Leaching of plant protection products and their transformation products

Proposals for improving the assessment of leaching to groundwater in the Netherlands --- Version 2

J.J.T.I. Boesten, A.M.A. van der Linden, W.H.J. Beltman and J.W. Pol

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Assessment of leaching of plant protection products to groundwater is an important aspect of the environmental risk assessment of these substances. Analysis of available Dutch groundwater monitoring data for these substances triggered a critical review of the current Dutch leaching assessment. As a result, proposals were developed for improving this assessment. These include: (i) a procedure for correcting systematic errors in measured sorption coefficients, (ii) a preliminary procedure for a quality check of Freundlich exponents, (iii) a flow chart for obtaining parameters describing the relationship between the organic-matter/water distribution coefficient, K_{om}, and the pH for weak acids, (iv) a procedure for obtaining a K_{om} endpoint from a population of K_{om} values including lower and upper limits, (v) a procedure for estimating the total amount of substance in soil from a concentration profile (needed for assessment of degradation half-lives from field experiments). This report is an update of the proposals reported in 2011 by the same authors based on testing the feasibility of the proposals to a few dossiers.

Keywords: plant protection products, leaching, groundwater, adsorption, degradation, sorption coefficient, Freundlich sorption exponent

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Preface

The work reported here was initiated in 2005 shortly after a decision tree for leaching of plant protection products was introduced in the Dutch registration procedure that was based on the GeoPEARL model. The background was that the Dutch association for drinking-water producing companies (VEWIN) at the moment of the introduction of the decision tree expressed their doubts whether this new tree would provide enough protection of individual drinking-water abstractions. These doubts were based on groundwater monitoring data collected by companies that were part of VEWIN. Based on this, the precursors of the Dutch Ministries of Infrastructure and the Environment and of Economic Affairs decided in 2005 that the decision tree should be critically reviewed in the light of the groundwater monitoring data provided by VEWIN. Therefore they established a scientific workgroup with members from Alterra, RIVM and Ctgb which has produced the report Boesten, J.J.T.I., A.M.A. van der Linden, W.H.J. Beltman and J.W. Pol, 2011. *Leaching of plant protection products and transformation products; Proposals for improving the assessment of leaching to groundwater in the Netherlands* (Alterra report 2630). The current report is an update of that report, correcting flaws and weaknesses that were detected upon application of the guidance proposals. The testing of the guidance proposals by the working group is reported in *Evaluation of the Dutch leaching decision tree with the substances bentazone, MCPA and mecoprop* (RIVM Report 2015-0095).

Samenvatting

Een analyse van beschikbare monitoringsgegevens in Nederlands grondwater gaf aan dat bentazon, MCPA en mecoprop de enige moederstoffen zijn die (i) in meer dan één drinkwateronttrekkingsgebied zijn aangetroffen, en (ii) zijn toegelaten in Nederland. Daarom zijn deze stoffen geselecteerd om de NL beoordeling van uitspoeling naar grondwater te testen. Deze drie stoffen zijn zwakke zuren die relatief zwak adsorberen en een pH-afhankelijke sorptie vertonen.

De oorspronkelijke opzet van de studie was om de bestaande NL beslisboom voor uitspoeling te evalueren door deze toe te passen op deze drie stoffen. Tijdens deze evaluatie bleek echter dat onderdelen van de bestaande richtsnoeren (zowel op NL als EU niveau) niet duidelijk of volledig genoeg waren of niet conform de stand van de wetenschap. Daarom werden voorstellen ontwikkeld om deze onderdelen te herzien.

Deze voorstellen richten zich op verbeteringen van de richtsnoeren voor het afleiden van de invoergegevens van de stoffen in de modelberekeningen. Toepassen van deze verbeterde richtsnoeren zal in het algemeen tot hogere inschatting van de uitspoeling leiden; dit geldt vooral voor zwak sorberende stoffen zoals bentazon, MCPA en mecoprop.

De procedure die thans gebruikt wordt om de systematische fout in de sorptiecoëfficiënt te beoordelen in kader van de NL uitspoelingsbeoordeling, moet worden herzien omdat deze procedure is gebaseerd op de werkelijke waarde van de sorptiecoëfficiënt. Dit is inconsistent met de toepassing van deze procedure op dossiers die alleen gemeten waarden bevatten. Daarom is een herziene procedure ontwikkeld die gebaseerd is op gemeten waarden. Verdere analyses gebaseerd op deze herziene procedure gaven aan dat gebruik van de zogenaamde indirecte methode van het OECD-106 richtsnoer niet uitsluit dat de sorptiecoëfficiënt met 100% overschat wordt. Een dergelijke overschatting zou leiden tot een sterke onderschatting van de uitspoeling. Ten einde deze systematische overschatting van de sorptiecoëfficiënt te voorkomen, adviseren we het volgende: (i) corrigeer sorptiecoëfficiënten gemeten met deze indirecte methode op basis van de gemeten massa in het systeem aan het eind van de studie, en (ii) beschouw deze gecorrigeerde sorptiecoëfficiënten als ondergrenzen van de werkelijke sorptiecoëfficiënt. Als deze correctie de sorptiecoëfficiënt verlaagt tot nul, dan adviseren we uitvoering van bodemkolomstudies om de sorptiecoëfficiënt te meten.

Zoals beschreven in de vorige alinea, is de procedure voor het inschatten van het effect van systematische fouten in de sorptiecoëfficiënt opnieuw bekeken en verbeterd. Deze controle was echter onmogelijk voor de toevallige fouten omdat hiervoor onvoldoende tijd beschikbaar was. We bevelen aan om de sorptiecoëfficiënt op nul te zetten als het product van de gemeten sorptiecoëfficiënt en de grond-water verhouding kleiner is dan 0,1 omdat de toevallige fout in de sorptiecoëfficiënt dan erg groot wordt. Deze 0,1 is echter niet gebaseerd op statistische analyses. Daarom adviseren we om dit criterium te onderbouwen of verbeteren op basis van statistische analyses van de toevallige fouten in beschikbare sorptiestudies gebaseerd op schudproeven.

De K_{om} is een belangrijk invoergegeven voor de uitspoelingsberekeningen. Berekeningen voor stoffen zonder pH-afhankelijke sorptie dienen uit te gaan van een centrale waarde gebaseerd op alle betrouwbare en relevante waarden (normaliter tenminste vier waarden voor moederstoffen). Voor zwak sorberende stoffen wiens sorptie niet afhangt van de pH, blijkt de selectie van relevante K_{om} metingen uit beschikbare dossiergegevens zo ingewikkeld te zijn dat er 'expert judgement' voor nodig is. T.g.v. beperkte beschikbare tijd was het onmogelijk om ervaring op te doen met deze selectie via bestudering van een aantal dossiers. Gezien het belang van deze parameter voor de uitspoelingsbeoordeling bevelen we aan om: (i) de K_{om} gegevens van een tiental dossiers in detail te analyseren, (ii) op basis hiervan verdere richtlijnen te ontwikkelen die het 'expert judgement' zo veel mogelijk overbodig maken, en (iii) een software tool (een 'expert system') te ontwikkelen dat deze selectie van de relevante K_{om} gegevens uitvoert op basis van deze richtlijnen.

De Freundlich sorptie exponent heeft aanzienlijke invloed op de berekende uitspoelingsconcentraties. We geven in dit rapport weliswaar enkele criteria om te beoordelen of gemeten waarden acceptabel zijn maar we bevelen aan om procedures te ontwikkelen om de gemeten Freundlich exponenten te beoordelen en om daarna een statistische analyse uit te voeren op basis van alle betrouwbare metingen waarbij getoetst wordt of de Freundlich exponent een stofeigenschap is. Verder bevelen we aan (zolang de resultaten van deze studie nog niet beschikbaar zijn) om als standaardwaarde N = 0,9 te gebruiken voor deze exponent (voor zowel moederstof als metabolieten) en om alleen van deze waarde af te wijken als tenminste drie betrouwbare N metingen beschikbaar zijn.

We bevelen aan om een N waarde alleen als voldoende betrouwbaar te beschouwen als deze waarde is gebaseerd op tenminste drie beginconcentraties met tenminste een factor 100 verschil tussen de hoogste en de laagste concentratie en als de correctie van de sorptiecoëfficiënt gebaseerd op de teruggevonden hoeveelheid aan het eind van de studie kleiner is dan 20%. Deze aanbeveling is gebaseerd op ‘expert judgement’. Daarom adviseren we verder onderzoek om deze aanbeveling te onderbouwen of herzien.

De ontwikkeling van richtsnoeren voor de beoordeling van de sorptie van zwakke zuren met een pH-afhankelijke sorptie bleek zo ingewikkeld dat hiervoor een beslisschema ontwikkeld moest worden. Dit schema geeft aan dat de K_{om} - pH relatie alleen gefit dient te worden als er tenminste vier gemeten K_{om} - pH paren beschikbaar zijn en als het verschil tussen de hoogste en de laagste pH waarde tenminste 3 is. Verder bleek dat pH waarden in dossiers gebaseerd zijn op drie verschillende meetmethoden (metingen in gedestilleerd water, in 0,01 mol/L $CaCl_2$ en in 0,1-1 mol/L KCl). Op basis van alle beschikbare gegevens konden wij lineaire verbanden afleiden tussen de pH waarden gemeten met deze verschillende methoden.

Voor de beoordeling van de sorptie van zwakke zuren adviseren wij om alle gemeten pH waarden terug te rekenen naar de pH meetmethode die gebruikt werd om het uitspoelscenario af te leiden (om inconsistenties tussen de pH meetmethoden te voorkomen). Voor de NL uitspoelingsbeoordeling is dit de pH_{KCl}. Als de meetmethode van de pH in een dossier onbekend is dan bevelen wij aan om standaard uit te gaan van een meting in water.

Het eindresultaat van de beoordeling van de sorptie van een zwak zuur is een verband tussen de K_{om} en de pH. Voor het fitten van dit verband is een software pakket nodig dat niet-lineaire functies aan kan. Diverse pakketten zijn hiervoor geschikt. Wij bevelen echter aan om hiervoor gespecialiseerde software (b.v. geprogrammeerd in *R*) te ontwikkelen die ook de pH waarden kan omrekenen en deze omgerekende waarden in een grafiek kan weergeven. Deze software dient publiek beschikbaar te zijn.

De bestaande richtlijnen voor het schatten van de totale hoeveelheid in de bodem bij veldpersistentie-studies bleken onvoldoende gedetailleerd te zijn, vooral als een significant percentage aanwezig is in meerdere bemonsterde lagen. Daarom hebben we een gedetailleerde richtlijn gemaakt om deze totale hoeveelheid in het bodemprofiel te schatten uit concentratieprofielen (als onderdeel van de veldpersistentiestudies voor het schatten van de *DegT50* in de bodem).

De huidige NL procedure voor de uitspoelingsbeoordeling dekt niet alle stoffen die de bodem kunnen bereiken: er worden op EU niveau geen gegevens gevraagd over afbraakproducten van gewas-beschermingsmiddelen die op bladoppervlakken gevormd worden door fotolyse. De beoordeling van de uitspoeling van deze stoffen is dus onmogelijk binnen het huidige toelatingskader. Dergelijke gegevens worden wel gevraagd voor afbraakproducten die op het bodemoppervlak gevormd worden door fotolyse.

Veldexperimenten op aardappelvelden met ruggen en voren hebben aangetoond dat uitspoeling in een dergelijk teeltsysteem aanzienlijk hoger kan zijn dan in gewassen die op vlak land geteeld worden. Dit komt vooral doordat de neerwaartse waterstroming onder de voren sterker is dan wordt aangenomen in berekeningen voor vlak land. Deze hogere uitspoeling treedt echter alleen op als de stof in de voor aanwezig is. Dus de toedieningsmethode bepaalt of de verwachte uitspoeling voor een ruggensysteem hoger of lager is dan voor vlak land. Wij hebben tien verschillende toedieningsmethoden geïdentificeerd voor gewasbeschermingsmiddelen in NL aardappelteeltsystemen. Voor twee van deze tien is de verwachte uitspoeling voor het ruggensysteem hoger dan voor vlak land terwijl voor vier van deze tien de verwachte uitspoeling lager is dan voor vlak land; voor de resterende vier is de uitspoeling naar verwachting gelijk voor beide systemen. Aangezien de huidige uitspoelingsbeoordeling niet verdedigbaar is voor aardappelteelt op ruggen, bevelen we aan om hiervoor een adequate uitspoelingsbeoordeling te ontwikkelen.

Summary

Analysis of the available monitoring data in Dutch groundwater showed that bentazone, MCPA and mecoprop were the only parent substances that: (i) were found in more than one drinking water abstraction area and (ii) have still a registration in the Netherlands. Therefore these substances were selected to test the current Dutch leaching assessment. These substances are all weak acids whose sorption is comparatively weak and a function of the pH of the soil.

The original intention of the study was to evaluate the Dutch decision tree on leaching by applying the tree to these three substances. However, while working on this evaluation it appeared that parts of the existing guidance (both at NL and EU level) were not clear or complete enough or not state-of-the-art scientifically. Therefore guidance proposals were developed to revise these parts.

The proposals focus on improvements of the guidance for deriving substance input parameters for the simulation models. Using this improved guidance will in general lead to higher estimates of leaching especially for weakly sorbing substances such as bentazone, MCPA and mecoprop.

The procedure currently used to assess the systematic error of the sorption coefficient in the Dutch leaching assessment needs to be revised because this procedure is based on the true value of the sorption coefficient. This is inconsistent with the use of the procedure for assessment of dossiers which contain only measured values. Therefore a revised procedure was developed that is based on measured values. Further analysis based on this revised procedure showed that following the so called indirect method of OECD-106 guideline does not exclude that the sorption coefficient is overestimated by 100%. Such an overestimation would lead to a strong underestimation of leaching. To avoid systematic overestimation of the sorption coefficient, we recommend to correct sorption coefficients measured with this indirect method based on the measured recovered amount at the end of the study and to consider the corrected sorption coefficients as lower limits of the true sorption coefficient. If this correction lowers the sorption coefficient to zero, we recommend to perform soil column studies to assess the sorption coefficient.

As described in the previous paragraph, the procedure for accounting for the effect of systematic errors in the sorption coefficient has been reviewed and improved. However, this was impossible for the effect of random errors due to lack of time. For assessment of leaching of parent substances, we recommend setting sorption coefficients to zero if the product of the measured sorption coefficient and the solid-liquid ratio is smaller than 0.1 because the random error in the sorption coefficient becomes very large for such systems. However, this value of 0.1 is not based on statistical analyses. Therefore we recommend to underpin or modify this criterion on the basis of statistical analyses of the random errors in available batch sorption studies.

The K_{om} is an important input parameter for the leaching calculations. A central value of all reliable and relevant values (usually at least four values for parent substances) has to be used for these calculations for pesticides with no pH-dependent sorption. For weakly sorbing substances with no pH-dependent sorption the selection of relevant K_{om} measurements from all available data in the dossier is so complicated that it requires expert judgement. Due to time constraints in the project, it was impossible to gain experience with this selection by studying a number of dossiers. In view of the importance of this parameter for the leaching assessment we recommend: (i) analysing the K_{om} data in some ten dossiers in detail, (ii) developing from this analysis further guidance that eliminates the need of expert judgement as much as possible, and (iii) making a software tool that selects the relevant K_{om} measurements based on this guidance.

The Freundlich sorption exponent is a major factor influencing the calculated leaching concentrations. We give a few acceptability criteria for the exponent, but we recommend developing procedures for evaluating measured Freundlich exponents and performing thereafter a statistical analysis of all

reliable measurements of the Freundlich exponent to test whether this exponent is a substance property. As long as the results of such a study are not available, we recommend to use as a default value a Freundlich exponent of $N = 0.9$, for both parent substances and metabolites, and to deviate only from this value if at least three reliable measurements of N are available.

We recommend to consider an N value reliable only if it is based on at least three initial concentrations with at least a factor of 100 between highest and lowest concentration and if the correction of the sorption coefficient based on the measured recovered amount at the end of the study is smaller than 20%. This advice is based on expert judgement. Therefore we recommend to perform further research to underpin or revise this advice.

The development of guidance to assess the sorption of weak acids whose sorption is a function of the pH appeared to be so complicated that we had to develop a decision flow chart for this. The flow chart indicates that a fit of the K_{om} -pH relationship should only be carried out if at least four pairs of measurements of K_{om} and pH are available and if the range of pH values is at least 3. Furthermore, it appeared that pH values in dossiers are based on three different measurement methods (measurements in distilled water, in approx. 0.01 mol/L $CaCl_2$ and in 0.1 - 1 mol/L KCl). After collecting all available data we were able to establish linear relationships between the pH values measured with these different methods.

When evaluating the sorption of a weakly acidic substances, we recommend to calculate all measured pH values back to the measurement method of the pH that was used to derive the leaching scenario (to avoid inconsistencies between pH measurement methods). For the Dutch leaching assessment this is the pH_{KCl}. If the measurement method of a pH in a dossier is unknown, we recommend to assume measurement in water as the default measurement method.

The end result of the assessment of the sorption of a weak acid is a relationship between the K_{om} and the pH. The procedure for fitting this relationship requires a software package capable of fitting non-linear functions to data. Several packages are capable of this. It is however recommended to develop dedicated software (e.g. programmed in R), that can also convert the pH values and indicate converted values in a graph. This software should become publicly available.

The available guidance for estimating the total amount of substance in soil in field persistence studies appeared to be not sufficiently detailed especially if a significant fraction of the substance is present in more than one sampled layer. Therefore we propose detailed guidance for estimating the total amount in the soil profile from concentration profiles (as part of field persistence studies to estimate the *DegT50* in soil).

The current Dutch leaching assessment procedure does not cover all substances that potentially reach the soil. There are, at the EU level, no data requirements for identification of degradation / transformation products of plant protection products formed on plant surfaces due to photolysis. So their leaching assessment is impossible within the current regulatory framework. Such data requirements exist for soil photometabolites.

Field studies with ridged potato fields have shown that leaching for full-field spray applications in such tillage systems may be considerably higher than for applications to crops grown on flat surfaces mainly because the downward water flow below the furrows is larger than assumed in calculations for flat surfaces. However, this higher leaching happens only if the substance is present in the furrows. Thus the application method determines whether the leaching expected for the ridged system is larger or smaller than for the flat system. We identified ten different application methods for pesticides in Dutch potatoes. For two of these the leaching expected for the ridged systems is larger whereas for four the leaching expected for the ridged systems is smaller than for the flat system; for the remaining four application methods the leaching is expected to be equal for both systems. As the current leaching assessment is not defensible for ridged potato systems, we recommend to develop an adequate leaching assessment methodology for these systems.

1 Introduction

The original aim of the workgroup was to test whether the Dutch decision tree as described by Van der Linden *et al.* (2004) offers sufficient protection of Dutch groundwater used for the production of drinking water. The procedure followed was: (i) to select the three plant protection products[1] that occur most frequently in deep groundwater as monitored by Dutch drinking water companies, (ii) to apply the decision tree to these three substances to test whether the decision tree was conservative enough to prevent groundwater contamination problems in future. However, the evaluation of the three substances showed that parts of the existing guidance (both at NL and EU level) were not clear or not complete enough or not state-of-the-art scientifically. Therefore these parts were revised and this revised guidance is described in this report. The evaluation of the decision tree is described in a separate report (Van der Linden *et al.* 2015).

The procedures described in this guidance report are based on the assumption that lower sorption and slower degradation of a substance will lead to more leaching. This is usually true for parent substances (Boesten and Van der Linden, 1991). However, it may not be true for the sorption or degradation of a parent substance if the leaching of a metabolite is the aim of the assessment. For example, a higher sorption coefficient of the parent substance may lead to a longer residence time in the top 30 cm of this parent which may lead to more formation of a certain metabolite and thus may lead to higher leaching concentrations of this metabolite. Such cases are beyond the scope of this report and have to be addressed later and, for the moment, dealt with on a case by case basis.

In the assessment of exposure of soil organisms, higher sorption may lead to a more conservative risk assessment (eg higher sorption may lead to higher concentrations in total soil in the top centimetres). As a consequence, the guidance in this report is also not applicable to the assessment of exposure of soil organisms.

Chapter 2 describes the selection of the three substances that occur most frequently in deep groundwater as monitored by Dutch drinking water companies and the remainder of the report describes the proposed revised guidance.

This report is an update of the proposals made in Boesten *et al.* (2011). Section 5.1 about lysimeter studies has been removed because this guidance was not in line with FOCUS (2009) and because the Standing Committee took in 2014 note of FOCUS (2009). Section 5.3 (dealing with deposition and dissipation on the crop and wash-off) has been removed, because EFSA guidance on this subject is expected to become available in 2015 (see EFSA, 2014b).

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[1] In this report the term 'plant protection product' (abbreviated to PPP) indicates the active substance (so not the formulated product).

2 Selection of relevant plant protection products based on groundwater monitoring data

On the basis of aggregated measured concentrations of plant protection products reported by the drinking water companies via REWAB in the period 1991-2004, a list has been compiled of 30 active ingredients found in raw water from groundwater abstractions[2] with at least one exceedence of the drinking water standard of 0.1 μg/L. Of these active ingredients Vewin has asked all measurements in raw water from the drinking water companies. The reported measurements have been analysed on:

1. Is the substance an active ingredient in a plant protection product or a relevant metabolite?
2. Is or was the active ingredient authorised in the Netherlands?
3. Is the measurement a single positive, never confirmed afterwards?

If the substance did not fulfil these conditions, it was not taken into account. After this analysis thirteen active ingredients remained. They are listed in Table 1. Some details of the 30 active ingredients and the reasons for exclusion for each of the seventeen excluded substances are given in Annex 1.

During this study also a WFD assessment was finalised, reporting concentrations of active ingredients in shallow and in deep groundwater in 2003/2004 (provinces of Noord-Brabant and Zuid-Holland) and 2006 (remaining provinces) (Van der Linden *et al.*, 2007). Substances found twice or more times in concentrations above 0.1 μg/L in deep groundwater have been added to Table 1[3]. Van der Linden *et al.* used an operational definition for deep groundwater as being samples taken from a filter of which the top of the filter was 7 m below soil surface or lower. At some locations samples were taken more than once in the covered period. The results of those samples were averaged.

In the WFD column of Table 1 the 0 and 1 times positive (criteria in header Table 1) are presented because for those substances our REWAB criteria were positive. In the REWAB column of Table 1 the lower four WFD substances with zero's were added because for these substances our WFD criteria were positive (see header of Table 1 for explanation of criteria).

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[2] Only measurements in raw water have been used, no measurements in pumping wells or observation wells.

[3] Van der Linden *et al.* (2007) present results of both shallow and deep groundwater measurements in their Tables 2.7 - 2.9. The result shown here is based on the measurements in deep groundwater (data from T. van der Linden, April 2008). Samples can be taken from two depths (x,y,z), hence maximal two measurements per location (x,y) are availble.

Table 1
Active substances found in deep groundwater in concentrations above 0.1 µg/L. Our criterion for including an active substance based on the REWAB data was that it was found in one or more abstraction above 0.1 µg/L more than once. The number of abstractions in which this was observed is stated. Our criterion for including an active ingredient based on the WFD data (Van der Linden et al., 2007) was that it was found in deep groundwater in concentrations above 0.1 µg/L at two or more sampling points. The ratio of the number of sampling points with exceedences (n) to the total number of measurements (A) is stated. The authorization status of each active ingredient is given as background information.

Active ingredient	**REWAB Number of abstractions**	**WFD *n/A***	**Authorised in NL and first expiry date**
bentazone	10	18/547	Yes, 31-12-2015
bromacil	6	2/3	No, since early nineties
chloorbromuron	1	0/0	No, since 1998
dichlobenil	1	1/535	No, since 2008
dichloorprop (2,4-DP)	1	3/16	No, since 1999
dikegulac-sodium	2	0/0	No, since early nineties
diuron	2	0/537	No, since 1999 (as PPP) and 2005 (as biocide)
DNOC (2-methyl-4,6-dinitrofenol)	1	0/478	No, since 1999
ethyleenthioureum (ETU) (metabolite of e.g. the substances: mancozeb, maneb and metiram)	1	0/58	Yes
MCPA	2	1/537	Yes, 01-03-2015
mecoprop	4	15/547	Yes (only mecoprop-p), 01-01-2023
metobromuron	1	0/0	No, since 2000
metoxuron	1	0/537	No, since 2007
Added because of WFD analysis			
atrazine	0	2/537	No, since 1999
dicloran	0	4/6	No, since 2000
endosulfan	0	3/8	No, since 1990
glyphosate	0	2/537	Yes, 31-12-2015

In the WFD assessment eight active ingredients were found twice of more in deep groundwater. DEET and 1,2--dichloropropane are not listed in Table 1 because they are not considered to be plant protection products. AMPA is not listed because it is considered to be a non-relevant metabolite. The data in Table 1 were not checked with the criteria given by Cornelese *et al.* (2003), like e.g. has the active ingredient been used in the infiltration area of the filter.

Three substances labeled as substances with concerns for abstraction of groundwater are also found in deep groundwater in the WFD assessment: bentazone, mecoprop and bromacil. MCPA was not found in deep groundwater. Of the four substances not labeled as substances with leaching concerns, but found in deep groundwater, only glyphosate is still registered in the Netherlands.

In 2008 two more monitoring studies on plant protection products in groundwater performed in 2007 became available.

In the Province of Zuid-Holland groundwater samples from 10 m depth contained at more than one location bentazone (2/21) and mecoprop-P (2/21), and at 25 m depth bentazone (3/28) and) ziram/metam-sodium (2/28) (Dassen, 2008). In view of the analysis method used by Dassen (2008), the ziram/metam-sodium detections reported by Dassen are questionable[4]. The results of Dassen (2008) correspond with the results presented in Table 1. Hence, it is not needed to reconsider the selection of substances with leaching concerns.

In the Dutch part of the Meuse catchment groundwater samples from 10 m depth contained at more than one location atrazine (2/112), bentazone (4/112), diuron (2/112), glyphosate (6/112), glufosinate-ammonium (6/112), kresoxim (2/112), o-fenylfenol (3/112) and simazine (4/112) (Verhagen *et al.*, 2008). Gluphosinate-ammonium, kresoxim-methyl, o-fenylfenol and simazine were not selected via the REWAB and WFD data. O-fenylfenol never had a registration in the Netherlands, hence has not been evaluated. Glufosinate-ammonium should be considered in this study as well; however the priority has been given for the substances that were selected from the REWAB data because those substances are found in groundwater abstraction areas.

Bentazone, MCPA and mecoprop-P were selected to evaluate the decision tree because they were found in more than one abstraction and they still have an authorisation in the Netherlands (as per 2014). Dichlobenil's metabolite BAM, also found in more than one abstraction area, was not selected because BAM is considered to be a non-relevant metabolite in the Netherlands.

It is remarkable that these three selected substances are weakly-acidic with pK_a values between 3 and 4 (Van der Linden *et al.*, 2015).

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[4] Since no specific analytical methods are available for the individual active substances belonging to the dithiocarbamate group, a screening residue definition was established in Regulation (EC) No 396/2005 as 'dithiocarbamates (dithiocarbamates, expressed as CS_2, including maneb, mancozeb, metiram, propineb, thiram and ziram)'. In case of positive findings further investigations are necessary to identify the origin of the CS_2 residue (EFSA, 2009).

3 Guidance proposals on the estimation of sorption parameters

3.1 Introduction

Chapter 2 indicates that the main substances with leaching concerns are bentazone, mecoprop and MCPA. These substances have in common that their sorption is low and that it depends on the pH of the soil. Boesten and Van der Linden (1991) showed that leaching is very sensitive to the sorption parameters if the sorption is low.

Careful analysis of the past leaching assessments of these substances showed weaknesses in the available Dutch guidance for estimation of sorption parameters as described by Mensink *et al.* (1995, 2008). The following sections describe the proposed solutions to these weaknesses.

This available guidance is based on a criterion for the P-value as described in the next section. This criterion has so far been used only in the Dutch evaluation procedures, so not in evaluations at the EU level.

An Excel workbook consisting of a series of spreadsheets has been developed to assist in deriving the sorption endpoints for leaching assessments. Based on information directly obtained from the description and the results of the experiments, the spreadsheets calculate estimates of the K_{om} (conservative where appropriate) and assess the quality of the Freundlich exponent. An up-to-date workbook can be downloaded from www.ctgb.nl as soon as the methodology is implemented.

3.2 Proposal for evaluation procedure of sorption coefficients derived from batch adsorption studies

3.2.1 Overview of existing guidance for batch adsorption studies

Batch adsorption studies for regulatory assessments are commonly carried out following the procedures in guideline OECD-106 (OECD, 2000). This guideline prescribes that measured adsorption coefficients are acceptable if the decrease in the concentration in the liquid phase is greater than 20% (see item 59 of OECD, 2000), and the recovery at the end of the study (mass balance) is at least 90%[5] (see item 64 of OECD, 2000). If these criteria are fulfilled, OECD-106 bases the calculation of the adsorption coefficient on the assumption that there were no loss processes. So the decrease in concentration in the liquid phase is then completely attributed to adsorption (see Eqn 3 on p. 14 of OECD, 2000, and the testing scheme in Annex 1 of OECD, 2000). However, accepting a recovery of 90% implies also that a loss of 10% is considered acceptable.

Boesten (1990) showed that the experimental error of sorption coefficients in batch sorption studies is controlled by a dimensionless quantity *P*:

$$P \equiv \frac{M\,K}{V} \qquad (1)$$

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[5] Recovery is here (OECD 106) defined as the total amount recovered from aqueous and solid phase at equilibrium (sorption phase) compared to the nominal amount. The extraction efficiency should be 95% or above.

where:
M = mass of solid phase in study (kg)
V = volume of liquid phase in study (L)
K = adsorption coefficient (L/kg)

He showed that this experimental error goes to infinity if P goes to zero. So P values close to zero indicate high uncertainty and have to be prevented in the measurement procedures for sorption. There is a unique relationship between P and the percentage decrease in the concentration in the liquid phase. This percentage increases with increasing P. So this analysis is in correspondence with the requirement in OECD (2000) of at least 20% decrease in the concentration in the liquid phase.

Mensink *et al.* (1995) wrote that the sorption coefficient of a batch adsorption study is not accurate or reliable if P is smaller than 0.1 (see their Table 5 and p. 30). So as a consequence, they consider studies with P values above 0.1 reliable. However, they did not provide an argument for setting the boundary at P = 0.1.

3.2.2 Development of a correction procedure to account for losses during batch adsorption studies

The leaching of plant protection products is very sensitive to sorption coefficients. It is therefore necessary to consider the effect on the sorption coefficient of a possible loss of substance of 10% in combination with a decrease in the concentration in liquid phase of at least 20% as considered acceptable by OECD (2000).

Boesten (1990) analysed the experimental error of sorption coefficients of batch adsorption studies. In his analysis the true sorption coefficient is assumed to be a known quantity. In reality, true values are not available: only measured values are available. Therefore we redid his analysis but now considering measured sorption coefficients as a basis for the assessment.

Our aim is to derive expressions for the relative error of the sorption coefficient as a function of system properties. We define K_E as the measured sorption coefficient ('E' from experimental) and K as the 'true' sorption coefficient. Furthermore we define the relative error of the sorption coefficient as:

$$r_K \equiv \frac{K_E - K}{K} \tag{2}$$

Boesten (1990) described an error analysis based on r_K and showed that r_K is the following function of the relative error in the PPP mass in the system, r_m:

$$r_K = \left(1 + \frac{1}{P}\right) r_m \tag{3}$$

The definition of r_m used by Boesten (1990) was similar to that for r_K:

$$r_m \equiv \frac{m_A - m_R}{m_R} \tag{4}$$

where m_A is the mass of test substance added to the system and m_R is the mass of test substance in the system recovered at the end of the study. As described before, OECD (2000) accepts the assumption that m_R is equal to m_A if the recovery is at least 90%.

Let us consider the case where the mass at the end of the study is measured by organic solvent extraction. Let us assume that at the end of the study a fraction φ of the mass of the test substance is recovered (as a fraction of the initial mass in the system). Then φ is defined by:

$$\varphi \equiv \frac{m_R}{m_A} \tag{5}$$

This fraction φ should be based on the true value of m_R so m_R should be corrected for the extraction efficiency.

It can be derived from Eqn 4 that:

$$r_m = \frac{1-\varphi}{\varphi} \tag{6}$$

As described before, there is a complicating factor in the leaching assessment procedure: the true *K* is unknown, so errors have to be evaluated on the basis of measured K_E values. It can be derived from Eqn 2 that:

$$K_E = (1 + r_K)K \tag{7}$$

So the measured K_E value is systematically a factor (1+ r_K) larger than the true value due to loss processes such as transformation. So the measured *P* value (with symbol P_E, '*E* ' from experimental) can be written as:

$$P_E \equiv \frac{M\,K_E}{V} = P\,(1 + r_K) \tag{8}$$

Elimination of *P* from Eqns 3 and 8 leads to the following expression:

$$r_K = \left(\frac{P_E + 1}{P_E - r_m}\right) r_m \tag{9}$$

Let us consider regulatory practice: then we have experimental values of P_E, K_E and φ and we want to know the true sorption coefficient *K*. Let us first define the multiplication factor Φ as follows:

$$\Phi \equiv \frac{K}{K_E} \tag{10}$$

Then K = $\Phi\, K_E$, so we have to multiply the measured sorption coefficient by Φ to obtain the true sorption coefficient. It can be derived from Eqn 2 that:

$$\Phi = \frac{1}{1 + r_K} \tag{11}$$

Combining Eqns 8, 9 and 11 gives:

$$\Phi = \frac{\varphi(P_E + 1) - 1}{P_E} \tag{12}$$

So Eqn 12 gives the multiplication factor for correcting K_E.

Let us consider some extreme cases in order to understand Eqn 12 better. If there is no loss from the system, φ = 1 and then also Φ = 1, so measured and true sorption coefficient are equal. Another extreme case is Φ = 0, which implies that the true sorption coefficient would be zero. Because sorption coefficients will usually be not negative, it seems necessary to require that $\Phi \geq 0$. Eqn 12 shows that this results in:

$$P_E > \frac{1-\varphi}{\varphi} \tag{13}$$

If, for instance, φ = 0.9 (i.e. a recovery of 90% of the test substance at the end), then Eqn 13 results in P_E >0.111. So if for such a recovery, a P_E value below 0.111 is found, this means that the decrease in the concentration of test substance was completely attributable to loss processes such as degradation instead of adsorption.

