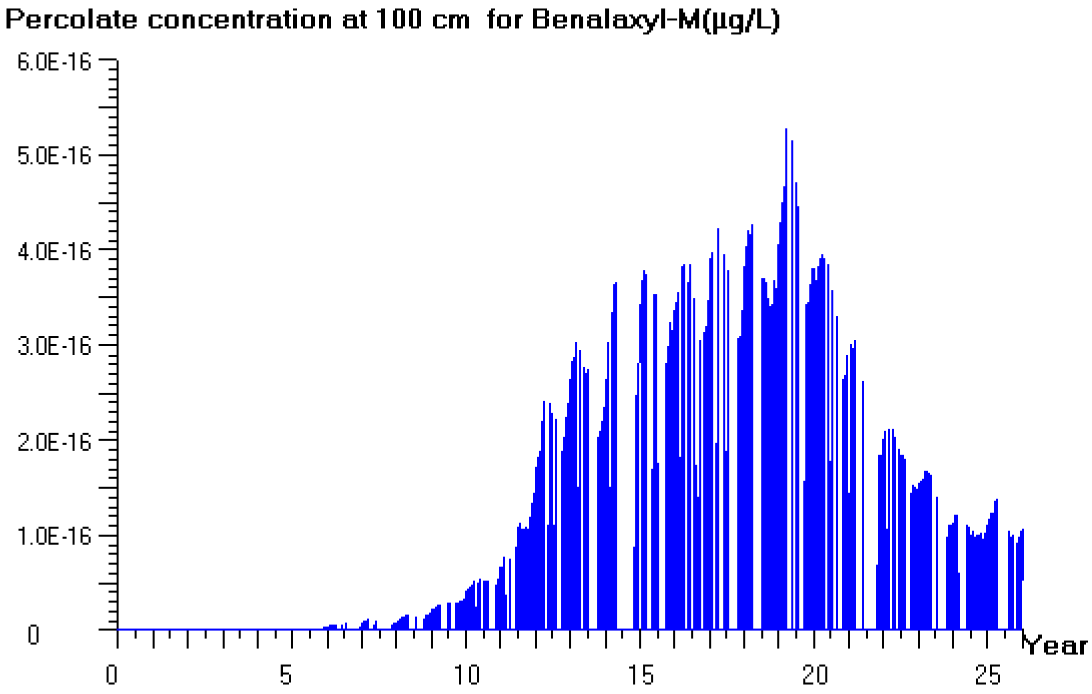


Figure 7-59: Time dependent concentration in the percolate for benalaxyl-M

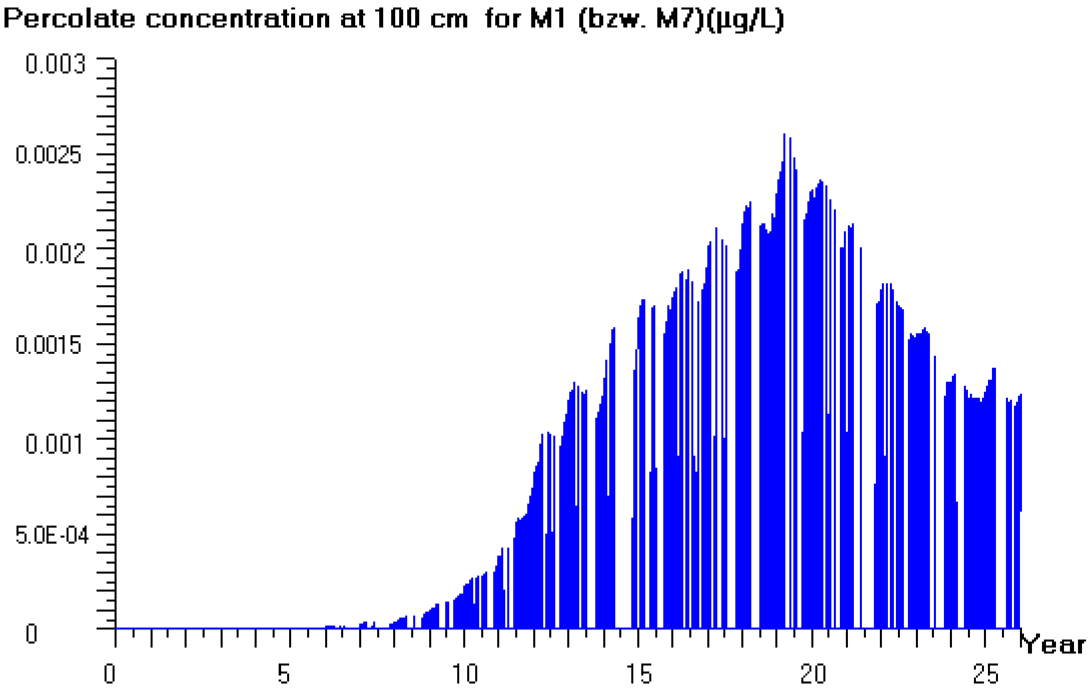


Figure 7-60: Time dependent concentration in the percolate for M1 (or M7)

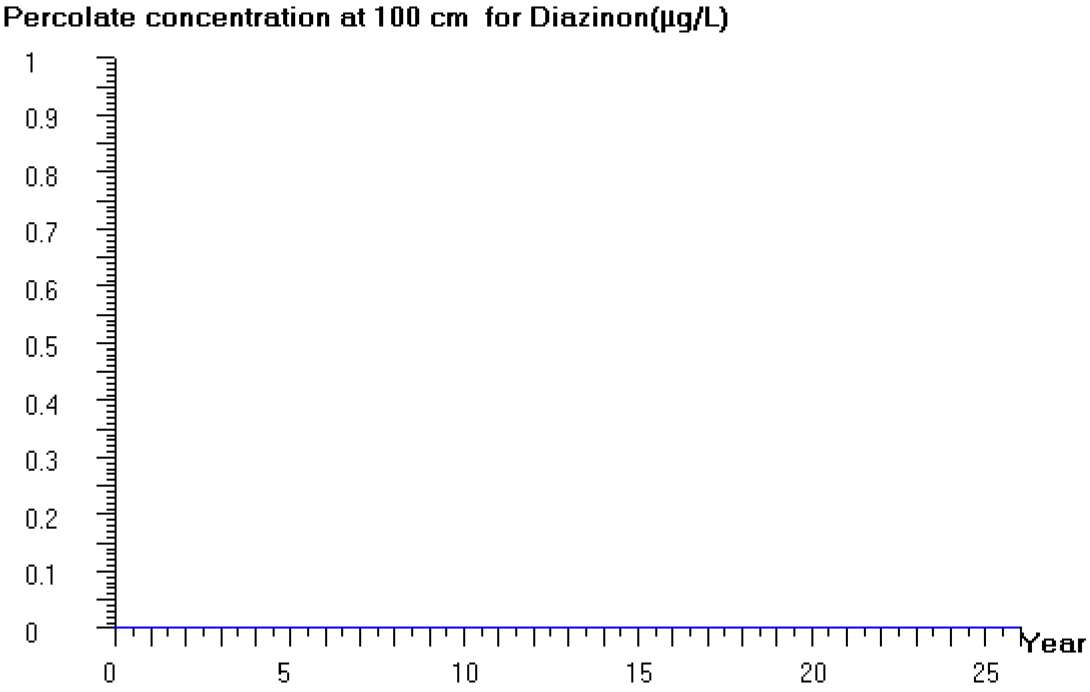


Figure 7-61: Time dependent concentration in the percolate for diazinon

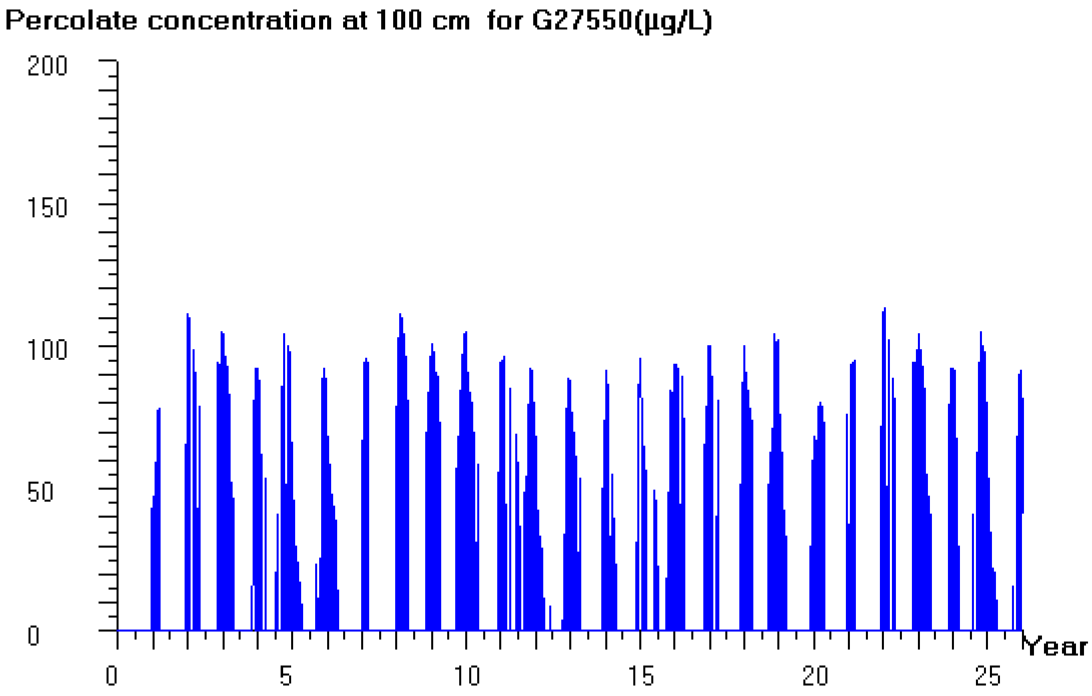


Figure 7-62: Time dependent concentration in the percolate for G27550

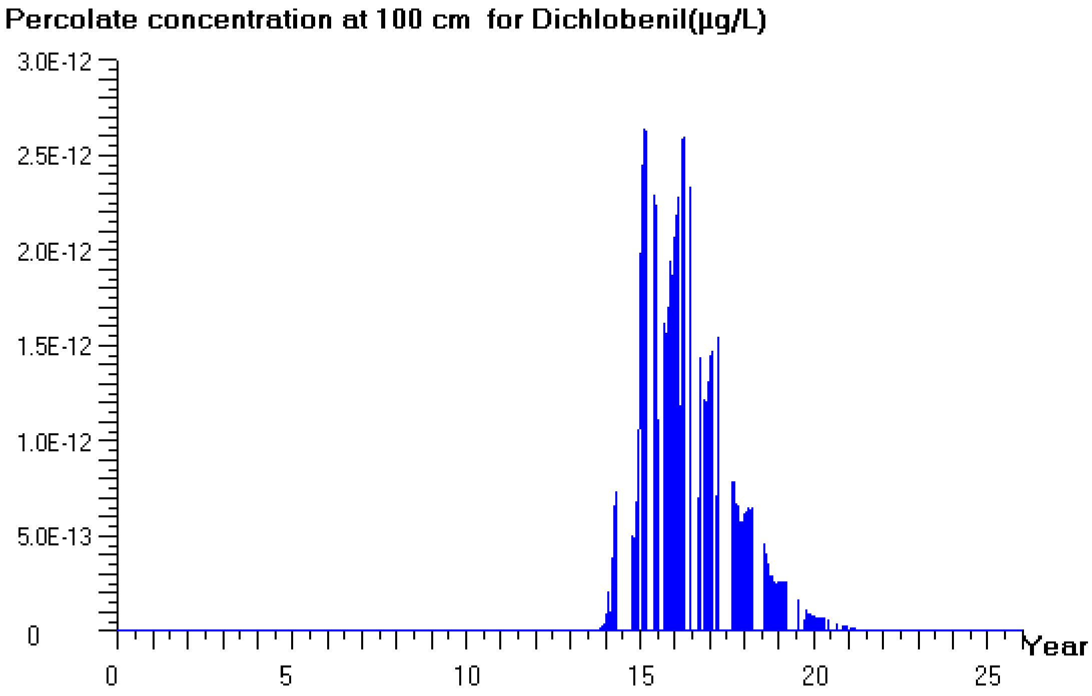


Figure 7-63: Time dependent concentration in the percolate for dichlobenil

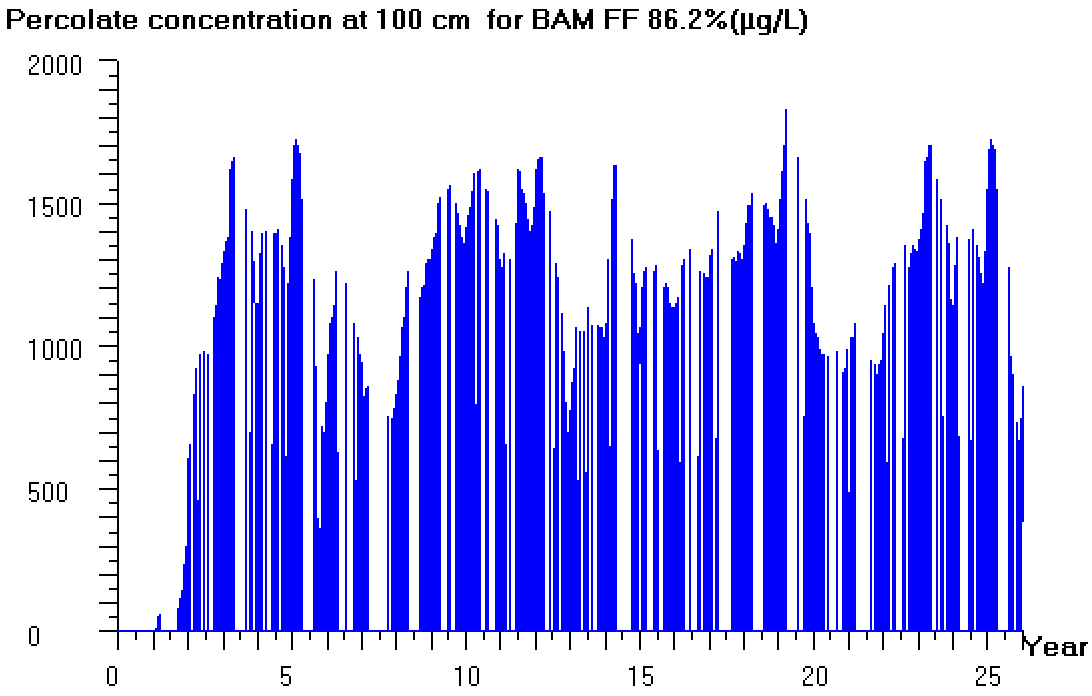


Figure 7-64: Time dependent concentration in the percolate for BAM

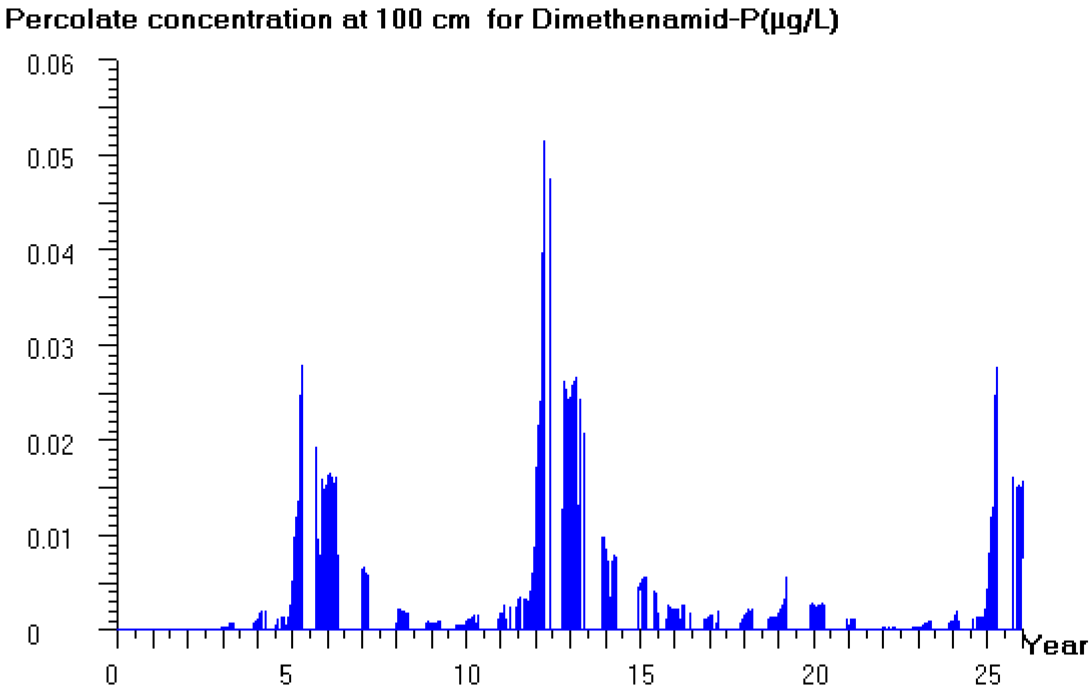


Figure 7-65: Time dependent concentration in the percolate for dimethenamid-P

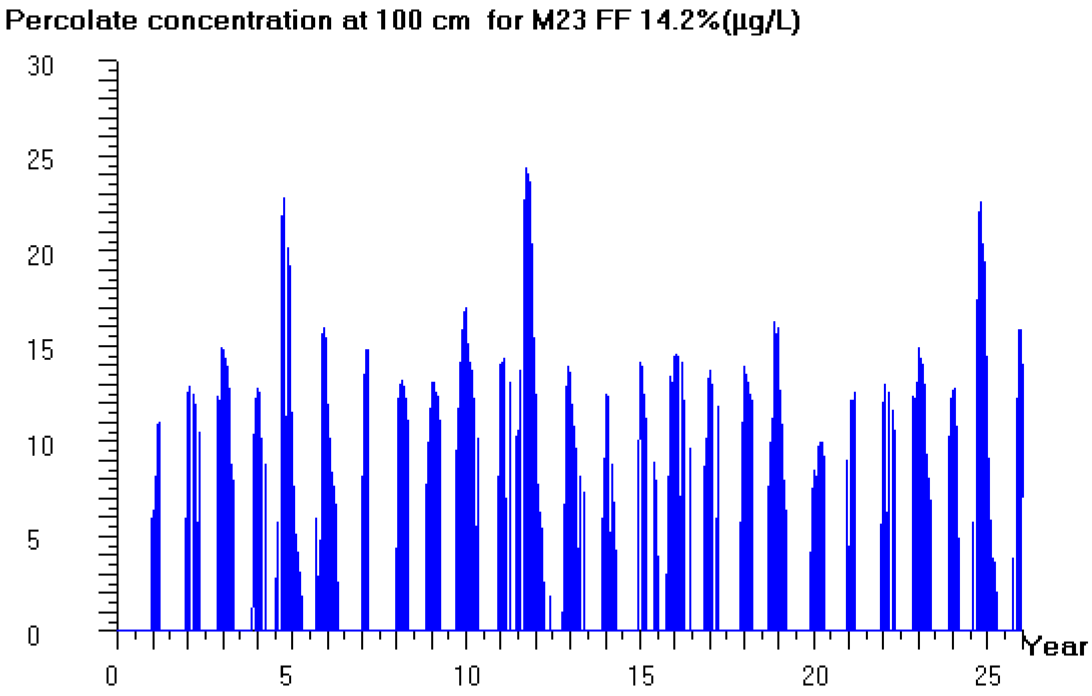


Figure 7-66: Time dependent concentration in the percolate for M23

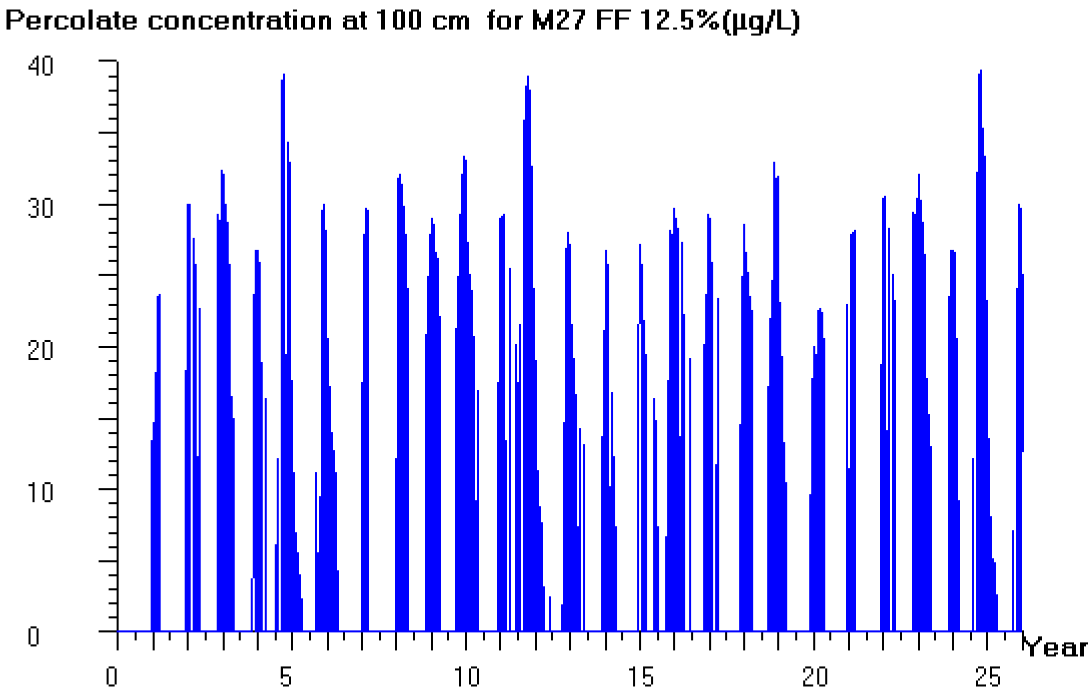


Figure 7-67: Time dependent concentration in the percolate for M27

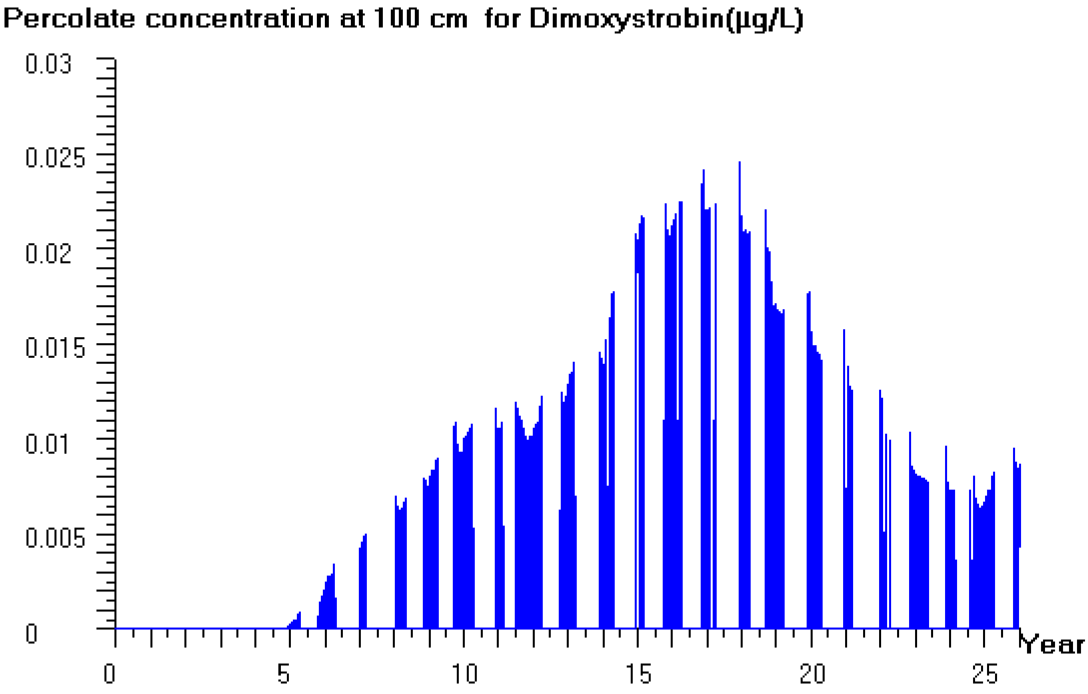


Figure 7-68: Time dependent concentration in the percolate for dimoxystrobin