The last extreme case is when P_E is infinity. Eqn 12 shows that then $\Phi = \varphi$. Figure 1 shows that Φ increases continuously with P_E. So the maximal value of Φ is φ.

Figure 1 shows that Φ is much smaller than 1 if the loss is 10% and that it is usually quite close to 1 if the loss is as small as 1%. The lines in Figure 1 intersect the horizontal axis indicating that the overestimation may be more than 100%. Combination of Eqns 6 and Eqn 12 shows that this limit is reached when P_E becomes as low as r_m. If the overestimation of the sorption coefficient is more than 100%, a negative sorption coefficient would be obtained which is in general difficult to justify (although not impossible for anions), so in this case it is recommended to set the sorption coefficient to zero.

There is a unique relationship between P_E and the fractional decrease in liquid phase, δ, defined by:

$$\delta \equiv \frac{m_A - Vc_e}{m_A} \tag{14}$$

where c_e is the concentration in the liquid phase at end of the study. The relationship can be derived from Eqn 14 and using Eqn 7 from Boesten (1990). It is given by:

$$P_E = \frac{\delta}{1-\delta} \tag{15}$$

or:

$$\delta = \frac{P_E}{P_E + 1} \tag{16}$$

So Eqn 11 can be rewritten as:

$$\Phi = \frac{\varphi + \delta - 1}{\delta} \tag{17}$$

We define the fraction of test substance lost, λ, as 1 - φ. Then Eqn 17 can be further simplified to:

$$\Phi = \frac{\delta - \lambda}{\delta} \tag{18}$$

The correctness of Eqn 18 can be understood conceptually if we realise that δ - λ is the true fraction of test substance adsorbed whereas δ is the assumed fraction of test substance adsorbed.

Please note that r_m and λ are not equal as a result of their definitions. Their relationship is described by:

$$r_m = \frac{\lambda}{1-\lambda} \tag{19}$$

Figure 2 shows that contour lines of equal Φ values are straight lines in the δ-λ plane. Let us consider again the extreme cases of the graph. If there is no loss ($\lambda = 0$) then Φ is 1 by definition (so at the horizontal axis of the graph). If the decrease in liquid phase is equal to the loss ($\delta = \lambda$), then the whole decrease is the result of disappearance. So then Φ is zero. As described before, OECD (2000) prescribes only that the decrease should be larger than 20% and the loss less than 10%. Figure 2 and Eqn 18 show that this leads to the restriction $\Phi \geq 0.5$, to obtain a reliable sorption coefficient. In this limiting case the true adsorption coefficient is only 50% of the measured adsorption coefficient. So if we interpret a recovery of 90% as a loss of 10% of the test substance, then OECD-106 accepts an overestimation of up to 100% of the adsorption coefficient (i.e. measured value is twice the true value). Such an overestimation may lead to a considerable underestimation of the leaching. Therefore we recommend to correct sorption coefficients based on the measured recovery at the end of the study using Eqn 18.

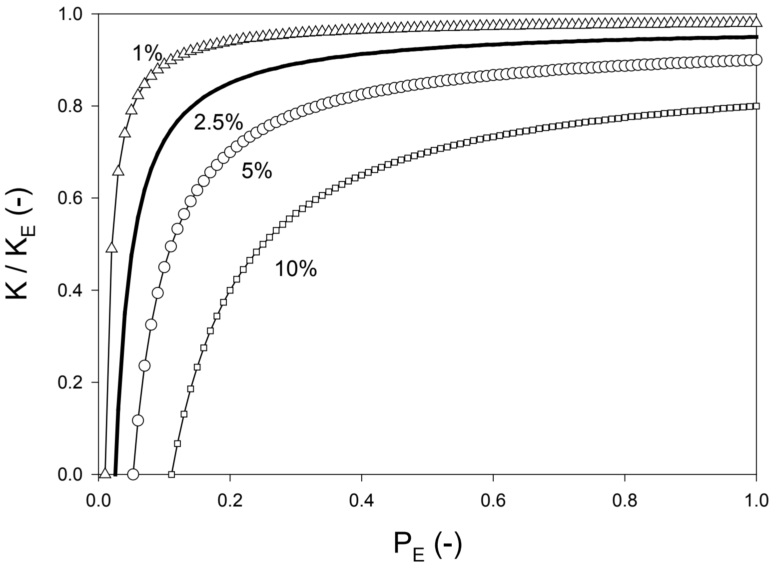

Figure 1 *Ratio of the true sorption coefficient divided by the measured sorption coefficient ($\Phi \equiv K/K_E$) as a function of P_E calculated with Eqn 12 for fractions of the test substance lost (λ) of 1, 2½, 5 or 10% (i.e. φ = 0.99, 0.975, 0.95 and 0.90 respectively).*

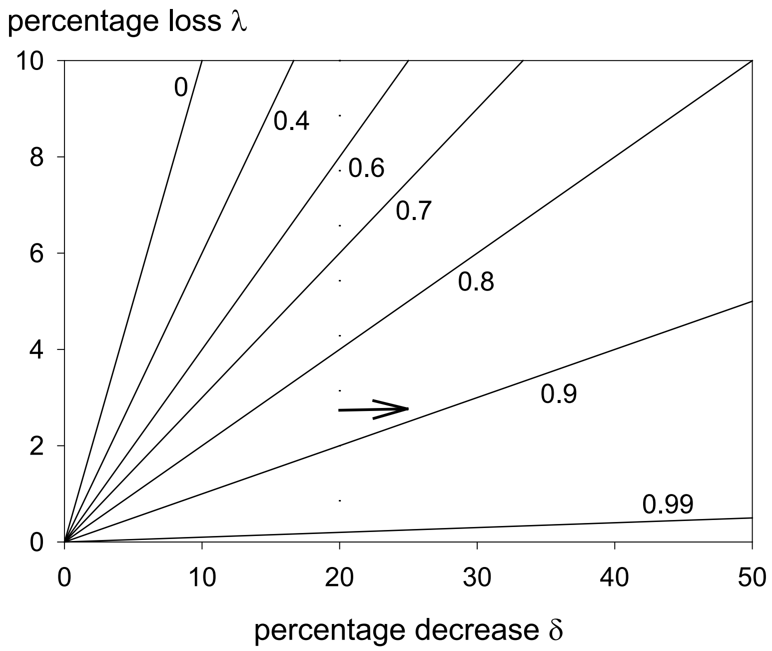

Figure 2 *Contour plot of the ratio between the true sorption coefficient divided by the measured sorption coefficient ($\Phi \equiv K/K_E$) as a function of the fractional decrease in the liquid phase, δ, and the fraction of the test substance lost, λ. The solid lines are contour lines with values of Φ as indicated and were calculated with Eqn 18. The dashed line and the arrow indicate the criterion δ >20% as prescribed by OECD (2000).*

OECD-106 recommends to analyse both soil and aqueous phases if less than 90% of the test substance is recovered in the material balance (see item 64 of OECD, 2000). In the absence of information on the material balance we recommend to use 10% loss of the test substance as a default (so $\lambda = 0.10$). Usually it will be possible to base λ values on the recovery of the test substance after the adsorption study. If information on the recovery is lacking and, based on additional information, loss is suspected to exceed 10%, we recommend to consider results of indirect batch adsorption experiments not reliable.

It is our experience that a considerable fraction of the sorption studies in the dossiers do not fulfill the criterion of 20% decrease of the concentration in the liquid phase. So on the basis of OECD-106, the results of these studies should be discarded. Our correction procedure (Eqn 18) makes it possible to use results of such studies in the authorisation procedures.

If equilibrium has not been attained in the study, the sorption of a substance will be underestimated, in general. It is considered not necessary to qualify results as unreliable if it is uncertain whether equilibrium was reached. Including the results, with appropriate corrections as described in this paragraph, will render conservative (i.e. low) estimates of the sorption coefficient. Further analysis, however, may show that non-equilibrium results should be considered outliers.

The above analysis considers only systematic errors leading to an unaccounted loss of the substance considered. Many sorption studies are done with ^{14}C labelled substances and sorption is calculated from the difference in the initial and final ^{14}C concentrations. If part of this radioactivity is transformed to a metabolite during the study, the sorption behaviour of the metabolite determines whether the true sorption coefficient of the parent substance is higher or lower than measured (if the metabolite sorbs stronger, the sorption of the parent is overestimated and if the metabolite sorbs weaker, the sorption of the parent is underestimated). The effect of such processes on the error in the sorption coefficient is difficult to capture in generic guidance recommendations.

3.2.3 Proposal for evaluating sorption coefficients including the effect of random errors

The above analysis considers only the effect of systematic errors. Boesten (1990) showed that also random errors in the sorption coefficient are directly proportional to $(1 + 1/P)$. Thus when P becomes as low as 0.1, the random error in the sorption coefficient increases sharply (going to infinity as P approaches zero).

Therefore it is recommended to use $P_E > 0.1$ as a general requirement for all adsorption batch studies (also for very persistent and non-volatile substances with low losses during the experiment). So if $P_E < 0.1$, then the study should result in a K value of 0 in any case. This recommendation has a weak scientific basis because it is not based on a criterion on the accuracy of the sorption coefficient. This would require further study that is beyond the scope of this report. We recommend to start such research (first step should be to analyse random experimental errors in available batch sorption studies, second step to simulate the effects of such errors on the error in the sorption coefficient after which a P value can be derived on the basis of the required accuracy of the sorption coefficient).

When calculating the P_E, it should be noted that Eqn 3 applies only to batch adsorption experiments in which the adsorption is derived from the decline of the concentration in liquid phase. If the adsorption is derived from an extraction of the soil with (organic) solvent immediately after the adsorption equilibration, then P_E has to be calculated from Eqn 8 using the volume of liquid phase just before the addition of the organic solvent (see Boesten, 1990). The value of δ should be based on this revised P_E using Eqn 16. OECD-106 recommends extraction of the soil for $0.1 < P_E < 0.3$ (see item 71 of OECD, 2000).

So the proposal is to use the correction procedure described in Section 3.2.2 (i.e. multiply the measured sorption coefficient K_E with the factor Φ from Eqn 18) in combination with the rule that if $P_E < 0.1$, the study should result in a K value of 0.

Let us consider how the above proposal works for an example study. The study consists of sorption measurements for four soils. The solid-liquid ratio was 0.5 g/mL. For each soil four initial concentrations were used. Each sorption measurement was done in duplicate (so two batch systems for each concentration). The adsorption equilibration time was 16 h. For one of the concentration levels, the remaining soil was extracted with organic solvent after the last desorption step. The concentrations in the supernatants and in the organic solvent were measured by ^{14}C and HPLC. It was reported that >99% of the radioactivity was the substance considered.

Table 2

Results of a hypothetical example sorption study and the results of the correction procedure based on Eqn 18.

Name of soil	**Reported Freundlich sorption coefficient (L/kg)**	**P_E (-)**	**Fractional decrease in liquid phase δ (%) at the reference concentration of 1 mg/L**	**Recovery (%) of substance in duplicate batch systems**	**Fraction lost λ (%)**	**Φ (-)**	**Corrected Freundlich sorption coefficient (L/kg)**
Wageningen	0.09	0.045	4.3	100 and 99	2	0.54	0
Rhenen	0.38	0.19	16.0	96 and 98	4	0.75	0.28
Renkum	0.24	0.12	10.7	97 and 97	4	0.63	0.15
Bennekom	0.8	0.4	28.6	95 and 93	7	0.76	0.60

Based on the results shown in Table 2, λ values were estimated as follows. In view of the small differences between the duplicate samples, it was considered appropriate to estimate different λ values for the four different soils. So average loss percentages were calculated for each of the four soils and 1% was added to this average to account for the uncertainty in the identity of the measured radioactivity. Using these λ values, Φ was estimated with Eqn 18 and corrected sorption coefficients were calculated as given in the last column for all but the Wageningen soil. The sorption coefficient of the Wageningen soil was set to zero because its P_E value was 0.045, so below 0.1.

In the above example, the uncertainty in the identity of the measured radioactivity was accounted for by attributing this to the loss percentage. This is a conservative approach when deriving sorption constants for use in leaching assessments as it leads to lower (corrected) K_{om} values. In specific cases, it may be justified, not to attribute this uncertainty to the loss percentage but attribute it to the liquid phase or assume that it is proportional to the distribution of the radioactivity over the different phases (so same behaviour of the substance considered). If no impurity is reported and if two distinct radioactive peaks are observed in a chromatogram of the application or control solution (representing the substance considered and the impurity), and if the smaller peak is not observed in the chromatogram of the solution after the sorption phase, it is reasonable to assume that the radioactivity of the smaller peak is an impurity that is more strongly sorbed than the substance considered. In such a case we recommend to include the fraction radioactivity in the smaller peak in the value of λ in Eqn 18. If the unknown peak decreases proportionally to the decrease of the peak of the substance considered, no correction is needed.

The Freundlich sorption coefficient has the same value as the linear sorption coefficient only at a reference concentration in the liquid phase of 1 mg/L. So the calculated decrease in the liquid phase in Table 2 is only valid for a sorption point with an equilibrium concentration in the liquid phase of 1 mg/L. This is of course a simplification. This procedure can be refined by using Eqn 18 for correcting the contents sorbed for the individual sorption points and thereafter fitting a new value of the Freundlich sorption coefficient by linear regression as usual.

3.3 Assessment of the Freundlich exponent from batch adsorption studies

3.3.1 Background and considerations

The Freundlich exponent N (often also indicated as 1/n) describes the curvature of the Freundlich sorption isotherm:

$$X = K_F \, c_R \left(\frac{c}{c_R} \right)^N \tag{20}$$

in which:

X = content sorbed (mg/kg)

K_F = Freundlich sorption coefficient (L/kg)

c = concentration in the liquid phase (mg/L)

c_R = reference concentration in the liquid phase (1 mg/L)

Nearly all measured N values are between 0.7 and 1.1 although sometimes values as low as 0.6 or as high as 1.2 have been measured (e.g. Allen and Walker, 1987; Boesten and Van der Pas, 1988; Brouwer *et al.*, 1990; Van der Pas *et al.*, 1999; Scorza *et al.*, 2004). It is already known since the beginning of the nineties that the Freundlich exponent may have a large effect on the leaching concentration. If all other parameters are kept constant, the leaching concentration may decrease more than a factor 100 when the Freundlich exponent decreases from 1.0 to 0.8 (Figure 2 of Boesten, 1991; also Figure C1 of Beltman *et al.*, 2008). So it is important that N is measured accurately.

Let us consider the guidance that is currently available at EU level for the Freundlich exponent. FOCUS (2000, p. 93) stated: 'For models which require the Freundlich adsorption coefficient (see above) the exponent of the isotherm (*N)* is also required and this is determined in each experiment. However where the results of a number of adsorption coefficient determinations are averaged then the average value of *N* should also be used (note that *N* is sometimes also referred to as *1/n)*. When there is no data, a default value of 0.9 should be used.'

FOCUS (2001, p. 201) stated 'Information on the mechanism of sorption should generally be available from the dossier used to establish the monograph of the substance. If the kinetics of sorption follow the Freundlich adsorption kinetics model one of the regression coefficients available will be the *N* -value. For models, which require the Freundlich adsorption coefficient, the exponent of the isotherm (*N)* is also required and values of this parameter are typically determined in each sorption experiment. If a number of *N* have been determined (e.g. for a number of soils), the average value of *N* should also be used. A default value of 0.9 is assumed if no information on the *N* value is present. If a linear relation for sorption has been determined the value may be set to 1.'

So the guidance provided by FOCUS (2000) and FOCUS (2001) is almost exactly the same. However, these guidance documents provide no justification for their recommendations. So there is a huge gap between on the one hand the uncertainty resulting from the estimation of the Freundlich exponent and on the other hand the lack of scientific underpinning of the recommendations by FOCUS (2000) and FOCUS (2001). Probably the guidance by FOCUS (2000; 2001) was inspired by Boesten and Van der Linden (1991) who recommended to use 0.9 as a default for Dutch scenario calculations on the basis of the argument that it was the average of the values found in a literature review by Calvet (1980). No guidance instructions are available how to check the accuracy of Freundlich coefficients. In the literature no error analyses of Freundlich exponents are available. Such analyses could be based on hypothetically generated sorption isotherms using Monte Carlo techniques.

There are no systematic studies on whether the Freundlich exponent is mainly a soil property or mainly a PPP property (the latter is assumed by FOCUS, 2000, 2001); to the best of our knowledge no analyses similar to EFSA (2007) but directed to the Freundlich exponent instead of the Q10, are available in literature. Such analyses are urgently needed to improve the quality of the leaching assessment.

Within PRAPeR meeting nr. 32, the experts agreed that if soil adsorption of soil metabolites was only measured at a single experimental concentration (so if only linear sorption coefficient *K* value could be determined) subsequent FOCUS modelling simulations should be carried out using a *N* value of 1 (based on the argument that only a linear sorption coefficient was measured). They agreed that in this situation a *N* of 0.9 (FOCUS guidance default) should not be used (personal communication W. Pol, 2009). We do not agree with this recommendation firstly because it is inconsistent with the use of a default *N* value of 0.9 for the parent substance. There are no reasons to assume that there are systematic differences between the population of *N* values of metabolite molecules and the population of *N* values of parent molecules. There is a second reason for disagreement with this PRAPeR recommendation. The accuracy of sorption coefficients is determined by both systematic and random errors. Measuring at more than one concentration level decreases the random error but does in principle not decrease the systematic error. So the issue is which type of error (random or systematic) is most important in adsorption studies. Based on our analysis in Section 3.2 we consider systematic errors in PPP sorption studies in general to be more important than random errors.

3.3.2 Proposed guidance

Given the lack of guidance we recommend to use *N* = 0.9 as a default value, for both parent substances and metabolites and to deviate only from this value if three or more reliable measurements of *N* are available for a substance. The minimum number of three is in line with current data requirements for metabolites. If three or more reliable data are available, the arithmetic mean is used. This in line with the vulnerability concept in current risk assessment approaches in which vulnerability is attributed to the scenario and central values are used for substance parameters. Implicitly the assumption is made that the Freundlich exponent is a substance parameter.

So also when only one sorption point is available for a soil metabolite, in line with the above, we recommend calculating K_F from Eqn 20 assuming a N value of 0.9 and a c_R of 1 mg/L.

In the absence of (i) detailed scientific analyses of the accuracy of the Freundlich exponent and (ii) tests of the hypothesis whether the exponent is a soil or PPP property, a pragmatic procedure is proposed for the evaluation of measured *N* values:

1. The overall quality of the experiment should be at least moderate, i.e. moderate or good.
2. Accept Freundlich exponents only from studies of which sorption coefficients are accepted to be included in further analysis. This is based on the argument that, if the sorption coefficient is considered not sufficiently reliable the curvature has to be unreliable as well.
3. The correction of the sorption coefficient, according to equation 18 is less than 20% (cf Figure 2), which implies that at least $\Phi \geq 0.8$ (for the indirect method) and $P_E \geq 0.1$.
4. Accept Freundlich exponents only from studies that included at least three different initial concentrations and in which the difference between the highest and the lowest initial concentration was at least a factor[6] of 100 (this instruction for the measuring procedure relaxes to some extent the recommendations in OECD 106, section 72, which states: 'Five test substance concentrations are used, covering preferably two orders of magnitude.', see OECD, 2000).
5. The R^2 value of the logarithms of the measured concentrations and the logarithms of measured contents sorbed is not less than 0.975.

This third requirement is more or less a minimum requirement because it is difficult to defend that a curvature would be reliable if the ratio between content sorbed and concentration in liquid phase would be more than 20% wrong or if the measurement of the sorption coefficient is very unreliable. Further research on the factors controlling the accuracy of the Freundlich exponent is strongly recommended.

In view of the absence of a database of reliable *N* measurements we recommend not to set strict limits to the *N* values of sorption isotherms of a specific substance-soil combination. Therefore values in the range 0.6 – 1.2 are considered acceptable, see par. 3.3.1. However, if the arithmetic mean *N* value exceeds 1.0, a value of 1.0 should be used because we consider an exponent higher than 1.0 physically unrealistic for the soil matrix. Background is that sorption sites in agricultural soils are expected to show a decreasing affinity for the concentration in the liquid phase for contents sorbed that are far below the content sorbed that corresponds to a monolayer of molecules sorbed. We do not recommend to use this restriction $N \leq 1$ for individual sorption isotherms because this would lead to a systematic bias.

We realize the risk that the mean measured *N* may lead to an *N* value between 0.9 and 1 in which case the higher-tier measured *N* will give more leaching than the default *N*. This is of course undesirable in a tiered approach but this is the consequence of the guidance recommendations by FOCUS (2000, 2001).

3.4 Guidance for estimating sorption coefficients from soil column studies

3.4.1 Background and considerations

According to European Commission (2013) column leaching studies in at least four[7] soils shall be carried out where in the batch adsorption and desorption studies provided it is not possible to obtain reliable adsorption coefficient values due to weak adsorption (such as K_{oc} < 25 L/kg). It is of course possible that e.g. two of the four required adsorption studies are considered acceptable. In such a case it seems not necessary to us to provide column leaching studies with four soils as long as reliable

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[6] In the accompanying spreadsheets, a factor of 95 is used to account for issues inherent to reporting.

[7] Three soils for metabolites.

sorption coefficients can be derived for in total four soils; so in case two acceptable adsorption studies are available, two soil column studies would suffice.

The experimental set-up for determining sorption of chemicals to soils from column study is described in OECD 312 (OECD, 2004). Guidance on how to derive sorption coefficients, compatible with those from batch experiments, is described below.

Chromatographic theory (assuming piston flow) leads to the following relationship:

$$Z = \frac{W}{\theta + \rho K} \qquad (21)$$

where *Z* is the average penetration depth (m), *W* is the water layer leached through the column, θ is the volume fraction of water in the soil column, ρ is the dry bulk density in the column (kg/L), and *K* is the linear sorption coefficient (L/kg). This leads to the following expression for *K*:

$$K = \frac{W - \theta Z}{\rho Z} \qquad (22)$$

The volume fraction of water and the dry bulk density can be experimentally determined. If not given, default values can be used. Equation 22 shows that a conservative (low) value of *K* is obtained for high values of θ and of ρ. Therefore default values $\theta = 0.43$ and $\rho = 1.5$ kg/L are recommended (assuming a density of the solid phase of 2.65 kg/L); a dry bulk density of 1.5 kg/L is rather high for soils in the top layer, so considered adequate for obtaining conservative estimates.

For sorption coefficients determined on the basis of the mass in the column, the piston flow method underestimates the sorption coefficient. Hence the estimated sorption coefficient is a lower limit value. The sorption coefficient is underestimated because the effect of no dispersion across the upper boundary is neglected (see Annex 2). This underestimation increases with decreasing penetration depth. As a higher tier, the effect of dispersion can be included in the estimation of the sorption coefficient. The theoretical background and the procedure is described in this section.

Jury and Gruber (1990) derived an analytical solution for the centre of mass Z_1 (m) of the convection-dispersion equation (D59, p.181). Beltman *et al.* (2009) extended their equation with linear sorption and first order transformation in the liquid phase:

$$Z_1(t) = \sqrt{\frac{Dt}{\pi R}}\, exp\left(-a^2 \frac{t}{R}\right) + \frac{D}{2v}\left[\left(1 + 4a^2 \frac{t}{R}\right) erfc\left(-a\sqrt{\frac{t}{R}}\right) - erfc\left(a\sqrt{\frac{t}{R}}\right)\right] \qquad (23)$$

where $R = 1 + \frac{\rho}{\theta}K$, $a = \frac{v}{2\sqrt{D}}$, and $D = v\,L_d$, with *v* the flow velocity (m/d), *t* time (d) and *D* the dispersion coefficient (m^2/d).

In this solution the transformation rate coefficient is not present, because transformation has no effect on the distribution of the concentration in the column (Beltman *et al.*, 2009, see also Figure A2.2 in Annex 2).

Figure 3 shows the sorption coefficient as a function of the penetraton depth based on piston flow and based on convection dispersion (calculated for column study set-up recommended in OECD 312), using a realistic value of *W* and the default values of θ and ρ. The figure shows that *K* becomes infinitely high when *Z* approaches zero. The consequence is that uncertainties in estimated sorption constants become larger with smaller penetration depth as the precision with which penetration depth can be measured is approximately 1 cm. For example, the uncertainty at a penetration depth of 5 cm is approx. 25% (assuming piston flow). Figure 3 shows that the underestimation by the piston flow method increases with decreasing penetration depth as well. The difference is becoming less than 20% when the penetration depth exceeds 10 cm. So this method is mainly useful for penetration depths above 10 cm, so *K* values below 1 L/kg. This adds on top of the uncertainty due to imprecision in the determination of the penetration depth.

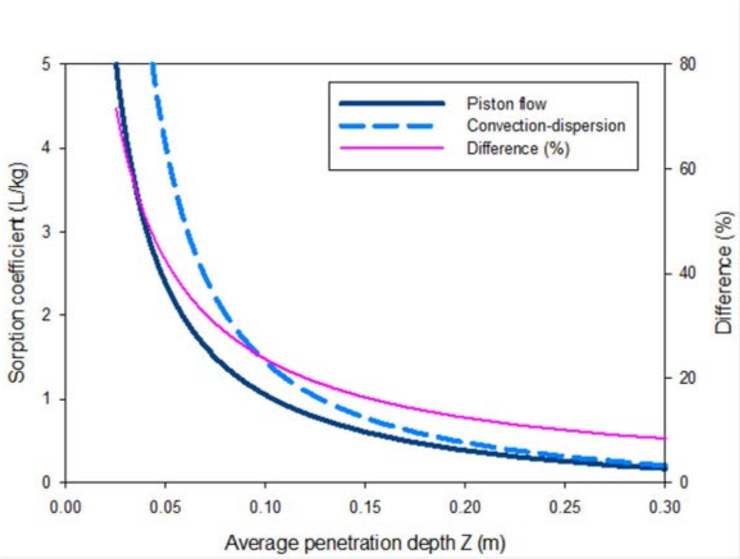

Figure 3 *Adsorption coefficient K as a function of the average penetration depth as calculated with (a) piston flow equation (Eqn 22) and, (b) convection dispersion (Eqn 23), assuming θ = 0.43, ρ = 1.5 kg/L, W = 20 cm in 48 hours, and* L_d *= 2.5 cm (only for convection dispersion). The difference between the two methods is indicated on the right axis in percent (calculated as (sorption coefficient convection dispersion – sorption coefficient piston flow)/ sorption coefficient piston flow).*

3.4.2 Proposed guidance

Column studies are considered only if at least following experimental conditions and results are reported: the water layer, the water flow rate, and the penetration depth in the column or the column length when most of the remaining substance has leached out of the column.

There are two distinct cases for the outcome of a soil column experiment: (A) more than 50% of the recovered mass has leached out of the column at the end of the experiment, (B) less than 50% of the recovered mass has leached out of the column at the end of the experiment. For each of the two possibilities the procedure is given. If the recovered mass is distributed equally between the column and percolated water the column results are used to determine the sorption coefficient.

A. More than 50% of the recovered mass has leached out of the column.
In the interpretation of the leached mass in percolated water two options are available; using the sample volume or do a best guess of the percolated volume (e.g. when percolated fractions are 200 and 300 mm, use 250 mm). Both options are incorporated in the procedure.

1. Determine the percolated volume W_1 preceeding the sample in which cumulative recovered substance = 50% of total recovered substance, and
2. Estimate the percolated volume W_2, volume at which recovered substance = 50% of total recovered substance.
3. Use eqn (22) for piston flow to calculate K_1 and K_2 for W_1 and W_2, with Z = length of the column (m) and W = water layer (m) necessary for leaching 50% of the recovered mass from the column[8].
4. Calculate the K_{om} from K_1 and report the K_{om} as lower limit value.
5. Calculate the K_{om} from K_2 and report the K_{om} as best guess value.

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[8] Eqn (23) for convection-dispersion can be used as well, but it is expected that K values will be higher than K values calculated by the piston flow equation (see Annex 2).

To refine the estimation of the sorption coefficient from a column study where more than 50% of the mass is leached, the data of the column study can be fitted with the convection-dispersion equation to include the effect of dispersion[9] (see Annex 2).

If only the total mass leached is known, the sorption coefficient can be estimated via:

1. Determine the length of the column, moisture concent in the column, dry bulk density, and the percolated volume.
2. Use the analytical solution of Jury & Roth (1990) assuming a dispersion length of 2.5 cm. Calculate the leached fraction for the total percolated volume. Optimise the value of the sorption coefficient to obtain the leached fraction that is equal to the leached fraction measured.

See also, the calculation that was done for a column study with bentazone (Section 2.1 in Van der Linden *et al.*, 2015).

B. Less than 50% of the recovered mass has leached from the column.

In the interpretation of the penetration depth two options are available; using the soil section or do a best guess of the depth in the soil section. Both options are incorporated in the procedure.

1. Determine the depth Z_1, where Z is the bottom of the soil section where cumulative recovered substance = 50%.
2. Estimate the penetration depth Z_2, the depth in the soil section where recovered substance = 50% of total recovered substance.
3. Use Eqn (22) for piston flow or use Eqn (23) to calculate K_1 and K_2 for Z_1 and Z_2, with Z = penetration depth (m) and W = percolated water layer (m). If Eqn (23) is used and the column study complies with OECD 312, i.e. column length is 30 cm, percolation rate is 0.2 m in two days, K can be determined from the curve in Figure 3. If the setup of the column study is different K can be calculated using eqn (23).
4. Calculate the K_{om} from K_1 and report the K_{om} as lower limit value Calculate the K_{om} from K_2 and report the K_{om} as best guess value.

If the value of K calculated with Eqn (22) is below zero, K is set to zero.

Soil column studies can only be used to estimate the linear sorption coefficient so they do not allow estimation of the Freundlich exponent. Soil column studies will only be relevant for the leaching assessment for plant protection products with K_{om} values that are so low that batch studies cannot give accurate sorption measurements. By definition, no accurate Freundlich exponents will be available for such products. Therefore we recommend to use for soil column studies the default value of 0.9 for the Freundlich exponent.

As a consequence the linear sorption coefficient derived from a soil column study has to be calculated back to the corresponding Freundlich sorption coefficient. The equation for the linear isotherm reads $X = K\, c$. So from the column leaching experiment we have derived a value of K. This is valid either for the concentration in the liquid phase in the percolate at the moment when 50% of the substance has leached from the soil column or it is valid for the concentration in the liquid phase at the average penetration depth at the end of the study (to be called c_{st}). The concentration in the percolate can be derived from the study itself. The c_{st} concentration can be estimated using the concentration in total soil of the substance at the average penetration depth and the volume fraction of water and dry bulk density of the soil column:

$$c_{st} = \frac{c^*}{\theta + \rho\, K} \qquad (24)$$

where c^* is the concentration in total soil (mg/L). Combining Eqns 20 and 23 gives then the following expression for K_F :

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[9] If Z > 30 cm justify the dispersion length (values above 2.5 may be justifiable).

$$K_F = K \left(\frac{c_{st}}{c_R} \right)^{1-N} \tag{25}$$

So if e.g. K = 1 L/kg and c_{st} = 0.3 mg/L, then K_F is calculated to be 0.89 L/kg.

3.5 Guidance for estimating sorption coefficients from soil TLC studies

3.5.1 Background and considerations

Soil TLC studies are nowadays not recommended for deriving sorption constants of substances. Such studies however may be available as legacy studies. If such studies are available, they may be considered to complete the dataset if, after evaluation, an insufficient number of data obtained with batch or column experiments remain. Therefore guidance for interpretation of soil TLC studies is described below.

Soil TLC studies comprise both thick layer (layer thickness > 2 mm) and thin layer (layer thickness ≤ 2 mm) studies. Thin layer studies are more common than thick layer studies and therefore the following text refers to thin layer studies. It is assumed that results are applicable to thick layer studies as well. In both types, sieved soil (2 mm, sieving to smaller mesh than 2 mm may result in incompatible results with batch and column studies as the fraction of finer particles is relatively enriched) is brought on a plate as a slurry or a paste and spread to form a layer of homogeneous thickness. Pretreatment of the soil should not differ from the handling prior to batch or column experiments, i.e. soils should not become too dry in order to avoid changes in soil organic matter. Water is evaporated before use of the plates. The test chemical is spotted on the plate at (approximately) 1.5 cm from the base. Reference chemicals may be spotted as well. The plates are immersed with the base down at some angle from the vertical in a closed chromatographic chamber containing an aqueous solution at a height of 0.5 cm. The aqueous solution (front) is allowed to migrate to (approximately) 11.5 cm from the base (i.e. 10 cm net migration of the water front). After migration, the relative mobility of the test substance is determined using a suitable detection method (for example plate scanning or zonal extraction). The test is usually replicated several times. The migration phase may last up to approximately 10 hours, dependent on the texture of the soil. Movement of the water / solution is relatively fast immediately after the start and slowing down towards the end.

The relative mobility, R_{TLC}, can be determined according to several definitions:

1. Distance between the centres of mass of the test substance at beginning and end.
2. Distance between the centre of mass of the test substance at the beginning and the front of the mass at the end.
3. Distance between the fronts of mass of the test substance at beginning and end.

All relative to the migration distance of the aqueous solution. R_{TLC} according to the second definition is usually referred to as R_F (frontal R). We recommend using option 1, the centre-of-mass approach, (if possible) because this is more accurate.

The moving distance can be determined automatically when an advanced scanning apparatus is available. Such equipment is ideal to determine R_{TLC} according to definition 1 as the response intensity is used to determine the centre of mass. The centre of mass at the start is measured as well or defined as the middle of the application spot. If such advanced equipment is not available, the R_{TLC} can be determined manually using a ruler or a measuring tape. The centre of mass at the beginning is defined as above, whereas the front at the beginning can be determined from the spreading of the solutionwater on the plate upon application. The centre of mass and front at the end are determined based on expert judgement and depending on the visualisation technique. The front can be taken as the upper end of the spot, whereas the spot is defined as being visually different from background. The centre of mass can be determined as the location with the highest (colour, radio activity, …) intensity or the location with the greatest width.

As stated above, the results of soil TLC studies are commonly expressed in terms of the factor R_{TLC} defined as:

$$R_{TLC} \equiv \frac{S}{W} \tag{26}$$

where S is the distance over which the substance has moved during the chromatography process and W is the distance over which the water has moved during this process; so R_{TLC} is always between 0 and 1 (Helling, 1971; SCP, 2002).

Assuming a linear sorption isotherm K (L/kg) and chromatographic theory then leads to the following expression:

$$R_{TLC} = \frac{\theta}{\theta + \rho K} \tag{27}$$

where θ is the volume fraction of water in the thin soil layer and ρ is the dry bulk density in this layer. Note that thisR_{TLC} is the inverse of the retardation factor in soil for which usually the symbol R is used. These conventions are somewhat confusing.

Eqn 27 leads to the following expression for K:

$$K = \frac{\theta\left(1 - R_{TLC}\right)}{\rho\, R_{TLC}} \tag{28}$$

As with soil column studies, soil TLC studies are not suitable for PPP that sorb highly to soil; if the movement of the PPP is low, the sorption cannot be determined precisely. R_{TLC} lower than 0.3 will in general not be reliable because of limitations in determining the travel distance adequately (see Figure 4). Measurement uncertainties above this R_{TLC}-value will have little influence on the estimated sorption constant. The relative uncertainty in the measurement will not become much less beyond this point. In addition to this uncertainty, it should be realised that TLC studies in general deliver lower estimates of the sorption constant because of the experimental conditions leading to relatively high flow velocities, thus short contact times, in the early phase of the experiment.

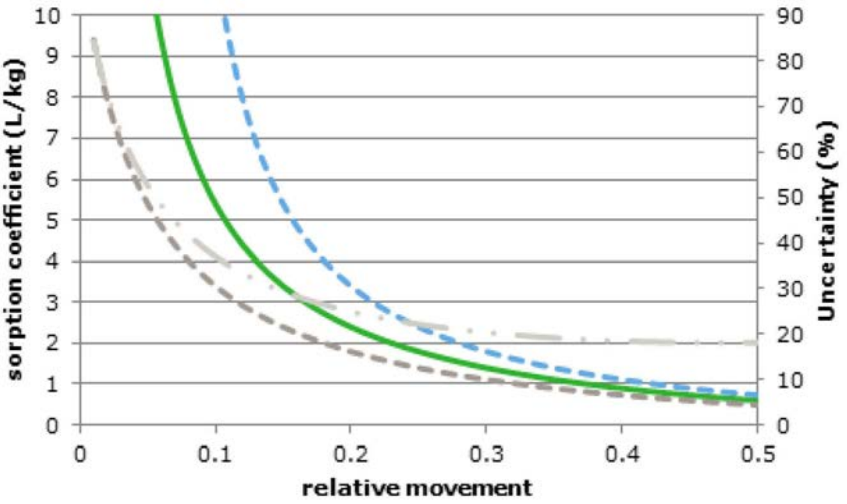

Figure 4 *Uncertainty in sorption constant because of uncertainty in the measurement of the relative substance movement. The solid line indicates the estimated sorption constant whereas the dashed lines indicate the lower and upper limit, based on the assumption that the (absolute) uncertainty in the measured distance is 5 mm. The dash-dotted line gives the % uncertainty defined as 100 x (estimated value – lower limit)/estimated value. The lines are calculated with* $\theta = 0.6$ *and* $\rho = 1$ *kg/L.*

High concentrations of the PPP in the solution establishing the dot may lead to less reliable or even unreliable results:

- smearing may occur due to exceeding the sorption capacity of the soil or the solubility of the substance in the aqueous solution
- underestimation of the sorption constant may occur due to the curvature of the equilibrium sorption curve.

The concentration in the application solution therefore should not exceed the solubility of the PPP in water and it is recommended to apply a maximum amount equivalent to the recommended application dose and to apply a series of lower concentrations as well.

In soil TLC studies θ and ρ are not measured so these have to be estimated. A low θ and a high ρ will lead to low K values. One may expect that a soil slurry on a TLC plate has not a high bulk density. Therefore it is defensible to assume as default value $\rho = 1.0$ kg/L. One may also expect that the water flow is unsaturated in view of the experimental procedure. We propose to use as a conservative θ value of 0.30 as a default; this is about half the porosity assuming a bulk density of the solid phase of 2.65 kg.

SCP (2002) discussed the methodology and concluded that soil TLC studies produce lower limits of sorption coefficients based on the following arguments:

1. There is only limited contact time between substance and the soil material during the transport process (the initial water flow rate may be rapid in soil TLC studies).
2. The chromatographic theory for R_{TLC} is based on the average transport distance of the substance whereas often the front is measured; so measured R_{TLC} values based on average transport would be lower.

We doubt whether in soil TLC studies usually the front is measured: in our view TLC studies are usually evaluated with radioactive measurements (with a scanner) and usually average transport distances are measured. So we do not agree with the second argument of the SCP. However, we agree that soil TLC studies produce lower limits in view of the limited contact time.

In case of high corrections of the sorption constant which are based on default assumptions (see section 3.4) it may be desirable to have lower limits of the sorption constant based on TLC studies. If only R_F values are available, it can be assumed that $R_{TLC} = 0.95 * R_F$.

3.5.2 Proposed guidance

TLC studies can only be used to estimate the linear sorption coefficient so they do not allow estimation of the Freundlich exponent. TLC studies will only be relevant for the leaching assessment for plant protection products with K_{om} values that are so low that batch studies cannot give accurate sorption measurements. In general, no accurate Freundlich exponents will be available for such products. Therefore we recommend using the default value of 0.9 for the Freundlich exponent using and Eqn 25 to convert the linear sorption coefficient to the Freundlich coefficient. In this case c_{st} has to be estimated from the applied mass and the extension of the 'solute dot' at the end of the experiment. This can be done as follows:

i. measure the surface area of the 'dot' (usually available);
ii. estimate or measure the thickness of the soil layer;
iii. use these quantities to calculate the volume of the dot;
iv. using the applied mass, the average total concentration in the dot, $c*$, can thus be calculated.

Next c_{st} can be calculated from Eqn 24.
In case c^* cannot be estimated from the experimental results, but the initial concentration in the dot solution is available, a conservative approximation is taking 1% of that concentration. Estimates in this study were 4% or above.

Eqn 25 shows that K_F decreases with increasing c_{st}, so low values of c_{st} are conservative. So high values of θ and ρ lead to conservative estimates of c_{st}. We recommend ρ = 1 kg/L as a high value so this should be appropriate here as well. For θ we recommend to use 0.6[10] which is about the porosity consistent with ρ = 1 kg/L.

Examples of application of this guidance for TLC studies are given by Van der Linden *et al.* (2015) for bentazone, MCPA and for mecoprop (Section 2 of Chapters 2, 3 and 4).

3.6 Estimating sorption coefficients for weak acids with pH-dependent sorption

3.6.1 Introduction

The guidance in this section concerns weak acids with one dissociation constant, especially those with a dissociation constant between 2 and 8. Substances with more dissociation constants might exhibit complexation reactions, for which the theory given below might not be valid (e.g. Nicholls and Evans, 1991a). For such substances the mobility not necessarily increases with pH because within-molecule complexation with bivalent or trivalent cations may take place, rendering an uncharged or even positively charged complex. Furthermore, there is evidence (e.g. Nicholls and Evans, 1991b; Kah, 2007) that the theory is not universally applicable to weak bases. In view of this we recommend for weak bases to perform studies with the full range of pH values encountered in agricultural practice with a sufficient number of studies to establish a quantitative relationship between the sorption coefficient and pH.

Surfaces of soil solids in temperate regions are usually negatively charged. This is important for the sorption of weak acidic substances in two ways. Firstly, the negative charge repulses anions from the surface of the soil solid phase. Sorption of anions therefore is generally negligible or very weak and

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[10] Note that this value of 0.6 differs from the value of 0.3 used to calculate a conservative value of *K* (described above Figure 4). For the calculation of the Freundlich sorption coefficient from the linear sorption coefficient, the use of 0.6 is conservative.

even exclusion might occur. Secondly, the negative charge attracts counteracting cations: the concentration of cations in the so-called diffuse double layer is higher than in the bulk solution and increasing towards the surface. Partly the cations consist of H^+-ion and therefore the H^+-concentration close to the surface is higher than in the bulk solution. The pH close to the soil surface is lower.

The dissociation reaction of a weak acidic substance in water is given by:

$$\mathrm{HA} \Leftrightarrow \mathrm{H}^+ + \mathrm{A}^- \tag{29}$$

with:

HA	the weak acidic substance, further called 'weak acid'
H^+	the hydrogen ion
A^-	the conjugated base, further called 'anion'

The equilibrium constant of the dissociation reaction is characterised by:

$$\mathrm{K}_{\mathrm{eq}} = \frac{\left[\mathrm{H}^+\right]\left[\mathrm{A}^-\right]}{\left[\mathrm{HA}\right]} \tag{30}$$

with:

K_{eq}	the equilibrium constant

The acid dissociation constant, K_a, is defined as the K_{eq} at which the concentrations, or better the activities, of A^- and HA are equal. The negative logarithm of K_a, pK_a, is then equal to the pH of the solution in which the activities of A^- and HA are equal.

As can be seen from the equations, the pH of the soil solution influences the ratio of the concentrations of the weak acid and the anion. Now, the pH at the soil surface is lower than in the bulk solution and therefore the equilibrium will be shifted to the left, i.e. towards the acid. As the acid is not repulsed by the soil surface, the sorption may be expected to be higher than foreseen from the pH of the soil solution.

Applying the theory for weak acidic substances to the soil system the following equation is obtained for the $K_{om,pH}$ (see Leistra *et al.*, 2001, for details):

$$\mathrm{K}_{\mathrm{om,pH}} = \frac{\mathrm{K}_{\mathrm{om,acid}} + \mathrm{K}_{\mathrm{om,anion}} \dfrac{\mathrm{M}_{\mathrm{anion}}}{\mathrm{M}_{\mathrm{acid}}} 10^{\mathrm{pH}-\mathrm{pK}_{\mathrm{a}}-\Delta\mathrm{pH}}}{1 + \dfrac{\mathrm{M}_{\mathrm{anion}}}{\mathrm{M}_{\mathrm{acid}}} 10^{\mathrm{pH}-\mathrm{pK}_{\mathrm{a}}-\Delta\mathrm{pH}}} \tag{31}$$

in which:

$K_{om,pH}$	the pH-dependent organic-matter/water sorption coefficient, L kg^{-1}
$K_{om,acid}$	the K_{om} for the weak acid, L kg^{-1}
$K_{om,anion}$	the K_{om} for the anion, L kg^{-1}
M	the molar mass of the anion and the weak acid, g mol^{-1}
ΔpH	a constant accounting for the surface acidity
pK_a	the negative logarithm of the acid dissociation constant

Figure 5 gives an example of the $K_{om,pH}$ as function of the pH of the soil. For this example $K_{om,acid}$ is 500 L/kg, $K_{om,anion}$ is 5 L/kg and the pK_a is 5, indicated by the vertical dotted line. It is obvious from the graph that the ΔpH is equal to one, the breakpoint is at pH = 6 i.e. one pH-unit above the pK_a. So the line has shifted one pH-unit to higher pH-values compared to the dissociation curve of the molecule.

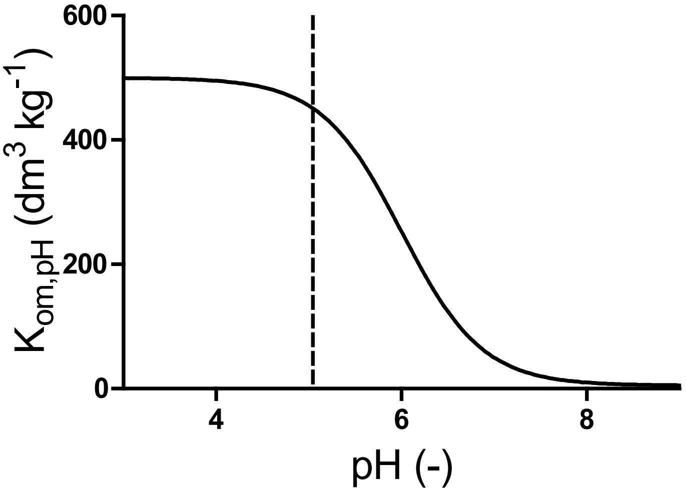

Figure 5 *Example curve of the K_{om} as function of soil pH calculated with Eqn 31 for $K_{om,acid}$ = 500 L/kg, $K_{om,anion}$ = 5 L/kg, M_{acid} = 200 g/mol, M_{anion} = 199 g/mol, pK_a = 5 and ΔpH = +1. The vertical line indicates pH = 5 (ie the pK_a).*

The substance properties $K_{om,acid}$, $K_{om,anion}$ and ΔpH have to be supplied to PEARL / GeoPEARL by the user in order to be able to calculate the leaching of weak acids. The following paragraphs give guidance on deriving appropriate input values for calculations. The principle of this guidance is that Equation 31 can be fitted to experimental data using any software package capable of fitting non-linear functions to data. Because of the existence of three different pH measuring techniques (see next Section), the pH values have to be brought in line with the evaluation scenario. For example, in case of GeoPEARL calculations for the Netherlands, pH values should be converted to the pH_{KCl} measurement method because the GeoPEARL soil database contains pH values based on this method.

So the first issue to be addressed is to establish the relationships between the three pH measurement methods (Section 3.6.2). Thereafter these relationships are used in Section 3.6.3 as a basis for defining the dataset of K_{om}-pH pairs and for establishing the guidance to estimate the sorption parameters.

3.6.2 Quantitative relationships between methods for measuring pH of soil

The principle of a pH measurement is that the pH is measured in the solution after soil and solution have been gently shaken and the particles have settled for a couple of hours. ISO (2005) has attempted to standardise the determination of soil pH, but still three different methods occur in the guidance. The protocol prescribes to measure the pH with a glass electrode in a 1:5 soil:solution suspension, but allows choosing between pure H_2O, 0.01 mol dm^{-3} $CaCl_2$ solution and 1 mol dm^{-3} KCl solution for suspending the soil. The methods are referred to as pH_{H2O}, pH_{CaCl2} and pH_{KCl} in the rest of this text. Earlier versions of the ISO protocol also prescribe a soil:solution ratio of 1:5. Other ratios have been used. A soil:solution ratio of 1:2.5 was adopted by the International Society of Soil Science (Peech, 1965, cited by Fotyma *et al.*, 1998) and has long been the standard in Europe (Schachtschabel *et al.*, 1989; Fotyma *et al.*, 1998). More recently, a 1:10 ratio for the pH_{CaCl2} method was introduced (Houba *et al.*, 1986; Fotyma *et al.*, 1998). Vanhoof *et al.* (2007) report an increase in pH of approximately 0.38 pH-units when going from a 1:1 soil:solution ratio to a 1:10 ratio.

The composition of the solution influences the soil and therewith the result of the measurement. The extension of the diffuse double layer is influenced by the salt concentration of the solution, the higher the salt concentration the more compressed the diffuse double layer is, which results in higher concentrations of cations in the diffuse double layer. Cations compete with H^+ ions in the diffuse double layer. Therefore, the pH in a measurement with $CaCl_2$ or KCl is expected to be lower than in a measurement with water. Comparing the $CaCl_2$ and KCl measurements, the pH in the KCl measurement is usually lower than the pH in the $CaCl_2$ measurement. The latter is mainly attributable to the higher salt content of the KCl solution. The pH measurement methods give, therefore, not the same result. Schachtschabel *et al.* (1989) report a difference between pH_{H2O} and pH_{CaCl2} measurements of on average 0.6 pH units for agricultural soils in Germany, for measurements with a 1:2.5 soil:solution ratio and 0.01 mol/L $CaCl_2$. Fotyma *et al.* (1998) compared results obtained with the pH_{KCl} (1 mol/L KCl, ratio 1:2.5) method with results obtained with the pH_{CaCl2} (0.01 mol/L $CaCl_2$, ratio 1:10) and found that the differences decreased with increasing pH. pH-values were found to be lower for the method with the 1 mol/L KCl solution.

As the value of the pH is influenced by the measurement method, it is important that a consistent dataset is derived when performing leaching calculations and that the dataset is compatible with the pH measurement method of the soil of the scenario. In a registration dossier of a plant protection product pH_E values according to several methods may be reported. The subscript E is used to indicate that it is a measured value from any experiment. Therefore it may be necessary to convert pH_E values in order to obtain a consistent analysis or evaluation. Below, simple linear conversion procedures are described in order to derive consistent datasets.

Seven data sets were found to elaborate on the relation between $pH_{E,H2O}$, $pH_{E,CaCl2}$ and $pH_{E,KCl}$ (Table 3). Data were checked on their origin and excluded if not originating from temperate areas. In general, soils originated from Europe and North-America; samples from Brasil, Indonesia and most African countries were discarded. Also, volcanic soils were discarded. Otherwise no data processing took place.

Table 3

Available pH datasets and number of pH measurements contained in them.

	Source	Global indication of origin of samples	soil:solution ratio	pH_{KCl} (1 mol/L)	pH_{CaCl2} (0.01 mol/L)	pH_{H2O}
1	Barrere *et al.*	France	1:2.5	29 [u]		29
2	BIS-Alterra[1]	Netherlands	1:2.5	452		452
3	Dyson *et al.*	USA, UK, France	1:2		15	15
4	Eijgenraam[2]	world, temperate areas	[w]	82 [uv]	81 [uv]	82
5	Gottesbüren[3]	world, temperate areas	1:5		155	155
6	De Groot *et al.*	Netherlands, Belgium	1:5	40	49	49
7	Rutgers *et al.*	Netherlands, Belgium	1:5	532		532

[w] unknown ratio

[u] unknown concentration

[v] variable concentration

[1] personal communication F. de Vries, Alterra, the Netherlands

[2] personal communication B. Eijgenraam, Alterra, the Netherlands. Each sample was measured 8 - 651 times in a kind of ring test; the average of all measurements was used here.

[3] personal communication B. Gottesbüren, BASF, Germany

[2,3] temperate: soils originating from locations between 35° and 65° northern latitude, resp. southern latitude; in case of uncertainty, samples were excluded.

We decided to use all pH_{KCl}, pH_{CaCl2} and pH_{H2O} data in Table 3 to obtain regression relationships between these three measurement methods. So, differences between the molarity of the solutions and the soil:solution ratio are ignored and only three methods are distinguished: pH_{KCl}, pH_{CaCl2} and pH_{H2O}. Arguments for this decision are:

1. Description of the analysis method is not always complete, i.e. ratio or molarity is sometimes not stated.
2. The soil:solution ratio is approximate for many samples, especially when fresh material was the starting point for the analysis.

3. The salt concentration is approximate as it also depends on the salt content of the sample, which depends on eg the nutrient status of the soil.
4. From the dataset of Eijgenraam, it is known that variation in results obtained from different laboratories using the same method is as large as variation obtained with different methods (Eijgenraam, personal communication, 23-02-2009).

The datasets were combined and analysed according to model II linear regression (also called orthogonal regression or Demming linear regression) using GraphPad Prism version 5.00 for Windows, GraphPad Software, San Diego California USA, www.graphpad.com. This method is different from ordinary linear regression as it assumes both X and Y variables are uncertain whereas in ordinary linear regression all uncertainty is attributed to the Y variable. The analyses of the datasets revealed linear relationships between the pH measurement methods, with the slope of the regression line statistically significant different from the value of 1. For the conversion the appropriate equation should be chosen from one of the following:

$pH_{CaCl2} = 1.018\ pH_{H2O} - 0.660$ [32a]
$pH_{H2O} = 0.982\ pH_{CaCl2} + 0.648$ [32b]

$pH_{KCl} = 1.109\ pH_{CaCl2} - 0.804$ [33a]
$pH_{CaCl2} = 0.902\ pH_{KCl} + 0.725$ [33b]

$pH_{KCl} = 1.163\ pH_{H2O} - 1.723$ [34a]
$pH_{H2O} = 0.860\ pH_{KCl} + 1.482$ [34b]

The equations in each pair denote the same line. Graphical representations of the fitted lines against the measured values and the data pairs themselves are given in Figure 2. Standard deviations of the slopes are 0.013, 0.024 and 0.011 respectively in the first appearing regression of equations 4, 5 and 6. The corresponding standard deviations in the intercepts are 0.089, 0.15 and 0.066 respectively. All intercepts are significantly different from 0. The slopes of the regression lines in Figures 2A and 2C are significantly different from 1. The slope of the regression of the pH_{CaCl2} results on the pH_{H2O} results (Figure 7) is not significantly different from 1. R^2 values for the three regression lines were respectively 0.95, 0.95 and 0.91.

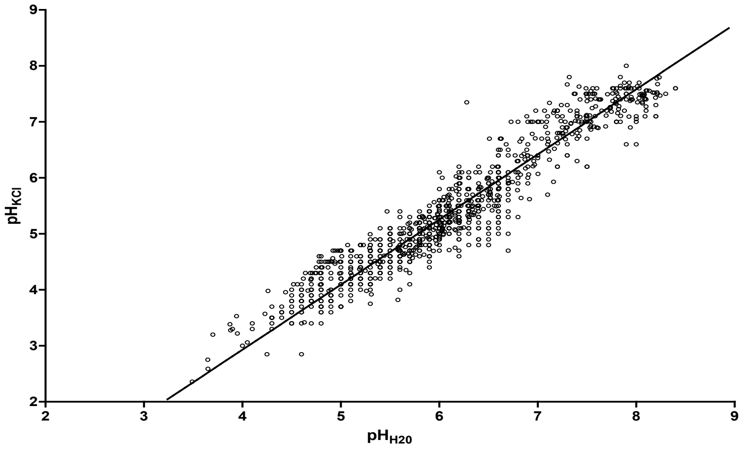

Figure 6 *Orthogonal regression of pH_{H2O} versus pH_{KCl}. The dots indicate the 1135 individual data pairs, the line gives the orthogonal regression of Eqn 34. Individual data may overlap. Data sources (see Table 3): 1, 2, 4, 6.*

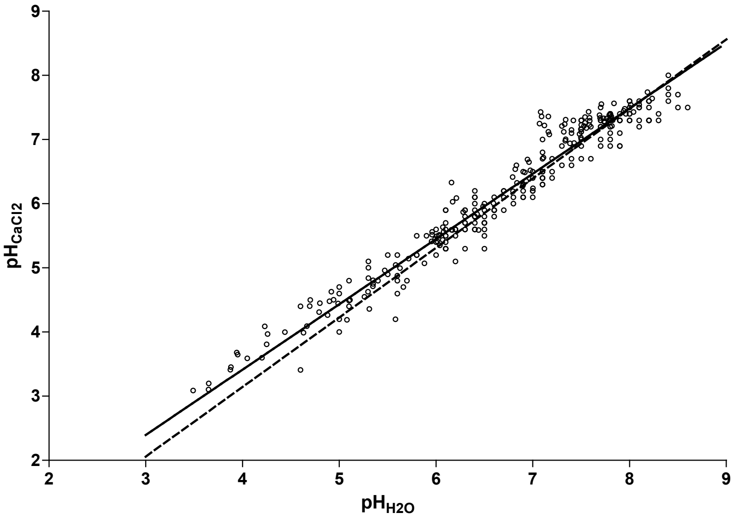

Figure 7 *Orthogonal regression of pH$_{H2O}$ versus pH$_{CaCl2}$. The dots indicate the 300 individual data pairs; the solid line gives the orthogonal regression of Eqn 32 and the dashed line gives Eqn 36 obtained by Kissel et al. (2004). Individual data may overlap. Data sources (see Table 3): 3, 4, 5, 6.*

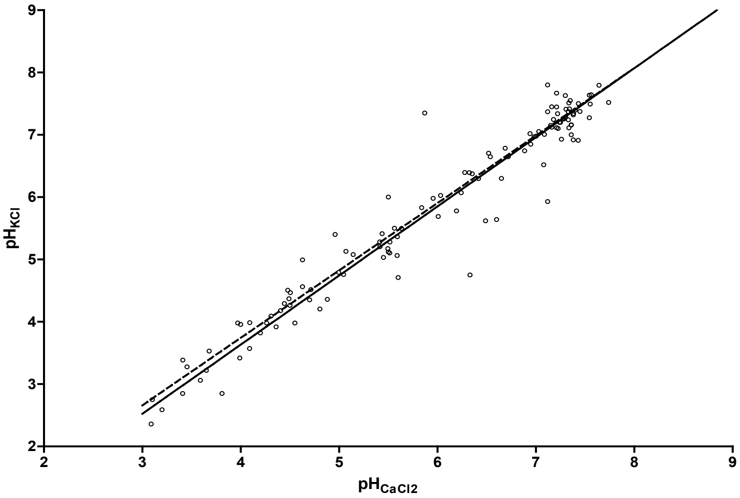

Figure 8 *Orthogonal regression of pH$_{CaCl2}$ versus pH$_{KCl}$. The dots indicate the 121 individual data pairs, the solid line gives the orthogonal regression of Eqn 33. Individual data may overlap. Data sources (see Table 3): 1, 6. The dashed line is the orthogonal regression obtained from Blgg (Eqn 35; data not in figure).*

Vanhoof *et al.* (2007) report a linear relation between pH$_{KCl}$ and pH$_{H2O}$ based on approximately 50 datapoints and found the difference to increase with increasing pH, so different from the relation in Figure 6. The R^2 value of 0.72 was rather low.

Termorshuizen (Blgg, personal communication, 2008, www.blgg.nl) performed an orthogonal regression on pH$_{KCl}$ - pH$_{CaCl2}$ data pairs from 3657 soil samples (mainly Dutch), which were analysed according to the ISO protocol (1:5 soil:solution ratio, 1 molar KCl and 0.01 molar CaCl$_2$, respectively; ISO, 2005). Measurements were in duplo, averages of the duplo measurements were used for the regression analysis. The regression line:

$$pH_{KCl} = 1.08\ pH_{CaCl2} - 0.59 \quad (35a)$$

$$pH_{CaCl2} = 0.92\ pH_{KCl} + 0.54 \quad (35b)$$

was obtained with a R^2 of 0.92. This line is shown in Figure 8 along with the regression line obtained for the datasets described in Table 3. Figure 8 indicates that the Blgg results compare very well with the results for the datasets in Table 3. The regression coefficient and the intercept are not significantly different from the values in equation 33. It cannot be excluded that the dataset of Termorshuizen partly overlaps the datasets of BIS, De Groot and Rutgers mentioned in Table 3. The data of Blgg are not available for further analyses and therefore equation 33 is used.

Kissel *et al.* (2004) report a linear relationship between pH_{CaCl2} and pH_{H2O} for soils originating from the south-eastern USA. Using ordinary linear regression, they found the regression line (R^2 = 0.9088):

$$pH_{H2O} = 0.92\ pH_{CaCl2} + 1.10 \qquad (36)$$

The measurements were performed on approximately 3000 soil samples, using a 1 : 1 soil : solution ratio. Although the fitting procedure was different, the resulting line is close to our line (see Figure 7).

In addition, Kissel *et al.* (2004) studied the influence of the salt concentration used in the determination of the pH. They selected three soils from the Coastal Plain of Georgia and rinsed these with deionised water to make them 'salt free'. After air drying and sieving, pH was measured in a soil:solution ratio of 1:1, prepared with 0 and 10^{-5} - 10^{0} molar $CaCl_2$ solutions. Very low concentrations of $CaCl_2$ did not affect the pH, but a nearly linear decrease of pH with log($CaCl_2$) was observed at concentrations above 0.0001 mol/L. At the highest salt concentration, the measured pH was 1.7 lower than in the 'salt free' soil. Herewith, they confirmed the potential large effect of the salt concentration on the measured pH.

For the further guidance development in the next section, we need also information on the difference between the pH values from the different measurement methods. We can calculate the difference between pH_{H2O} and pH_{KCl} from Eqn 34b:

$$pH_{H2O} - pH_{KCl} = + 1.482 - 0.140\ pH_{KCl} \qquad (37)$$

Similarly we can calculate the difference between pH_{CaCl2} and pH_{KCl} from Eqn 33b:

$$pH_{CaCl2} - pH_{KCl} = + 0.725 - 0.098\ pH_{KCl} \qquad (38)$$

The difference between pH_{CaCl2} and pH_{H2O} can be calculated from Eqn 32b:

$$pH_{H2O} - pH_{CaCl2} = + 0.648 - 0.018\ pH_{CaCl2} \qquad (39)$$

We use pH_{KCl} as the reference pH in this context because Dutch pH data are available for pH_{KCl}. Therefore the right-hand side of Eqn 39 is rewritten into a function of pH_{KCl} using Eqn 33b:

$$pH_{H2O} - pH_{CaCl2} = + 0.635 - 0.0162\ pH_{KCl} \qquad (40)$$

Figure 9 shows that the range of pH_{KCl} for Dutch arable soils in the GeoPEARL database is 3.5 to 7.5 which is more or less consistent with observations by Reijneveld *et al.* (2009) showing a range from about 4 to 8 for four regions in the Netherlands. Figure 10 shows that in the pH range from 3.5 to 7.5 the difference between pH_{H2O} and pH_{KCl} decreases from about 1.0 at pH_{KCl} = 3.5 to about 0.4 at pH_{KCl} = 7.5. The average difference pH_{H2O}- pH_{KCl} over this range is 0.7. The figure shows also that the difference between pH_{CaCl2} and pH_{KCl} decreases from about 0.4 at pH_{KCl} = 3.5 to about 0 at pH_{KCl} = 7.5. The average difference pH_{CaCl2} - pH_{KCl} over this range is 0.2. Figure 10 shows also that the difference pH_{H2O}- pH_{CaCl2} does only vary slightly between pH_{KCl} = 3.5 and pH_{KCl} = 7.5. The average difference over this range is 0.5. These average differences are summarized in Table 4.

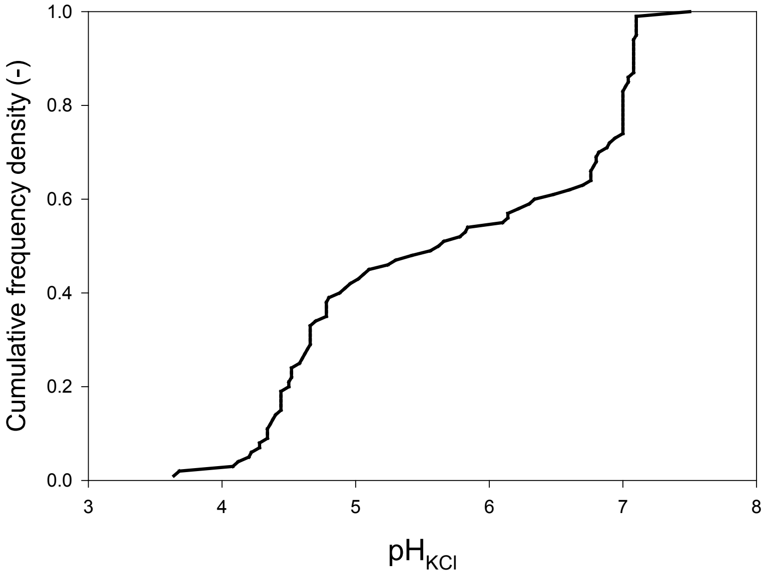

Figure 9 *Cumulative frequency density of pH_{KCl} of Dutch arable soils based on the GeoPEARL database (personal communication R. Kruijne, 2010).*

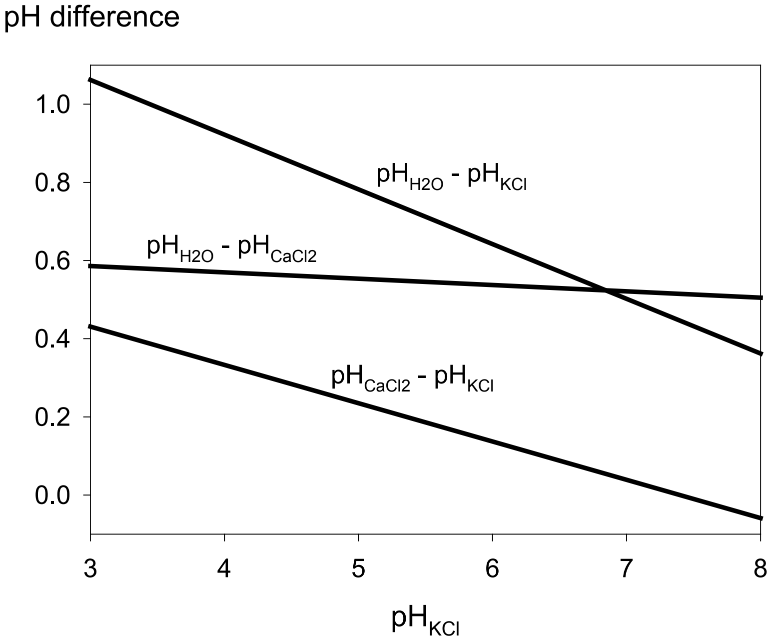

Figure 10 *Differences between the three pH measurement methods as a function of pH_{KCl} as calculated with Eqns 37, 38 and 40.*

Table 4

Average pH differences between the pH measurement methods for the range of pH_{KCl} from 3.5 to 7.5 based on Eqns 37, 38, 40.

Difference considered	Average value of difference
pH_{H2O} - pH_{KCl}	0.7
pH_{H2O} - pH_{CaCl2}	0.5
pH_{CaCl2} - pH_{KCl}	0.2

3.6.3 Guidance for estimating K_{om} values of weak acids for scenario calculations

This section describes the guidance for estimating K_{om} values of weak acids. This guidance is valid for both Tier 1 and Tier 2 of the Dutch assessment scheme for leaching to groundwater as described by Van der Linden *et al.* (2004). Tier 2 is based on GeoPEARL and the GeoPEARL soil database contains pH_{KCl} values. Therefore the guidance below is based on the pH_{KCl} as the default measurement method. However, the guidance is described in such a way that it it should be easy to use also for the other default measurement methods.