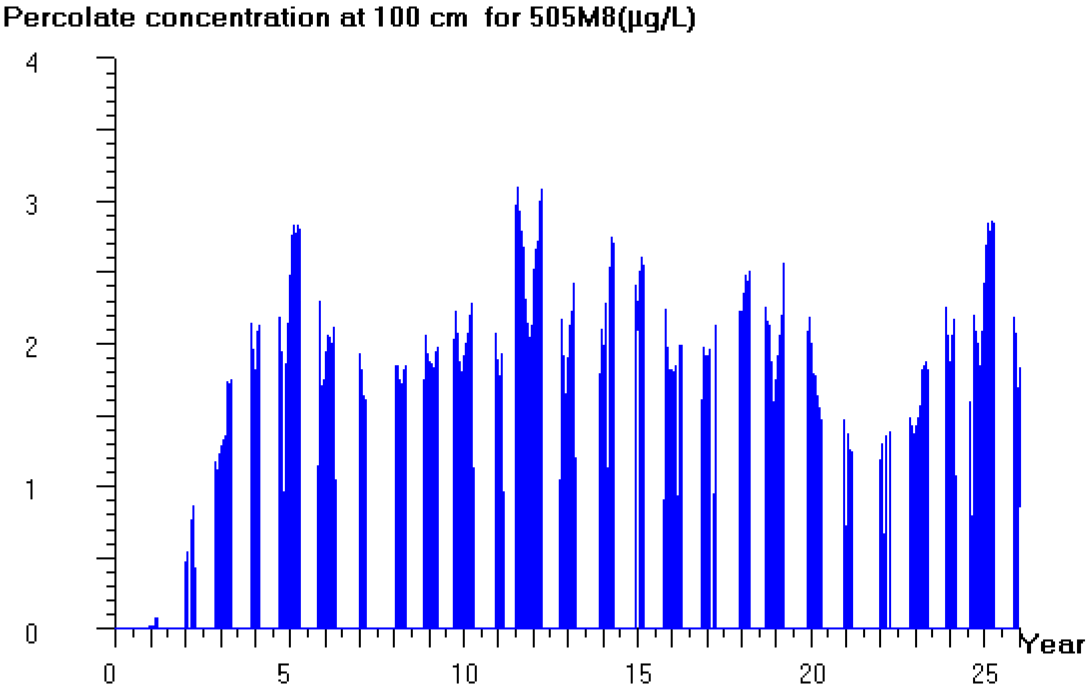


Figure 7-69: Time dependent concentration in the percolate for 505M8

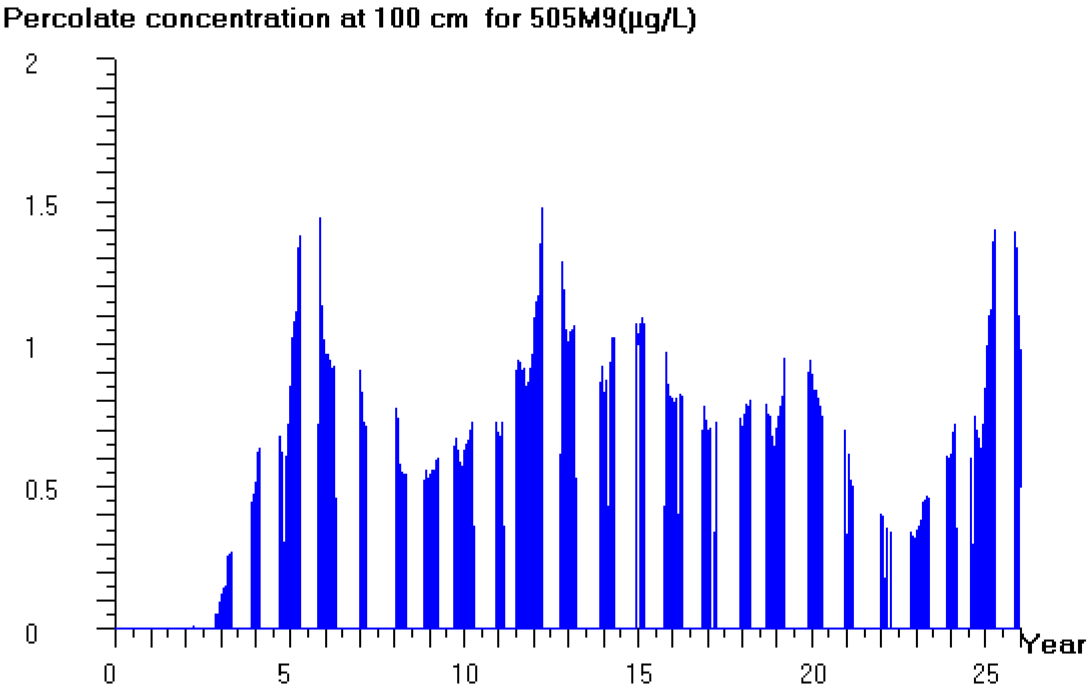


Figure 7-70: Time dependent concentration in the percolate for 505M9

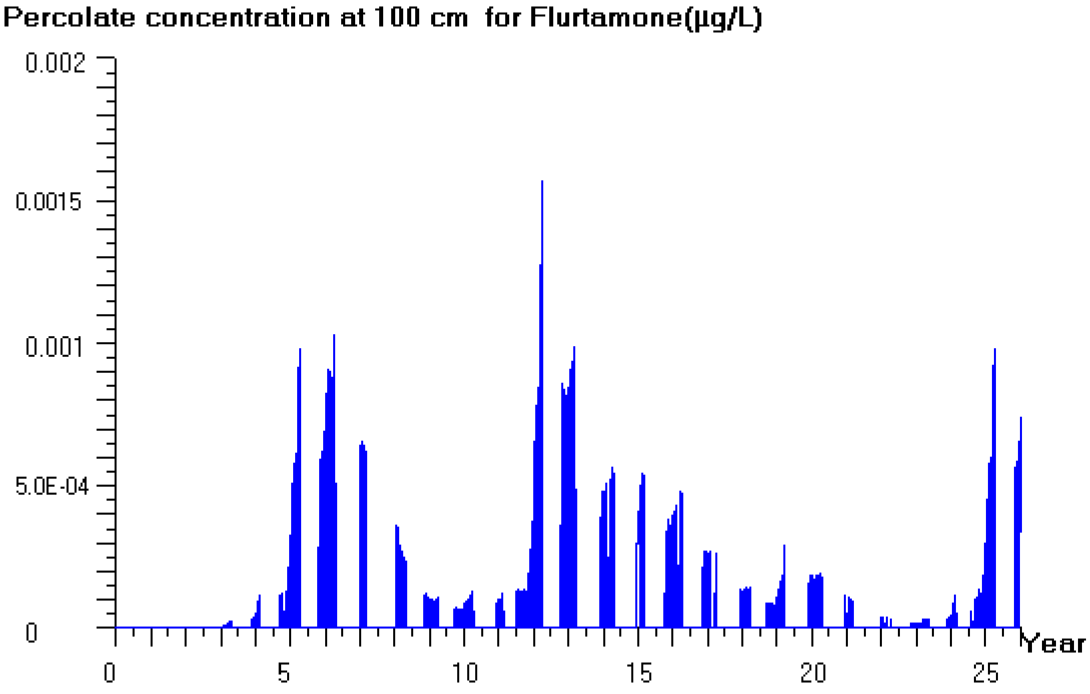


Figure 7-71: Time dependent concentration in the percolate for flurtamone

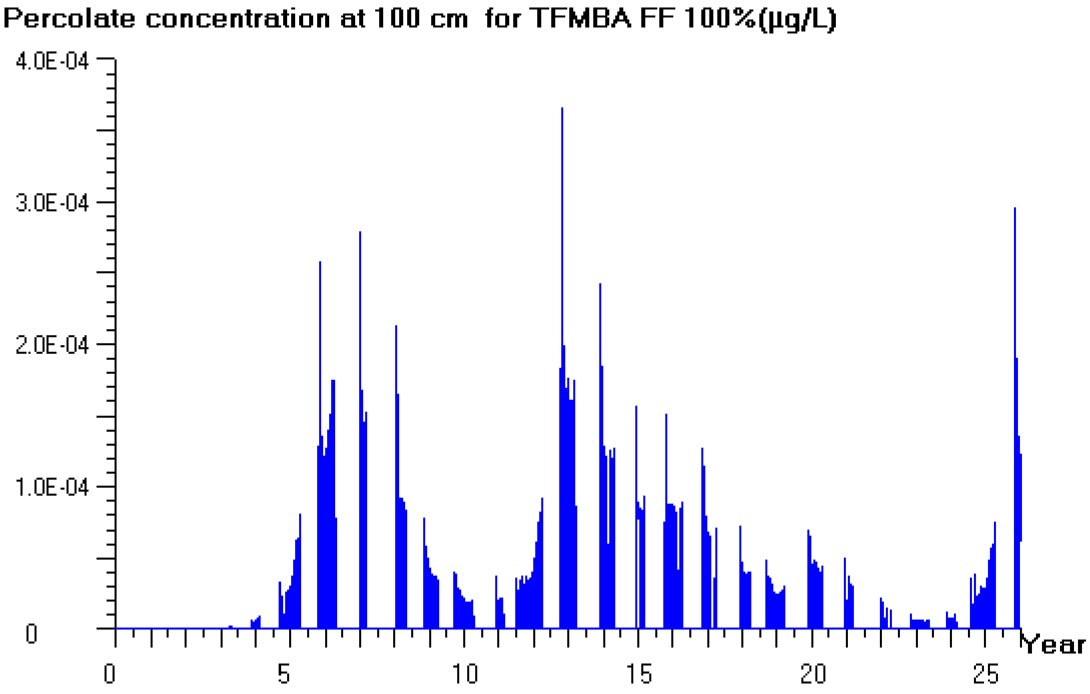


Figure 7-72: Time dependent concentration in the percolate for TFMBA

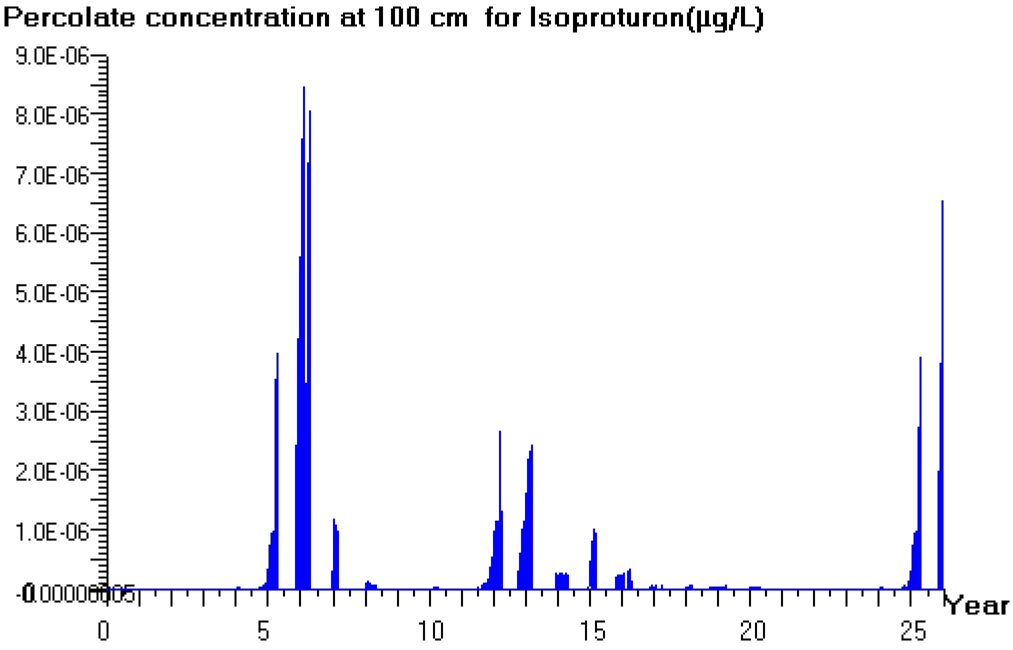


Figure 7-73: Time dependent concentration in the percolate for isoproturon

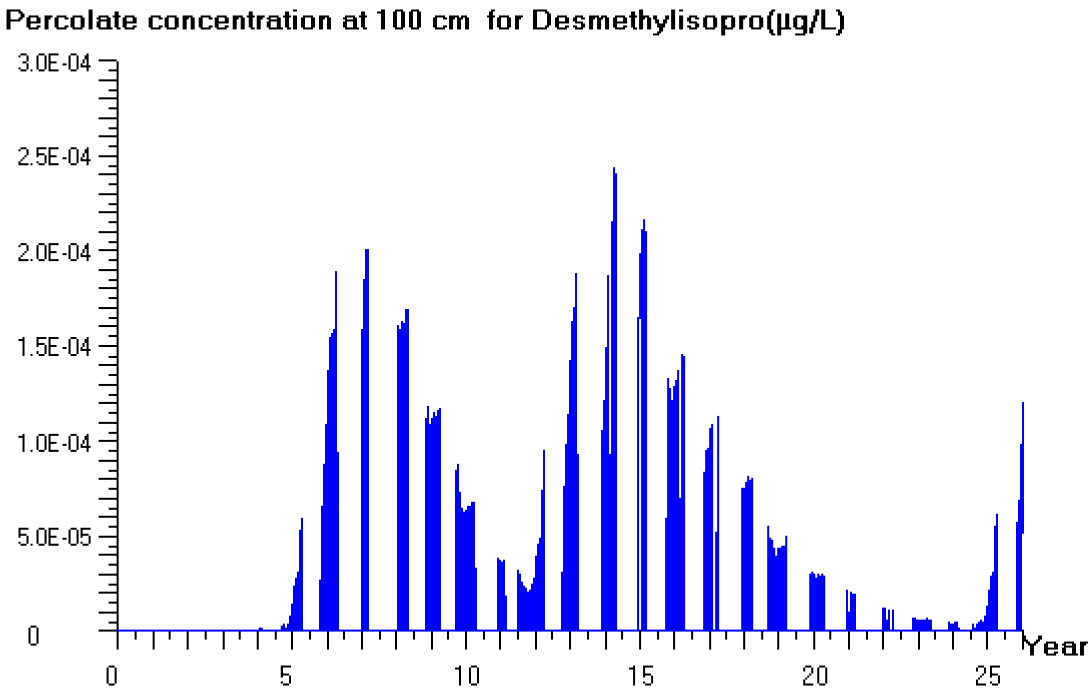

Percolate concentration at 100 cm for Desmethylisopro(µg/L)

Figure 7-74: Time dependent concentration in the percolate for desmethyl isoproturon

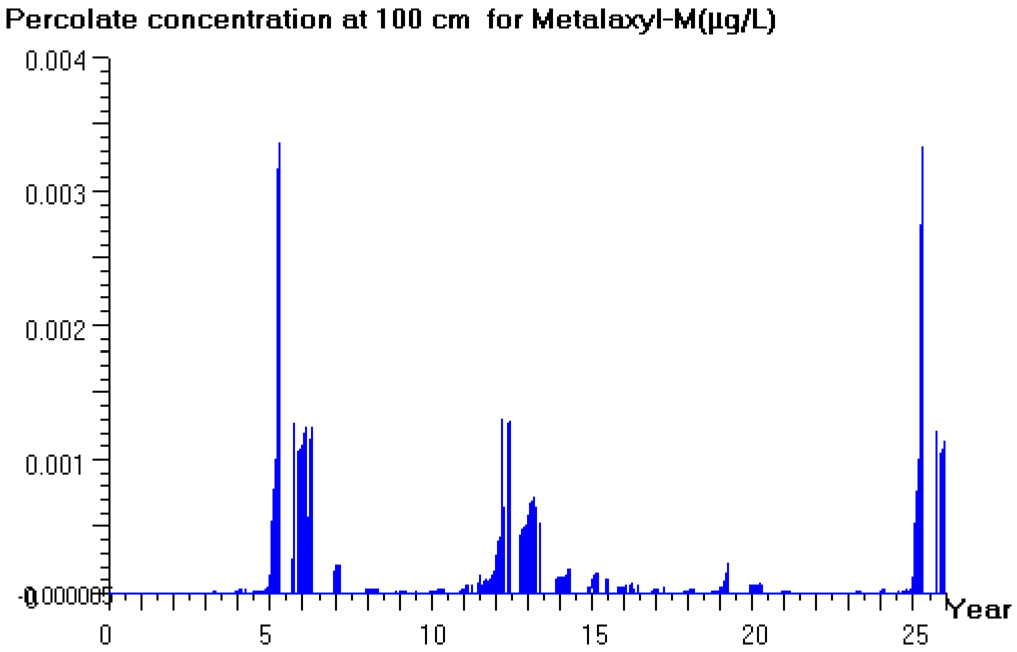

Percolate concentration at 100 cm for Metalaxyl-M(µg/L)