As stated above, the pH of the soil will influence the sorption of weak acidic substances. It is recommended to always take account of pH-dependent sorption of such substances if the pK_a of the substance is between[11] 2 and 8. pK_a-values below 2 will identify substances that are usually fully negatively charged in normal agricultural soils (also in the diffuse double layer) irrespective of the pH of the soil and there will be no contribution of the neutral molecule to the sorption. It will also be impossible to find soils with sufficiently low pH to see any effect on the sorption process. Similarly values above 8 will identify substances that are always in the neutral form in normal agricultural soils. Guidance is given for cases where there is one pK_a.

For substances with more than one pK_a in the range 2 to 8 the situation may be more complex. The behaviour of such substances with pH is not predictable and expert judgement is required. Guidance for such substances is not given in this document. In case sorption presumably is pH dependent it is recommended to select test soils in a broad pH range to achieve a curve to fit adequate input parameters in the leaching models.

If the pK_a of a substance is between 2 and 8, the data handling has to follow the next steps:

1. Evaluate the quality of the individual sorption data and exclude all data that are considered to have insufficient quality from further analyses. Include results of batch, column and TLC studies. A soil should occur in the selection only once. If more data for the same soil[12] are available consider averaging when these can be considered true replicates, in other cases choose the most appropriate / reliable one and deselect other values. Continue only if at least four K_{om} values are left. Quality criteria are:
    a. Soil samples from top layer, if not: value not suitable for inclusion in dataset;
    b. Organic carbon content of the soil is at least 0.3% (see OECD106);
    c. pH value given; if not: unreliable;
    d. Sorption constant (K_D, K_F, K_{OC}, K_{om}) reported as an upper limit, if so: unreliable;
    e. Missing soil/solution ratio, if so: unreliable;
    f. Wrong or uncertain calculation method while basic experimental data not available (if basic data are available, the sorption data can be recalculated), if so: unreliable;
    g. Influence of transformation/degradation probably larger than accounted for in default correction (expert judgement);
    h. Unknown water layer in column studies, if so: unreliable;
    i. Unknown water flow rate in column studies, if so: unreliable;
    j. Unknown penetration depth or column length, if so: unreliable.
2. Determine the pH measurement method of the scenario or the scenarios for which calculations have to be performed; for the Dutch leaching assessment this is the pH_{KCl} method because the pH in the GeoPEARL soil database has been measured with this method.
3. Check whether the pH measurement method is known for each single measurement, assign pH_{H2O} as the measurement method when not (this is a conservative approach as will be explained below).
4. Select pH - K_{om} data pairs and convert, when necessary, pH values to the pH measurement method of the scenario using the appropriate equation of equations 4 - 6. If for a soil sample

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[11] The risk assessment should investigate whether dissociation of the molecule (parent or metabolite) is possible in the pH range, also when the pK_a is not provided. If so, pH dependent sorption is assumed and the guidance provided in this section applies.

[12] With regard to sorption, soils are considered to be the same when they originate from the same field.

pH-values according to several methods are available, select the one according to the scenario method and do not convert. In the report state values and measurement methods for both the experimental values and the converted values.

5. Plot all data in a K_{om} -pH plot analogously to Figure 16 in Section 3.9, such that best-guess values[13] and lower limit values (see earlier sections) can be distinguished. This step is similar to the first step of the evaluation of the sorption of substances not showing pH-dependent sorption. In addition, plot converted pH-K_{om} data pairs such that original and corrected values can be visually distinguished (see Van der Linden *et al.* (2015) for examples).
6. On a case by case basis, judge from the graph whether lower limit values can be taken into account in the further analysis of the data. Lower limit values may unduly influence the curve because a correction based on default assumptions may be too large. In such cases, the data pair should be discarded. Reasons for deselection include (be careful however for soil with default pH correction, i.e. when pH measurement method is unknown):
    a. TLC studies always provide lower limits (up to a factor of three too low), if higher K_{om}-values are available for soils in the same pH range or higher pH then these TLC results are deselected;
    b. If a batch value is based on default corrections, this can be deselected when, in soils within the same pH range, higher values or higher lower limit values are available;
    c. Sorption values based on default corrections are deselected when, in the same pH range, higher values but with smaller correction are available. In case all values in the range are based on default corrections, only the 0-values are deselected because correction was cut-off at 0;
    d. If there are plenty of data, data with unknown pH measurement method can be deselected if 10 or more values remain (either all or none of the (remaining) data with unknown pH measurement method are deselected at this point);
    e. The value being considered an outlier and based on default correction. A value is considered an outlier if the value differs a factor 5 from the average in the same pH range;
    f. The value being considered an outlier.

After following this data handling procedure, we recommend using the flow chart in Figure 11 to obtain the sorption parameters. This flow chart is based on the assumption that higher K_{om} values lead to less leaching. In case the degradation is dependent on soil properties as well, the procedure may not be conservative. Van der Linden *et al.* (2009) found maximal leaching at intermediate pH for a substance with both sorption and degradation dependent on soil pH. The flow chart checks first whether there are at least four K_{om} values. We consider four K_{om} values the minimum to estimate sorption parameters in case of pH-dependent sorption as three parameters have to be fitted. So the minimum number of three values for metabolites as requested in the data requirements is insufficient for this fitting procedure. The next step is to check whether the range of pH values is at least 3. We consider this as a minimum to estimate adequate parameters for Eqn 31. Admittedly, this is a conservative requirement which may be relaxed when more experience has been gained with this procedure. If this requirement is fulfilled, the right branch of the flow chart has to be followed. We will first describe this right branch and come back later to the left branch. In this right branch, the instruction is to fit Eqn 31 to the data (thus generating values for $K_{om,acid}$, $K_{om,anion}$ and ΔpH) under the following constraints:

a. Use the molar masses of the acid and the anion as fixed input;
b. Use the pK_a value of the substance as fixed[14] input;
c. $K_{om,acid}$ and $K_{om,anion}$ are ≥ 0.0 and $K_{om,acid} \geq K_{om,anion}$ (the requirement for the constants to be ≥0 originates from PEARL and GeoPEARL limitations).

Eqn 31 can be fitted to experimental data using any software package capable of fitting non-linear functions to data. An example of this fitting is given in Section 3.6.4. If the fit is successful (i.e. the

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[13] Based on earlier sections in the report, corrections may have been applied to the results. A best guess corrected result is obtained when corrections are based on information in the report of the experiment. A lower limit is obtained when a correction is based on one or more default assumptions.

[14] Usually only one value will be available in a registration dossier, if applicable. If more than one pK_a values are available for the same dissociation reaction, the selected value should be justified.

software package successfully terminates the fitting procedure), plot the fitted line along with the selected measurement values in a figure. Next step is to determine whether the fit is visually acceptable and whether the fitted ΔpH-value is within the acceptable range.

Examples of the application of this guidance are given for bentazone, MCPA and mecoprop in Van der Linden *et al.* (2015).

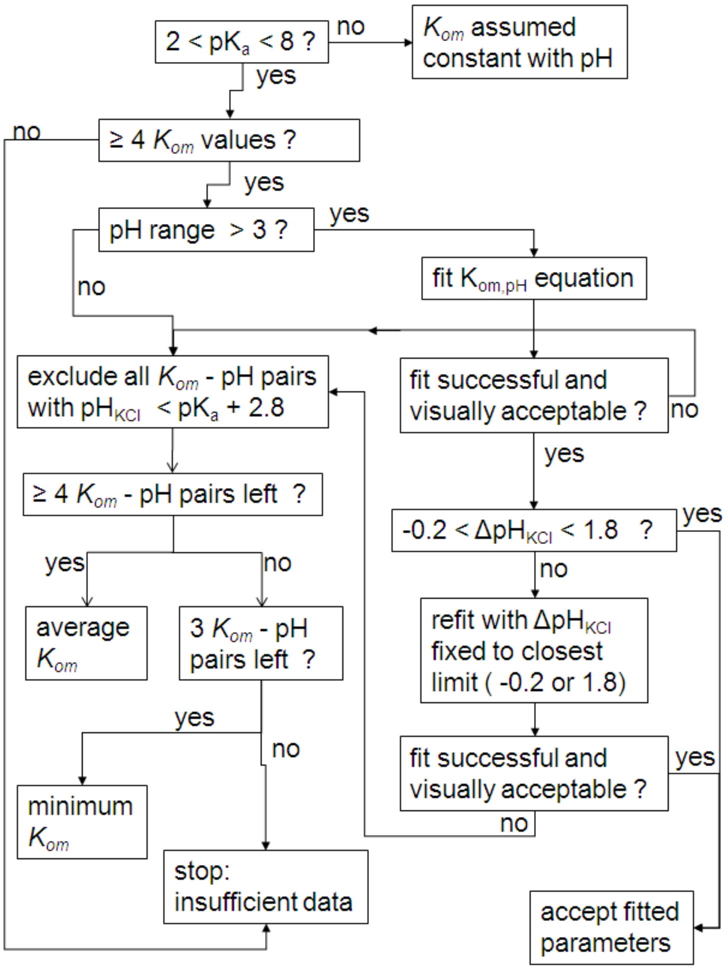

Figure 11 *Flow chart for estimating sorption parameters for weak-acidic substances with pH-dependent sorption (based on* pH_{KCl} *as the preferred measurement method; see text for modifications needed for other measurement methods). The left-hand branch of the scheme is not valid for substances for which also degradation is dependent on soil properties.*

So for that purpose we have to define the acceptable range of ΔpH. Nicholls and Evans (1991 mention a value of 1.8 pH units for the surface acidity effect, which means that the pH at the surface would be 1.8 pH units lower than in the bulk solution. However, Nicholls and Evans (1991) provide no source for this 1.8. Moreover, Fontaine *et al.* (1991) found that they could describe the pH dependency of the sorption of the weak acid flumetsulam to a range of soils without including any surface acidity effect. So we conclude that the surface acidity effect is likely to be considerably less than these 1.8 pH units. Besides the variability in composition and presence of competing cations, also experimental conditions with regard to soil:solution ratio and ionic strength (Vanhoof *et al.*, 2007) and variability in the pH measurement itself lead to the conclusion that it is reasonable to accept a range in ΔpH-values. Further analysis of the dataset of Eijgenraam (dataset 4 in Table 3) with respect to the variability in pH measurements for individual soil samples led to a standard deviation of the measurements of approximately 0.2 pH-units, irrespective of the measurement method and the average pH of the soil sample. In view of this variability, we consider that there will be a real difference in soil pH when the difference in pH between two soils is 0.3 pH units.

Based on the previous paragraph we cannot exclude that the surface acidity effect may be about 1 pH unit. Combining this with the variability in the pH measurements described above, we conclude that a range of ΔpH of 2 is acceptable when measured in a 0.01 normal salt solution. An acceptable range in ΔpH-values would then be 0 - 2 for the pH_{CaCl2} measurement method. As different pH measurement methods may lead to different pH in the bulk soil solution, it is to be expected that the observed ΔpH-values, i.e. the difference in pH at the solid surfaces and in the bulk solution, will also depend on the measurement method. From the combination of Eqn 3, Figure 5 and the lines in Figure 2, it can be derived that the ΔpH value will increase in the order KCl < $CaCl_2$ < H_2O, for agricultural soils with pH_{KCl} values in the range of approximately 3 - 8. In other words, the ΔpH value found when fitting a series based on pH_{KCl} is expected to be lower than when fitting a pH_{CaCl2} series or a pH_{H2O} series. This is illustrated with Figure 12 which shows an example of $K_{om,pH}$ as a function of pH for the three measurement methods.

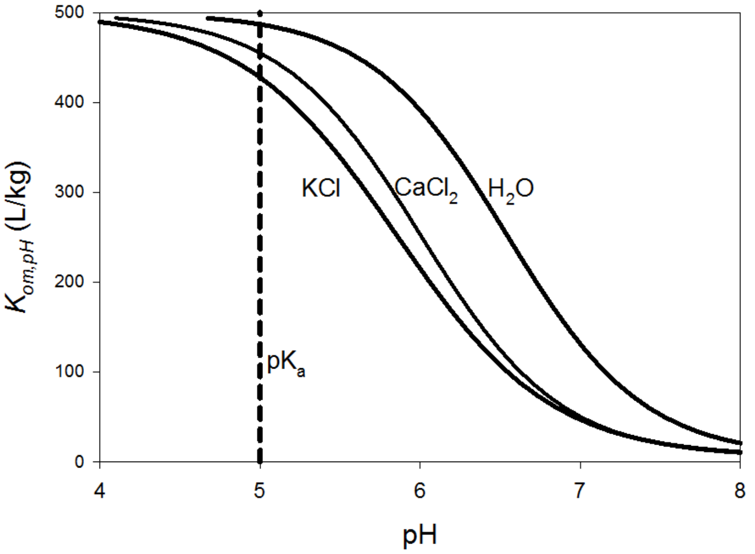

Figure 12 *Example of a relationship between $K_{om,pH}$ and pH for the three different pH-measurement methods. The line for $CaCl_2$ was calculated with Eqn 31 for $K_{om,acid}$ = 500 L/kg, $K_{om,anion}$ = 5 L/kg, M_{acid} = 200 g/mol, M_{anion} = 199 g/mol, pK_a = 5 and ΔpH = +1. The line for H_2O was calculated from the line for $CaCl_2$ using Eqn 32b for the difference in pH and the line for KCl was calculated from the line for $CaCl_2$ using Eqn 33a for the difference in pH.*

Using the average difference between the different measurement methods in Table 4 and assuming that the acceptability range for ΔpH_{CaCl2} is 0 - 2, the acceptability range for ΔpH_{H2O} is 0.5 - 2.5, and the acceptability range for ΔpH_{KCl} is -0.2 - 1.8. In Figure 11, we assumed that the pH_{KCl} is the preferred measurement method. In case other measurement methods are used, a modified version of Figure 11 can be used where the range of ΔpH_{KCl} is replaced by the ranges of ΔpH_{H2O} or ΔpH_{CaCl2}.

Figure 11 shows that if the fitted ΔpH value is outside the appropriate range, the ΔpH value must be fixed to the closest limit value (ie -0.2 if the fitted ΔpH_{KCl} was below -0.2 or +1.8 if the fitted ΔpH_{KCl} was above 1.8) and Eqn 31 fitted again. Then it is again checked whether the fit was successful and visually acceptable.

In order to gain insight into the accurateness of the fit and uncertainty in the parameters, a 95% confidence interval band around the fitted curve is plotted, where possible. So, finally a figure showing the selected values, the fit and the 95% confidence limits is produced if the right hand branch of the scheme is applicable.

We now consider the left branche of the flow chart in Figure 11. The flow chart shows that this left branch has to be followed if the fitting in the right branch is not OK or if the pH range of the ≥4 K_{om} values is less than 3. First step is to check whether there are at least four K_{om} -pH pairs with pH_{KCl} above pK_a+2.8. This is based on the requirement that $pH_{CaCl2} > pK_a + 3$ which implies that $pH_{KCl} > pK_a+2.8$ (Table 4). If this is the case, the average K_{om} of these pairs can be used to estimate the $K_{om,anion}$ conservatively.

The background of the criterion $pH_{CaCl2} > pK_a + 3$ is that only at such high pH values it is guaranteed that only the sorption of the anion is measured and not some mixture of the weak acid and the anion. This is illustrated by the example in Figure 12 which shows that at $pH_{CaCl2} = 8$ (ie $pH_{CaCl2} = pK_a + 3$) the K_{om} is very close to that of the anion. Following the same reasoning, for pH_{H2O} the criterion becomes $pH_{H2O} > pK_a + 3.5$.

If there are no four such K_{om} -pH pairs, it is tested in Figure 11 whether there are at least three such pairs. If yes, the minimum of these three is used to estimate the $K_{om,anion}$ as a conservative result. If less than three pairs are available, the data are considered insufficient to estimated sorption parameters meaningfully.

It happens regularly in a dossier that a pH value is reported without the corresponding measurement method. So then the measurement method is unknown. We recommend to assume then that the pH_{H2O} was the measurement method. We consider this to be a conservative approach, because it implies that the pH value has to be converted from a pH_{H2O} value to either a pH_{CaCl2} or a pH_{KCl} value, so the point will shift to the left along the pH-axis. This shift to the left can be observed from Figures 2A and 2B because pH_{CaCl2} and pH_{KCl} values are always lower than pH_{H2O} values in the relevant pH range for temperate non-volcanic agricultural soils. As a consequence, this approach will lead to relatively low values for the $K_{om,pH}$, i.e. the $K_{om,pH}$ is lower than the value (at the same pH) than obtained without correction because $K_{om,acid}$ is larger than $K_{om,anion}$. In the fitting procedure, the shifted point will then relatively contribute more to the $K_{om,acid}$ and less to the $K_{om,anion}$. The conservativeness of the use of pH_{H2O} will be further illustrated by the example in Section 3.6.4.

The selection of the acceptable range of ΔpH_{KCl} values (-0.2 - 1.8) enables us to illustrate that sorption of weak-acidic substances with pK_a less than 2 is usually limited to sorption of the anion in Dutch soils. Figure 9 showed that the lowest pH_{KCl} for Dutch arable soils is about 4. The example in Figure 13 shows that only for the upper limit of $\Delta pH_{KCl} = 1.8$ there may be a significant contribution of the weak acid between $pH_{KCl} = 4$ and $pH_{KCl} = 5$. We consider it justifiable to keep the lower limit of the pK_a in the upper box of Figure 11 at 2, instead of using a lower limit of 1, because it is unlikely that dossiers will contain only sorption studies in pH_{KCl} range 4-5 in view of the recommendations by OECD (2000). Item 20 of this reference says: 'For ionisable test substances, the selected soils should cover a wide range of pH, in order to evaluate the adsorption of the substance in its ionised and unionised forms.' We interpret this wide range as at least three pH-units in view of the range of pH values of the soils described by OECD (2000); these are also described in our Table 11. Therefore we consider the error made in the average K_{om} of all soils (which is further used in the leaching assessment as described in Section 3.9) sufficiently small to justify a pK_a of 2 as the lower limit.

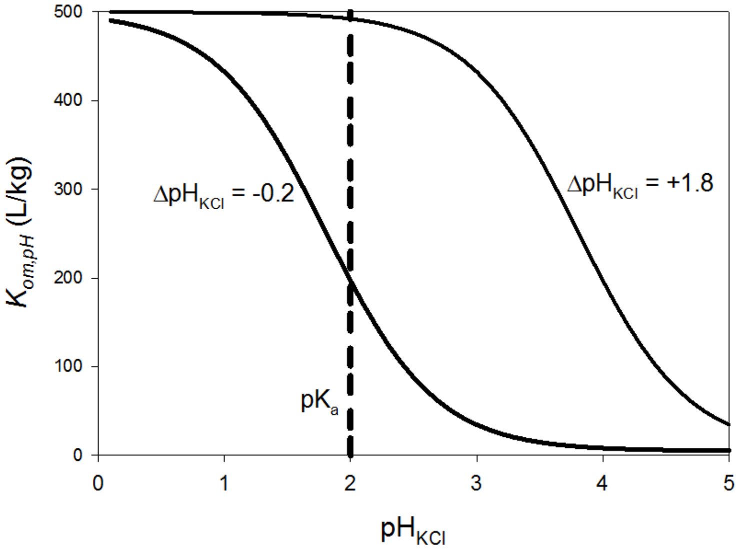

Figure 13 *Relationship between $K_{om,pH}$ and pH_{KCl} calculated with Eqn 31 for $K_{om,acid}$ = 500 L/kg, $K_{om,anion}$ = 5 L/kg, M_{acid} = 200 g/mol, M_{anion} = 199 g/mol, pK_a = 2 and the two ΔpH_{KCl} values as indicated.*

As described at the start of this section, the above guidance is intended to be used both for Tier 1 and Tier 2 of the Dutch assessment for leaching to groundwater. As described by Van der Linden *et al.* (2004), Tier 1 has to be based on a conservative estimate of the K_{om}. This conservative estimate can be based on: (i) the box 'average K_{om}' of Figure 11, (ii) the box 'minimum K_{om}' of Figure 11, or (iii) the $K_{om,anion}$ as derived from the box 'accept fitted parameters' of Figure 11. Tier 2 can best be based on the fitted parameters as derived from the flow chart in Figure 11. If it would be impossible to parameterise Eqn 31 using the flow chart of Figure 11, it is also acceptable to use for Tier 2 conservative estimates derived from the boxes 'average K_{om}' and 'minimum K_{om}' in this flow chart.

3.6.4 Examples of the fitting procedure

We give in this section two examples to demonstrate how the proposed guidance may work. In the first example we show how the fit procedure works in general. In the second example, we show how the procedure works in case the measurement method is unknown for part of the pH values. This second example will also demonstrate that using pH_{H2O} as the default measurement method is a conservative approach.

Table 5 describes a hypothetical dataset 'A' of sorption constants for a weak acidic substance with a molar mass of 200 g mol^{-1} and a pK_a of 6. The dataset A was generated by calculating with Eqn 31 $K_{om,pH}$ values for 20 randomly chosen pH_{KCL} values in the range 4 - 8, with a $K_{om,acid}$ of 500 L kg^{-1}, a $K_{om,anion}$ of 5 L kg^{-1} and a ΔpH value of +0.5. After calculating the values with Eqn 31, uncertainty was introduced assuming a normally distributed error with a coefficient of variation for each single sorption constant of 15%. The generated datapoints are given in Table 5. Figure 14 shows that the generated datapoints are consistent with the relationship used to generate them.

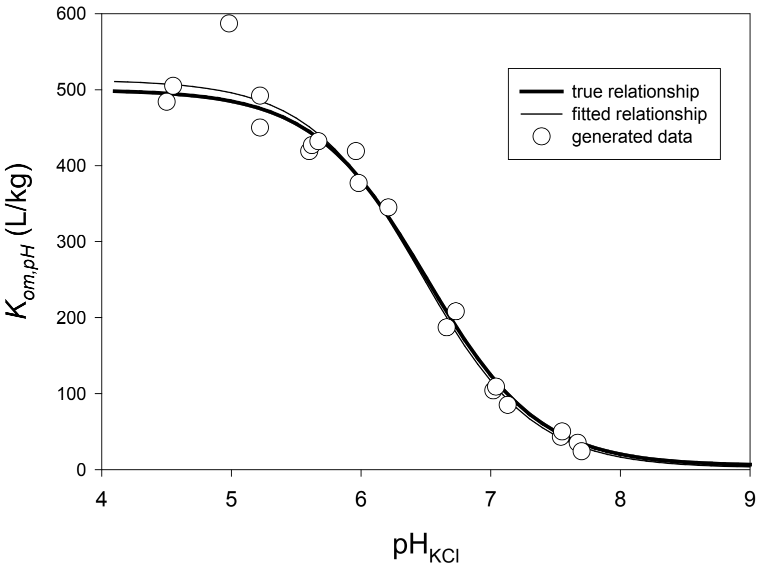

Figure 14 *$K_{om,pH}$ as a function of pH. The thick solid line was calculated with Eqn 31 for $K_{om,acid}$ = 500 L/kg, $K_{om,anion}$ = 5 L/kg, M_{acid} = 200 g/mol, M_{anion} = 199 g/mol, pK_a = 6 and ΔpH = +0.5. The data points were generated assuming a normal distribution with a coefficient of variation of 15% (dataset A in Table 5). The thin solid line is the result of fitting Eqn 31 to the data point (see Table 6 for parameter values).*

Figure 14 shows also that the fitted line was very close to the true line. Table 6 shows that the fitted $K_{om,acid}$ was close to the true value (513 versus 500 L kg^{-1}). The fitted $K_{om,anion}$ was 2 L kg^{-1}, so somewhat lower than the true value of 5 L kg^{-1}. The fitted ΔpH was 0.46 which is close to the true value of 0.5.

In order to illustrate that use of pH_{H2O} as the default measurement method is conservative (for the leaching assessment of parent substances; see Chapter 1) when the measurement method is unknown, a hypothetical dataset B was generated from the hypothetical dataset A. Randomly, ten data pairs of dataset A were selected and the pH measurement method set to unknown (see Table 5). Next the pH_{KCl} values of these ten datapairs were calculated from the original pH values assuming that these were pH_{H2O} values using Eqn 34a (see Table 5). Table 5 and Figure 15 show that this led to a shift to lower pH values as could be expected. Next step was to fit dataset B to Eqn 31. Figure 15 shows that the fitted line for dataset B to the left of the line for dataset A (as a result of the shift of half of the pH values to lower values). This can also be derived from the lower value of ΔpH_{KCl} fitted for dataset B as shown in Table 6. Figure 15 illustrates that the approach of using pH_{H2O} as the default measurement method is conservative: the line for dataset B is below that for dataset A.

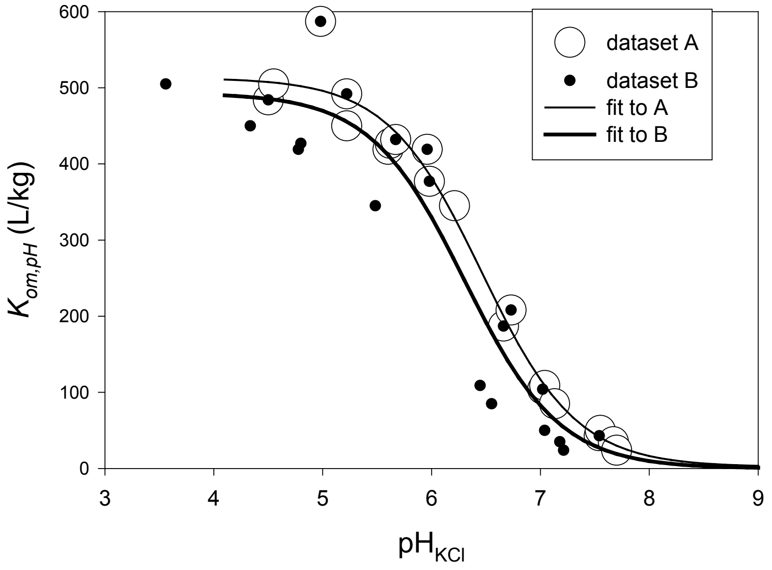

Figure 15 *Datasets A and B and their fits to the relationship between $K_{om,pH}$ and pH of Eqn 31. See Table 6 for parameter values of the fitted lines.*

Table 5

Two hypothetical example data sets. Dataset A was generated using Eqn 31 with $K_{om,acid}$ = 500 L/kg, $K_{om,anion}$ = 5 L/kg, M_{acid} = 200 g/mol, M_{anion} = 199 g/mol, pK_a = 6 and ΔpH = +0.5 and generating data points assuming a normal distribution with a coefficient of variation of 15%. Dataset B was based on dataset A but assuming that the measurement method of 10 of the 20 datapoint was unknown. The pH values in the column 'estimated pH_{KCl}' were calculated with Eqn 34a assuming that the measurement method was pH_{H2O}.

Dataset A		**Dataset B**		
pH_{KCl}	**K_{om} (L kg^{-1})**	**pH**	**measurement method**	**estimated pH_{KCl}**
4.50	484	4.50	KCl	4.50
4.55	505	4.55	unknown	3.56
4.98	587	4.98	KCl	4.98
5.22	492	5.22	KCl	5.22
5.22	450	5.22	unknown	4.34
5.60	419	5.60	unknown	4.78
5.62	427	5.62	unknown	4.80
5.67	432	5.67	KCl	5.67
5.96	419	5.96	KCl	5.96
5.98	377	5.98	KCl	5.98
6.21	345	6.21	unknown	5.48
6.66	187	6.66	KCl	6.66
6.73	208	6.73	KCl	6.73
7.02	104	7.02	KCl	7.02
7.04	109	7.04	unknown	6.45
7.13	85	7.13	unknown	6.55
7.54	43	7.54	KCl	7.54
7.55	50	7.55	unknown	7.04
7.67	35	7.67	unknown	7.18
7.70	24	7.70	unknown	7.21

Table 6

Results and statistical characteristics of fitting the $K_{om,pH}$ - pH relationship to the datasets A and B given in Table 5. True values for both dataset A and B were: $K_{om,acid}$ = 500 L/kg, $K_{om,anion}$ = 5 L/kg and ΔpH_{KCl} = 0.5.

Fitted parameter	Dataset	Best fit value	Standard error	95% confidence interval
$K_{om,acid}$ (L/kg)	A	513	13	485-540
	B	493	25	440-546
$K_{om,anion}$ (L/kg)	A	2	17	0-39
	B	0	33	0-69
ΔpH_{KCl}	A	0.46	0.08	0.30-0.63
	B	0.30	0.15	0.00-0.61

3.7 Estimating sorption coefficients from batch studies for substances whose with sorption coefficient depends depending on other soil properties than pH or organic matter

In Tier 2 of the Dutch decision tree, calculations have to be made with the GeoPEARL model. This model offers the option that the sorption coefficient K_F of the substance is a linear function of the mass fractions of organic matter, sand, silt, clay and sesqui-oxides (see Eqn 45 of Tiktak *et al.*, 2004). If there is evidence that the sorption coefficient is related to sand, silt, clay or sesqui-oxides, then we recommend to perform a linear regression analysis using this equation to estimate these GeoPEARL input parameters. Eqn 45 of Tiktak *et al.* (2004) reads:

$$K_{F,eq} = K_{F,eq,0} + m_{om} K_{om,eq} + m_{sand} K_{sand,eq} + m_{silt} K_{silt,eq} + m_{clay} K_{clay,eq} + c_{sox} K_{sox,eq} \tag{41}$$

where:
$K_{F,eq}$ (m^3 kg^{-1}) is the overall Freundlich sorption coefficient,
$K_{F,eq,\,0}$ (m^3 kg^{-1}) is the Freundlich equilibrium sorption coefficient for sorption not attributable to a particular soil parameter,
m_{om} (kg kg^{-1}) is the mass fraction of organic matter,
$K_{om,eq}$ (m^3 kg^{-1}) is the coefficient for sorption to organic matter,
m_{sand}, m_{silt} and m_{clay} (kg kg^{-1}) are the mass fractions of sand, silt and clay,
$K_{sand,eq}$, $K_{silt,eq}$ and $K_{clay,eq}$ (m^3 kg^{-1}) are the coefficients for sorption to sand, silt and clay, respectively,
c_{sox} (mmol kg^{-1}) is the soil content of sesqui-oxides and
$K_{sox,eq}$ (m^3 $mmol^{-1}$) is the coefficient for sorption to sesqui-oxides.

GeoPEARL uses Eqn 41 with the restriction that all sorption coefficients have to be greater than or equal to zero. Furthermore the sum of the mass fractions of sand, silt and clay has to be 1.

Tier-1 calculations may be performed by estimating the lowest possible K_F for Dutch soils from Eqn 41 based on the probability densities of the independent variables as presented in Section 5.6. The procedure is then to use lower limits of the independent variables because this gives the minimum K_F value. These lower limits will differ from crop to crop. Therefore we recommend to establish a list of minimum values of the mass fractions of organic matter, sand, silt, clay and of the content of sesqui-oxides for all crops used in GeoPEARL.

3.8 Estimation of sorption coefficients of minor metabolites with QSARS

At PRAPeR meeting nr. 32, the experts agreed that estimation of K_{oc} values using QSAR approaches was only ever acceptable for minor (<10% of AR, i.e. applied radioactivity) metabolites (personal communication W. Pol, 2009). For major (>10% of AR) metabolites experimentally derived values should always be provided, following when necessary (i.e. when there were practical reasons why a standard guideline batch adsorption study was not practical) the principles in Scientific Committee on Plants (2002). They agreed that appropriately calculated QSAR approaches could be accepted for minor (<10% of AR) metabolites for decision making at the EU level when there was a margin of safety against the decision making trigger/s and other conservative assumptions had been combined when making the groundwater/ surface water exposure calculations. However they also considered that for a majority of substances where such assessments were accepted at the EU level, that a requirement should be identified for appropriate experimental adsorption determinations to be provided for national product authorisation decisions, where the pattern of use being assessed might be more challenging regarding groundwater and surface water concentrations.

We do not agree with these recommendations because we have no information available on the accuracy of these QSAR approaches and because a literature review of the accuracy of these approaches is beyond the scope of the report. We consider the proposed distinction between minor and major metabolites a risk management decision because there is scientifically no strong link between the risk associated with a metabolite and its formation fraction: the dosage and the toxicity to humans and organisms may be more important than the formation fraction. The statements 'when there was a margin of safety' and 'other conservative assumptions' are qualitative and therefore they are in the context of the Dutch leaching assessment not helpful to us.

3.9 Calculation of endpoints of model input parameters related to sorption in soil if the K_{om} does not depend on soil properties

With respect to sorption, the base line for the tiered Dutch leaching assessment is that the K_{om} is independent of soil properties such as sand, silt, clay or sesqui-oxide contents. If this is the case, the estimation of the K_{om} is the same for Tier 1 and Tier 2. If this is not true, then in Tier 1 a conservative estimate of the K_{om} is needed because Tier 1 considers only the Kremsmünster soil profile whose selection was based on the assumption that the K_{om} is independent of soil properties. Sections 3.7 and 3.8 describe the estimation procedures for the K_{om} if it depends on soil properties. In this section we propose procedures for the case where the K_{om} is independent of soil properties such as sand, silt, clay or sesqui-oxide contents. In these proposals only studies with relevant soils are considered (see Section 5.6 for a discussion on relevance of soils).

The first step of the assessment of the K_{om} values is to evaluate the quality of the individual sorption data and exclude all data that are considered to have insufficient quality from further analyses (see Section 3.6.3: quality criteria given in point 1). The guidance in Section 3.2.3 implies that each K_{om} value derived from a batch study has to be corrected, if not derived from the direct batch method. So the further assessment may be based on a list of corrected K_{om} values. Part of these values may be 0. Moreover we may have at the end a population of K_{om} values based on different measuring methods (batch, soil column, TLC). Thus it should be assessed whether a sorption result has added value to the population of sorption results.

So, we should keep in mind that the correction of batch sorption coefficients as described in Section 3.2.3 is recommended to avoid use of unrealistically high sorption coefficients. This does not imply that the correction procedure results in accurate sorption coefficients. Instead, corrected sorption coefficients should be seen as lower limits. Thus the averaging should not be done blindly. Let us consider the example case of Table 7.