Figure 7-75: Time dependent concentration in the percolate for metalaxyl-M

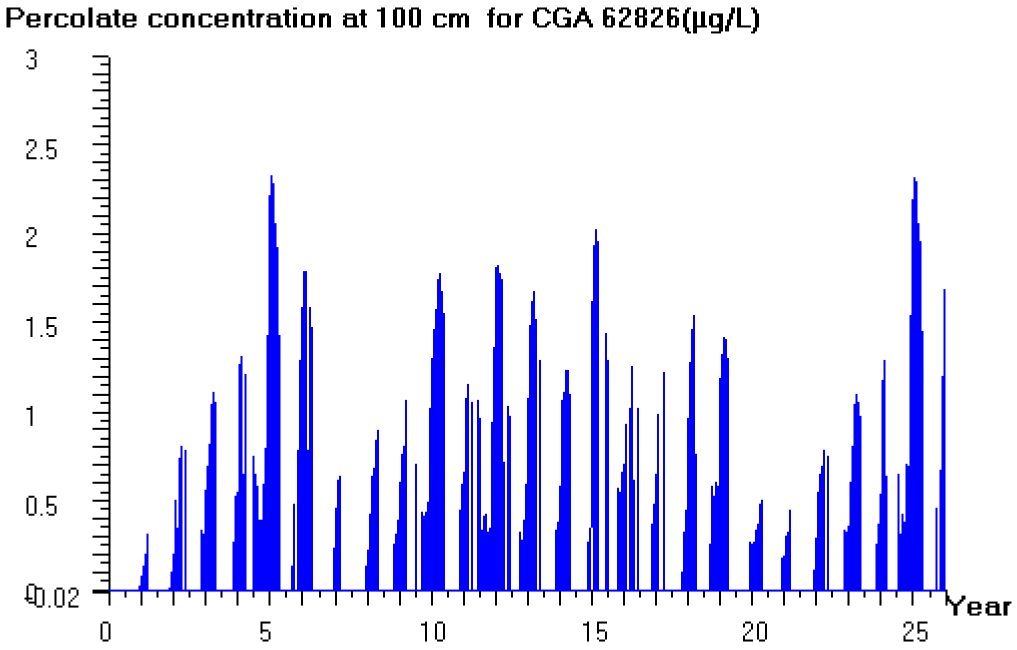


Figure 7-76: Time dependent concentration in the percolate for CGA 62826

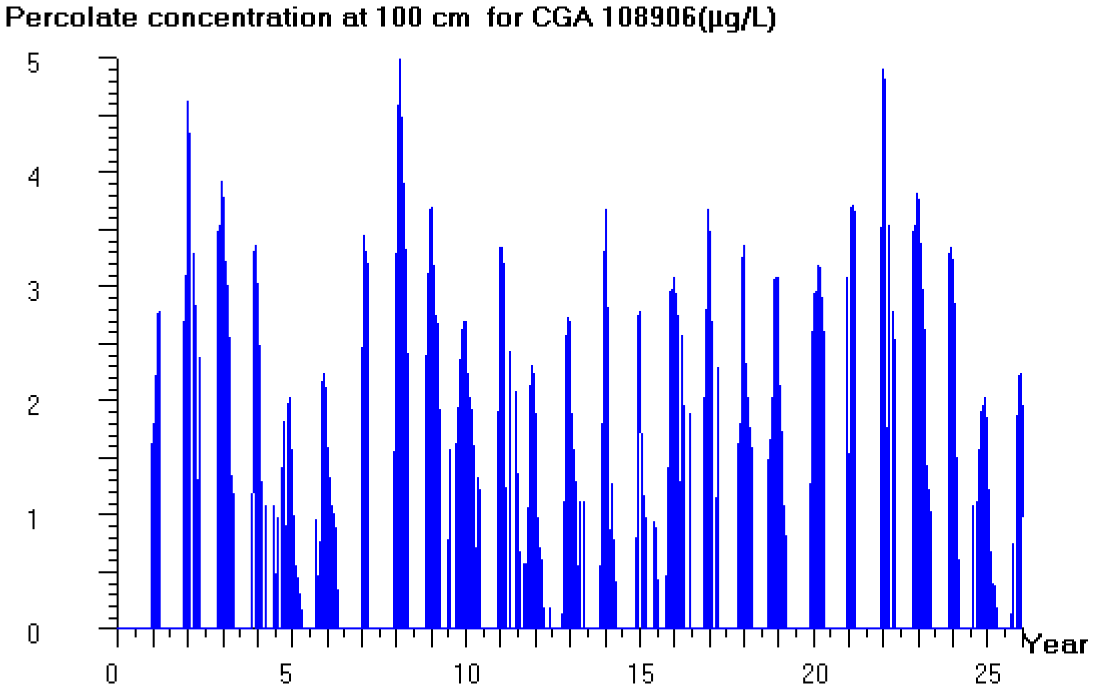


Figure 7-77: Time dependent concentration in the percolate for CGA 108906

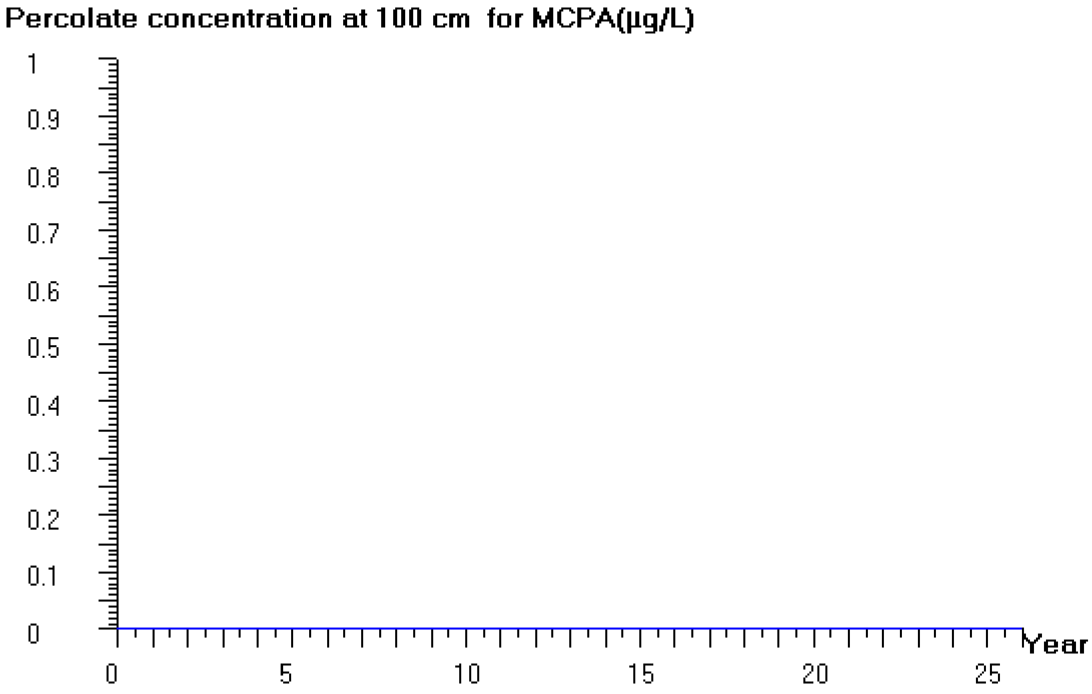


Figure 7-78: Time dependent concentration in the percolate for MCPA

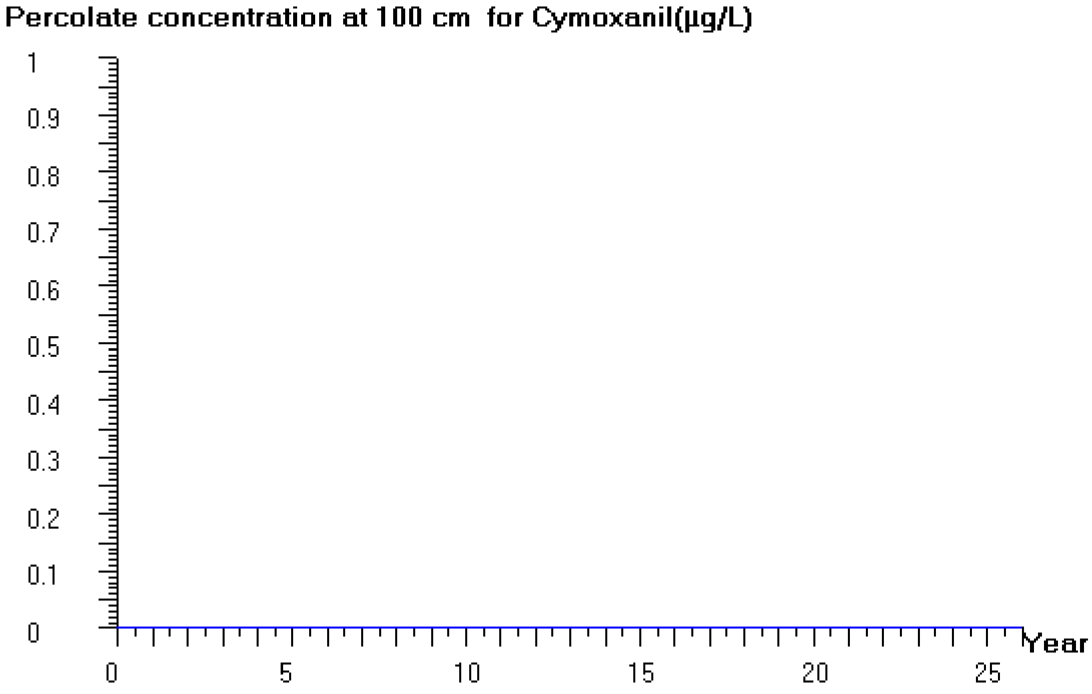


Figure 7-79: Time dependent concentration in the percolate for cymoxanil

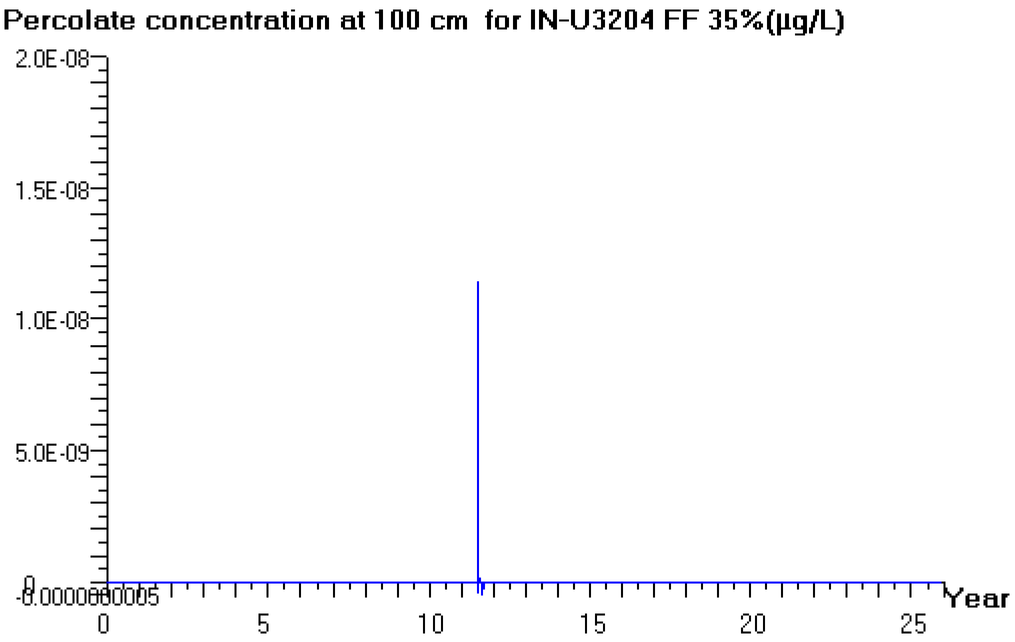


Figure 7-80: Time dependent concentration in the percolate for IN-U3204

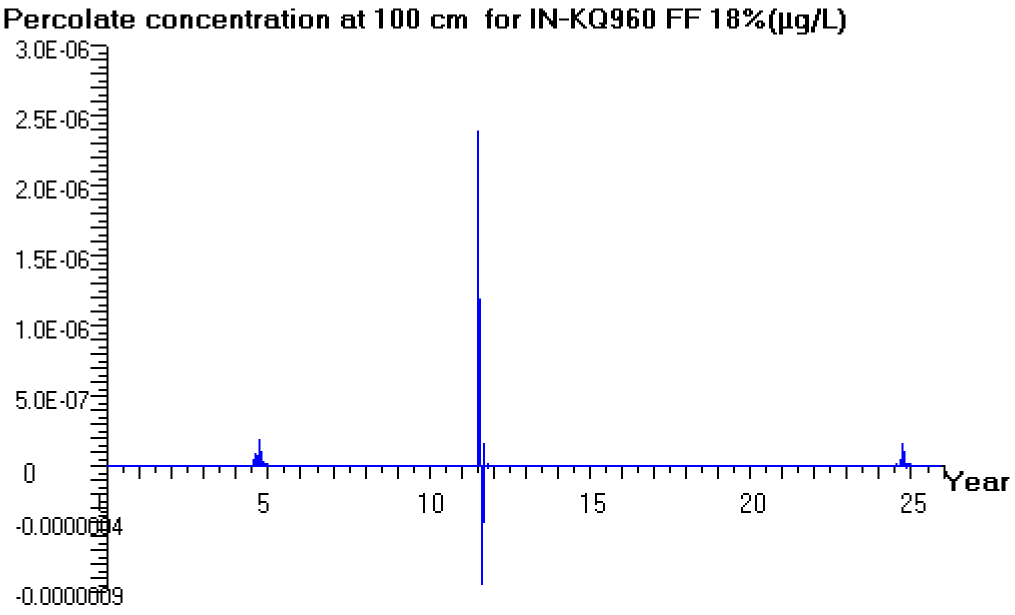


Figure 7-81: Time dependent concentration in the percolate for IN-KQ960

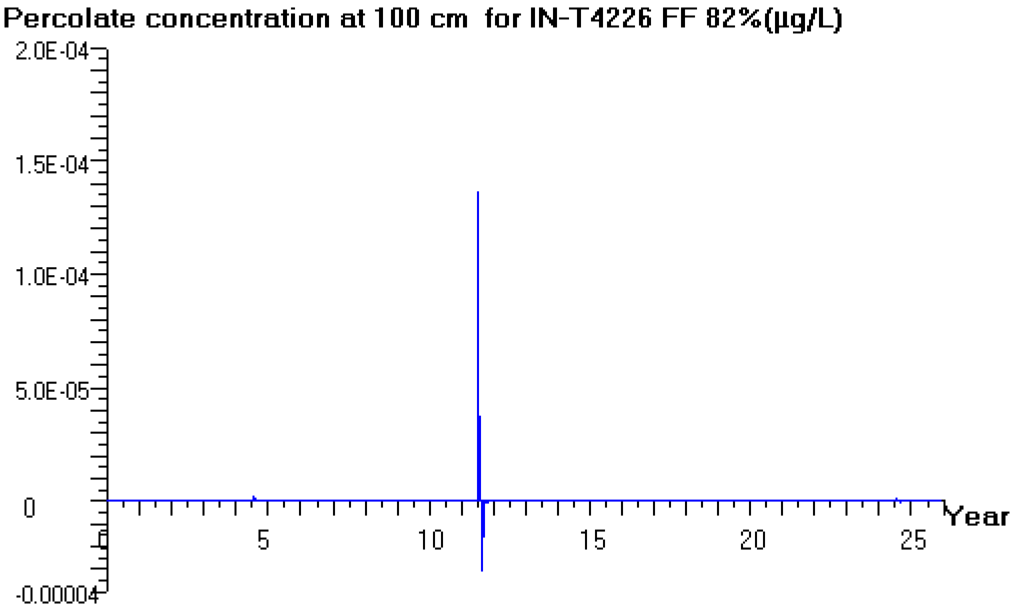


Figure 7-82: Time dependent concentration in the percolate for IN-T4226