Table 7

Example case of K_{om} values available for a certain PPP.

Soil	K_{om} (L/kg)				
	batch uncorrected	batch corrected	soil column or TLC	value selected	value used for calculation of geomean
A	20	>16		16	16
B	18	>12		12	12
C	14	>0	6	6	6
D	30	>0		0	1
E			8	8	8
geomean					6

In this case the zero batch value of soil C can be discarded because there is a more reliable value from the TLC or soil column study for soil C. We recommend to use in general only one K_{om} value for one soil (i.e. the best value).

Based on EFSA (2014a) the geomean of all relevant values should be calculated, and used in the leaching calculations. However, use of a geomean is incompatible with a zero K_{om}. EFSA (2014a) recommends the geomean based on the assumption that the K_{om} is log-normally distributed whereas a log-normal distribution excludes zero values. For weakly sorbing pesticides it seems difficult to defend that zero values are impossible (e.g. for anionic pesticides the K_{om} may even be negative because of anion exclusion). We propose as a pragmatic solution to replace all zero K_{om} values by 1 L/kg. The arguments for this are that it is practically impossible to distinguish experimentally between $K_{om} = 0$ and $K_{om} = 1$ L/kg and that the leaching simulated for $K_{om} = 0$ will usually be very close to the leaching simulated for $K_{om} = 1$ L/kg.

This pragmatic solution was applied in Table 7 and resulted in a geomean of 6 L/kg. Omission of this 1 L/kg from the geomean calculation in Table 7 would have resulted in a geomean of 10 L/kg, so the procedure for handling zero K_{om} values may have considerable effect on the K_{om} endpoint.

Let us next consider the example in Figure 16, which contains the data of Table 7 amended with three additional data. The first point is that the result of soil F is considered the most reliable result as it is based on a correction based on reported values. The second point is that a correction based on defaults may become rather large (for example the result of soil nr. D). In this case, the uncorrected value is high whereas the corrected value is zero. The difference between the two values suggests a high uncertainty, because the range of uncertainty is very wide and an estimate is obtained that is smaller than values obtained with column and TLC studies (the latter is expected to deliver a lower limit value). So we suggest to discard the value of soil D. The correction for soil H is much smaller than the correction for soil D but the corrected K_{om} (based on the default 10% loss) is also smaller than those obtained with column and TLC studies so we suggest also to discard the K_{om} of soil H.

So the assessment of the K_{om} of soils D and H indicates that a K_{om}, that is based on default corrections, has no added value if lying outside the range of the other K_{om} values. The argument for this is that the corrected K_{om} based on the default 10% loss is a lower limit. If corrections are based on actual measured recoveries, the resulting K_{om} values are not considered as lower limits but as best-guess values. This is illustrated with the example of soil F.

Another interesting case would be a value that, after correction based on default values, is still significantly higher than the uncorrected values for the other soils. This is for example the case for the K_{om} value of 48 at $pH_{KCl} = 6.18$ (Figure 3-3 in Van der Linden *et al.* 2015). In that case, the corrected K_{om} value is about a factor of four higher than other K_{om} values in the same pH range. Such a value could be considered a true outlier and discarded from the population. We recommend in such a case to evaluate whether the corrected value is outside the 95% confidence range of the other values and if so discard the value. In the fitting procedure for the data shown in this Figure 3-3, deleting this point has however little influence on the final results. Datasets are usually so small that expert judgement is recommended to identify outliers.

We realize that this is complicated guidance and that this has not yet been tested thoroughly. Therefore we recommend as a next step to test this guidance proposal by applying it to a number of dossiers that show considerable difference in the variation between the different K_{om} values and combinations of different measurement methods (batch, TLC, columns).

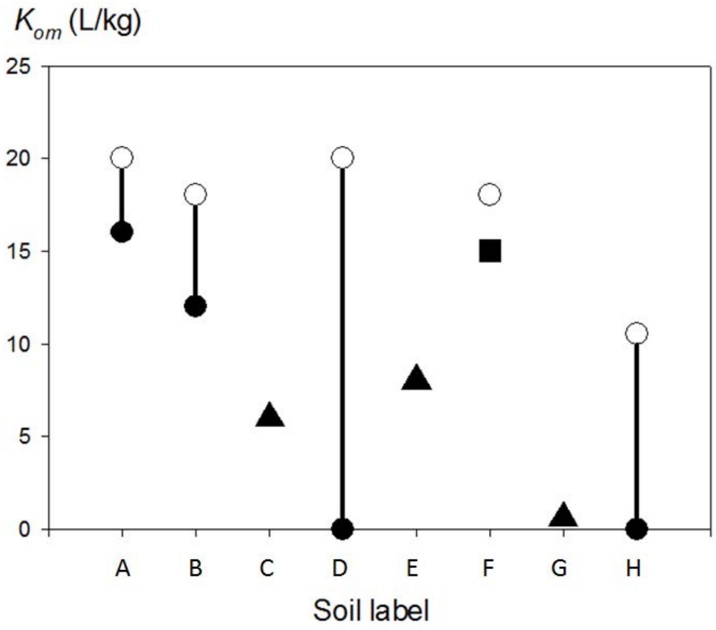

Figure 16 *Example case of K_{om} values available for a certain PPP. Open circles are uncorrected batch values; closed circles are batch values that are corrected based on the default 10% loss during the study; the square for soil F is a batch value that is corrected based on measured recovery in the study; the triangles for soils C, E and G are values based on soil column or TLC studies. The line segments indicate the uncertainty in the K_{om} values because of the use of the default 10% loss.*

With respect to the Freundlich exponent *N* we recommend to average all reliable values (see Section 3.3.2 for the reliability criteria) and to use the arithmetic mean, for parents as well as metabolites, if the number of reliable values is three or larger. If less than three reliable data are available, the default of 0.9 should be used.

4 Guidance proposals on the estimation of degradation parameters

4.1 Introduction

Chapter 2 indicates that the main substances with leaching concerns are bentazone, mecoprop and MCPA. These substances have in common that their sorption is low. Boesten and Van der Linden (1991) showed that leaching is very sensitive to the degradation rate if the sorption is low and the leached concentration is at a level of 0.1 μg/L.

Careful analysis of the past leaching assessments of these substances showed weaknesses in the available guidance for estimation of the degradation rate parameters. The following sections describe the proposed solutions to these weaknesses.

4.2 Arrhenius activation energy

We recommended to use the guidance by EFSA (2007) for estimating the Arrhenius activation energy because this is an analysis based on the most recent data. This implies a default value of 65.4 kJ/mol.

4.3 Guidance for deriving *DegT50* values for the degradation rate within the soil matrix from field persistence studies

4.3.1 Introduction

DegT50 values derived from field persistence studies are used as input to models for PPP leaching to groundwater and PPP accumulation in a top layer. For both purposes it is important that the measured *DegT50* reflects degradation within the soil and not some loss process in the top millimeters of soil. EFSA (2010a) provides guidance for the assessment of the *DegT50* from such studies. We provide in the next sections guidance on reporting of the sampling procedure, calculation of the total amount in soil, weighting of data in the fitting procedure and handling of data based on too few sampling times or too few sampling spots. These are issues at a more detailed level than those covered by EFSA (2010a).

In general it is unlikely that it is possible to derive *DegT50* values of secondary metabolites from field persistence studies because of the large number of parameters that has to be fitted or estimated for secondary metabolites. No guidance for such metabolites will be provided here.

4.3.2 Reporting and evaluation of the procedure of sampling of soil

Coefficients of variation of areic masses (mass per surface area) in the field may be expected to be in the order of 50-100% for sampled surface areas in the order of magnitude of 10 to 100 cm^2: Walker and Brown (1983) found coefficients of variation ranging between 40 and 70% for simazine residues within a 40 x 40 m field. They used soils cores with diameters ranging from 2.5 to 6 cm. Walker and Brown made calculations on the confidence interval of the areic mass in a soil sample comprising 30 cores bulked and mixed together. They found that the 95% confidence interval ranged between 75 and 125% of the true mean value. NAFTA (2006) cite a presentation by R. Jones who compiled confidential information from notifiers. Jones reports a CV of 110% of individual sampling points assuming a lognormal distribution (R. Jones, personal communication, 2008).

An adequate sampling strategy for such areic masses is e.g. as follows: sample 20 spots in the field with a diameter of 5 cm each and mix groups of five samples before extraction and analysis. This is expected to give an acceptable estimate of the average areic mass in the field and an acceptable estimate of the standard deviation of this average.

In view of the potentially very large variability of the remaining fractions in the field, it is necessary to include plot sizes and a detailed description of the sampling procedure (including diameters of the soil core). Also the mixing procedure of the soil samples should be reported.

4.3.3 Guidance for estimating total amount in soil from concentration profiles

Estimating the total amount in soil from concentration profiles is not straightforward because part of the soil samples will have contents below the LOQ or LOD. Usually the LOQ will have been calculated as three times the LOD (ENV-ISO, 1998).

The content of plant protection product in soil can be estimated for all sampled layers. The next step is to convert these into the estimated total areic mass, A (mg/m^2), of plant protection product in the soil profile. This is defined as:

$$A = \int \rho m \, dx \tag{42}$$

where ρ = dry bulk density of soil (kg/L) and x is depth in soil (m). If measurements of the dry bulk density are available, then these should be used. If such measurements are not available, a constant value of 1.5 kg/L for the whole soil profile should be used. If this constant value is used, the areic mass is directly proportional to this value. As a consequence, this constant value has no effect on the fitted *DegT50*: the areic amounts for the different times are based on the same bulk density.

In the following, it is assumed that the field experiment is not yet interpreted with an inverse modelling technique. This section addresses the quantification of the remaining mass of a substance in field experiments in order to establish degradation rates.

Results of field dissipation studies usually are reported in tabular format, with substance contents listed with respect to both depth and time. As substance concentrations change with time and depth and contents may be or become below measurable amounts, guidance on the handling of such results in view of deriving degradation values is necessary as different interpretations may lead to significantly different results. The following text provides a rather pragmatic guidance. This guidance is based on the guidance provided by FOCUS (2006), but extends it with respect to the depth aspect.

FOCUS (2006), in their Table 6-1, has given three examples on how to deal with values below LOQ and/or LOD. Their approach is dealing with the time aspect only and is pragmatic as it does not rely on statistical approaches on contents below the limit of detection. In field studies, also the depth aspect should be taken into account, because the substance may be transported through the soil to deeper layers. FOCUS (2006) prescribes to assume that a substance is present at half the limit of detection (LOD) the first time it is not detected anymore, i.e. the first time after the last detect. That principle is extended here to the depth aspect. The examples of FOCUS assume that the LOD is known and that results are quantified if the content is at or above LOD. In practice, results may be given with the limit of quantification (LOQ) as the lowest level. This requires an analogous, but slightly different, approach.

Table 8 provides a theoretical example of results of a field experiment for which results are reported with LOQ and LOD both known. The columns indicate sampling points in time, with T1 not necessarily the first sampling point in time, but at least fulfilling the requirements laid down in EFSA (2012) for excluding influences of surface dissipation processes. The rows indicate the sampled layers. Based on FOCUS (2006) the following rules apply for cases where both LOD and LOQ are given and contents between LOD and LOQ are either reported as a content or reported as LOD ≤ content < LOQ:

- all values between LOD (inclusive) and LOQ are set to the actual measured values. If the actual measured values are not reported, use 0.5 * (LOQ + LOD)

- all values <LOD are set to ½ LOD
- all values after the first non-detect (<LOD), with respect to depth and/or time, are omitted unless values >LOQ are reported for a shallower respectively deeper layer or for the same layer at an earlier respectively later point in time. In that case additional layers and points in time are included, analogously to example 3 in FOCUS (2006, Table 6-1).

Table 9 shows the results of applying the rules to the theoretical example of Table 8.

Table 8

Theoretical example of results of a field experiment with both LOQ and LOD reported. Tx points in time, Lx layers, M measured value ≥LOQ, X content between LOD and LOQ quantified or not.

Time	T1	T2	T3	T4	T5	T6
layer						
L1	M	M	<LOD	<LOD	<LOD	<LOD
L2	M	M	LOD≤X<LOQ	LOD≤X<LOQ	<LOD	<LOD
L3	M	M	M	LOD≤X<LOQ	<LOD	<LOD
L4	LOD≤X<LOQ	M	LOD≤X<LOQ	<LOD	<LOD	<LOD
L5	<LOD	LOD≤X<LOQ	LOD≤X<LOQ	<LOD	<LOD	<LOD
L6	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
L7	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Table 9

Handling of results of a field experiment with both LOQ and LOD reported. Tx points in time, Lx layers, M measured value ≥LOQ, – result is not used for quantification of the remaining mass.

Time	T1	T2	T3	T4	T5	T6
layer						
L1	M	M	LOD/2	LOD/2	-	-
L2	M	M	(LOQ+LOD)/2 #	(LOQ+LOD)/2 #	LOD/2	-
L3	M	M	M	(LOQ+LOD)/2 #	LOD/2	-
L4	(LOQ+LOD)/2 #	M	(LOQ+LOD)/2 #	LOD/2	-	-
L5	LOD/2	(LOQ+LOD)/2 #	(LOQ+LOD)/2 #	LOD/2	-	-
L6	-	LOD/2	LOD/2	-	-	-
L7	-	-	-	-	-	-

Replace (LOQ+LOD)/2 with actually measured value if that is reported.

The approach changes slightly if all results below LOQ are reported as <LOQ. Table 10 gives the equivalent of Table 8 for this situation. The result <LOQ indicates that the substance has not been quantified. Analogously to FOCUS (2006) the following rules apply for cases where all results below LOQ are reported as <LOQ:

- all values below LOQ are set to ½ LOQ
- all values after the first <LOQ, with respect to depth and/or time, are omitted unless values >LOQ are reported for a shallower respectively deeper layer or for the same layer at an earlier respectively later point in time. In that case additional layers and points in time are included, analogously to example 3 in FOCUS (2006, Table 6-1).

Table 11 shows the results of applying the rules to the theoretical example of Table 10.

It should be noted that in some cases the approach for this situation, where results are only reported with respect to LOQ, may not be conservative. I.e. higher remaining masses would be calculated if the results were reported with respect to LOD and some values indeed are between LOD and LOQ. In other cases, the approach for this situation may be too conservative. If the content in reality was below LOD, the approach leads to too high estimates of the remaining mass. Given all other uncertainties in this approach to obtain half-lives from field experiments, it is considered not appropriate to make further assumptions on values <LOQ.

Table 10

Theoretical example of results of a field experiment with only LOQ reported. Tx indicate points in time, Lx indicate layers, M measured value ≥LOQ.

Time	T1	T2	T3	T4	T5	T6
layer						
L1	M	M	<LOQ	<LOQ	<LOQ	<LOQ
L2	M	M	<LOQ	<LOQ	<LOQ	<LOQ
L3	M	M	M	<LOQ	<LOQ	<LOQ
L4	<LOQ	M	<LOQ	<LOQ	<LOQ	<LOQ
L5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
L6	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
L7	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

Table 11

Handling of results of a field experiment with only LOQ reported. Tx indicate points in time, Lx indicate layers.

Time	T1 $	T2	T3	T4	T5	T6
layer						
L1	M	M	1/2LOQ	-	-	-
L2	M	M	1/2LOQ	-	-	-
L3	M	M	M	1/2LOQ	-	-
L4	1/2LOQ	M	1/2LOQ	-	-	-
L5	-	1/2LOQ	-	-	-	-
L6	-	-	-	-	-	-
L7	-	-	-	-	-	-

$ See text for handling values at T immediately after application

The procedure estimating total mass in the soil profile has been applied for bentazone in Van der Linden *et al.* (2015).

We recommend to test this guidance proposal in points 1 to 10 by applying it to a number of datasets because it is almost impossible to foresee all possible complications with respect to concentration profiles. This testing is beyond the scope of this report.

To be able to identify down to which layer the substance penetrated (and therefore LOD should be used) Boesten *et al.* (2011) proposed to estimate the 90% penetration depth of plant protection product (defined as the depth above which 90% of the PPP amount is located) on the basis of an equation for the average penetration depth of plant protection product in soil assuming chromate-graphical transport theory and piston flow. However, the 90% penetration depth calculated with this equation appeared not sufficiently robust to estimate the 90% penetration depth in soil dissipation studies. See Annex 4 for the equation and the test of the equation resulting in this conclusion.

4.3.4 Procedure for weighting of data in the fitting procedure

When replicate samples are available, often the variability in residues immediately after application is much larger than for later sampling points. Therefore weighting of data in the fitting procedure may be an important issue. FOCUS (2006, p. 70) states: 'Ideally, the method of weighting fits to data should represent the measurement precision or uncertainty of the experimental data. More weight should be given to fitting to data that are measured to greater precision or with less uncertainty. Statistical criteria to evaluate the goodness of fit should account for any weighting of fits to the data. Weighting should be used as a tool to reflect the uncertainty associated with each data point. However, weighting should not be performed merely to change the fit, when the weighting is not reflected in the uncertainty of the data.' Subsequently at p. 72, FOCUS (2006) states: 'Under field conditions, pesticide degradation is influenced by a large number of environmental factors, which are spatially variable at a small scale. It is not clear whether differences between individual points within the field increase or decrease as time progresses. Therefore, establishing general rules for weighting fits of kinetics to field data is difficult so the use of unweighted fits to untransformed data is recommended as a first step. Alternative methods can be applied if a satisfactory fit cannot be achieved.'' We do not agree with this recommendation if there are large differences (e.g. more than a factor three) between the variability in residues from sampling time to sampling time. In such a case we recommend to give each average areic mass a weight that is inversely proportional to its standard deviation.

4.3.5 Procedure for estimating the *DegT50* in case of too few sampling times or too few sampling spots

In many field experiments as reported in dossiers, there is only one bulked soil sample available for each sampling time and therefore the uncertainty in the remaining fraction is unknown. To explore the resulting consequences for the uncertainty in the *DegT50* values, Monte Carlo simulations were carried out on the relationship between the standard error of the *DegT50* and the number of sampling times and the number of soil samples (see Annex 5). The results show that the number of soil samples at each sampling time becomes a critical factor when this number decreases below 10.

FOCUS (2006, p. 68) suggests also a minimum of five sampling times but uses this not as a strict criterion. The results in Annex 5 indicate that for five sampling times and 20 soil samples, the standard error in the *DegT50* is about 20%. This seems a comparatively small uncertainty. Moreover this has been so far more or less the standard approach for performing such experiments. Therefore we propose as a pragmatic rule that the accuracy of the *DegT50* is acceptable if it is based on at least five sampling times and 20 soil samples per sampling time. This is also in line with the recommendations by Jones as cited by NAFTA (2006).

If these criteria are not met, we recommend that the resulting *DegT50* value is labelled as potentially unreliable and that this label is considered when determining the geomean *DegT50* endpoint used for the leaching assessment using the flow chart of Figure 17. If the resulting *DegT50* is longer than the geomean endpoint (including this *DegT50* in the calculation of this geomean endpoint), then this endpoint is conservative so can be used (box 2). However, if the *DegT50* is shorter than the geomean endpoint, then there are two options: (i) eliminate the *DegT50* from the population of *DegT50* values and recalculate this geomean (box 5), or (ii) assess the uncertainty of this *DegT50* in more detail (box 6). If after performing the activities in the boxes 4, 5 or 6, the leaching concentration is acceptable (box 7) then the leaching assessment can stop. If not, the notifier can consider further actions (e.g. carry out field experiments with adequate numbers of soil samples or remaining sampling times (box 8). Please note that the number of sampling times should be based on the remaining sampling times used for the *DegT50*; so e.g. sampling times that have to be discarded following the guidance of EFSA (2014) should not be taken into account when determining this number.

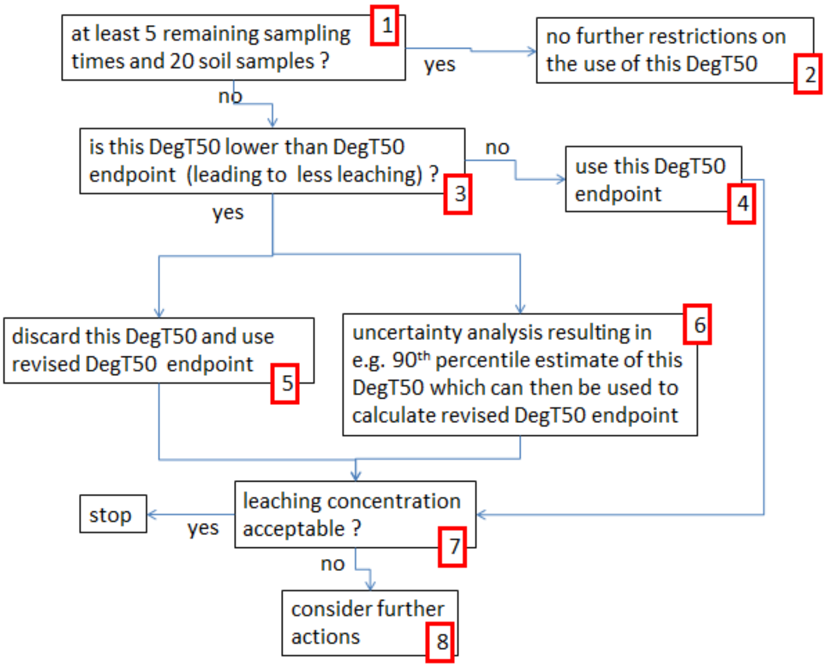

Figure 17 *Flow chart for the assessment of the DegT50 in case this is based on too few sampling points or sampling times.*

This uncertainty assessment could be based on a statistical analysis of the accuracy of the *DegT50* value (following a procedure similar to Annex 5 and based on the actual number of soil samples, the actual sampling times in the field experiment, the actual estimated *DegT50* and a CV of individual soil samples of 110% assuming a lognormal distribution). On the basis of this, e.g. the 90th percentile of the *DegT50* could be calculated and used as the endpoint of the field persistence study in the further risk assessment. It may be useful to develop standard software for this. It is important that in this statistical analysis of the accuracy of the *DegT50* exactly the same procedure is followed for estimating the 90th percentile as was done for estimating the *DegT50* (so if unweigthed fractions were used for estimating the *DegT50*, then also unweighted fractions should be used for the accuracy analysis). The justification for this procedure is that this more conservative and laborious approach is only needed if the notifier has provided less samplings than is generally considered acceptable.

Please note that, in the case of a metabolite, the proposed procedure implies that the measurements used in the evaluation start after some time after application; so the initial areic mass of the metabolite will usually not be zero. Thus this initial areic mass becomes then also a fitting parameter. This will also usually be the case for parent substances because it is unlikely that enough rain falls between application and first sampling to satisfy the penetration-depth criterion of Eqn 1.

4.4 Estimation of *DegT50* for substances whose *DegT50* depends on other soil properties than soil temperature, soil moisture or soil depth

In Tier 2 of the Dutch decision tree, calculations have to be made with the GeoPEARL model. This model offers the option that the *DegT50* of the substance for top soil at 20 °C and pF = 2 is a linear function of the mass fractions of organic matter, clay and the pH (see Eqn 62 of Tiktak *et al.*, 2004). If there is evidence that the *DegT50* is related to clay, organic matter or pH, we recommend to perform a linear regression analysis using this equation to estimate these GeoPEARL input parameters. Eqn 62 of Tiktak *et al.* (2004) reads:

$$DegT50_{plot} = DegT50_r + f_{om}(m_{om} - m_{om,r}) + f_{clay}(m_{clay} - m_{clay,r}) + f_{pH}(pH - pH_r) \quad (43)$$

where:
$DegT50_{plot}$ (d) is the half-life of the pesticide in the top soil of a plot in GeoPEARL at 20 °C and pF = 2,
f_{om} (d), f_{clay} (d) and f_{pH} (d) are factors for the effect of organic matter, clay and pH,
m_{om} (kg kg^{-1}) and m_{clay} (kg kg^{-1}) are the mass fraction of organic matter and clay.
The suffix *r* refers to the conditions for a reference soil that can be arbitrarily defined.

When using Eqn 43 it is important that the *DegT50* input value is consistent with the pH measurement method of the soil scenario that is used for the calculation (similar to the procedure used for estimating a pH dependent K_{om} in Section 3.6). So for GeoPEARL calculations for the Netherlands, the pH in Eqn 43 has to be the pH_{KCL}.

There is the additional specification in this Eqn 62 that if $DegT50_{plot}$ is calculated to be less than a user-specified minimum value $DegT50_{min}$ then $DegT50_{plot}$ = $DegT50_{min}$ and similarly that if $DegT50_{plot}$ is calculated to be higher than a user-specified maximum value $DegT50_{max}$ then $DegT50_{plot}$ = $DegT50_{max}$. The minimum and maximum values are added to prevent the calculation of unrealistic (zero or negative) *DegT50* values for soils with extreme properties.

If a notifier wishes to limit the assessment to Tier-1 calculations, these must be performed by estimating the highest possible *DegT50* for Dutch soils from Eqn 43 based on the probability densities of the independent variables as presented in Section 5.6. This highest possible *DegT50* may have to be derived from Monte-Carlo simulations using these probability densities and Eqn 43.

The pH dependency of sorption may be accompanied by pH dependency of transformation of the substance (e.g. mesotrione). Because the type of relationship of degradation with pH is unknown on beforehand, it is recommended to select test soils for degradation experiments in a relevant pH range in relation to relevant crops for the active substance under consideration.

4.5 Calculation of endpoints of model input parameters related to degradation in soil

With respect to *DegT50* values, the base line for the tiered Dutch leaching assessment is that the *DegT50* is independent of soil properties other than soil temperature, moisture and depth. If this is the case, the estimation of the *DegT50* is the same for Tier 1 and Tier 2. If this is not true, then in Tier 1 a conservative estimate of the *DegT50* is needed because Tier 1 considers only the Kremsmünster soil profile whose selection was based on the assumption that the *DegT50* is independent of soil properties. Section 4.4 describes the estimation procedures for the *DegT50* if it depends on soil properties. In the sections below we propose procedures for the case where the *DegT50* is independent of soil properties other than soil temperature, moisture and depth.

For half-lives we recommend calculating the individual *DegT50* values using the flow chart of FOCUS (2006, p. 114). We recommend calculating the endpoint *DegT50* from the geomean of all accepted values (FOCUS, 2006, p. 235). For formation fractions we recommend to use the arithmetic average of all accepted values (FOCUS, 2006, p. 235).

When the standard deviation of the natural logarithms of the *DegT50* values is smaller than 0.2 or larger than 0.6 the set of *DegT50* values should be evaluated more critically, e.g. via an expert opinion. The range of 0.18 to 0.58 is based on values of laboratory measurements and field studies summarized in Table 2 of EFSA (2010a). An example of a dataset of *DegT50* values with a standard deviation smaller than 0.18 is mecoprop with a standard deviation of Ln(*DegT50*) of 0.09 as described by Van der Linden *et al.* (2015).

An Excel workbook consisting of a series of spreadsheets has been developed to assist in deriving the *DegT50* endpoint for leaching assessments. Based on information directly obtained from the description and the results of the experiment, the spreadsheets calculate estimates of the *DegT50* (conservative where appropriate). An ap-to-date workbook can be downloaded from www.ctgb.nl as soon as the methodology is implemented.

5 Guidance proposals on further aspects of the leaching assessment

5.1 Leaching assessment for potato fields with ridges and furrows

Studies with PPP leaching in Dutch ridged potato fields for granules incorporated before the ridge-furrow formation and for a spray application after the ridge-furrow formation have shown that leaching for such tillage systems may be considerably higher than leaching in tillage systems with a level surfaces (Smelt *et al.*, 1981; Leistra and Boesten, 2010) because there is more downward water flow below the furrows than below the ridges and because substance may runoff from the ridges into the furrows. However if the substance is e.g. incorporated in the ridge the leaching may be lower than for systems with a level surface (see Hammel & Schröder, 2014). This implies that the current Dutch leaching assessment based on PEARL and GeoPEARL scenarios for level soils may either be too conservative or not conservative enough depending on the application method of the pesticide.

Figure 18 shows a schematic representation of the ridge-furrow system for Dutch potatoes. This scheme is based on the convention to define the level of the soil surface in a furrow-ridge system as the hypothetical plane that corresponds with the soil level that existed before this system was formed. We call this the ‘zero level’ (indicated as the zero level in Figure 18). In the Netherlands it is common practice to place the seed potato with its top just (so say 1 cm) below this zero level for clayey soils and 2 to 3 cm deeper on sandy soils (see Figure 38 of van der Zaag, 1992, and p. 36 of Veerman, 2003). Let us assume that the seed potato has a diameter of 5 cm and that its top is at 2.5 cm below the zero level; then its centre is 5 cm below the zero level (as is shown in Figure 18).

Table 5.1 lists the current pesticide applications in Dutch potatoes and their expected leaching when compared with the type of application that Ctgb currently uses as a proxy for calculations with PEARL or GeoPEARL (so considering a tillage system with a level surface). The basis of the assessment of the expected leaching was that the effect of the excess of water on the leaching concentrations is expected to be strongly non-linear (e.g. Leistra, 1985).

The results of the assessment in Table 12 show that of the ten application types two have more expected leaching and four have less expected leaching and for the remaining four application types the leaching is expected to be the same. This shows that for potatoes the application method has a very large effect on the leaching assessment.

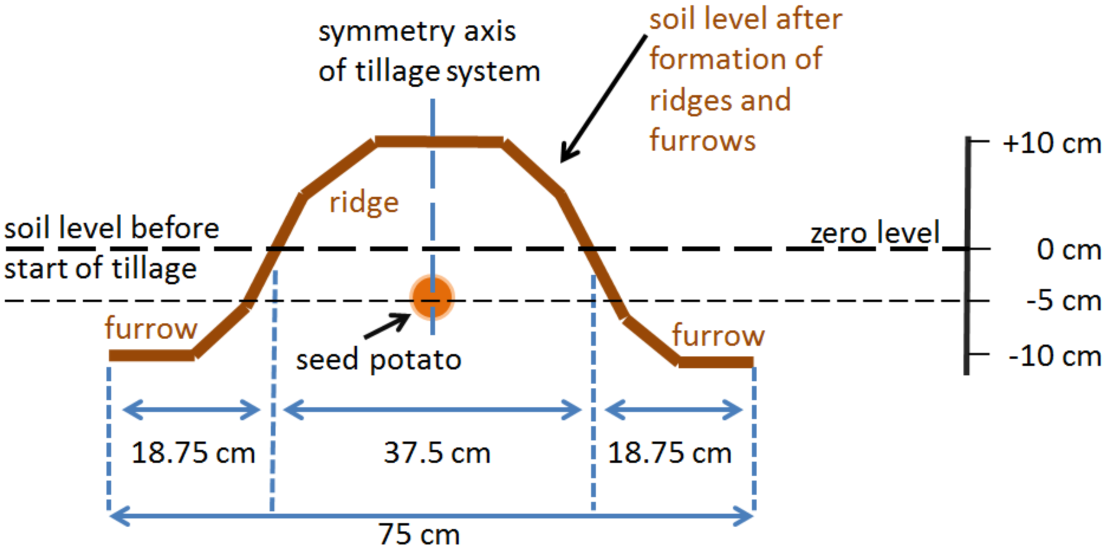

Figure 18 *Schematic representation of the potato tillage system as practised in the Netherlands. The scheme assumes that the whole field is build up of such units (so assuming that potatoes are planted at a distance of 75 cm). So only half the width of each furrow is shown.*

Table 12

Different application types of pesticides in Dutch potatoes and their effect on the leaching compared with the leaching expected when using PEARL or GeoPEARL assuming a tillage system with a level soil surface. The expectation is based on expert judgement as indicated by the argumentation in the last column. The depths indicated are based on the hypothetical level of the soil surface as indicated by the zero-level in Figure 18.

Application type	Timing	Further application details	Application method used in PEARL or GeoPEARL	More or less leaching than expected when using PEARL or GeoPEARL
Injection of soil fumigants without subsequent plastic cover	Months before setting		Injection at the injection depth	No effect because soil fumigants have dissipated before ridge-furrow formation
Injection of soil fumigants with subsequent plastic cover	Months before setting	Plastic cover is present several weeks after application	Injection at the injection depth	No effect because soil fumigants have dissipated before ridge-furrow formation and plastic cover has opposite effects on leaching: less infiltration of water (less leaching) and less volatilisation (more leaching)
Incorporation of granules over whole surface of the field	Day(s) before the ridge-furrow formation or on same day (but before ridge-furrow formation)	Usually incorporated to a depth of -20 cm	Incorporation to the incorporation depth	More leaching because a significant part of the substance is below the furrow during the growing season
Pre-emergence spray before ridge-furrow formation	Week(s) before the ridge-furrow formation		Spraying onto bare soil	A little bit less leaching because most of the pesticide is found back in the ridge after the ridge-furrow formation

Application type	Timing	Further application details	Application method used in PEARL or GeoPEARL	More or less leaching than expected when using PEARL or GeoPEARL
Treatment of seed potato with powder	Before setting		Injection at the depth of the centre of the potato	Less leaching because of less downward water movement in the ridge
Spray in trench made for setting of seed potato or put granules in this trench	At setting time	Similar to next application method but with the difference that application is over full length of the trench before the potato is set	Injection at the depth of the centre of the potato	Less leaching because of less downward water movement in the ridge
Spray in setting hole	At setting time	First spray in hole, set potato and then overspray potato in hole	Injection at the depth of the centre of the potato	Less leaching because of less downward water movement in the ridge
Pre-emergence spray after ridge-furrow formation	Week(s) after ridge-furrow formation		Spray application to the soil surface	More leaching because part of the substance is sprayed in the furrow plus part of the substance sprayed on the ridge will runoff to the furrow
Overspray of crop	June-July	Mostly weekly applications of fungicides	Spray application to the soil surface with interception specified by user	No effect because of complex counteracting factors: stem flow of rain water reduces leaching but wash off of substance into furrow may increase leaching
Overspray intended to kill the leaves/crop	One week before harvest of seed potatoes	At harvest the soil is grubbed in such a way that the soil surface becomes level again	Incorporation over 20 cm depth at time of overspray	No effect because the reality corresponds well with the assumed application

The above considerations are limited to ridge-furrow systems for potatoes. The dimensions of the ridge-furrow system for e.g. asparagus are different from those of the potato system (asparagus has much larger ridges and the soil is also covered with plastic for several months). Providing recommendations for other systems than potatoes was not possible in the time frame of this project.