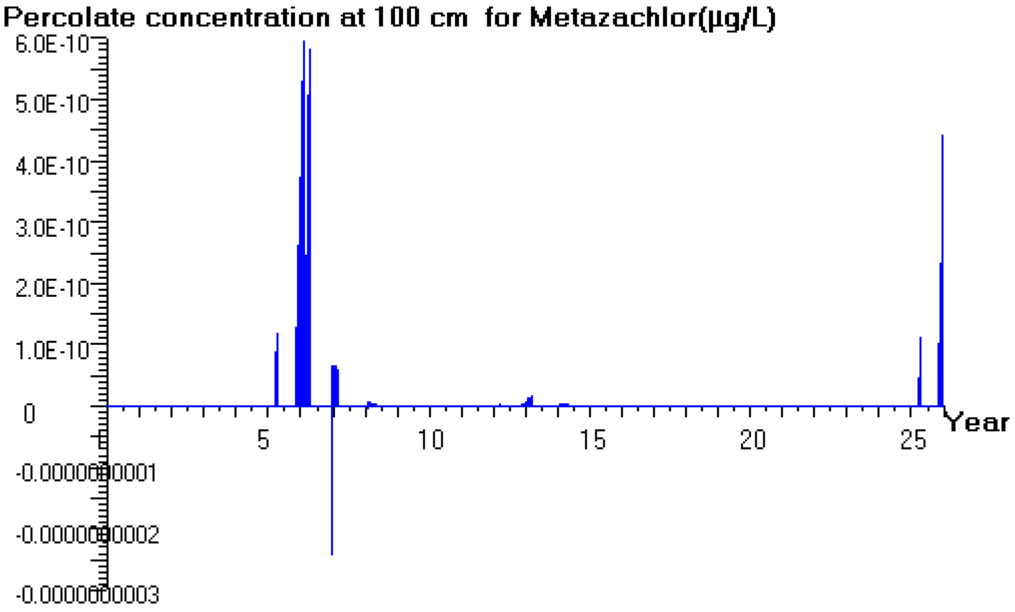


Figure 7-83: Time dependent concentration in the percolate for metazachlor

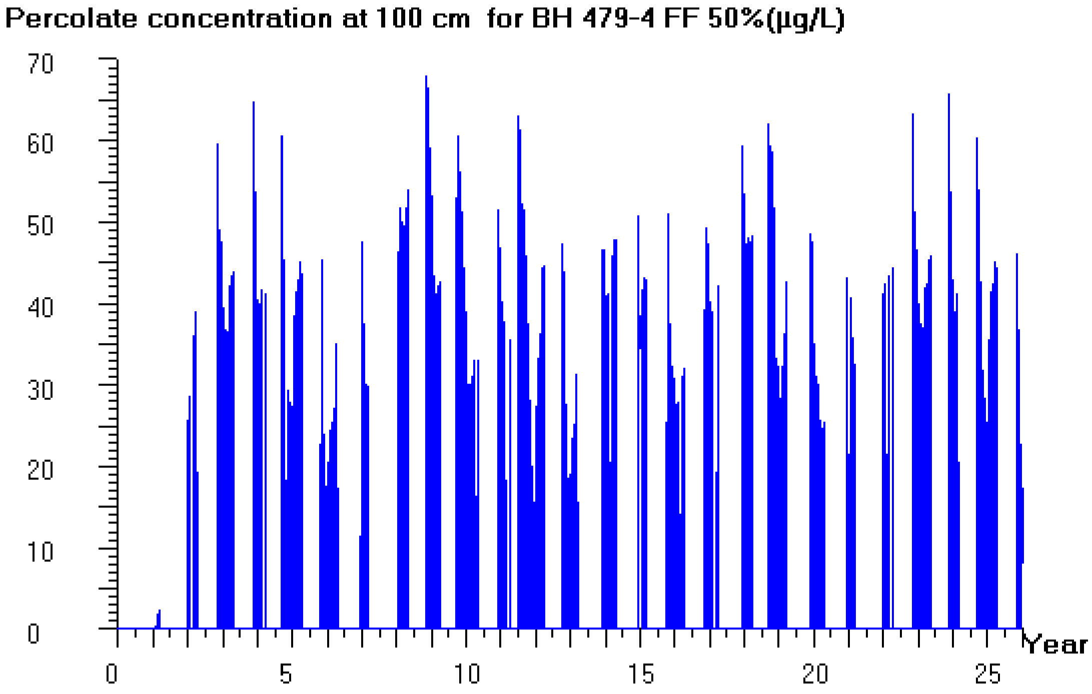


Figure 7-84: Time dependent concentration in the percolate for BH 479-4

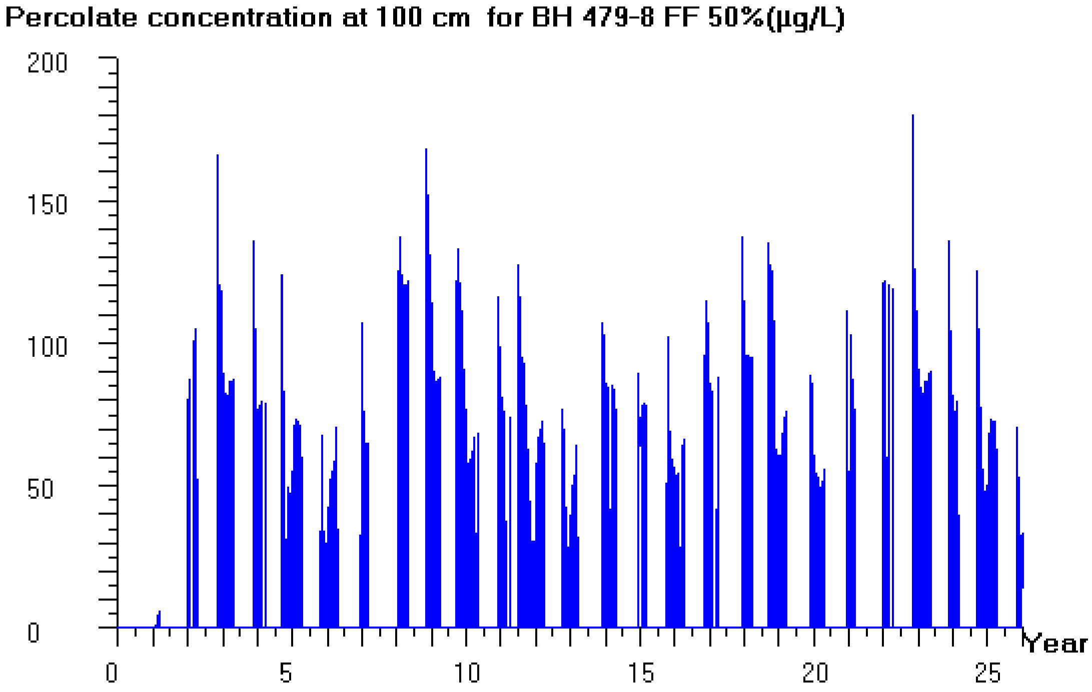


Figure 7-85: Time dependent concentration in the percolate for BH 479-8

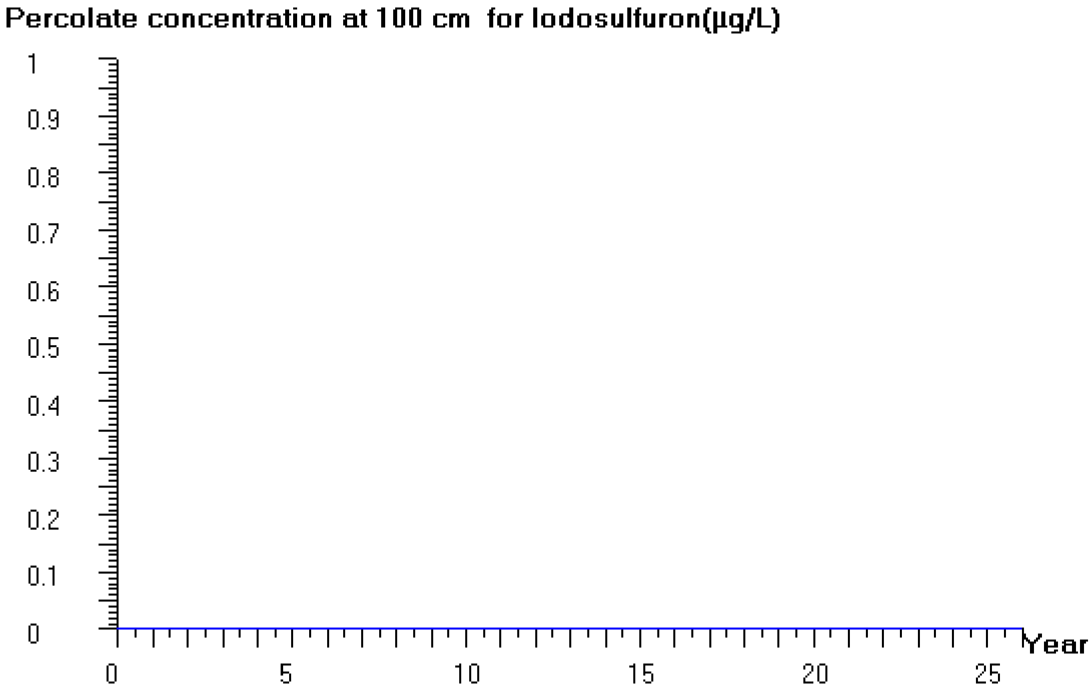


Figure 7-86: Time dependent concentration in the percolate for iodo sulfuron

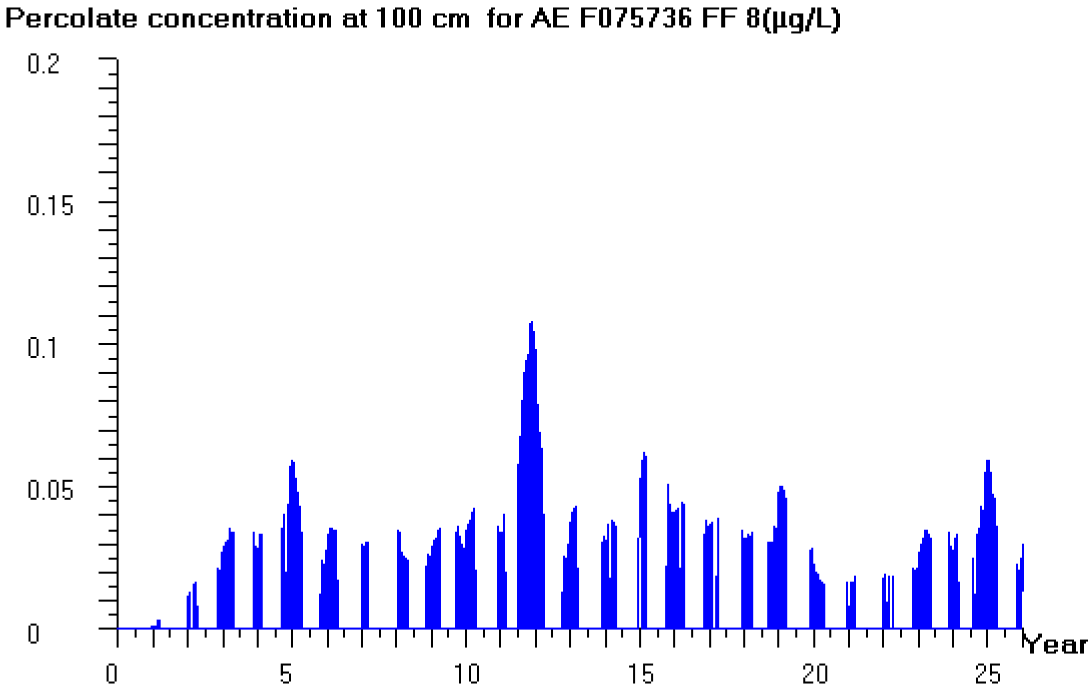


Figure 7-87: Time dependent concentration in the percolate for AE F075736

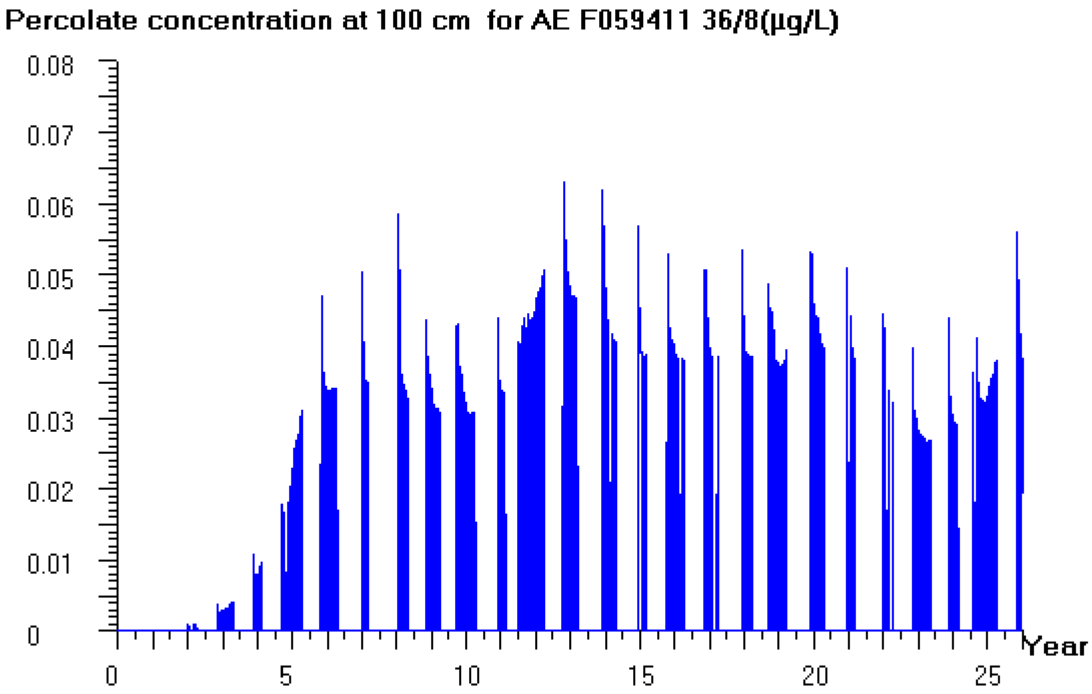


Figure 7-88: Time dependent concentration in the percolate for AE F059411

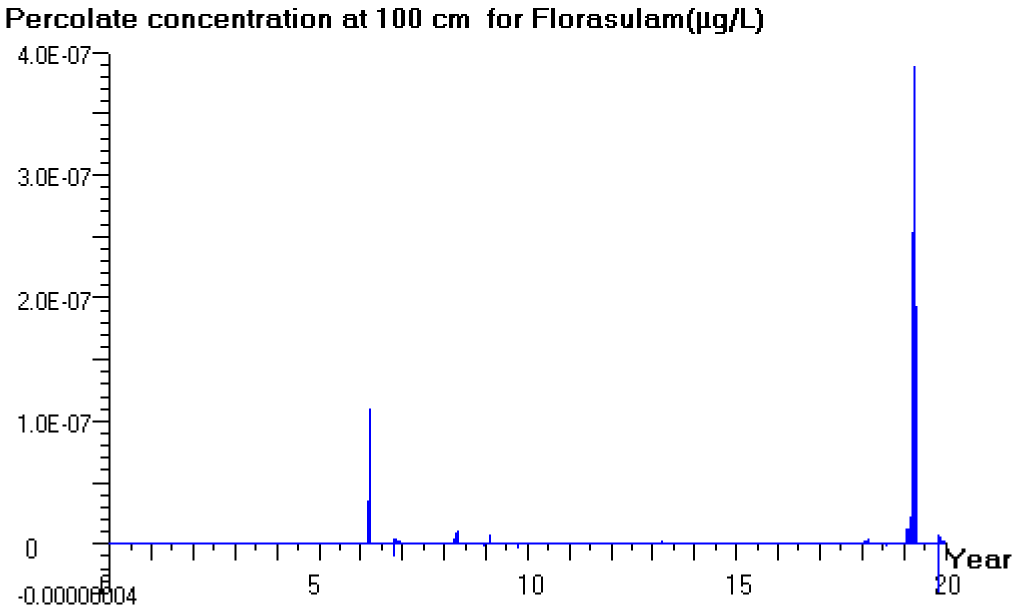


Figure 7-89: Time dependent concentration in the percolate for florasulam

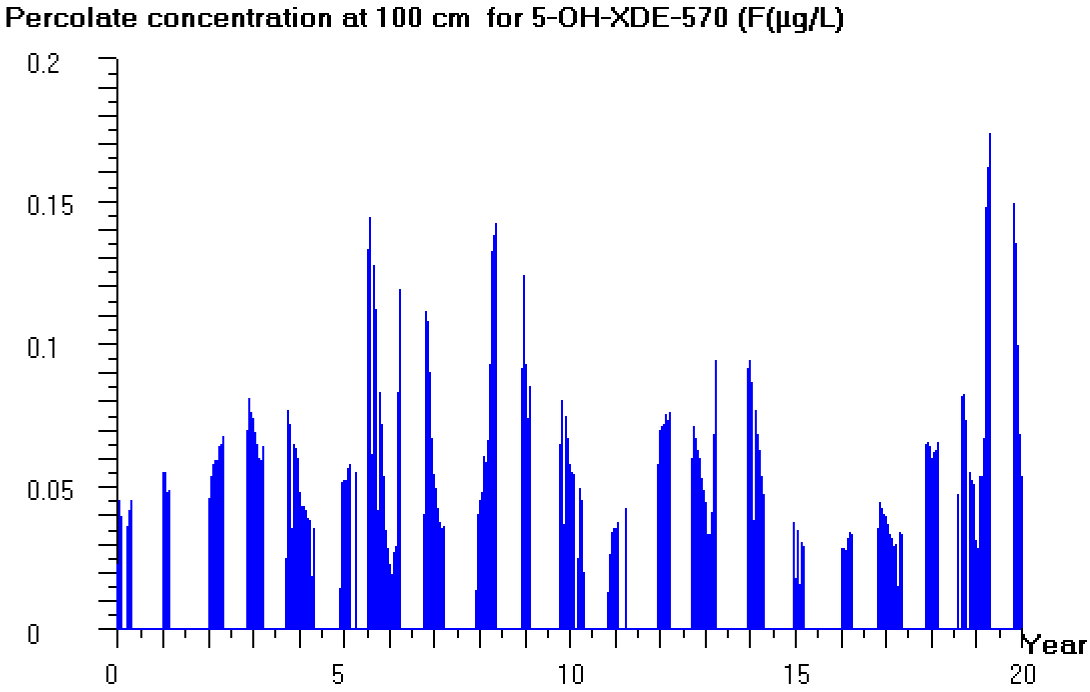