5.2 Guidance for assessment of metabolites resulting from soil photolysis

Plant protection products may be sprayed onto bare soil. As long as little rain falls, the substance is concentrated in the top millimetres of soil. This may last for several weeks in spring in the Netherlands. So in principle there is a few weeks available for photodegradation. It seems therefore relevant to assess the leaching of soil photometabolites to groundwater. This assessment of leaching of soil photometabolites has to take place at the level of the first tier of the leaching assessment. We recommend to revise the leaching flow chart of Ctgb (2014; Annex 1) to include this point.

In the dossier there is always one soil photolysis study available (OECD, 2002). This OECD guideline recommends to perform such a study with only one soil type (see point 23 of this guideline) so usually only one study will be available. If this shows amounts of metabolites corresponding to formation fractions above 10% (this 10% is based on Annex II/III of the EU regulation) then we recommend the following procedure for each metabolite that exceeds this 10% limit:
- estimate formation fraction from soil photolysis experiment
- perform measurements of sorption and degradation properties
- perform measurements of water solubility, saturated vapour pressure and if relevant the pK_a

- perform leaching calculations in which the total amount of metabolite formed is assumed to be applied to the soil surface as a parent substance
- as a higher tier, calculations could be made with leaching models that include soil photolysis in the top millimetres of soil as a separate process.

In the current EU procedure there is one additional trigger for photometabolites that do not exceed this 10%. If such a photometabolite is also formed under dark conditions, the metabolite is also considered in the groundwater risk assessment if (a) the metabolite, at least two sequential time points, accounts for more than 5% of the amount of active substance added, of if (b) at the end of the study the content of the photometabolite is still increasing.

The European Commission (2003) wrote in the guidance document on the relevance of metabolites for groundwater, an instruction (on p. 6) stating that, as a minimum, degradation products must be characterised and identified by the notifiers to the extent that is technically feasible and their relevance must be assessed, if one of the following conditions applies:

a. metabolites, which account for more than 10% of the amount of active substance added in soil at any time during the studies (soil metabolism/degradation or soil photolysis studies); or
b. which account for more than 5% of the amount of active substance added in soil in at least two sequential measurements during the soil metabolism/degradation studies; or
c. for which at the end of soil metabolism/degradation studies the maximum of formation is not yet reached.

The 10% trigger for soil photometabolites is based on risk management considerations. If 10% of a PPP dose of 1 kg/ha would leach to groundwater, this will result in groundwater concentrations in the order of 10 μg/L (Boesten and Van der Linden, 1991). So this 10% trigger does not lead to protection of groundwater at a level of 0.1 μg/L.

Plant protection products on plant surfaces may also be transformed and plant photometabolites may reach the soil via wash-off. At present these plant photometabolites are no subject of the fate and behaviour assessment. The Annexes II/III of the EU regulation do not require additional fate data for photometabolites on plant surfaces based on Annex II point 6.1. Thus a risk assessment of leaching of plant photolysis metabolites is impossible based on the EU regulation.

5.3 Clarification of criteria on the applicability of Tier 1 in the Dutch leaching assessment

Van der Linden *et al.* (2004) described the tiered approach for leaching to groundwater as is currently used in Dutch registration. Tier 1 consists of calculations with the FOCUS Kremsmünster scenario and Tier 2 of GeoPEARL calculations. As described in Section 2.3.1 of Van der Linden *et al.* (2004), there are a number of restrictions with respect to the use of Tier 1. The text in this Section 2.3.1 has appeared to be confusing in a number of cases in regulatory practice.

Therefore we give below a new description of these restrictions.

A. Skip Tier 1 and start immediately with Tier 2 if one of the following statements is true:
1. the vapour pressure of the PPP is at 20 °C higher than 10^{-4} Pa and it is injected or incorporated into the soil,
2. the geometric mean *DegT50* under reference conditions is shorter than ten days and the geomean K_{om} is smaller than 10 L/kg.

B. Use a conservative estimate of the K_{om} in the Tier-1 calculations if the K_{om} does depend on soil properties (other soil properties include pH, sand, silt or clay content, sesqui-oxide content).

C. Use a conservative estimate of the *DegT50* in the Tier-1 calculations if the *DegT50* does depend on soil properties other than moisture, temperature or soil depth (other soil properties may include pH, clay content, organic matter).

By performing a number of simulations for a few substances, a few application times and all crops associated with the Kremsmünster location, it was found that leaching concentrations calculated for different crops did not differ very much from each other and that highest leaching concentrations were for winter wheat (E. Smit, 2009, personal communication). Therefore, winter wheat was chosen to obtain conservative leaching estimates when the crop does not occur in the Kremsmünster crop list. If the crop does occur in this crop list, the recommendation is to base the Tier-1 calculation on a Kremsmünster calculation with this crop.

In Tier-2 calculations with GeoPEARL it is possible to include dependencies of the sorption coefficient to other soil properties than organic matter and dependencies of the *DegT50* to soil properties (see Sections 3.6 and 3.7 for guidance on the parameterisation of the sorption coefficient in GeoPEARL and Section 4.4 for guidance for the parameterisation of the *DegT50* in GeoPEARL).

5.4 Criteria for properties of soils to be used for sorption and degradation studies

Risk assessment procedures on fate and exposure of PPP in general require that sorption and degradation parameters are obtained from experimental studies with top soils, i.e. soils from the plough layer or down to the depth of maximally 25 cm of agricultural soils. In the current assessment procedures at both the European and Dutch national level, vulnerability to leaching is entirely attributed to the scenarios, so central values should be used when performing leaching calculations. As stated in previous chapters, the geometric mean of the *DegT50* values and the K_{om} values are used in the assessments when the transformation and sorption processes are not dependent on soil properties.

An implicit requirement is that the individual *DegT50* and K_{om} values are obtained in experiments with soils that are collectively considered representative of the area for which the assessment is performed. With regard to the Netherlands, this would mean that values from experiments with tropical and volcanic soils should be excluded when calculating the central values. Values obtained from experiments with soils from temperate regions in general are acceptable as long as soil properties are not extreme.

Models that are currently used for leaching assessments need as input *DegT50* and K_{om} values, which are standardised to reference conditions. Sorption and degradation constants derived from experiments with sub-soils should not be used to estimate reference values for sorption and degradation in top-soils. Values derived from experiments with soils from deeper layers, however, may be used for deriving appropriate depth-dependency relationships.

OECD guideline 307 (OECD, 2002b) recommends to perform experiments with soils representative of the area of use of a substance whereas OECD guideline 106 (OECD, 2000) gives recommended ranges for clay content, organic carbon and pH_{CaCl2} (see Table 13 for these ranges).

For sorption studies it is required that the organic matter content of the soil used is > 0.5% or > 0.3% OC, because lower organic matter contents are considered not representative for Dutch agricultural soils.

As leaching calculations for the evaluation of PPP in the second tier are performed with GeoPEARL, one option would be to set acceptability criteria with respect to soil properties based on ranges of soil characteristics as included in the 456 soil profiles in the GeoPEARL database. However, we consider this database not suitable for this purpose because the properties of these soil profiles are averages of a large number of soil profiles. Therefore the true range of the values in Dutch agriculture is expected to be considerably wider than the range in this database.

Reijneveld *et al.* (2009) reported averages and standard deviations of properties of samples of arable soils (excluding maize) taken in four regions in the Netherlands (at least 160 samples per region). The results in Table 14 indicate that the clay content may range from <8% to >32% and that organic matter content may range from < 1% to > 15% (Reijneveld *et al.*) show for the second region that the frequency distribution of organic carbon differs systematically from a normal distribution so the estimation of ranges from the given average and standard deviations is not straightforward). These are very wide ranges whereas these regions cover not all arable land in the Netherlands. So based on the available information it does seem not meaningful to prescribe restrictions that go further than the wide ranges shown in Table 13.

Table 13
Ranges of soil properties for sorption studies as described by OECD (2000; their Table 1).

Soil type	**pH (in 0.01 M $CaCl_2$)**	**Organic carbon content (%)**	**Clay content (%)**	**Soil texture**
1	4.5-5.5	1.0-2.0	65-80	clay
2	>7.5	3.5-5.0	20-40	clay loam
3	5.5-7.0	1.5-3.0	15-25	silt loam
4	4.0-5.5	3.0-4.0	15-30	loam
5	<4.0-6.0	<0.5-1.5	<10-15	loamy sand
6	>7.0	<0.5-1.0	40-65	clay loam / clay
7	<4.5	>10	<10	sand / loamy sand

Table 14
Properties of arable soils in four regions of the Netherlands taken from Reijneveld et al. (2009). Values shown are averages and standard deviations (±) of the population of four regions (defined by zip codes). Numbers of samples per region ranged in 1984/1985 from 682 to 3277, in 1999/2000 from 165 to 1541 and were at least 160 in 2003. Organic matter was calculated by multiplying organic carbon with 1.724. The pH_{KCl} was based on a KCl concentration of 1 mol/L. Arable land was defined as land where potatoes, sugar beets, cereals or flower bulbs were grown (so excluding maize).

Regions in the Netherlands		**Sampling years**	**Clay (%)**	**pH_{KCl}**	**Organic carbon (g/kg)**	**Organic matter (%)**
Description	**Zip codes**					
Marine clay, south-west	32, 43-46	1984/1985			13	
		1999/2000			12	
		2003	20 ± 7	7.4 ± 0.3	13 ± 6	2.2 ± 1.0
Marine clay, west-central	11, 13, 38, 82, 83	1984/1985			20	
		1999/2000			23	
		2003	22 ± 10	7.4 ± 0.2	17 ± 9	2.9 ± 1.6
Reclaimed peat, north-east	78, 94-96	1984/1985			63	
		1999/2000			64	
		2003	<8	4.9 ± 0.3	59 ± 29	10.2 ± 5.0
Loess, south	61-64	1984/1985			14	
		1999/2000			14	
		2003	14 ± 2	6.6 ± 0.6	14 ± 4	2.4 ± 0.7

5.5 Use restrictions of the 2004 decision tree

Van der Linden *et al.* (2004) described the Dutch decision tree for leaching to groundwater but did not indicate the domain of the tree. However, this tree was developed for normal uses on arable crops, permanent crops and grassland. So the tree does e.g. not include the following uses:

1. on hard surfaces;
2. artificial lawns;
3. in public green;
4. on covered crops (see EFSA, 2010b, for definition of covered crops);
5. in mushrooms grown inside;
6. on railway tracks;
7. under crash barriers or road signs.

5.6 Developments with respect to GeoPEARL

The core of Tier 2 of the decision tree is the leaching simulations with GeoPEARL. Since the release of the currently approved version several developments have taken place, both with regard to underlying (map) information and model development. It is recommended that a new GeoPEARL package is released, with up-to-date information and models.

It has been noted that the organic matter map contained in the current GeoPEARL package may overestimate organic matter contents in arable soils and underestimate these in grassland soils, in certain areas in the Netherlands. A new organic matter map has been established, based on a better separation of arable and grassland soils.

GeoPEARL 3.3.3 uses SWAP version 2.0.9.f (Van Dam *et al.* 1997). Later versions have become available (see for example Kroes *et al.* 2008), with additional options and improved descriptions of, amongst other, preferential flow. It is expected that calculated leaching concentrations will only slightly change when a newer version of SWAP is used and the option of preferential flow is switched off.

We suggest that, when the new package is released, it contains the Substances Plug-in (SPIN), so that risk assessors and other users do not have to enter substance parameters for the GeoPEARL package separately.

As described by van der Linden *et al.* (2015), GeoPEARL is not suitable for simulating wash off from plant surfaces because it is hydrologically based on only three crops (maize, potatoes and grass). So GeoPEARL does not simulate the wash off realistically. Therefore we recommend to improve the simulation of wash off from plant surfaces in GeoPEARL.

6 Consequences for existing guidance

The proposed guidance in Chapter 3 is likely to lead to sorption parameters that differ often from those that would be obtained following the current EU guidance (which is consolidated in Anonymous, 2011). The proposed guidance will for parent substances often lead to weaker sorption and therefore result in higher leaching concentrations.

Section 4.3 provides guidance on deriving *DegT50* values from field persistence studies on a number of detailed aspects that have not been considered so far in the FOCUS and EFSA workgroups. These are likely to lead to longer *DegT50* values and therefore to higher leaching concentrations.

Section 4.4 provides higher-tier guidance for substances with very specific degradation properties which is unlikely to cause conflicts with other guidance.

Implementation of this proposed guidance will also require a revision of the Dutch assessment scheme for leaching to groundwater as described by Van der Linden *et al.* (2004) because: (i) we recommend to include soil photometabolites in the first tier of the assessment scheme (Section 5.2), and (ii) we described new criteria for Tier 1 (see Section 5.3).

Including photometabolites in the first tier will lead to a more conservative assessment. However, this procedure is already being used at the EU level (W. Pol, personal communication, 2011). The new criteria for Tier 1 are a clarification of the old criteria and have therefore no consequences (except the need for updating the Dutch assessment scheme). The new guidance for crop interception and wash-off (EFSA, 2014b) will lead to higher leaching concentrations.

7 Conclusions and recommendations

7.1 Conclusions

Analysis of the available monitoring data in Dutch groundwater showed that bentazone, MCPA and mecoprop were the only parent substances that (i) were found in more than one drinking water abstraction area and (ii) have still a registration in the Netherlands. Therefore these were selected to test the current Dutch leaching assessment. These substances are all weak acids whose sorption is comparatively weak and a function of the pH.

The original intention of this report was to evaluate the Dutch decision tree on leaching by applying the tree to these three substances. However, while working on this evaluation it appeared that parts of the existing guidance (both at NL and EU level) were not clear or complete enough or not state-of-the-art scientifically. Therefore guidance proposals were developed to revise these parts.

The proposals focus on improvement of the guidance for deriving substance input parameters because they are based on application of the decision tree to these three substances. Using this improved guidance will in general lead to higher estimates of leaching especially for weakly sorbing substances such as the ones to be used for the evaluation of the decision tree.

The procedure currently used to assess the systematic error of the sorption coefficient in the Dutch leaching assessment needs to be revised because the original procedure is based on the true value of the sorption coefficient. This is inconsistent with the use of the procedure for assessment of dossiers which contain only measured values. Therefore a revised procedure was developed that is based on measured values. Further analysis based on this revised procedure showed that following the indirect method of the OECD-106 guideline does not exclude that the sorption coefficient is overestimated by 100%. Such an overestimation would lead to a strong underestimation of leaching.

The development of guidance to assess the sorption of weak acids whose sorption is a function of the pH showed that this guidance has to be based on a decision flow chart in view of its complexity. Furthermore, it appeared that pH values in dossiers are based on three different measurement methods (measurements in distilled water, in 0.01 mol/L $CaCl_2$ and in 1 mol/L KCl). After collecting all available data we were able to establish linear relationships between the pH values measured with these different methods.

The available guidance for estimating the total amount of substance in soil in field persistence studies appeared to be not sufficiently detailed especially if a significant fraction of the substance is present in more than one sampled layer.

The current Dutch leaching assessment procedure does not cover all substances that potentially reach the soil. There are no data requirements for identification of degradation products of plant protection products formed on plant surfaces due to photolysis at EU level. So their leaching assessment is impossible within the current regulatory framework. Such data requirements exist for soil photometabolites. However, their leaching is not assessed in the current Dutch decision tree for leaching.

The current procedure for assessment of leaching in ridged potato tillage systems is not defensible; it may either overestimate or underestimate this leaching depending on the application method.

7.2 Recommendations

7.2.1 Guidance recommendations for immediate use

To avoid systematic overestimation of the sorption coefficient via the indirect method, we recommend to correct measured sorption coefficients based on the measured recovered amount at the end of the study and to consider the corrected sorption coefficients as lower limits of the true sorption coefficient. If this correction lowers the sorption coefficient to zero, we recommend to perform soil column studies to assess the sorption coefficient.

For assessment of leaching of parent substances, we recommend setting sorption coefficients to zero if the product of the measured sorption coefficient and solid-liquid ratio is smaller than 0.1 because the random error in the sorption coefficient becomes very large for such systems.

We recommend to consider an N value reliable only if it is based on at least three initial concentrations with at least a factor of 100 between highest and lowest concentration and if the correction of the sorption coefficient based on the measured recovered amount at the end of the study is smaller than 20%.

When evaluating the sorption of a weakly acidic substances, we recommend to calculate all measured pH values back to the measurement method of the pH that was used to derive the soil scenario (to avoid inconsistencies between pH measurement methods). For the Dutch leaching assessment this is the pH measured in 1 mol/L KCl. If the measurement method of a pH in a dossier is unknown, we recommend to assume measurement in water as the default measurement method.

We recommend that a fit of the K_{om} - pH relationship of weak acids is only carried out if at least four pairs of measurements of K_{om} and pH are available and if the range of pH values is at least 3.

7.2.2 Recommendations for further guidance development

The K_{om} is an important input parameter for the leaching calculations. The geomean value of all reliable and relevant values (usually at least four values) has to be used for these calculations. For weakly sorbing substances the selection of relevant K_{om} measurements from all available data in the dossier is so complicated that it requires expert judgement. In view of the importance of this parameter for the leaching assessment we recommend (i) analysing the K_{om} data in some ten dossiers in detail, and (ii) developing from this analysis further guidance that eliminates the need of expert judgement as much as possible.

The fitting procedure for describing the relationship between K_{om} and pH requires a software package capable of fitting non-linear functions to data. Several packages, including the package used for the calculations in this report, are capable of this. It is however recommended to develop dedicated software (e.g. programmed in R), that can also convert the pH values and indicate converted values in a graph. This software should become publicly available.

In the past, an initial quality check of a sorption study was performed using Tables 5-2 and 5-3 of Mensink *et al.* (2008). We recommend to develop revised versions of these tables that are consistent with the proposals in this report.

Detailed guidance is proposed for estimating the total amount in the soil profile from concentration profiles (as part of field persistence studies to estimate the *DegT50* in soil). We recommend testing and improving the guidance proposal by applying it to a number of datasets.

Field studies with ridged potato fields have shown that leaching for full-field spray applications in such tillage systems may be considerably higher than for applications to crops grown on flat surfaces. Our interpretation of these studies indicates that the application method determines whether the expected leaching for this ridged system is larger or smaller than for the flat system. Moreover, we identified ten different application methods for pesticides in Dutch potatoes. We recommend to develop specific guidance for the assessment of the leaching for such ridged tillage systems.

We recommend including in a future GeoPEARL version the option to provide frequency distributions of organic matter, pH and clay content for the area of the crop considered in the leaching assessment. We recommend also to establish a list of parameters describing the frequency distributions of the mass fractions of organic matter, sand, silt, clay and of the content of sesqui-oxides for the areas of all crops used in GeoPEARL.

We recommend to include the evaluation of the leaching of soil photometabolites in the Dutch decision tree for leaching to groundwater.

7.2.3 Recommendations for further research

The recommendation to set sorption coefficients to zero if the product of the measured sorption coefficient and solid-liquid ratio is smaller than 0.1 is not based on statistical analyses. Therefore we recommend to underpin or modify this criterion on the basis of statistical analyses of the random errors in available batch sorption studies.

The Freundlich sorption exponent is a major factor influencing the calculated leaching concentrations. We recommend developing procedures for evaluating measured Freundlich exponents and performing thereafter a statistical analysis of all reliable measurements of the Freundlich exponent to test whether this exponent is a substance property.

The advice on the assessment of the reliability of the Freundlich exponent N is based on expert judgement. Therefore we recommend to perform further research to underpin or revise this advice.

In view of the inappropriateness of the current leaching assessment for application of pesticides in ridged potato tillage systems, we recommend to develop an adequate leaching assessment methodology for these systems. This will have to include simulations with a two-dimensional model because the ridged tillage system cannot be represented realistically with one-dimensional models.

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Abbreviations

Ctgb	Acronym for Dutch pesticide registration authority
CV	Coefficient of Variation
EC	European Commission
EFSA	European Food Safety Authority
EU	European Union
ISO	International Standards Organisation
FOCUS	FOrum for the Co-ordination of the USe of models in regulatory exposure assessments
HPLC	High-Pressure Liquid Chromatography
LOD	Limit Of Determination
LOQ	Limit of Quantification
MACRO	Acronym for model simulating pesticide behaviour in soil including macropore flow
OECD	Organisation of Economic Co-operation and Development
PEARL	Acronym for model simulating pesticide behaviour in soil
PEC	Predicted Environmental Concentration
PPP	Plant Protection Product
PRAPeR	Former unit of EFSA responsible for review of risk assessments of pesticides at EU level
PRZM	Acronym for model simulating pesticide behaviour in soil
Q10	Factor describing the increase of the degradation rate coefficient in soil for a temperature increase of 10^{o}C
QSAR	Quantitative Structure-Activity Relationship
REWAB	Database of Dutch drinking water companies containing measurements of pesticides in water pumped up for drinking water consumption
SCP	Scientific Committee on Plants
SE	Simulation Error
TLC	Thin Layer Chromatography
USES	Uniform System for the Evaluation of Substances
Vewin	Dutch association of companies producing drinking water
WFD	Water Framework Directive

Annex 1 Active ingredients found in raw water of groundwater abstractions

Table A1.1 presents some details on the active ingredients labeled as substances with leaching concerns in this study, of which the overview is given in Table 1 (Chapter 2).

Table A1.2 presents the compounds that were selected from the REWAB database, but are not considered as substances with leaching concerns in this study. Some details on the measurements and the rationale for not considering them as a substance with leaching concerns are given in the table for each compound. Two criteria were checked: (1) is the compound an active ingredient of plant protection product and (2) is the substance found more than once found at concentrations above 0.1 µg/L at a certain location. Compounds that are not listed in Tomlin (2003) or in the Ctgb database are not considered active ingredients of plant protection products.

Table A1.1
Some details on active ingredients labeled as substances with leaching concerns in this study.

Compound	**Abstractions in which standard is exceeded**	**Some details on number of exceedings *(n)* when occurring at one abstraction**
bentazone	Ten abstractions	
bromacil	Six abstractions	
chlorbromuron	Boerhaar	max 0.14 µg/L, *n* = 4, 1995
dichlobenil	Lith	max 0.23 µg/L, *n* = 4, 1993
dichlorprop (2,4-DP)	Hengelo (Overijssel)	max 0.12 µg/L, *n* = 12, 1992
dikegulac-sodium	Leersum	max 0.21 µg/L, *n* =3, 1995/1996/1998
	Groenekan	max 0.43 µg/L, *n* = 9, 1995/1996/ 1998-2004
diuron	Bilthoven	max 0.13 µg/L, *n* = 9, 1999
DNOC (2-methyl-4,6-dinitrofenol)	Bergen	max 0.15 µg/L, *n* = 4, 2002
ethylenethiourea (ETU)	Noordwijk	Six records instead of one in file for 1991, giving different concentrations. min 0.2 µg/L
MCPA	Almelo-Wierden	*n* > 10, 1997
(4-chloro-2-methylphenoxy acetic acid)	Hengelo (Overijssel)	*n* > 10, 1999
mecoprop (MCPP)	Four abstractions	
metobromuron	Zutphen - Vierakker	max 0.12 µg/L, *n* = 6, 1998
metoxuron	Espelo	max 0.19 µg/L, *n* =19, 2000

Table A1.2

Active ingredients not labeled as a substance with leaching concerns in this study with some details on the REWAB data, and why a compound is not considered a substance with leaching concern.

Compound	Abstractions in which standard is exceeded	Why not a substances with leaching concern?
1,2-dichloropropane	Ten abstractions	From 1 January 2003 onwards 1,2-dichloropropane is not considered as a plant protection product. It is not an active ingredient, but a byproduct. Its standard is 1.0 µg/L (MNP, 2006)
1-(3,4-dichlorophenyl)urea	Vessem, 2001 0.11 µg/L, *n* =1 Beegden, 2001 0.17 µg/L, *n* =1	No active ingredient
1-(4-isopropylphenyl)urea	Vierlingsbeek, 2001	No active ingredient
2-chloroaniline	De Steeg, 2003 and 2004 max 0.27 µg/L	No active ingredient
2-nitrophenol	Eindhoven, Aalsterweg 2003	No active ingredient
2,4-dinitrophenol	Witharen, 1997 max 0.12 µg/L, *n* = 12 Holten, 1995 max 0.12 µg/L, *n* = 12,	No active ingredient
2,6-dichlorobenzamide (BAM)	Eight abstractions	Metabolite evaluated as human toxicological not relevant (European Commission, 2003)
aldrin	Eindhoven, Aalsterweg 2000 1 µg/L, *n* = 1	Only one positive
ametryn	Manderveen, 2000 min 0.02, max 0.39, avg 0.14 µg/L, *n* = 3	Third measurement <0.1 µg/L, hence, only one positive
Aminomethylphosphonic acid (AMPA)	De Punt, 2003	Metabolite evaluated as human toxicological not relevant (European Commission, 2003)
atrazine	Lopik, 1992 0.13 µg/L, *n* = 1	Only one positive
beta-endosulfan	Velddriel, 1995 0.14 µg/L, *n* = 1	Only one positive
Heptachlor epoxide	Eindhoven, Aalsterweg 1999 8 µg/L, *n* = 1	Only one positive According to the Waterleidingbesluit (2001) the standard for aldrin, dieldrin, heptachloor and heptachloorepoxide is 0.030 µg/L
MCPB (4-(4-chloro-2-methylphenoxy)butanoic acid)	Helmond, 2001 0.27 µg/L, *n* = 1	Only one positive Known artefact (Bannink, Personal communication, 2008))
monuron	Six abstractions	Monuron has never been for sale Probably a methodical artefact, all positives were from same laboratory
naphtalene	Four abstractions	Sources e.g. inside of tubing (Bannink, Personal communication, 2008)
prometryn	Manderveen, 2000 min. 0.02, max. 0.26, avg 0.09 µg/L, *n* = 3	Third measurement <0.1 µg/L, hence, only one positive

References Annex 1

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Annex 2 Effect of dispersion and of transformation on estimation of sorption coefficients from column studies

Sorption coefficients can be determined in a simple way from the results of soil column studies using the piston flow method described in Section 3.4. The method is based on the assumption that dispersion can be ignored because dispersion affects transport of the mass through the column in a symmetrical way. However, for short columns dispersion cannot be ignored. This effect of dispersion on transport in columns is explained in this annex.

Transformation of the substance in the column decreases the mass remaining in the column and the mass leaching from the column. How to interpret studies in which the substance is transformed in the columns is explained in this annex.

Dispersion
In an infinite column dispersion makes the pesticide mass moving through the column according to a symmetrical distribution around the centre of mass. However, the column having a finite upper boundary leads to an asymmetric distribution pattern due to the inability of dispersive transport across the upper boundary of the column. In short columns this leads to the peak concentration occurring before 1 pore volume is leached, shown for a column of 15 cm length in Figure A2.1 by the curve for no transformation (*DegT50* = 1000 d used in the calculation). Hence the assumption of piston flow used in Section 3.4 diverges for short columns. This phenomenon is described by Jury and Roth (1990): 'The surface boundary condition, does not allow solute to diffuse upward. Because this breaks the symmetry of the diffusion process, the centre of mass of the solute pulse moves downward faster and spreads out slower than it would in an infinite medium. Only when the solute is far below the surface does the influence of the upper boundary disappear.'

Figure A2.2 (Figure 3.4 in Jury & Roth,1990) illustrates the effect of the upper boundary on the effective flow velocity and on effective dispersion in the column. V_{eff} and D_{eff} are calculated for the centre of mass (position where half of the mass is present before and the other half of the mass is behind). From approximately dimensionless time $T = 5$ the effective values approach the final values

For the example shown in Figure A2.1 the dimensionless time T after 1 day is 2 ($T = v^2t/D$, where $D = v.L_d = 5\times2.5 = 12.5$ cm^2/d). At $T = 2$, the effective flow velocity V_{eff} is 1.4, corresponding to the velocity in the example of $1.4\times5 = 7$ cm/d. This is the flow velocity for the centre of mass, i.e. the average velocity of the whole pulse (see Figure A2.2). In an infinite system the mass on the left side of the centre would travel further upstream due to dispersion. Because of the upper boundary this is not possible. The centre of mass at $t = 1$ d is located at 7.1 cm in the column (using Eq. D59, p.181 in Jury and Roth, 1990). In an infinite system the centre of mass at $t = 1$ d would be located at 5.0 cm ($= v\cdot t$). This smaller centre of mass shows that centre of mass moves faster in the finite system representing a column.

Now the effect of the upper boundary is quantified for column studies that are performed according to OECD 312. The column length should be at least 30 cm, and 20 cm of water is applied in two days, hence the percolation rate is 10 cm/d. Assuming a moisture content θ of 0.43, the flow velocity is 10/0.43 = 23.3 cm/d, and the dispersion coefficient $D = 23.3 \times 2.5$ (dispersion length) = 58 cm/d. According to EFSA guidance, column studies can be used for substances with $K_{oc} < 25$ L/kg. Using a bulk density of 1500 kg/m^3, organic matter content of the soil of 5% with $K_{oc} = 25$ L/kg ($K_{om} =$ 43 L/kg) the calculated average penetration depth would be 5.5 cm for piston flow and 7.6 cm with the convection-dispersion method. Using the 7.6 cm penetration depth (representing reality) to determine the K_{om} with the piston flow method results in a K_{om} of 29 L/kg. This case illustrates the extent of maximal the underestimation of the sorption coefficient by using the pistion flow method in stead of the convection-dispersion method.

Transformation
In column studies where the substance is transformed substantially the estimation of sorption coefficients is affected. To illustrate the effect of transformation on mass leaching from the column, the example calculation shown in Figure A2.1 for a column of 15 cm was extended with calculations for *DegT50* values of 2.25 and of 0.75 d. The figure shows that the shorter the *DegT50* the earlier the peak concentration occurs in the leachate. The remaining mass has been transformed in the column, as shown by the concentration distribution in the column shown in Figure A2.3 after percolation of 0.33 porevolumes.

The interpretation of column studies where more than 50% of the mass was leached needs further explanation. Some example calculations were done for the OECD column of 30 cm length with the simplified version of PEARL using 50 layers of 1 cm. OECD312 recommends at least 70% recovery of the substance. In the column test of 2 days, this corresponds with a *DegT50* of 3.9 days. However, when the substance is leached it is not transformed anymore. Therefore we consider a *DegT50* of 2 days (instead of 3.9 days), as realistic case for maximal transformation in the column. To show how the remaining mass tails in the column when more than 50% of the dose has leached out of the column an example is constructed using K = 0.5 L/kg. For three transformation rates, including the realistic maximal transformation with *DegT50* of 2 days, the concentrations in the column at the end of the study are shown in Figure A2.4. Virtual concentrations are shown for the distance greater than the column length of 30 cm, illustrating how the concentrations in the column are the tail of the whole substance mass.

The estimation of sorption coefficients with the piston flow method for transformed substances is checked using calculation results for the OECD column parameterisation and K = 0.1 L/kg. Figure A2.5 shows concentrations in leached water as a function of time for three transformation rates, indicating that the lower *DegT50*'s result in earlier leaching of 50% of recovered mass. Recovered mass is the sum of the mass remaining in the column and the mass leached, both at the end of the study. The calculation of the sorption coefficients is shown in Table 1. First the recovered mass (RM) was determined. The cumulative mass leached was calculated as a function of time, from which the time that 50% RM leached was selected. This selected time was multiplied with the percolation rate of 0.1 m/d to obtain W. The sorption coefficient K was calculated with the piston equation and determined for convection dispersion from Figure 6 (Section 3.4). As reference is given that for a substance with K = 0 and no transformation, 50% of RM is leached at t = 1.19 d.

The piston flow method gives sorption coefficients lower than 0.1 L/kg for all three cases. The convection-dispersion method gives sorption coefficients lower than 0.1 L/kg for substances that are transformed. However the difference from 0.1 L/kg is less than from the piston flow method.

Table A2.1

Sorption coefficients K calculated with piston flow method and with convection-dispersion method from the time that 50% of the recovered mass (RM) leached from the soil column of a substance with K = 0.1 L/kg.

DegT50 (d)	Mass in column at end of study (% of dose)	Mass leached (% of dose)	Recovered mass (RM) (%)	Time 50% of RM leached (d)	*W* (m)	*K* piston (L/kg)	*K* conv-disp (L/kg)
1000 (no trans-formation)	29.0	70.8	99.8	1.61	0.161	0.07	0.1
2	10.6	36.2	46.8	1.46	0.146	0.04	0.06
0.5	0.18	1.18	1.36	1.25	0.125	-0.01	0.02

Conclusion

Sorption coefficients from soil column studies are underestimated when they are determined with the piston flow method. This results in conservative sorption coefficients when used in the leaching assessment.

Sorption coefficients from soil column studies of substances that are transformed are underestimated when they are determined with the piston flow method and even so with the convection-dispersion method. This results in conservative sorption coefficients when used in the leaching assessment.