Figure 7-90: Time dependent concentration in the percolate for 5-OH-XDE-570

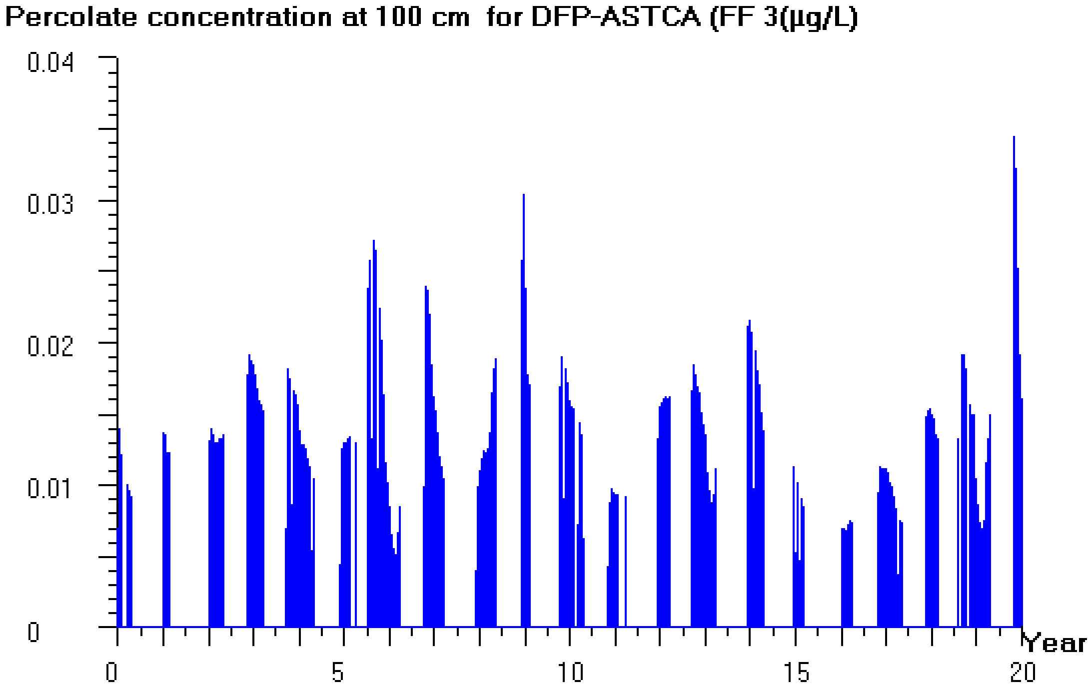


Figure 7-91: Time dependent concentration in the percolate for DFP-ASTCA

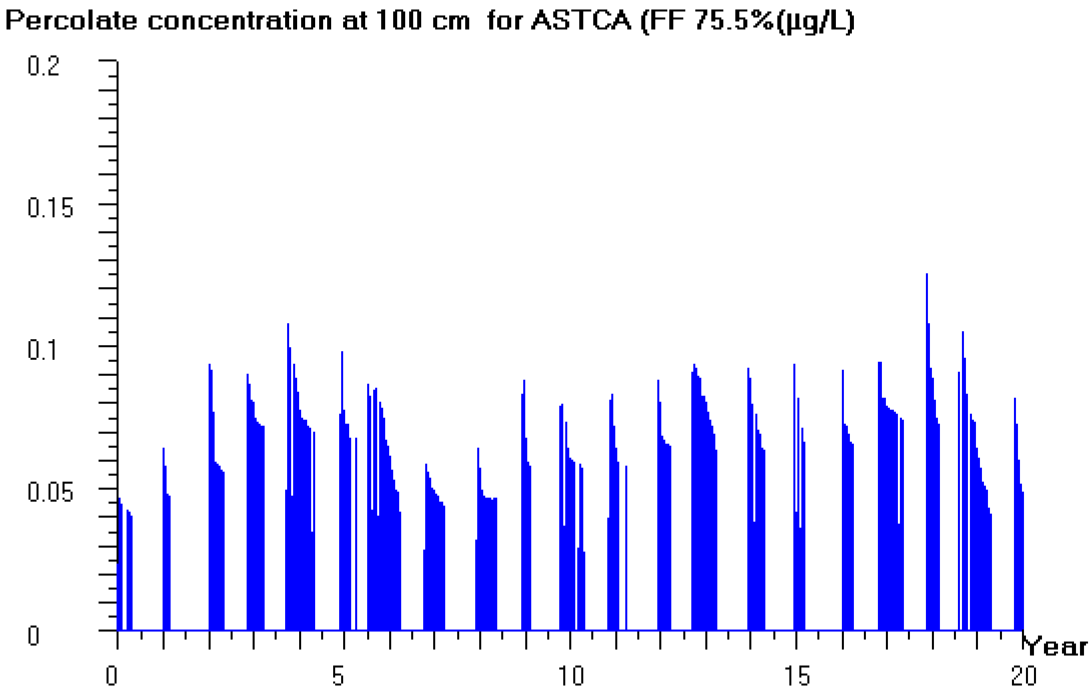


Figure 7-92: Time dependent concentration in the percolate for ASTCA

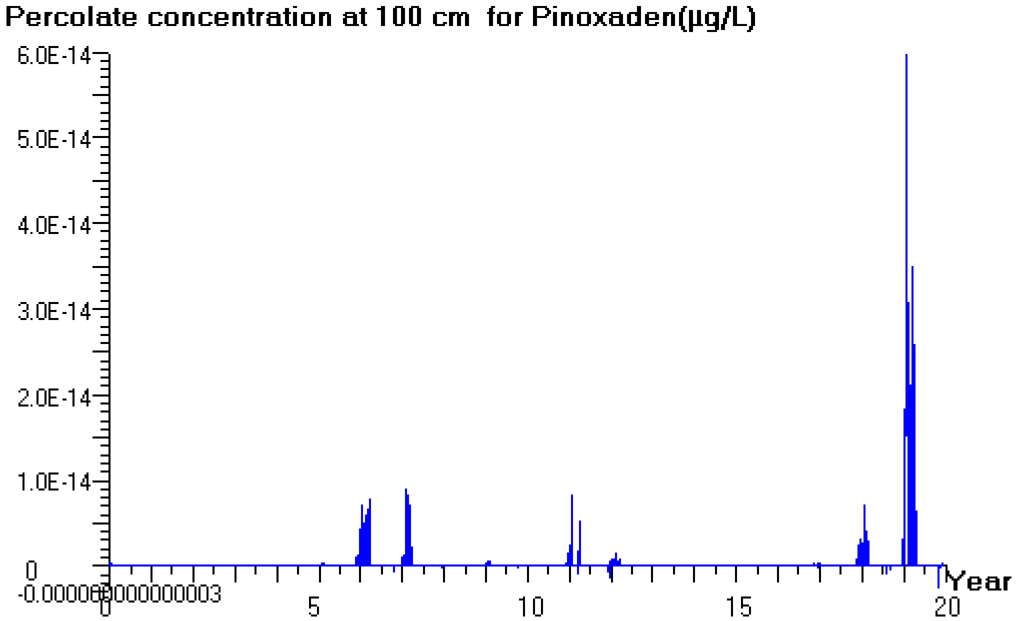


Figure 7-93: Time dependent concentration in the percolate for pinoxaden

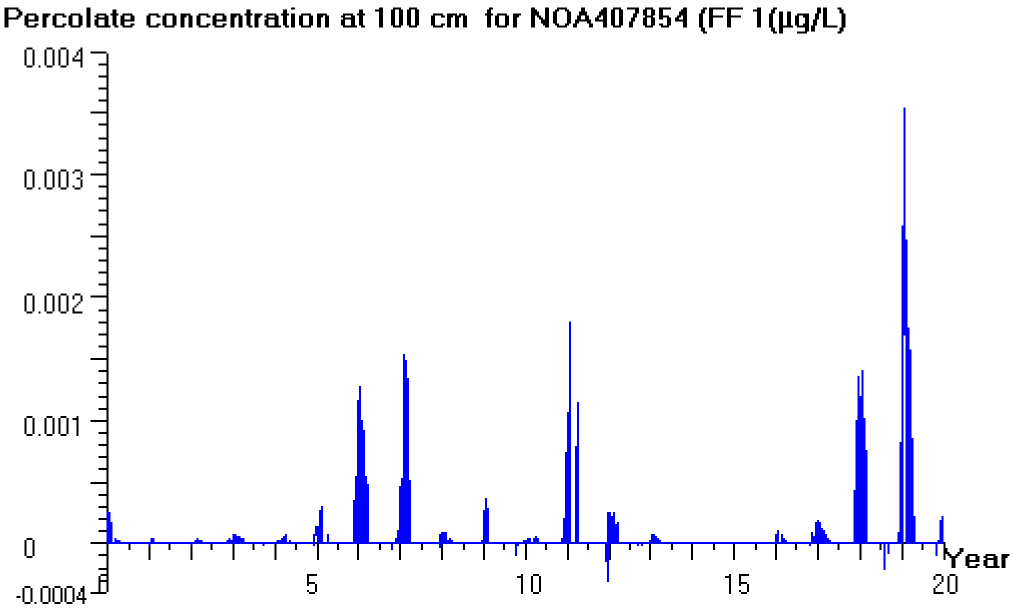


Figure 7-94: Time dependent concentration in the percolate for NOA407854

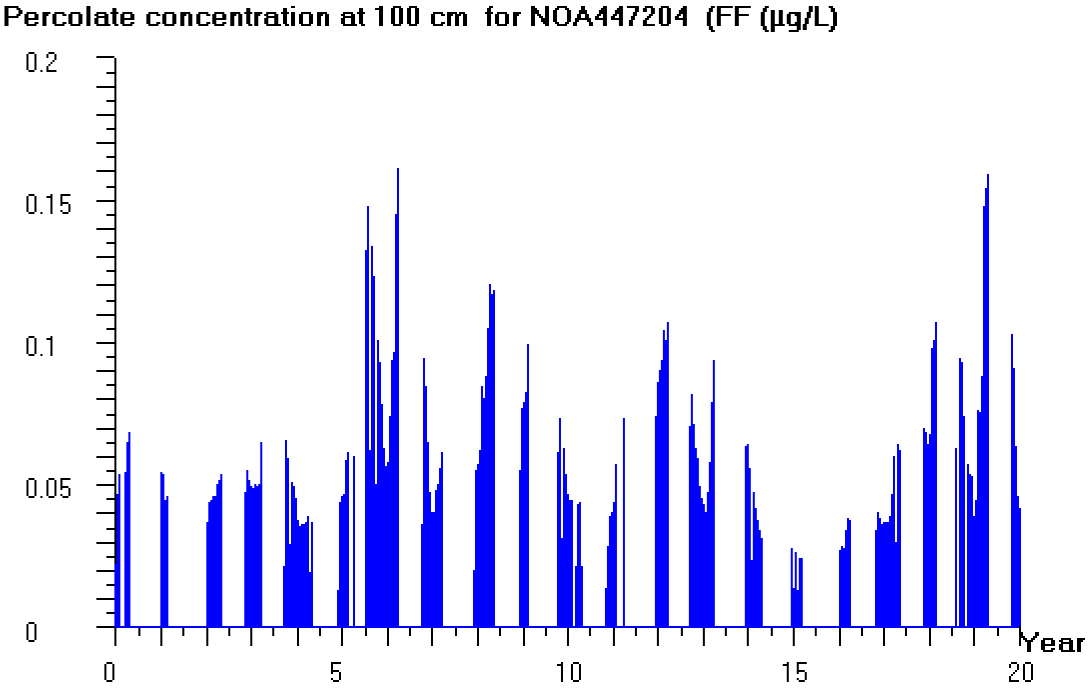


Figure 7-95: Time dependent concentration in the percolate for NOA447204

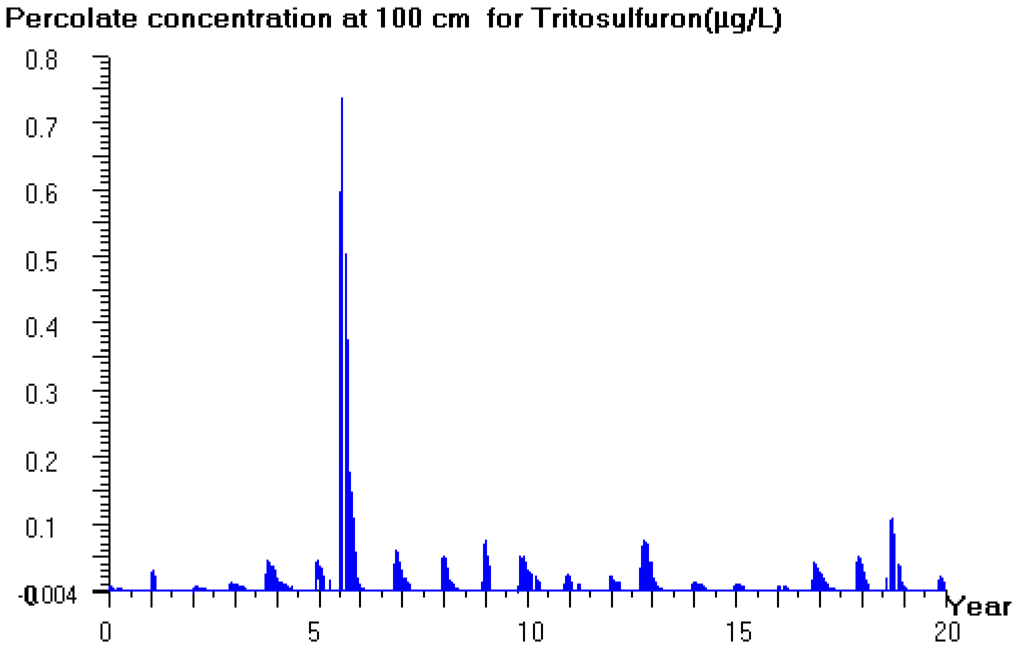


Figure 7-96: Time dependent concentration in the percolate for tritosulfuron

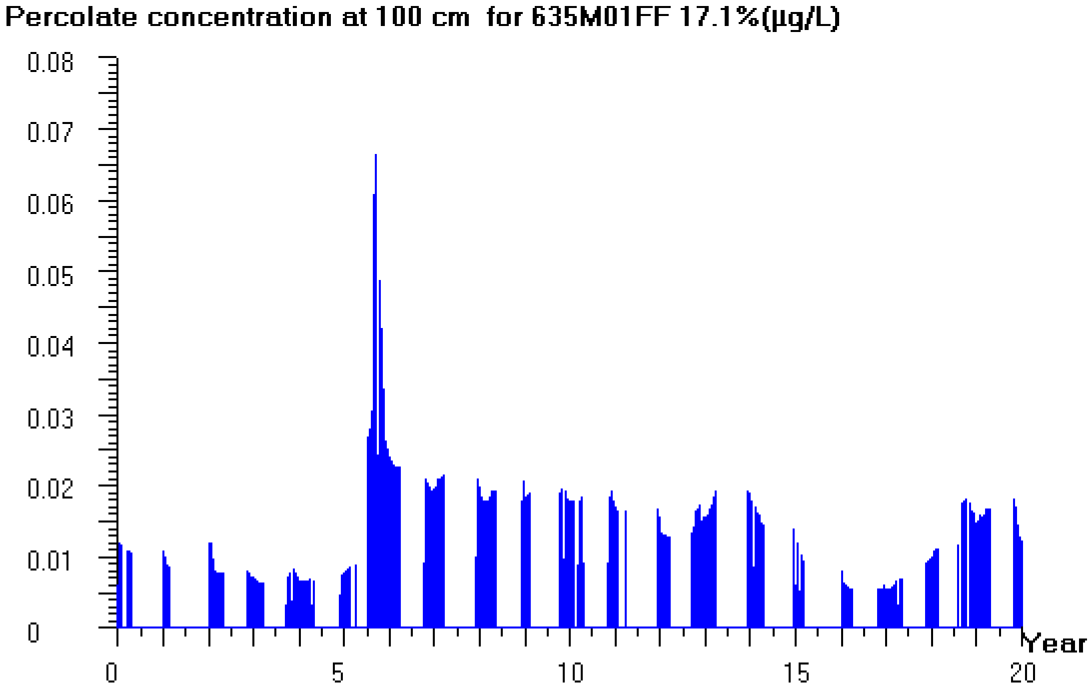


Figure 7-97: Time dependent concentration in the percolate for BH 635-4 (635M01)

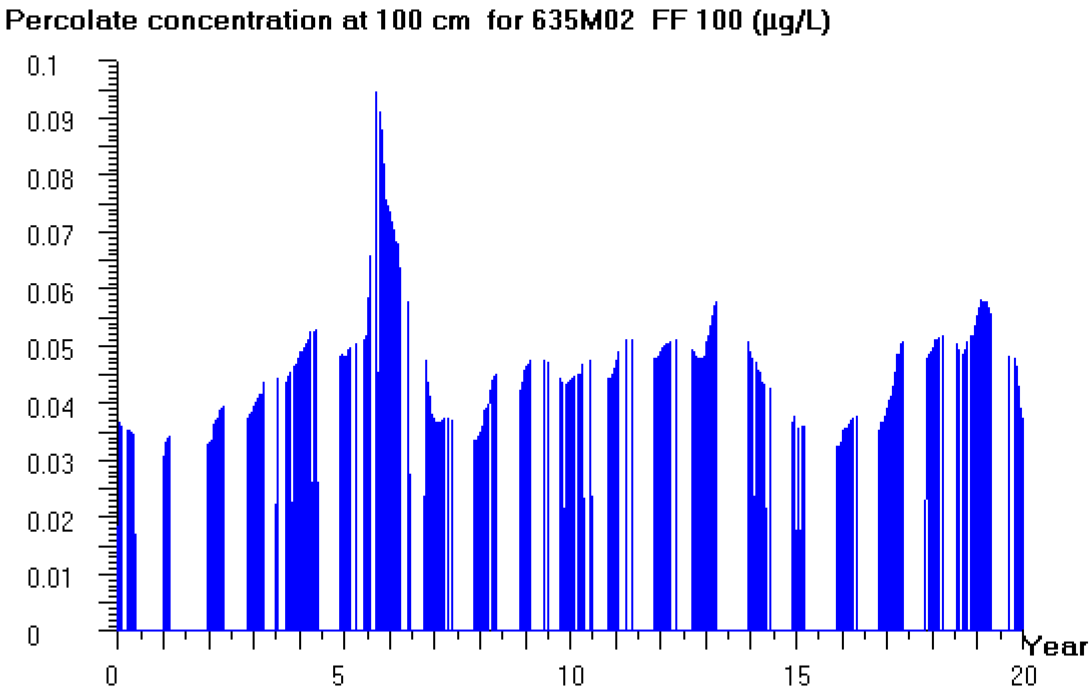


Figure 7-98: Time dependent concentration in the percolate for BH 635-2 (635M02)

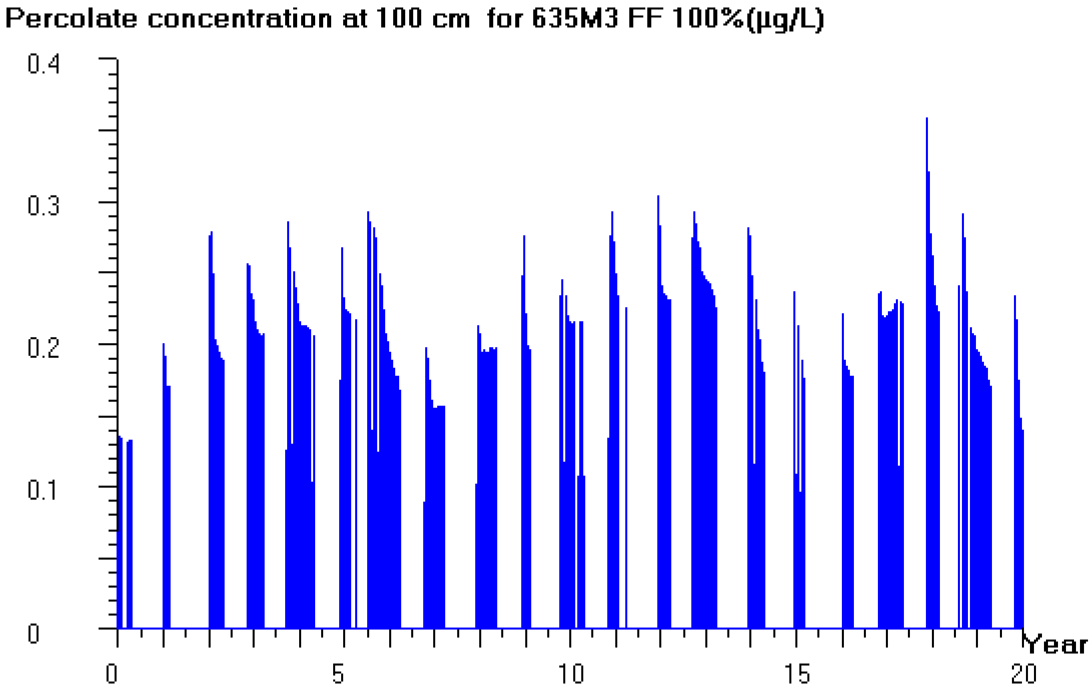


Figure 7-99: Time dependent concentration in the percolate for BH 635-3 (635M03)

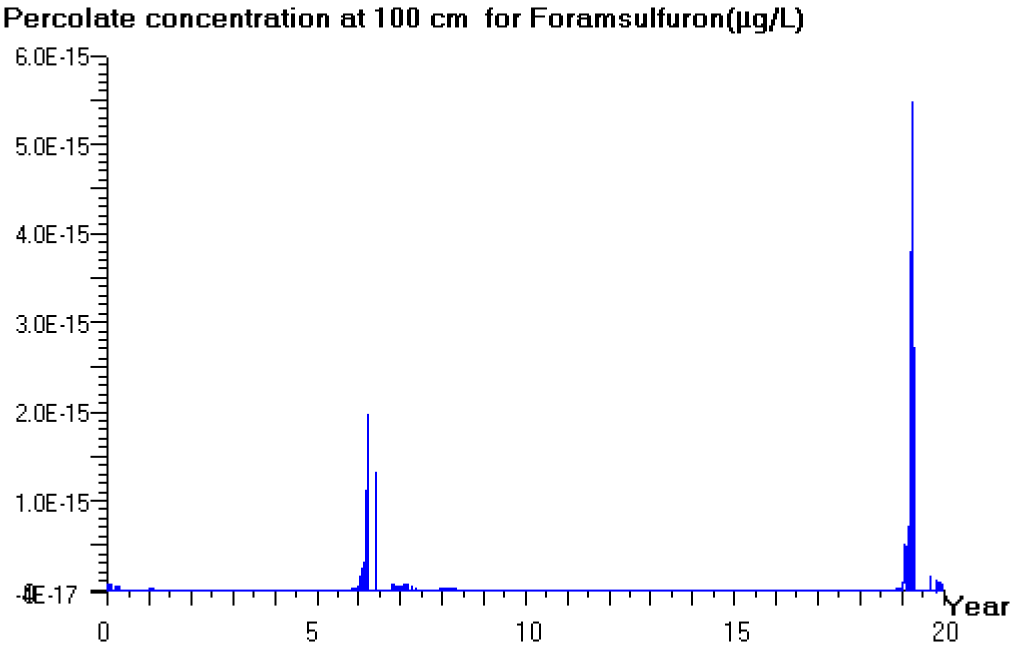


Figure 7-100: Time dependent concentration in the percolate for foramsulfuron

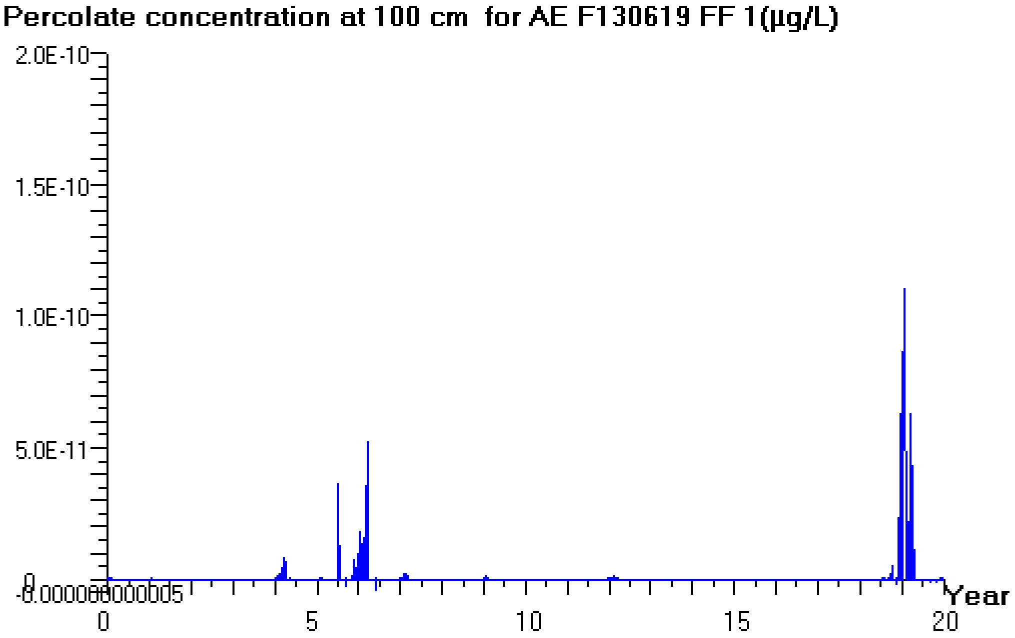


Figure 7-101: Time dependent concentration in the percolate for AE F130619

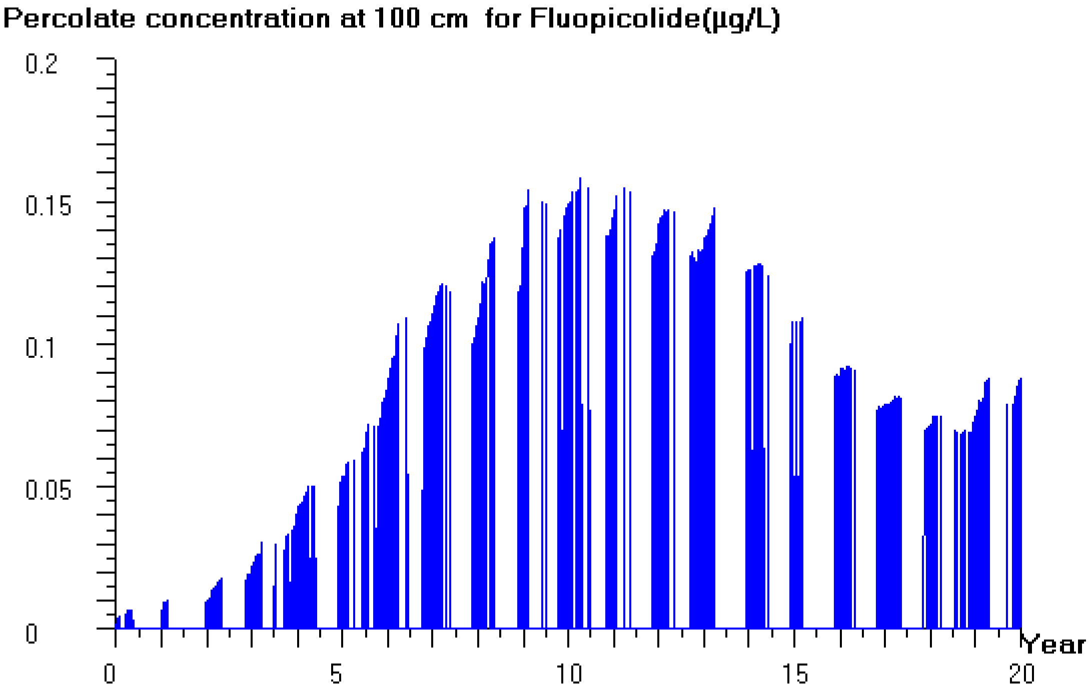


Figure 7-102: Time dependent concentration in the percolate for fluopicolide

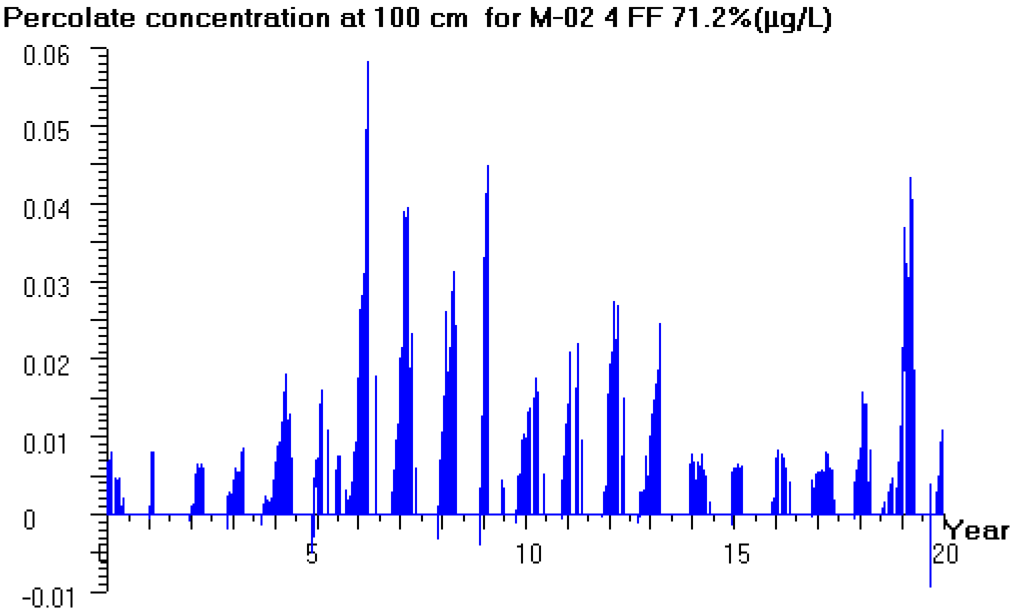


Figure 7-103: Time dependent concentration in the percolate for M-02 = PCA = AE C657188 (UMET/2)