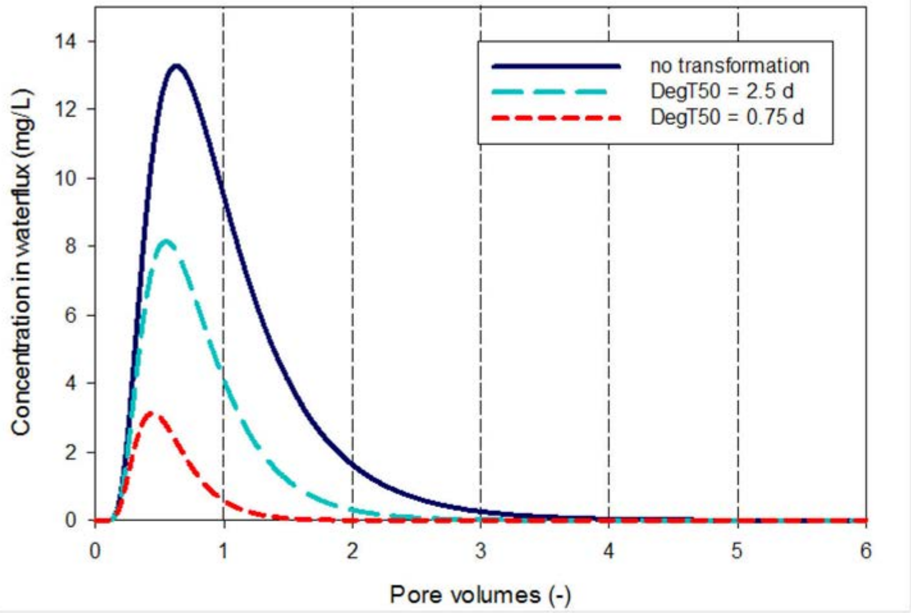

Figure A2.1 *Concentration in leachate (flux concentration) as a function of the number of percolated pore volumes, with K = 0 L/kg and three transformation rates. The column parameterisation is based on a column study with MCPA of Hiller et al. (2010). Column length = 15 cm, θ = 0.51, ρ = 1500 kg/m^3, v = 5 cm/d, dose 1.018 g/m^2. Dispersion length of 2.5 cm is derived from Vanderborght and Vereecken (2009); repacked columns with saturated flow (ponding) and a flow velocity of 1-10 cm/d: median value is 2 cm; on basis of flow rate is 3 cm. The pore volume is 0.15 L. The study is simulated with a simplified version of PEARL taking a semi-infinite system of 25 x 1 cm, where the flux concentrations at 15 cm depth are shown in the graph.*

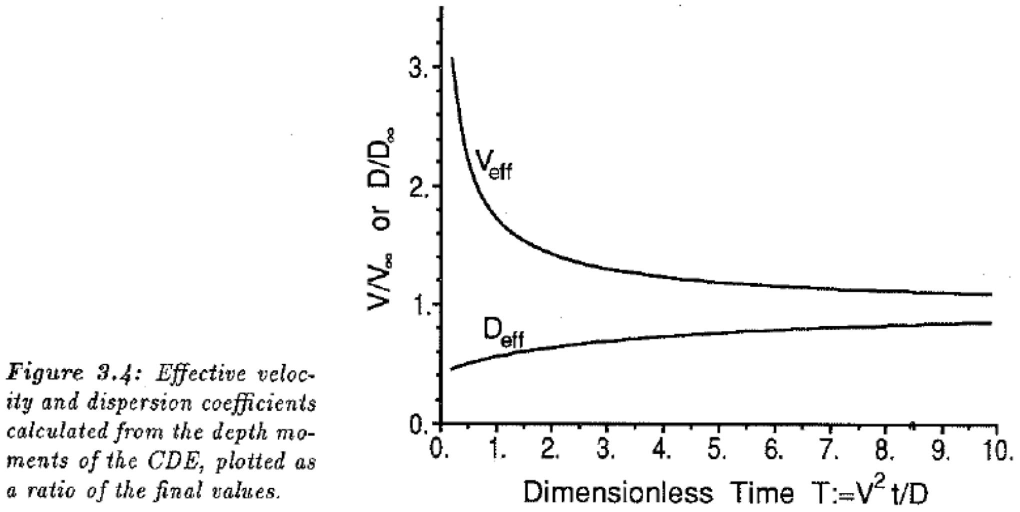

Figure 3.4: Effective velocity and dispersion coefficients calculated from the depth moments of the CDE, plotted as a ratio of the final values.

Figure A2.2 *Figure taken from Jury and Roth (1990).*

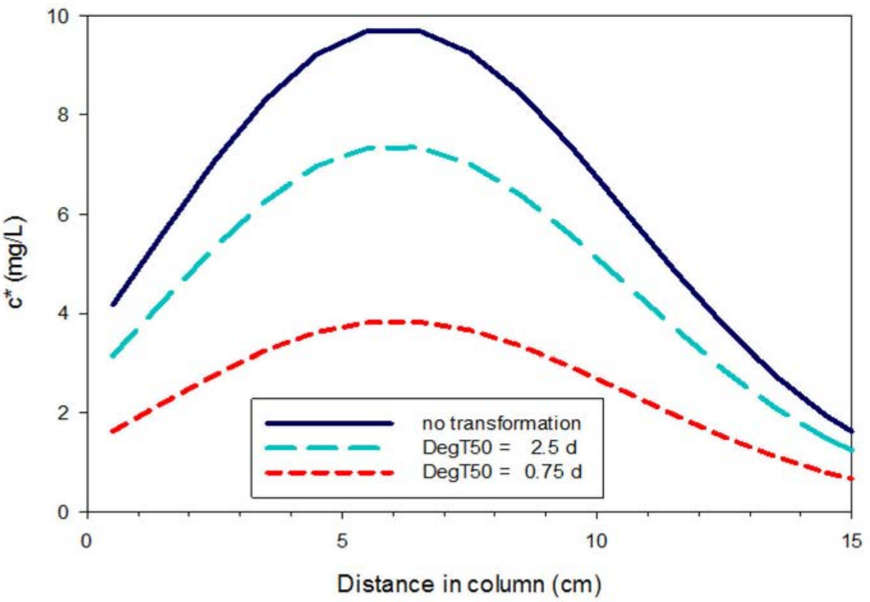

Figure A2.3 *Concentration as a function of the distance*[15] *in the column (resident concentration) after 1 day (0.33 porevolume), with K = 0 L/kg and three transformation rates. See caption of Figure A2.1 for details of the calculation.*

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[15] The concentration in Figure A2.3 is a resident concentration that can be linked to the flux concentration in Figure A2.1. E.g. for the no transformation curve the resident concentration (c_r) at 15 cm is 1.65 mg/L, multiplied with θ 0.51 gives 3.2 mg/L in pore water. Using this resident concentration in pore water in Eq. 3.14 of Jury and Roth ($c_f = c_r - D/v * (\delta c_r/\delta z)$) the flux concentration (c_f) is calculated as 6.3 mg/L at 1 day, equal to 0.33 porevolume.

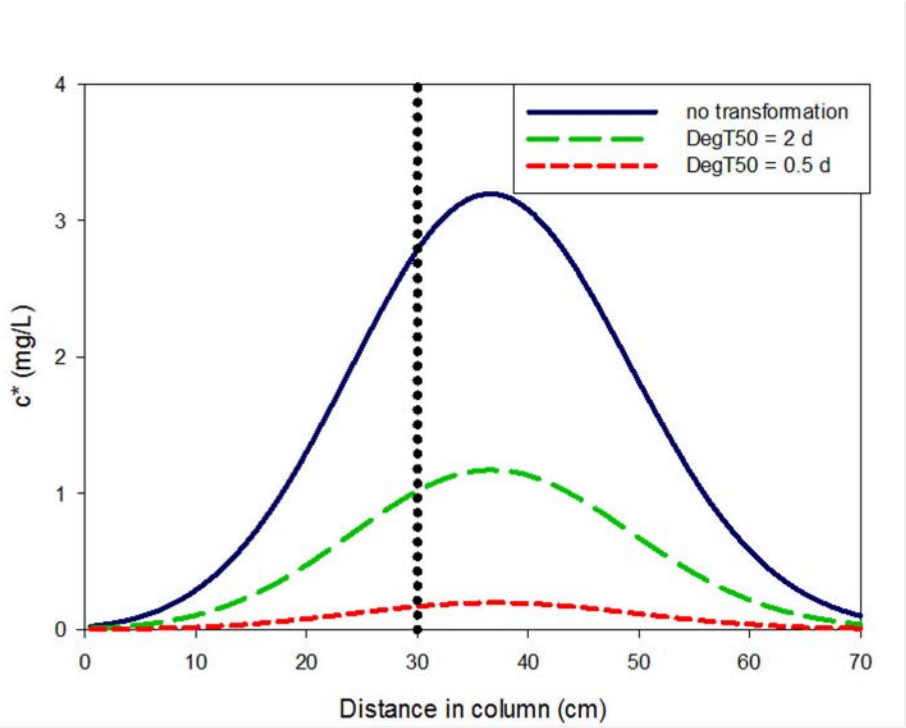

Figure A2.4 *Concentration as a function of the distance in the column of 30 cm after two days of percolation. The distance above 30 cm is virtual, because the substance has leached from the column at distance 30 cm. Concentrations are calculated with the convection dispersion equation, with* $\theta = 0.43$*,* $\rho = 1.5$ *kg/L, W = 20 cm in 48 hours,* $L_d = 2.5$ *cm, sorption coefficient K = 0.5 L/kg and three transformation rates.*

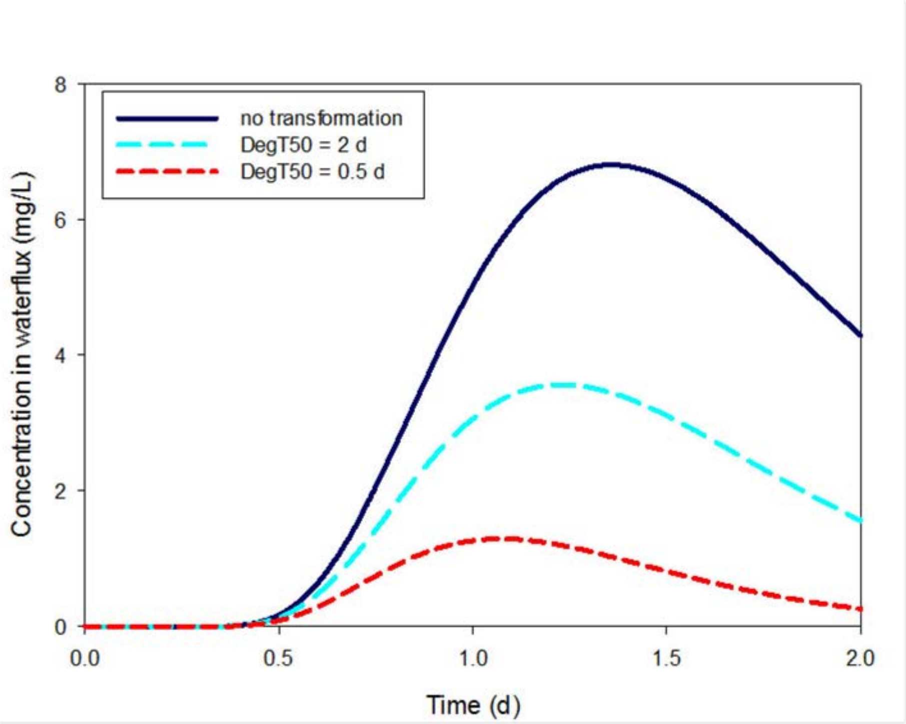

Figure A2.5 *Concentration in leached water as a function of time for OECD column parameterisation (see text), K = 0.1 L/kg and three transformation rates (indicated in figure). One pore volume is replaced in* $0.43 \times 30/10 = 1.29$ *d.*

References Annex 2

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Annex 3 The pH measurements used in Section 3.6 to establish quantitative relationships between pH$_{KCl}$, pH$_{CaCl2}$ and pH$_{H2O}$

Table A3-1

Data pairs of pH$_{H2O}$ and pH$_{CaCl2}$. Reference numbers in first column indicate the data source described in Table 3.

Reference nr.	pH$_{H2O}$	pH$_{CaCl2}$
3	4.6	4.4
3	5	4.6
3	5	4.7
3	5.1	4.8
3	5.3	5
3	5.3	5.1
3	5.5	5.2
3	5.6	5.2
3	6	5.6
3	6.1	5.9
3	6.4	6.1
3	6.4	6.2
3	7.1	6.8
3	7.5	7.3
3	7.7	7.5
4	7.73	7.33
4	7.11	6.72
4	6.16	5.59
4	7.94	7.45
4	8.23	7.64
4	7.34	7.00
4	4.79	4.31
4	6.01	5.50
4	7.79	7.31
4	7.55	7.18
4	6.97	6.52
4	5.63	5.00
4	7.74	7.28
4	7.80	7.38
4	5.90	5.50
4	4.92	4.63
4	5.30	4.63
4	4.94	4.50
4	4.90	4.48
4	7.38	6.94
4	6.79	6.19
4	6.79	6.42
4	6.17	5.59
4	6.90	6.28
4	5.58	5.05
4	7.80	7.34
4	4.99	4.44
4	7.53	7.21
4	6.07	5.44
4	6.01	5.42
4	7.50	7.16
4	6.03	5.51
4	5.99	5.45
4	7.58	7.43
4	4.88	4.26
4	6.07	5.63
4	7.00	6.24
4	6.84	6.32
4	7.76	7.33
4	7.84	7.56
4	6.08	5.56
4	5.11	4.50
4	6.93	6.35
4	7.81	7.36
4	7.42	6.89
4	7.71	7.55
4	4.67	4.09
4	5.95	5.41
4	7.58	7.23
4	6.92	6.49
4	5.35	4.81
4	8.10	7.54
4	4.69	4.40
4	8.18	7.74
4	5.96	5.52
4	7.70	7.34
4	3.65	3.10
4	7.43	6.95
4	7.74	7.28
4	7.83	7.30
4	7.79	7.38
4	7.82	7.21
4	7.50	7.03
4	6.82	6.54
4	7.59	7.34
4	5.72	5.14
4	3.88	3.45
4	4.44	4.00
4	6.42	5.84
4	6.59	6.01
4	8.01	7.54
4	6.49	5.96
4	5.66	4.70
4	5.35	4.71
4	7.96	7.40
4	3.87	3.41
4	7.34	6.98
4	7.48	7.09
4	7.59	7.29
4	6.94	6.69
4	6.17	6.03
5	6.4	5.9
5	7.9	7.1
5	6.5	5.7
5	6.8	6
5	6.1	5.5
5	7.9	6.9
5	6.6	5.9
5	8.4	7.7
5	7.9	7.3
5	8.1	7.2
5	7.8	7.3
5	7.7	7.2
5	7.7	7.3
5	7.7	7.2
5	7.6	7.2
5	7.95	7.48
5	7.8	7.4
5	7.8	7.2
5	7.8	7.3
5	7.5	7
5	6.1	5.3
5	5.96	5.56
5	6.2	5.6
5	6.2	5.6
5	6.9	6.1
5	6.5	5.3
5	5.8	5.5

Reference nr.	pH_{H2O}	pH_{CaCl2}
5	6.3	5.9
5	6.6	5.9
5	6.3	5.3
5	6.2	5.6
5	6.3	5.6
5	6	5.4
5	6.5	5.6
5	6.6	6.1
5	6.4	6
5	6.1	5.3
5	7.7	7
5	6	5.2
5	6.9	6.3
5	7.7	7.3
5	7.8	7.1
5	6.5	5.7
5	6.2	5.5
5	6.5	5.9
5	7.8	7.4
5	7.3	6.9
5	7.1	6.3
5	7.3	6.6
5	6.9	6.3
5	7	6.2
5	6.9	6.1
5	7	6.2
5	6.7	6.1
5	7.2	6.4
5	8	7.6
5	7.8	7.4
5	5.8	5.2
5	6.7	5.9
5	5	4.2
5	7.9	7.4
5	8.2	7.6
5	6.9	6.2
5	6.2	5.1
5	6.5	6
5	8	7.6
5	7.5	7.3
5	8.2	7.5
5	7.8	7
5	8	7.4
5	8.04	7.43
5	8.2	7.3
5	7.8	7.3
5	7.8	7.2
5	8	7.3
5	8.2	7.3
5	8	7.3
5	8.2	7.3
5	6.5	5.8
5	7	6.5
5	8.2	7.6
5	7	6.4
5	8.3	7.4
5	8.1	7.5
5	7.8	7.4
5	6.4	5.6
5	6.3	5.9
5	5.7	4.8
5	7.1	6.3
5	4.2	3.6
5	8.4	8
5	6.7	6.2
5	6.4	5.6
5	8.1	7.5
5	8.1	7.6
5	6.4	5.8
5	8.4	7.8
5	7.9	7.3
5	6.4	5.8
5	6.4	5.8
5	5.4	4.8
5	6.1	5.4
5	7.8	6.9
5	7.4	7.1
5	7.1	6.5
5	5.6	4.8
5	6.6	5.8
5	6.3	5.6
5	6.3	5.7
5	7.1	6.5
5	7.1	6.7
5	7.9	7.3
5	6.1	5.7
5	8.2	7.6
5	6.1	5.5
5	6.1	5.3
5	6.5	5.7
5	8	7.4
5	5.6	4.6
5	7	6.1
5	5	4
5	8	7.5
5	7.1	7
5	5.8	5.2
5	7.6	6.7
5	4.7	4.5
5	8.3	7.3
5	8.5	7.5
5	6.8	6.1
5	7.7	6.9
5	6.4	6.1
5	7.4	6.7
5	7.2	6.7
5	7.1	6.4
5	7.1	6.4
5	7.4	6.6
5	7.5	6.7
5	8.1	7.3
5	7.1	6.4
5	6.5	5.5
5	6.4	5.7
5	6.3	5.8
5	6.9	6.5
5	5.1	4.4
5	7.5	6.9
5	7.2	6.5
5	8.5	7.7
5	8.4	7.6
5	8.6	7.5
5	5.5	4.9
5	6.6	5.9
5	6.1	5.9
5	6.7	6.2
5	7.9	6.9
5	6.3	5.7
6	4.23	4.09
6	6.1	5.6
6	5.88	5.07
6	7.54	7.26
6	6.96	6.65
6	7.69	7.38
6	7.33	7.24
6	4.26	3.97
6	4.25	3.81
6	5.26	4.55
6	5.1	4.49
6	7.32	7.12
6	4.63	3.99
6	7.16	7.12
6	6.21	6.09
6	7.12	7.22
6	7.08	7.43
6	7.16	7.36
6	7.17	7.08
6	7.09	7.36
6	5.6	4.88
6	7.54	7.35
6	7.5	7.12
6	5.3	4.84
6	5.08	4.19
6	5.47	4.96
6	6.03	5.5
6	6.04	5.35
6	4.05	3.59
6	3.95	3.65
6	3.49	3.09
6	7.42	7.3
6	6.28	5.87
6	5.35	4.75

Reference nr.	pH_{H_2O}	pH_{CaCl_2}
6	7.5	7.23
6	7.34	7.31
6	6.83	6.6
6	6.44	5.59
6	3.65	3.2
6	5.58	4.2
6	4.6	3.41
6	7.07	7.25
6	4.8	4.45
6	5.31	4.36
6	7.3	7.21
6	7.4	7.15
6	7.5	7.16
6	3.94	3.68
6	6.16	6.33

Table A3-2

Data pairs of pH_{KCl} and pH_{CaCl_2}. Reference numbers in first column indicate the data source described in Table 3.

Reference nr.	pH_{CaCl_2}	pH_{KCl}
4	7.33	7.24
4	6.72	6.65
4	5.59	5.36
4	7.45	7.37
4	7.64	7.79
4	7.00	6.98
4	4.31	4.09
4	5.50	5.17
4	7.31	7.41
4	7.18	7.25
4	6.52	6.71
4	5.00	4.79
4	7.28	7.26
4	7.38	7.32
4	5.50	5.12
4	4.63	4.56
4	4.63	4.99
4	4.50	4.47
4	4.48	4.51
4	6.94	7.02
4	6.19	5.78
4	6.42	6.30
4	5.59	5.06
4	6.28	6.40
4	5.05	4.76
4	7.34	7.51
4	4.44	4.29
4	7.21	7.12
4	5.44	5.41
4	5.42	5.21
4	7.16	7.12
4	5.51	5.11
4	5.45	5.03
4	7.43	7.50
4	4.26	3.98
4	5.63	5.50
4	6.24	6.07
4	6.32	6.39
4	7.33	7.37
4	7.56	7.64
4	5.56	5.50
4	4.50	4.26
4	6.35	6.37
4	7.36	7.16
4	6.89	6.74
4	7.55	7.49
4	4.09	3.99
4	5.41	5.28
4	7.23	7.10
4	6.49	5.62
4	4.81	4.21
4	7.54	7.27
4	4.40	4.18
4	7.74	7.52
4	5.52	5.28
4	7.34	7.11
4	3.10	2.75
4	6.95	6.85
4	7.28	7.25
4	7.30	7.28
4	7.38	7.34
4	7.21	7.45
4	7.03	7.05
4	6.54	6.65
4	7.34	7.42
4	5.14	5.08
4	3.45	3.28
4	4.00	3.96
4	5.84	5.83
4	6.01	5.69
4	7.54	7.63
4	5.96	5.98
4	4.70	4.35
4	4.71	4.52
4	7.40	7.40
4	3.41	3.39
4	6.98	6.97
4	7.09	7.01
4	7.29	7.28
4	6.69	6.79
4	6.03	6.03
6	7.12	7.8
6	7.21	7.67
6	7.3	7.63
6	7.35	7.55
6	7.16	7.45
6	7.12	7.37
6	5.87	7.35
6	7.22	7.34
6	7.24	7.2
6	7.25	7.2
6	7.36	7.16
6	7.15	7.15
6	7.36	7
6	7.26	6.93
6	7.38	6.92
6	7.43	6.91
6	7.08	6.52
6	6.65	6.3
6	5.5	6
6	7.12	5.93
6	6.6	5.64
6	4.96	5.4
6	5.07	5.13
6	6.33	4.75
6	5.6	4.71
6	4.49	4.37
6	4.88	4.36
6	3.97	3.98
6	4.55	3.98
6	4.36	3.92
6	4.2	3.82
6	4.09	3.57
6	3.68	3.53
6	3.99	3.42
6	3.65	3.22
6	3.59	3.06
6	3.81	2.85
6	3.41	2.85
6	3.2	2.59
6	3.09	2.36

Table A3-3

Data pairs of pH_{KCl} and pH_{CaCl2}. Reference numbers in first column indicate the data source described in Table 3.

Reference nr.	pH_{H20}	pH_{KCl}
1	7.8	7
1	6.3	5.8
1	6.7	5.8
1	7.1	6.6
1	8.2	7.1
1	7.8	7
1	6.1	5.8
1	6.5	5.8
1	6.3	6.1
1	8	7.05
1	7.2	6.2
1	7.4	7.1
1	5.8	5.1
1	7	6.4
1	5.9	4.6
1	6.6	6.1
1	8.1	7.4
1	6.7	6.5
1	6.6	5.8
1	5.3	3.75
1	5.4	5.1
1	7.4	6.7
1	8.1	7.2
1	6.7	6.1
1	7.5	7.1
1	8.2	7.3
1	6.4	5.5
2	3.7	3.2
2	3.9	3.3
2	4.0	3.0
2	4.1	3.4
2	4.1	3.3
2	4.3	3.3
2	4.3	3.4
2	4.3	3.5
2	4.3	3.5
2	4.3	3.5
2	4.3	3.7
2	4.3	3.5
2	4.4	3.5
2	4.4	3.6
2	4.4	3.6
2	4.4	3.7
2	4.4	3.6
2	4.5	4.0
2	4.5	3.9
2	4.5	3.6
2	4.5	3.7
2	4.5	3.4
2	4.5	3.8
2	4.5	3.4
2	4.5	3.4
2	4.5	3.8
2	4.5	3.6
2	4.6	4.0
2	4.6	3.6
2	4.6	3.9
2	4.6	3.7
2	4.6	3.8
2	4.6	4.1
2	4.6	3.6
2	4.6	4.0
2	4.6	3.8
2	4.6	3.8
2	4.6	3.8
2	4.6	3.9
2	4.7	4.0
2	4.7	4.2
2	4.7	4.0
2	4.7	4.0
2	4.7	4.0
2	4.7	3.8
2	4.7	4.1
2	4.7	3.9
2	4.7	3.9
2	4.7	3.9
2	4.7	3.8
2	4.7	3.7
2	4.7	3.8
2	4.7	4.0
2	4.7	4.2
2	4.8	3.9
2	4.8	3.4
2	4.8	4.6
2	4.8	4.5
2	4.8	4.1
2	4.8	4.0
2	4.8	4.3
2	4.8	4.1
2	4.8	4.2
2	4.8	4.0
2	4.8	4.0
2	4.8	3.6
2	4.8	3.7
2	4.8	4.1
2	4.8	4.2
2	4.8	3.8
2	4.8	3.8
2	4.8	3.7
2	4.9	3.8
2	4.9	4.2
2	4.9	4.0
2	4.9	3.9
2	4.9	4.3
2	4.9	3.8
2	4.9	3.7
2	4.9	3.6
2	4.9	4.0
2	4.9	3.9
2	4.9	3.8
2	4.9	3.9
2	4.9	3.9
2	4.9	3.8
2	5.0	4.2
2	5.0	4.7
2	5.0	4.3
2	5.0	4.2
2	5.0	3.9
2	5.0	4.0
2	5.0	3.7
2	5.0	4.2
2	5.0	4.1
2	5.0	4.7
2	5.0	3.7
2	5.0	4.1
2	5.0	4.1
2	5.0	4.2
2	5.1	4.2
2	5.1	4.2
2	5.1	4.5
2	5.1	4.1
2	5.1	4.6
2	5.1	4.4
2	5.1	4.2
2	5.1	4.1
2	5.1	4.0
2	5.1	3.9
2	5.1	4.1
2	5.1	4.3
2	5.1	4.7
2	5.1	4.1
2	5.1	4.3
2	5.1	4.5
2	5.1	4.1
2	5.1	4.5
2	5.1	4.5
2	5.2	4.8
2	5.2	4.6
2	5.2	4.2
2	5.2	4.8
2	5.2	4.3
2	5.2	4.4
2	5.2	4.1

Reference nr.	pH_{H20}	pH_{KCl}
2	5.2	4.3
2	5.2	4.5
2	5.2	4.4
2	5.2	4.2
2	5.2	4.4
2	5.2	4.5
2	5.2	4.1
2	5.2	4.2
2	5.2	4.4
2	5.2	4.2
2	5.2	4.5
2	5.2	4.4
2	5.2	4.8
2	5.2	4.8
2	5.2	4.3
2	5.2	4.2
2	5.2	4.2
2	5.3	4.4
2	5.3	4.3
2	5.3	4.5
2	5.3	4.6
2	5.3	4.2
2	5.3	4.1
2	5.3	4.6
2	5.3	4.1
2	5.3	4.6
2	5.3	4.5
2	5.3	4.3
2	5.3	4.5
2	5.3	4.1
2	5.3	4.7
2	5.3	4.1
2	5.3	4.5
2	5.3	4.7
2	5.3	4.0
2	5.3	4.6
2	5.3	4.2
2	5.3	4.3
2	5.3	4.8
2	5.3	4.9
2	5.3	4.3
2	5.4	4.3
2	5.4	4.7
2	5.4	4.3
2	5.4	4.4
2	5.4	4.4
2	5.4	4.5
2	5.4	4.6
2	5.4	4.5
2	5.4	4.5
2	5.4	4.7
2	5.4	4.5
2	5.4	4.5
2	5.4	4.5
2	5.4	4.3
2	5.4	4.7
2	5.4	4.4
2	5.4	4.7
2	5.4	4.2
2	5.4	4.7
2	5.4	4.9
2	5.4	4.9
2	5.4	4.8
2	5.4	4.8
2	5.4	4.5
2	5.4	4.5
2	5.4	4.6
2	5.4	4.3
2	5.5	4.6
2	5.5	4.3
2	5.5	4.6
2	5.5	4.5
2	5.5	4.9
2	5.5	5.0
2	5.5	4.2
2	5.5	4.5
2	5.5	5.1
2	5.5	5.1
2	5.5	4.9
2	5.5	4.5
2	5.5	4.9
2	5.5	4.3
2	5.5	4.5
2	5.5	4.4
2	5.5	4.4
2	5.5	5.0
2	5.6	4.6
2	5.6	4.5
2	5.6	4.6
2	5.6	4.6
2	5.6	4.6
2	5.6	4.7
2	5.6	5.3
2	5.6	4.9
2	5.6	5.0
2	5.6	4.4
2	5.6	4.6
2	5.6	4.7
2	5.6	4.8
2	5.6	4.6
2	5.6	4.0
2	5.6	4.6
2	5.6	4.6
2	5.6	4.7
2	5.6	4.5
2	5.6	4.5
2	5.6	5.4
2	5.7	4.9
2	5.7	4.7
2	5.7	4.5
2	5.7	4.3
2	5.7	4.6
2	5.7	4.1
2	5.7	4.5
2	5.7	4.7
2	5.7	4.5
2	5.7	4.9
2	5.7	4.8
2	5.7	4.7
2	5.7	4.9
2	5.7	4.7
2	5.7	5.0
2	5.7	4.8
2	5.7	5.0
2	5.7	5.0
2	5.7	5.0
2	5.7	4.9
2	5.7	5.0
2	5.7	4.6
2	5.7	4.9
2	5.7	5.1
2	5.7	5.1
2	5.7	4.5
2	5.8	5.3
2	5.8	4.9
2	5.8	4.6
2	5.8	5.1
2	5.8	4.8
2	5.8	5.2
2	5.8	5.2
2	5.8	4.9
2	5.8	5.0
2	5.8	4.9
2	5.8	5.1
2	5.8	5.0
2	5.8	5.1
2	5.8	5.0
2	5.8	4.9
2	5.8	4.9
2	5.8	5.0
2	5.9	4.6
2	5.9	4.8
2	5.9	5.3
2	5.9	4.8
2	5.9	5.2
2	5.9	5.0
2	5.9	5.3
2	5.9	5.1
2	5.9	5.2
2	5.9	5.3
2	5.9	4.5
2	5.9	5.4

Reference nr.	pH$_{H20}$	pH$_{KCl}$
2	5.9	5.2
2	5.9	5.2
2	5.9	5.0
2	5.9	5.1
2	5.9	5.0
2	5.9	4.4
2	5.9	5.0
2	5.9	5.2
2	5.9	4.9
2	5.9	5.4
2	5.9	4.9
2	5.9	4.6
2	5.9	5.5
2	5.9	5.1
2	5.9	5.4
2	6.0	5.3
2	6.0	5.6
2	6.0	5.4
2	6.0	5.1
2	6.0	5.1
2	6.0	4.8
2	6.0	6.1
2	6.0	5.1
2	6.0	5.5
2	6.0	5.6
2	6.0	5.3
2	6.0	5.4
2	6.0	5.3
2	6.0	5.2
2	6.0	5.0
2	6.0	5.2
2	6.0	5.3
2	6.0	5.3
2	6.0	5.5
2	6.0	5.6
2	6.0	4.9
2	6.1	5.1
2	6.1	5.5
2	6.1	5.2
2	6.1	5.3
2	6.1	5.6
2	6.1	5.7
2	6.1	5.5
2	6.1	5.5
2	6.1	5.5
2	6.1	5.1
2	6.1	5.1
2	6.1	5.3
2	6.1	5.2
2	6.2	5.5
2	6.2	4.6
2	6.2	5.8
2	6.2	5.6
2	6.2	5.4
2	6.2	5.4
2	6.2	5.7
2	6.2	6.2
2	6.2	4.9
2	6.2	4.7
2	6.2	5.0
2	6.2	5.1
2	6.2	5.8
2	6.2	5.2
2	6.2	6.0
2	6.3	5.5
2	6.3	5.4
2	6.3	5.4
2	6.3	5.6
2	6.3	5.5
2	6.3	5.3
2	6.3	5.8
2	6.3	5.2
2	6.3	5.1
2	6.3	6.0
2	6.3	5.0
2	6.3	4.8
2	6.3	5.6
2	6.3	5.6
2	6.3	5.5
2	6.3	5.1
2	6.3	5.4
2	6.4	5.4
2	6.4	5.4
2	6.4	5.8
2	6.4	5.9
2	6.4	5.5
2	6.4	5.1
2	6.4	5.2
2	6.4	5.8
2	6.4	5.7
2	6.5	5.7
2	6.5	5.7
2	6.5	5.9
2	6.5	5.2
2	6.5	4.9
2	6.5	5.1
2	6.5	5.7
2	6.5	5.7
2	6.5	5.6
2	6.6	5.8
2	6.6	5.9
2	6.6	5.8
2	6.6	5.8
2	6.6	5.3
2	6.6	5.4
2	6.6	5.2
2	6.6	5.2
2	6.6	5.5
2	6.6	6.1
2	6.6	6.1
2	6.6	6.0
2	6.6	6.1
2	6.6	6.1
2	6.6	5.3
2	6.6	6.1
2	6.6	5.6
2	6.6	5.6
2	6.7	5.7
2	6.7	6.0
2	6.7	5.9
2	6.7	5.8
2	6.7	6.1
2	6.8	6.1
2	6.8	5.9
2	6.8	6.3
2	6.8	6.0
2	6.8	6.1
2	6.9	6.2
2	6.9	6.6
2	6.9	6.0
2	6.9	5.9
1	7	6.4
2	7.1	7.1
2	7.1	6.8
2	7.2	6.2
2	7.2	7.2
2	7.2	7.2
2	7.2	7.2
2	7.2	7.1
1	7.3	6.6
2	7.3	6.4
2	7.3	7.3
2	7.3	6.4
2	7.3	6.9
2	7.4	6.3
2	7.4	6.8
2	7.4	7.1
2	7.5	7.0
2	7.5	7.0
2	7.5	6.7
2	7.5	7.5
2	7.5	6.2
2	7.5	6.2
2	7.6	6.9
2	7.8	7.0
2	7.9	7.6
2	7.9	7.4
2	7.9	8.0
2	7.9	6.6
2	8.0	7.0
2	8.0	6.6
2	8.0	7.1