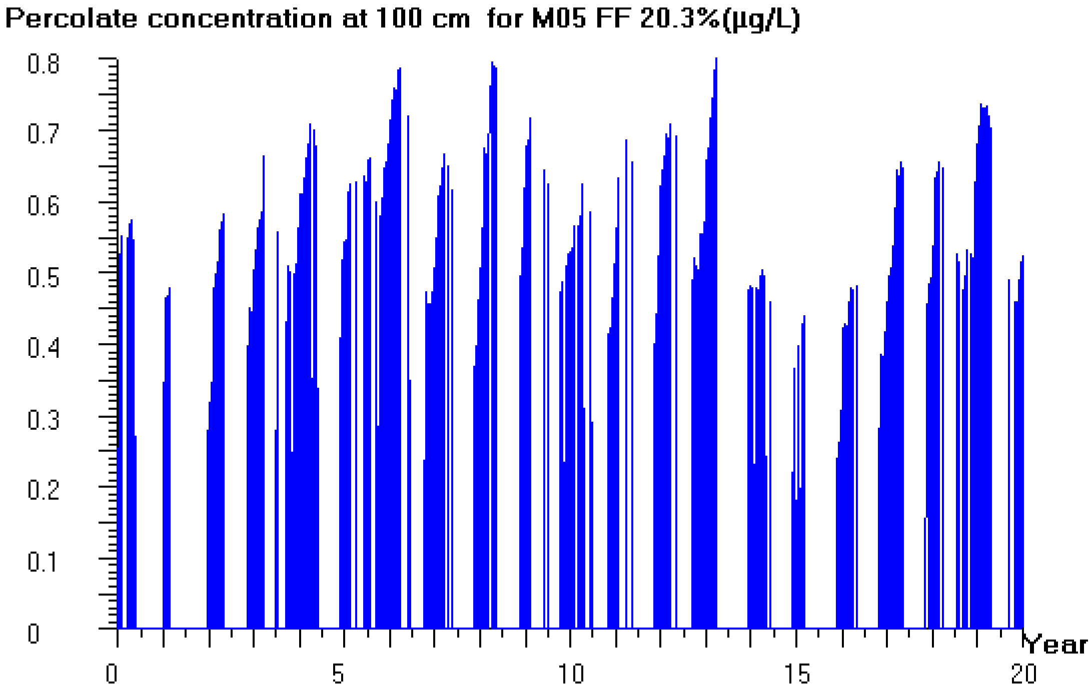

Percolate concentration at 100 cm for M05 FF 20.3%(µg/L)

Figure 7-104: Time dependent concentration in the percolate for M-05 = AE 1344122 = P1 (=RPA433497)

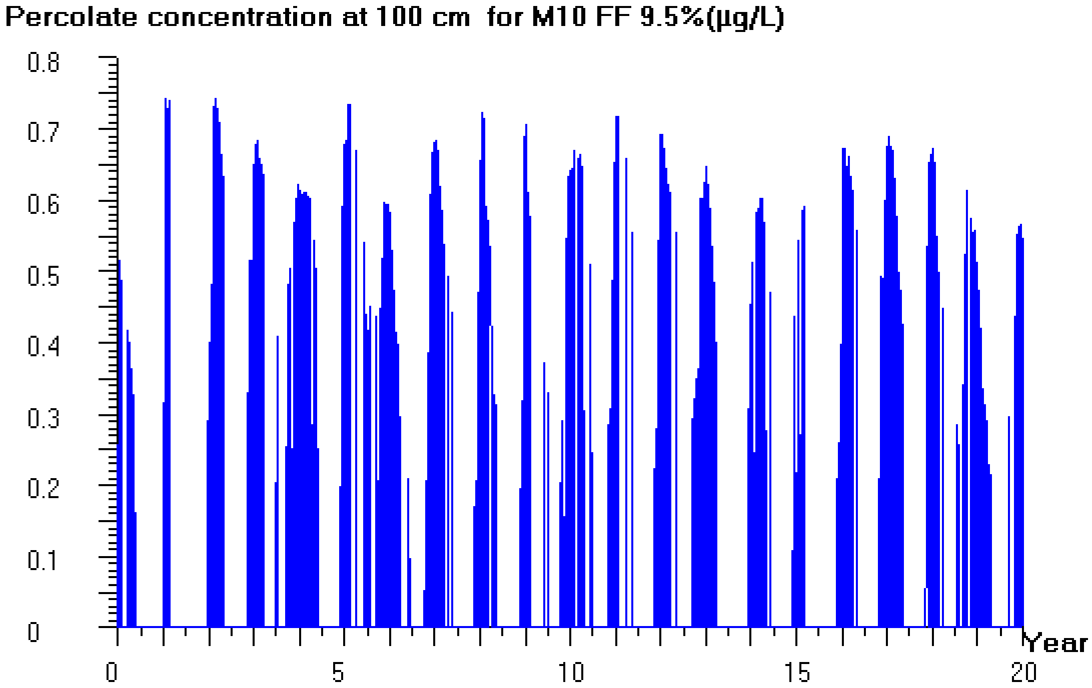

Percolate concentration at 100 cm for M10 FF 9.5%(µg/L)

Figure 7-105: Time dependent concentration in the percolate for M-10 = AE 1344123 = P4 (=RPA 433965)

## 7.6 Appendix 6: Methodology for the inverse modelling procedure

The inverse modelling optimisation was done using the software tool “inversePELMO” which combines the simulation model PELMO with the optimisation tool “PEST” (Klein 2011b).

According to FOCUS (2009/2014) inverse modelling studies are performed in order to obtain key parameters for risk assessment such as $Kf_{oc}$ (Freundlich sorption constant related to organic carbon) and $DegT_{50}$ (degradation time to 50%) from higher tier studies (e.g. outdoor studies) instead directly from standard laboratory studies on sorption and degradation. Aim of such a study is on one hand to get a deeper look into the processes that led to a certain lysimeter result. On the other hand inverse modelling studies can be used to improve the standard modelling on tier 1 by considering additional information from higher tier studies.

Generally, two steps have to be conducted when performing inverse modelling studies:

First, the hydrology in soil is optimised, followed by the optimisation of pesticide fate as shown in Figure 7-106

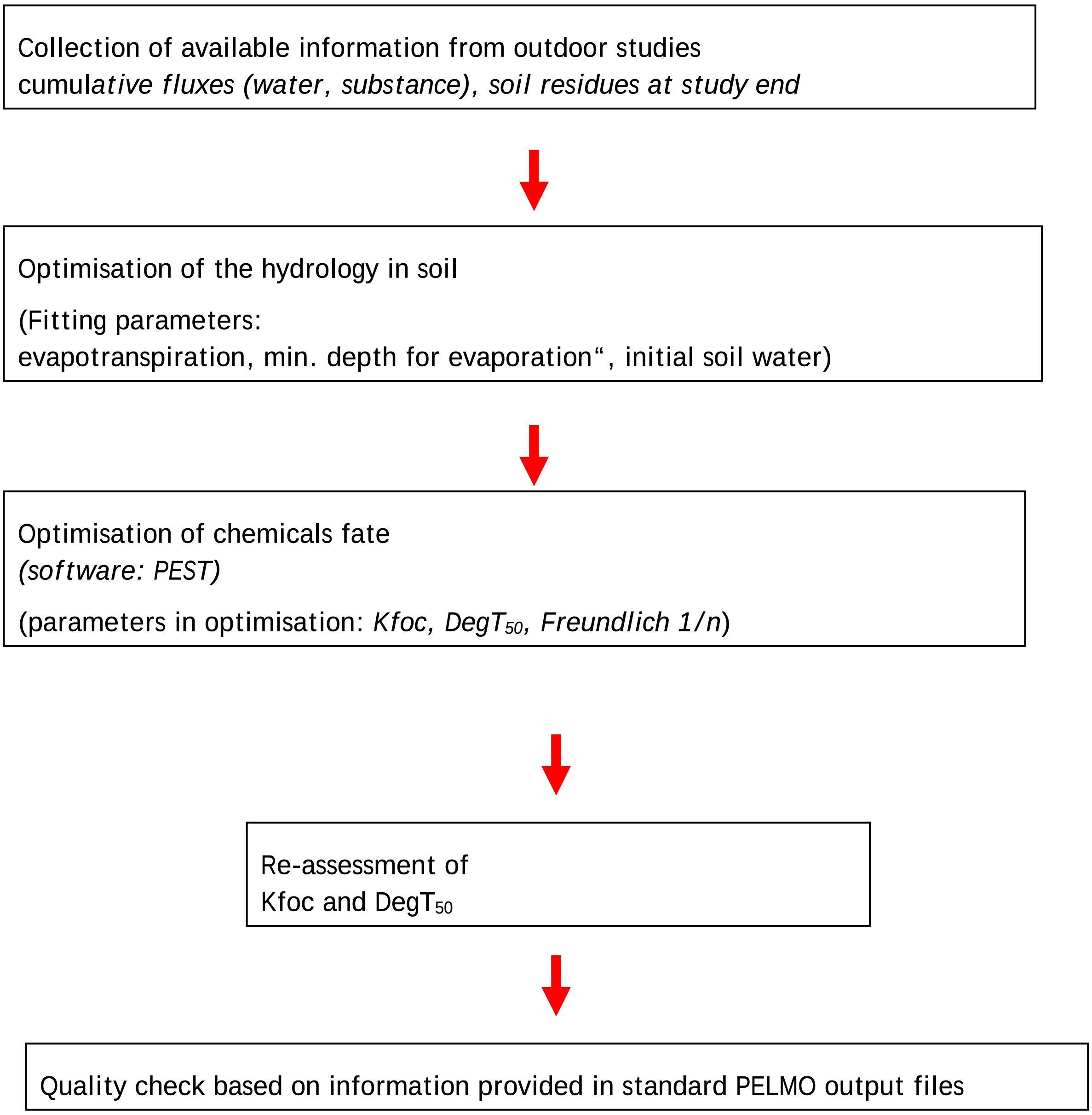


Figure 7-106: Flow chart: File handling of a flux optimisation with InversePELMO

PELMO (Klein 1995, Jene 1998, Klein 2011a) is the standard model for doing leaching simulations for registration purposes in Germany (Holdt et al. 2011) and in Europe FOCUS (2009/2014). However, PELMO with its normal shell is not designed to perform inverse modelling studies because these studies require several model runs including automatic modification of input files based on the comparison with experimental results.

A scheme that shows the file handling is presented in Figure 7-107 for an optimisation of pesticide properties based on cumulative fluxes in the leachate. All pesticide and application parameters are gathered in text files with extension “psm”. The scenario input data can be found in files with extension „sze”. Before starting the inverse modelling calculation a first simulation (with initial conditions for either the soil hydrology or pesticide properties) should be prepared using the normal shell (which can be called directly from InversePELMO).

The optimisation itself is done automatically by InversePELMO.

As shown in Figure 7-107 InversePELMO calls PEST which then reads the control file pest_pesticide.pst with all information about the parameters considered for the optimisation including their initial values and their allowed ranges. Also the experimental data (e.g. cumulative fluxes) can be found in pest_pesticide.pst.

According to the information in pesticide.tpl *PEST.exe* is able to create pesticide input files (pesticide.psm) for PELMO including the correct position for the input parameters used in the optimisation. After this file has been written PEST calls PELMO for a simulation. To make the interface between PELMO and PEST more stable a second program is always executed after PELMO (in the example presented in Figure 7-107: PELMO_results_pesticide.exe) which gathers the important simulation results (e.g. calculated cumulative pesticide fluxes) and writes them into the file pest.plm. After both programs (PELMO and PELMO_results_pesticide.exe) are finished PEST gets control again and will read the important simulation results listed in pest.plm (instructions for PEST to read pest.plm is given in pest.ins). According to the simulation results a new iteration is initiated with new $DegT_{50}$ and $Kf_{oc}$ data for the optimisation until the optimisation is finalised.

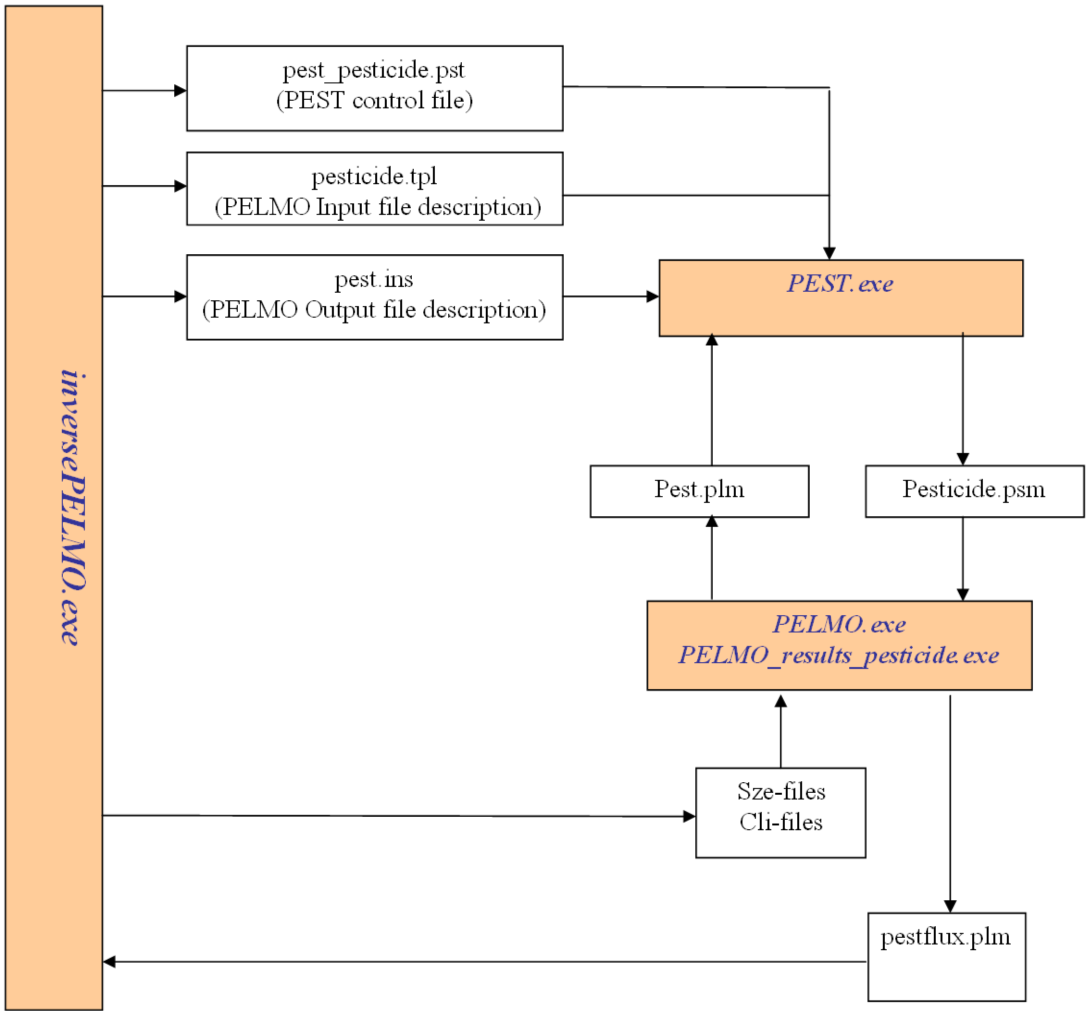


Figure 7-107: Flow chart: File handling of a flux optimisation with InversePELMO

## 7.7 Appendix 7: Detailed results of the inverse modelling simulations

Detailed information about the climate (temperatures, precipitation) and soil parameters (e.g. texture, organic carbon contents) are provided in this appendix 7.

Inverse modelling always begins with a calibration step to adequately describe the soil hydrology of the leaching study, in terms of both temporal and total fluxes.

In this appendix the following input parameters are used by inversePELMO for the calibration:

- Initial soil moisture (a single value for the whole soil core),
- Minimum depth for evaporation,
- Crop specific Kc-factors.

The crop specific Kc-factors are used to transpose the generic potential evaporation data to crop specific values. These factors are available for no-crop condition, mid-season and late season.

For the optimisation of the pesticide fate the parameters Kfoc and DegT50 in soil were used. All other parameters were set to the same values as in Part A I.

***<u>The rest of this appendix was separated as it may have contained confidential information.</u>***