Reference nr.	pH$_{H20}$	pH$_{KCl}$
2	8.2	7.1
2	8.3	7.5
2	8.4	7.6
2	8.4	7.6
4	7.73	7.24
4	7.11	6.65
4	6.16	5.36
4	7.94	7.37
4	8.23	7.79
4	7.34	6.98
4	5.80	5.06
4	4.79	4.09
4	6.01	5.17
4	7.79	7.41
4	7.55	7.25
4	6.97	6.71
4	5.63	4.79
4	7.74	7.26
4	7.80	7.32
4	5.90	5.12
4	4.92	4.56
4	5.30	4.99
4	4.94	4.47
4	4.90	4.51
4	7.38	7.02
4	6.79	5.78
4	6.79	6.30
4	6.17	5.06
4	6.90	6.40
4	5.58	4.76
4	7.80	7.51
4	4.99	4.29
4	7.53	7.12
4	6.07	5.41
4	6.01	5.21
4	7.50	7.12
4	6.03	5.11
4	5.99	5.03
4	7.58	7.50
4	4.88	3.98
4	6.07	5.50
4	7.00	6.07
4	6.84	6.39
4	7.76	7.37
4	7.84	7.64
4	6.08	5.50
4	5.11	4.26
4	6.93	6.37
4	7.81	7.16
4	7.42	6.74
4	7.71	7.49
4	4.67	3.99
4	5.95	5.28
4	7.58	7.10
4	6.92	5.62
4	5.35	4.21
4	8.10	7.27
4	4.69	4.18
4	8.18	7.52
4	5.96	5.28
4	7.70	7.11
4	3.65	2.75
4	7.43	6.85
4	7.74	7.25
4	7.83	7.28
4	7.79	7.34
4	7.82	7.45
4	7.50	7.05
4	6.82	6.65
4	7.59	7.42
4	5.72	5.08
4	3.88	3.28
4	4.44	3.96
4	6.42	5.83
4	6.59	5.69
4	8.01	7.63
4	6.49	5.98
4	5.66	4.35
4	5.35	4.52
4	7.96	7.40
4	3.87	3.39
4	7.34	6.97
4	7.48	7.01
4	7.59	7.28
4	6.94	6.79
4	6.17	6.03
6	7.32	7.8
6	7.3	7.67
6	7.42	7.63
6	7.54	7.55
6	7.5	7.45
6	7.5	7.37
6	6.28	7.35
6	7.12	7.34
6	7.33	7.2
6	7.07	7.2
6	7.16	7.16
6	7.4	7.15
6	7.09	7
6	7.54	6.93
6	7.69	6.92
6	7.08	6.91
6	7.17	6.52
6	6.96	6.3
6	6.03	6
6	7.16	5.93
6	6.83	5.64
6	5.47	5.4
6	5.88	5.13
6	6.16	4.75
6	6.1	4.71
6	5.1	4.37
6	5.6	4.36
6	4.26	3.98
6	5.26	3.98
6	5.31	3.92
6	5.58	3.82
6	4.23	3.57
6	3.94	3.53
6	4.63	3.42
6	3.95	3.22
6	4.05	3.06
6	4.25	2.85
6	4.6	2.85
6	3.65	2.59
6	3.49	2.36
7	4.52	4.1
7	4.56	4.1
7	4.6	3.4
7	4.62	4.2
7	4.64	4.3
7	4.69	4.3
7	4.7	3.4
7	4.71	4.3
7	4.74	4.3
7	4.75	4.3
7	4.75	4.4
7	4.78	4.5
7	4.78	4.6
7	4.79	4.3
7	4.8	3.6
7	4.8	3.7
7	4.8	3.7
7	4.8	4.4
7	4.81	4.4
7	4.84	4.5
7	4.86	4.5
7	4.87	4.4
7	4.88	4.5
7	4.88	4.5
7	4.91	4.5
7	4.92	4.7
7	4.94	4.5
7	4.94	4.7
7	4.97	4.7
7	4.99	4.5
7	4.99	4.7
7	5	3.7
7	5	3.7
7	5	4.4
7	5	4.5
7	5	4.7

Reference nr.	pH_{H20}	pH_{KCl}
7	5.01	4.6
7	5.07	4.8
7	5.1	3.8
7	5.1	4.1
7	5.1	4.2
7	5.1	4.5
7	5.11	4.7
7	5.16	4.6
7	5.19	4.37
7	5.2	4
7	5.2	4.3
7	5.2	4.5
7	5.2	4.6
7	5.2	4.8
7	5.23	4.8
7	5.25	4.34
7	5.29	4.75
7	5.3	4.1
7	5.3	4.69
7	5.3	4.7
7	5.3	4.8
7	5.35	4.9
7	5.38	4.46
7	5.4	4.4
7	5.4	4.5
7	5.4	4.5
7	5.4	4.5
7	5.4	4.7
7	5.4	4.7
7	5.4	4.8
7	5.43	4.50
7	5.44	4.61
7	5.5	4.5
7	5.5	4.6
7	5.5	4.6
7	5.5	4.7
7	5.5	4.7
7	5.5	4.8
7	5.5	4.8
7	5.5	4.9
7	5.5	5
7	5.5	5
7	5.5	5
7	5.5	5
7	5.5	5.1
7	5.53	4.87
7	5.58	4.72
7	5.59	4.7
7	5.59	4.73
7	5.6	4.5
7	5.6	4.6
7	5.6	4.7
7	5.6	4.7
7	5.6	4.8
7	5.6	5
7	5.6	5
7	5.6	5.1
7	5.62	5
7	5.62	4.86
7	5.63	4.65
7	5.64	4.63
7	5.64	4.63
7	5.64	5.01
7	5.64	5.1
7	5.65	4.65
7	5.66	4.77
7	5.67	4.91
7	5.68	5.18
7	5.69	4.65
7	5.7	4.6
7	5.7	4.7
7	5.7	4.7
7	5.7	4.7
7	5.7	4.8
7	5.7	4.8
7	5.7	4.8
7	5.7	4.9
7	5.7	4.9
7	5.7	5
7	5.7	5.1
7	5.7	5.1
7	5.7	5.1
7	5.7	5.2
7	5.7	5.3
7	5.72	4.65
7	5.72	4.7
7	5.73	4.57
7	5.73	4.9
7	5.74	4.71
7	5.76	4.63
7	5.76	4.75
7	5.76	4.86
7	5.76	5.18
7	5.77	5.2
7	5.77	4.77
7	5.8	4.7
7	5.8	4.7
7	5.8	4.8
7	5.8	4.8
7	5.8	4.8
7	5.8	4.8
7	5.8	4.8
7	5.8	4.87
7	5.8	4.9
7	5.8	5
7	5.8	5.1
7	5.8	5.1
7	5.8	5.1
7	5.8	5.1
7	5.8	5.2
7	5.8	5.2
7	5.8	5.2
7	5.8	5.2
7	5.8	5.2
7	5.8	5.2
7	5.8	5.2
7	5.8	5.3
7	5.8	5.3
7	5.8	5.3
7	5.8	5.4
7	5.80	4.84
7	5.82	4.8
7	5.83	5.32
7	5.83	4.9
7	5.83	5
7	5.83	5.29
7	5.84	5.08
7	5.84	5.3
7	5.85	4.63
7	5.85	5.27
7	5.85	5.1
7	5.86	4.8
7	5.86	5.21
7	5.87	4.96
7	5.88	4.93
7	5.90	4.73
7	5.9	4.8
7	5.9	4.8
7	5.9	4.8
7	5.9	4.8
7	5.9	4.9
7	5.9	4.9
7	5.9	5.1
7	5.9	5.1
7	5.9	5.1
7	5.9	5.1
7	5.9	5.2
7	5.9	5.3
7	5.9	5.3
7	5.9	5.4
7	5.9	5.4
7	5.9	5.4
7	5.93	4.93
7	5.94	4.70
7	5.94	5.07
7	5.95	5.57
7	5.96	5.1
7	5.96	4.89
7	5.97	4.94
7	5.97	4.95
7	5.97	5.16
7	5.98	4.82

Reference nr.	pH_{H20}	pH_{KCl}
7	5.98	5.36
7	5.99	5.34
7	5.99	5.49
7	6	4.7
7	6	4.9
7	6	4.9
7	6	5
7	6	5
7	6	5
7	6	5
7	6	5.1
7	6	5.1
7	6	5.1
7	6	5.1
7	6	5.1
7	6	5.1
7	6	5.1
7	6	5.1
7	6	5.2
7	6	5.2
7	6	5.2
7	6	5.2
7	6	5.2
7	6	5.43
7	6	5.5
7	6	5.6
7	6	5.8
7	6.00	4.93
7	6.00	4.96
7	6.00	5.10
7	6.02	5.15
7	6.02	5.30
7	6.03	5.07
7	6.03	5.11
7	6.03	5.24
7	6.03	5.60
7	6.03	5.06
7	6.04	5.08
7	6.04	4.98
7	6.04	5.60
7	6.04	5.00
7	6.05	5.14
7	6.05	5.66
7	6.05	5.20
7	6.05	5.04
7	6.06	5.2
7	6.08	5.3
7	6.08	5.5
7	6.09	5.65
7	6.09	5.68
7	6.09	5.55
7	6.1	5
7	6.1	5
7	6.1	5.1
7	6.1	5.2
7	6.1	5.2
7	6.1	5.2
7	6.1	5.2
7	6.1	5.22
7	6.1	5.3
7	6.1	5.3
7	6.1	5.3
7	6.1	5.3
7	6.1	5.3
7	6.1	5.4
7	6.11	5.21
7	6.11	5.3
7	6.12	5.38
7	6.12	5.4
7	6.12	5.43
7	6.13	5.63
7	6.13	5.80
7	6.16	5.08
7	6.16	5.25
7	6.16	5.33
7	6.17	5.22
7	6.17	5.87
7	6.18	5.77
7	6.19	5.5
7	6.2	4.9
7	6.2	5.2
7	6.2	5.2
7	6.2	5.2
7	6.2	5.2
7	6.2	5.2
7	6.2	5.2
7	6.2	5.2
7	6.2	5.23
7	6.2	5.3
7	6.2	5.3
7	6.2	5.3
7	6.2	5.3
7	6.2	5.4
7	6.2	5.4
7	6.2	5.4
7	6.2	5.4
7	6.2	5.6
7	6.2	5.9
7	6.2	6.1
7	6.21	5.24
7	6.21	5.9
7	6.21	6
7	6.22	5.1
7	6.22	5.5
7	6.23	6.1
7	6.25	5.11
7	6.28	5.6
7	6.28	5.7
7	6.29	5.33
7	6.29	5.5
7	6.29	5.8
7	6.30	5.41
7	6.3	5.3
7	6.3	5.3
7	6.3	5.3
7	6.3	5.3
7	6.3	5.3
7	6.3	5.4
7	6.3	5.5
7	6.3	5.5
7	6.3	5.5
7	6.3	5.6
7	6.3	5.8
7	6.3	6
7	6.31	5.25
7	6.33	5.58
7	6.33	5.48
7	6.33	5.34
7	6.34	5.44
7	6.34	5.5
7	6.34	5.5
7	6.34	5.7
7	6.35	5.34
7	6.35	5.37
7	6.37	6.1
7	6.39	5.5
7	6.39	5.6
7	6.39	5.46
7	6.4	4.8
7	6.4	4.9
7	6.4	4.9
7	6.4	5.1
7	6.4	5.3
7	6.4	5.3
7	6.4	5.5
7	6.4	5.6
7	6.4	5.7
7	6.4	5.8
7	6.4	5.8
7	6.4	6.2
7	6.41	5.83
7	6.41	6.1
7	6.43	5.6
7	6.44	5.67
7	6.45	5.44
7	6.49	5.78
7	6.49	6
7	6.5	4.8
7	6.5	5
7	6.5	5.1
7	6.5	5.5
7	6.5	5.9

Reference nr.	pH_{H20}	pH_{KCl}
7	6.5	6
7	6.51	6.7
7	6.51	5.75
7	6.52	5.64
7	6.52	5.65
7	6.52	5.73
7	6.52	5.7
7	6.52	5.8
7	6.52	6.1
7	6.54	5.94
7	6.54	5.42
7	6.54	6.2
7	6.56	5.5
7	6.56	5.60
7	6.58	5.49
7	6.59	5.6
7	6.59	6.2
7	6.6	5
7	6.6	5.1
7	6.6	5.4
7	6.6	5.6
7	6.6	5.8
7	6.6	5.9
7	6.6	6.2
7	6.6	6.4
7	6.6	6.4
7	6.6	6.5
7	6.61	5.82
7	6.61	5.67
7	6.61	6
7	6.62	6.5
7	6.62	6.7
7	6.63	6.7
7	6.68	6.6
7	6.7	4.7
7	6.7	5
7	6.7	5.3
7	6.7	5.4
7	6.7	5.6
7	6.7	5.95
7	6.7	6.4
7	6.71	5.91
7	6.73	7
7	6.74	5.93
7	6.77	6.4
7	6.78	6.1
7	6.8	5.3
7	6.8	6.3
7	6.8	7
7	6.83	6.06
7	6.84	6.7
7	6.86	6.43
7	6.87	6.33
7	6.88	6.17
7	6.89	6.5
7	6.89	7.1
7	6.9	6.4
7	6.9	7
7	6.91	6.06
7	6.93	7
7	6.95	7
7	6.95	6.21
7	6.97	6.24
7	6.98	7.2
7	7	6.36
7	7	7
7	7	7
7	7.01	7
7	7.04	6.7
7	7.04	7
7	7.1	5.7
7	7.1	6.7
7	7.11	6.47
7	7.12	6.32
7	7.17	7.2
7	7.20	6.72
7	7.2	6.8
7	7.20	6.62
7	7.22	6.8
7	7.22	6.8
7	7.24	7.014
7	7.24	7.3
7	7.25	6.8
7	7.25	6.9
7	7.25	7.1
7	7.26	6.79
7	7.26	6.75
7	7.28	7
7	7.28	6.69
7	7.29	6.83
7	7.29	6.9
7	7.35	6.78
7	7.37	7.5
7	7.38	7.5
7	7.4	7.2
7	7.41	7.01
7	7.43	7.09
7	7.43	7.4
7	7.45	6.97
7	7.45	7
7	7.49	7.10
7	7.49	7.5
7	7.49	7.6
7	7.52	7.5
7	7.53	7.01
7	7.53	6.9
7	7.54	6.86
7	7.54	7
7	7.54	7.4
7	7.56	7.5
7	7.56	7.5
7	7.56	7.6
7	7.57	6.92
7	7.58	7.5
7	7.6	7.6
7	7.62	6.89
7	7.62	7.4
7	7.63	7.4
7	7.64	7.4
7	7.65	7.2
7	7.7	7.2
7	7.75	7.18
7	7.76	7.51
7	7.76	7.6
7	7.77	7.6
7	7.79	7.54
7	7.8	7.6
7	7.82	7.23
7	7.84	7
7	7.84	7.4
7	7.84	7.6
7	7.84	7.8
7	7.84	7.11
7	7.88	7.2
7	7.88	7.7
7	7.89	7.6
7	7.9	7.5
7	7.9	7.5
7	7.92	7.6
7	7.93	7.10
7	7.93	7.63
7	7.93	7.7
7	7.94	6.9
7	7.95	7.4
7	7.95	7.45
7	7.95	7.6
7	7.98	7.6
7	8.01	7.35
7	8.03	7.43
7	8.03	7.60
7	8.03	7.70
7	8.04	7.49
7	8.06	7.50
7	8.06	7.36
7	8.06	7.48
7	8.07	7.33
7	8.07	7.47
7	8.07	7.49
7	8.08	7.49
7	8.09	7.41
7	8.09	7.10
7	8.09	7.42

Reference nr.	pH_{H20}	pH_{KCl}
7	8.10	7.56
7	8.11	7.56
7	8.13	7.56
7	8.17	7.53
7	8.20	7.43
7	8.21	7.78
7	8.21	7.53
7	8.22	7.50
7	8.22	7.68
7	8.24	7.47

Annex 4 Verification of equation for 90% penetration depth

Introduction

For the interpretation of field dissipation studies the amount of PPP in soil in deeper layers is sometimes calculated by using an estimation for 90% penetration depth of the substance. The equation for estimating 90% penetration depth was not verified before. The verification described in this annex shows that the equation is not sufficiently robust to estimate the 90% penetration depth in soil dissipation studies.

The calculation of 90% penetration depth is based on the cumulative precipitation since the application, and on the average penetration depth of plant protection product in soil assuming chromatographical transport theory and piston flow. This penetration depth is estimated using Eqn (A4-1):

$$X_p = \frac{R}{\theta + \rho\, OM\, K_{om}} \qquad \text{(A4-1)}$$

where:

X_p = average penetration depth of the PPP (mm)
R = cumulative rainfall since PPP application (mm)
θ = volume fraction of water at field capacity (-)
ρ = dry bulk density of soil (kg/L)
OM = mass fraction of organic matter (kg/kg)
K_{om} = organic-matter/water distribution coefficient of the plant protection product (L/kg)

This 90% penetration depth, X_p, is defined as the depth above which 90% of the PPP amount is located. To verify if this equation is a valid method to estimate the 90% penetration depth, the X_p calculated is compared with 90% penetration depths derived from PEARL simulations (Z_{90}) with selected FOCUS scenarios.

Eqn A4-1 may overestimate the 90% penetration depth because it ignores upward movement due to evaporation of water. However it may underestimate the 90% penetration depth because it calculates the average penetration depth. However, measurements of bromide penetration into sandy soil by Boesten (1986, p. 53) suggest that Eqn 43 is a reasonable approximation.

Methods

PEARL simulations were done with three substances for four FOCUS scenarios. For each calculation the 90% penetration depth is calculated with Eq. (43) and from the PEARL simulation, at 14, 28, 56 and 100 d after application. Only times for which more than 5% of the dosage remained in the profile are considered.

The 90% penetration depth of the PEARL result (Z_{90}) is calculated by (1), starting at the top of the profile, for each layer the cumulative mass in the above profile is calculated, (2) if between two layers 90% of the total mass is exceeded, then (3) the depths of the bottom of those two layers are used to (4) interpolate between those two depths, by weighing by the cumulative mass that was calculated for each layer.

Three combinations of K_{om} and *DegT50* were selected that covered the range of relevant substances and give about 1 µg/L leaching concentration in the Kremsmuenster scenario (sorption kinetics considered). The K_{om} and *DegT50* of the three substances are given in Table A4.1. Sorption kinetics parameter values used were: k_{des}=0.01 d^{-1} and f_{ne} = 0.5.

Table A4.1

K_{om} and DegT50 of the three substances used for the test.

Substance	K_{om} (L/kg)	*DegT50* (d)
S1	10	7
S2	40	24
S3	100	58

Four scenarios were selected to cover the different climate zones in the EU. Selected were Kremsmuenster, Chateaudun, Okehampton and Piacenza.

The dispersion length in the top horizon is changed from 0.05 into 0.025 m (Vanderborght and Vereecken, 2007) because this is more representative for the top of the profile. The standard discretization of the top horizon might be too course, therefore the layer thicknesses were decreased from 0.025 m into 0.0025 m.

For calculations with Eqn (A4-1) the bulk density, organic matter content and volume of water at field capacity of the top horizon were used (see Table A4.2). The volume of water at field capacity was obtained from Appendix A of FOCUS (2000).

Simulated is an application of 1 kg on May 1st on fallow soil (so no crop) every three years. Hence each run results in 20 values of the 90% penetration depth as a function of cumulative precipitation. For each application the cumulative precipitation and the penetration depth (Z_{90}) is determined at 14, 28, 58 and 100 days after the application. Precipitation occurring at the day of application is included in the calculation.

Table A4.2

Characteristics of the top horizon of the four FOCUS scenarios.

Scenario	Thickness horizon (m)	Bulk density (kg/L)	Organic matter content (%)	Volume of water at field capacity (%)
Kremsmuenster	0.3	1.41	3.6	33.4
Chateaudun	0.25	1.3	2.4	37.4
Okehampton	0.25	1.28	3.8	35.8
Piacenza	0.3	1.3	1.72	33.9

Simulations were done for Kremsmuenster with all three substances and for Chateaudun, Okehampton and Piacenza with substance S2.

Results

The 90% penetration depth calculated with Eqn (D-1) is given as a function of the 90% penetration depth calculated from the PEARL simulations. The results are shown in Figures A4.1 and A4.2.

Figure A4.1 shows the penetration depths of the three substances in the Kremsmuenster scenarios. From the graphs the following observations are done:

- Substance S1 (Figure A4.1-A): the criterion that remaining mass should be > 5% results in all penetrations after 100 days being not relevant (open triangles). The 90% penetration depth calculated from the PEARL simulations (Z_{90}) is larger than X_p after 14 and 28 days, and smaller after 56 days.
- Substance S2 (Figure A4.1-B): the 90% penetration depth calculated from the PEARL simulations is larger than or equal to the penetration depth X_p after 14, 28 and 56 days. However not after 100 days.

- Substance S3 (Figure A4.1-C): the 90% penetration depth calculated from the PEARL simulations is larger than or equal to the penetration depth X_p for all four times. After 100 days the maximum penetration depth is less than 0.16 m.

Figure A4.2 shows the penetration depths of substance S2 in the Chateadun, Oakhampton, and Piacenza scenarios. The penetration depth calculated from the PEARL simulations (Z_{90}) after 14, 28 and 56 days is systematic larger than the penetration depth X_p, except for Piacenza, where part of the 56 day Z_{90} and all 100 day Z_{90} values are smaller. The variation in the Piacenza results is larger than in the other scenarios.

The goodness of estimation of the 90% penetration depth Z_{90} by X_p depends on the substance properties and on the scenario, and changes in time. After 14 and 28 days after the application, X_p underestimates the 90% penetration depth. For long times; in some cases after 56 days and always after 100 days, X_p overestimates the 90% penetration depth calculated in the numerical simulations.

Conclusion
The 90% penetration depth X_p calculated with Eqn (A4-1) is not sufficiently robust to estimate the 90% penetration depth in soil dissipation studies.

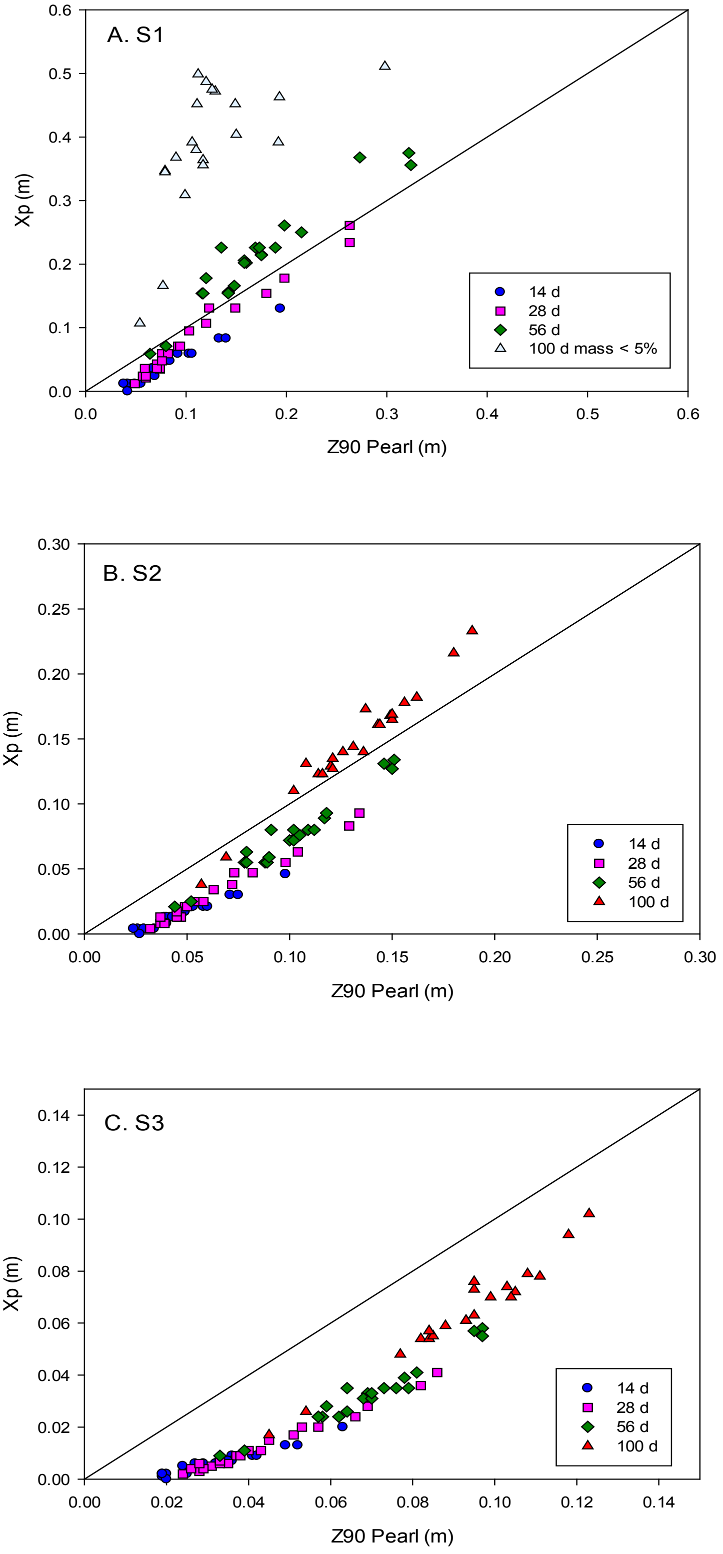

Figure A4.1 *Penetration depths calculated with Eqn (A4-1),* X_p*, as a function of penetration depth calculated from PEARL simulations,* Z_{90}*, for the Kremsmuenster scenario, with substances A. S1, B. S2 and C. S3.*

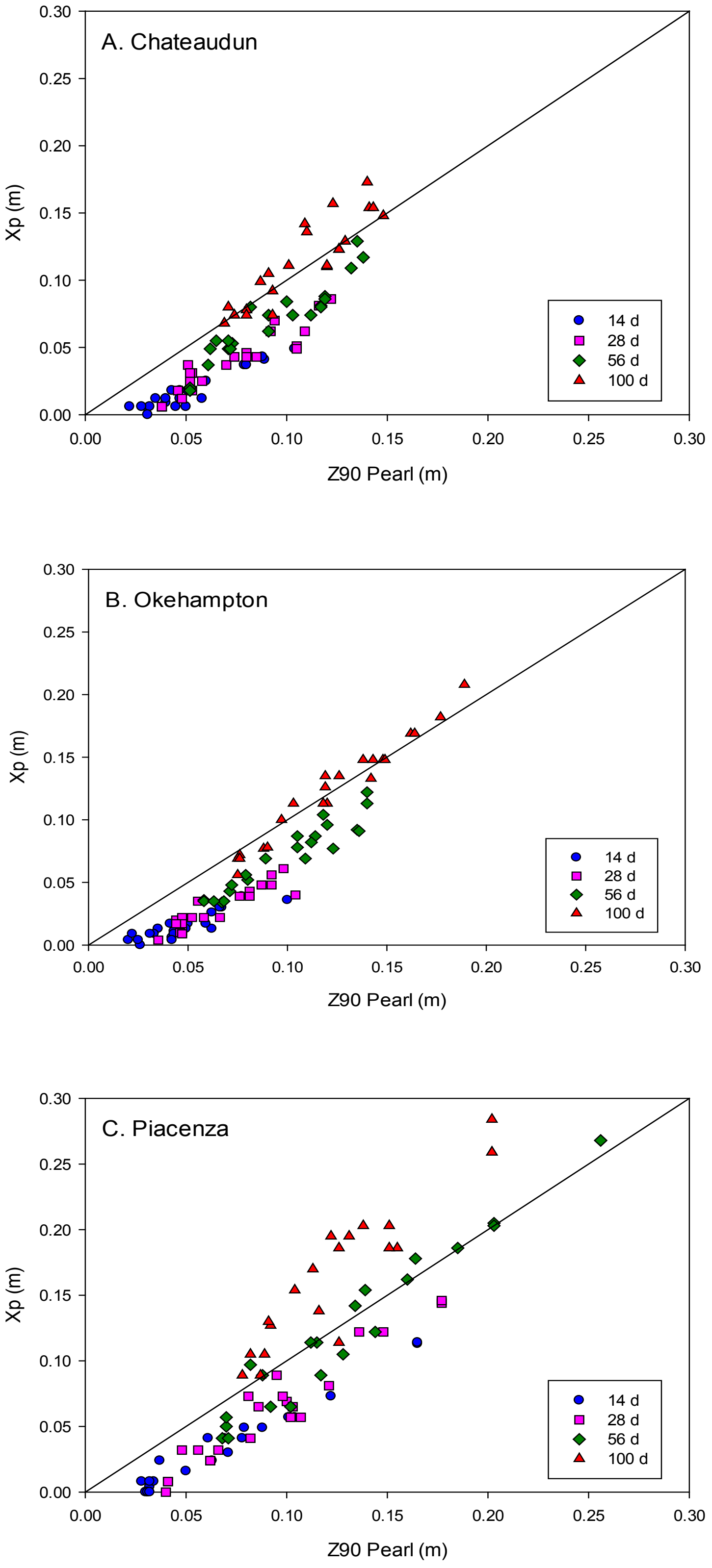

Figure A4.2 *Penetration depths calculated with Eqn (A4-1),* X_p*, as a function of penetration depth calculated from PEARL simulations,* Z_{90}*, for the A. Chateaudun, B. Okehampton and C. Piacenza scenario.*

Annex 5 Monte Carlo simulations for the standard error of *DegT50* values derived from field persistence studies

Often field persistence studies contain only one mixed soil sample for each sampling time and there is no information on the uncertainty in the concentration in this single soil sample. The derived *DegT50* value is a higher tier value so it is not meaningful to obtain a *DegT50* value that is too inaccurate. To assess the accuracy of *DegT50* values Monte Carlo simulations were made in which hypothetical field data sets were generated. The two variables in the simulations were: (i) the number of sampling times (ranging from three to ten), and (ii) the number of soil samples taken at each sampling time. Each simulation was based on 10000 draws of hypothetical field data sets. Simulations were made for *DegT50* values of 10, 50, 100 and 200 days. In the simulations, the sampling times were equally spaced over the period between start and until 10% of the dose was left based on the prescribed number of sampling times and the prescribed *DegT50* value. For these sampling times the true remaining fractions were calculated and subsequently random values of the remaining fractions were calculated. It was assumed that the fractions were lognormally distributed with an average equal to the true value and with a coefficient of variation, CV, of the individual soil samples of 110% (based on NAFTA, 2006).

The lognormal distribution was based on the following mean (μ) and standard deviation (σ) of the log transformed remaining fraction:

$$\mu = \ln\left(\frac{F}{\sqrt{1+CV^2}}\right) \qquad \text{(A5-1)}$$

$$\sigma = \sqrt{\ln(1+CV^2)} \qquad \text{(A5-2)}$$

where F = the true remaining fraction.

Then the *DegT50* was derived from each hypothetical field data set by linear regression (after logarithmic transformation) and the standard error of the 10000 generated *DegT50* values was calculated. In the regression procedure, all remaining fractions were given equal weight because this is the procedure recommended by FOCUS (2006): p. 72 states '… unweighted fits to untransformed data is recommended as a first step.'

Figure A5.1 shows results for the *DegT50* value of 50 d and lognormally distributed remaining fractions in terms of the CV. Results for other *DegT50* values are not shown because the CV's for these other values were always almost identical to those obtained for 50 d. Figure A5.1 shows that the CV of the estimated *DegT50* was only a weak function of the number of sampling times for 10, 15 and 20 soil samples. The surprisingly small effect of the number of sampling times is probably linked to the assumption in the simulations that the sampling times always cover the decline from 100 to 10% (also in the case of only two sampling times). The figure shows also that the effect of the number of sampling times becomes larger when only five soil samples are taken at each sampling time.
Figure A5.1 shows that the number of soil samples has only a small effect between ten and twenty soil samples. However, there is a considerable effect when the number of soil samples becomes smaller than 10.

It was tested whether the weight given to the fractions had a large effect on the estimated CV; this was done by performing calculations in which it was assumed that the weight of each fraction was equal to the inverse of this fraction. Thus the fractions at the different sampling times get an equal weight. The resulting CV's were considerably smaller than those shown in Figure A5.1 (e.g. the value for five sampling times and 20 samples was about 13% compared to about 20% in Figure A5.1).

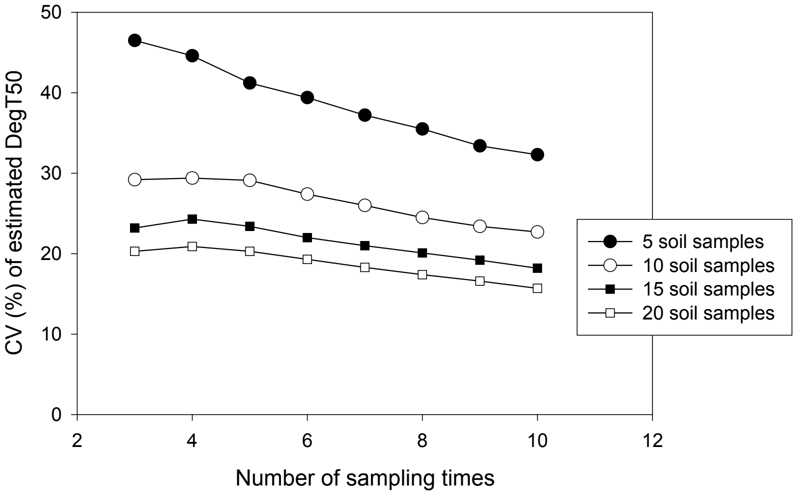

***Figure A5.1** Standard error of the DegT50 derived from hypothetical field studies as a function of the number of sampling times and number of soil samples in each study. Each point was calculated from 10000 datasets generated by Monte Carlo simulations. The remaining fractions were assumed to be lognormally distributed. All calculations were made for a true DegT50 value of 50 d.*

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Alterra Wageningen UR is the research institute for our green living environment. We offer a combination of practical and scientific research in a multitude of disciplines related to the green world around us and the sustainable use of our living environment, such as flora and fauna, soil, water, the environment, geo-information and remote sensing, landscape and spatial planning, man and society.

The mission of Wageningen UR (University & Research centre) is 'To explore the potential of nature to improve the quality of life'. Within Wageningen UR, nine specialised research institutes of the DLO Foundation have joined forces with Wageningen University to help answer the most important questions in the domain of healthy food and living environment. With approximately 30 locations, 6,000 members of staff and 9,000 students, Wageningen UR is one of the leading organisations in its domain worldwide. The integral approach to problems and the cooperation between the various disciplines are at the heart of the unique Wageningen Approach.