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Leaching of plant protection products and their transformation products

Proposals for improving the assessment of leaching to groundwater in
the Netherlands

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

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Proposals for improving the assessment of leaching to groundwater in the Netherlands

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Abstract

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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 an average K_{om} 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). We recommend to test the feasibility of proposals to a few dossiers before implementing them in the leaching assessment.

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 Environment and of Economic Affairs, Agriculture and Innovation 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 this report.

We would like to thank André Bannink (VEWIN¹) for help with collecting the groundwater monitoring data and for participating in the workgroup from 2005 to 2007. We would like to thank Aaldrik Tiktak (PBL) for participating in the workgroup in its early stage.

¹ André works currently for RIWA-Rijn.

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 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 improvements 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 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 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 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.

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 compounds, 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. The mean 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, (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 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 this study are not available, we recommend to use as a default value a Freundlich exponent of $N = 0.9$ and to deviate only from this value if reliable measurements of N are available with an arithmetic mean value that differs statistically significantly from $N = 0.9$.

We recommend to consider an N value reliable only if it is based on at least five 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 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 CaCl₂ and in 0.1 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 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_{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.

In view of the complexity and the preliminary nature of the proposed guidance for assessment of pH-dependent K_{om} values, we recommend to apply this guidance to the sorption of bentazone, MCPA and mecoprop and to revise the guidance thereafter. 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. We recommend further that such a fit 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.

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). Because of the complexity of this guidance we recommend testing and improving the guidance proposal by applying it to a number of datasets. As part of this guidance we proposed a simple equation for estimating the 90% penetration depth at the sampling time considered. We recommend to test this simple equation against a number of simulations with FOCUS groundwater scenarios.

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

Field studies with ridged potato fields indicate that leaching for full-field spray applications in such tillage systems may be considerably higher than for spray applications to crops grown on flat fields. Therefore we recommend to consider development of a separate leaching assessment procedure for such crop-tillage systems.

FOCUS (2009) developed guidance for evaluating lysimeter studies. This guidance is based on the principle that a lysimeter study is used to estimate the *DegT50* in the top soil using inverse modelling. However, this guidance has been formulated only at a general level and has not been tested in a few case studies. Therefore we recommend applying this guidance to a few lysimeters studies from regulatory dossiers and, based on this, developing more detailed guidance.

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 products² 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 complete enough or not state-of-the-art scientifically. Therefore these parts were revised and this revised guidance is described in this report. The workgroup intends to report the evaluation of these three substances at a later stage.

The procedures described in this guidance report assume 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.

² 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 abstractions³ 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 analyzed on:

- Is the compound an active ingredient in a plant protection product or a relevant metabolite?
- Is or was the active ingredient authorized in the Netherlands?
- Is the measurement a single positive, never confirmed afterwards?

If the compound 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 compounds are given in Appendix 1.

During this study also a WFD assessment was finalized, 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). Compounds found twice or more times in concentrations above 0.1 µg/L in deep groundwater have been added to Table 1⁴. 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. The results of those locations 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 compounds our REWAB criteria were positive. In the REWAB column of Table 1 the lower four WFD compounds with zero's were added because for these compounds our WFD criteria were positive (see header of Table 1 for explanation of criteria).

³ Only measurements in raw water have been used, no measurements in pumping wells or observation wells.

⁴ 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 available.

Table 1

Active ingredients found in deep groundwater in concentrations above 0.1 µg/L. Our criterion for including an active ingredient 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
ethylethioureum (ETU) (metabolite of e.g. the substances: mancozeb, maneb and metiram)	1	0/58	Yes
MCPA	2	1/537	Yes, 01-01-2012
mecoprop	4	15/547	Yes (only mecoprop-p), 01-06-2013
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, 01-07-2012

In the WFD assessment eight active ingredients were found twice or more in deep groundwater. DEET and 1,2-dichloropropane are not listed in Table 1 because they are not considered as 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 compounds labeled as substances with concerns for abstraction of groundwater are also found in deep groundwater in the WFD assessment; bentazon, mecoprop and bromacil. MCPA was not found in deep groundwater. Of the four compounds 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 bentazon (2/21) and mecoprop-P (2/21), and at 25 m depth bentazon (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 questionable⁵. 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). Glufosinate-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 compounds that were selected from the REWAB data because those compounds are found in groundwater abstraction areas.

Bentazon, MCPA and mecoprop-P were selected to validate the decision tree because they were found in more than one abstraction and they still have a registration in the Netherlands in 2008. Dichlobenil's metabolite BAM, also found in more than one abstraction area and registered in 2008, was not selected because BAM is considered to be a non-relevant metabolite in the Netherlands. However current discussions at EU level may lead to reconsideration of its non-relevancy.

⁵ 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 CS₂, including maneb, mancozeb, metiram, propineb, thiram and ziram)'. In case of positive findings further investigations are necessary to identify the origin of the CS₂ 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.

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% (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 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 PPP sorption coefficients in batch sorption studies is controlled by a dimensionless quantity P .

$$P \equiv \frac{M K}{V} \tag{1}$$

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:

$$r_K \equiv \frac{K_E - K}{K} \quad (2)$$

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 :

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

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

$$r_m \equiv \frac{m_A - m_R}{m_R} \quad (4)$$

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 and where it is assumed for the calculation of the adsorption that the mass at the end of the study is equal to the added mass. 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:

$$\varphi \equiv \frac{m_R}{m_A} \quad (5)$$

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:

$$r_m = \frac{1 - \varphi}{\varphi} \quad (6)$$

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:

$$K_E = (1 + r_K)K \quad (7)$$

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:

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

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

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

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:

$$\Phi \equiv \frac{K}{K_E} \quad (10)$$

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:

$$\Phi = \frac{1}{1 + r_K} \quad (11)$$

Combining Eqns 8, 9 and 11 gives:

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

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, $\varphi = 1$ and then also $\Phi = 1$, so measured and true sorption coefficient are equal. Another extreme case is $\varphi = 0$, which implies that the true sorption coefficient would be zero. Because sorption coefficients will usually be not negative, it seems necessary to require that $\varphi \geq 0$. Eqn 12 shows that this results in:

$$P_E > \frac{1 - \varphi}{\varphi} \quad (13)$$

If, for instance, $\varphi = 0.9$ (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:

$$\delta \equiv \frac{m_A - Vc_e}{m_A} \quad (14)$$

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:

$$P_E = \frac{\delta}{1 - \delta} \quad (15)$$

or:

$$\delta = \frac{P_E}{P_E + 1} \quad (16)$$

So Eqn 11 can be rewritten as:

$$\Phi = \frac{\varphi + \delta - 1}{\delta} \quad (17)$$

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

$$\Phi = \frac{\delta - \lambda}{\delta} \quad (18)$$

The correctness of Eqn 18 can be understood conceptually if we realise that $\delta - \lambda$ 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:

$$r_m = \frac{\lambda}{1 - \lambda} \quad (19)$$

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 $\Phi < 0.5$. 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 (ie 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.

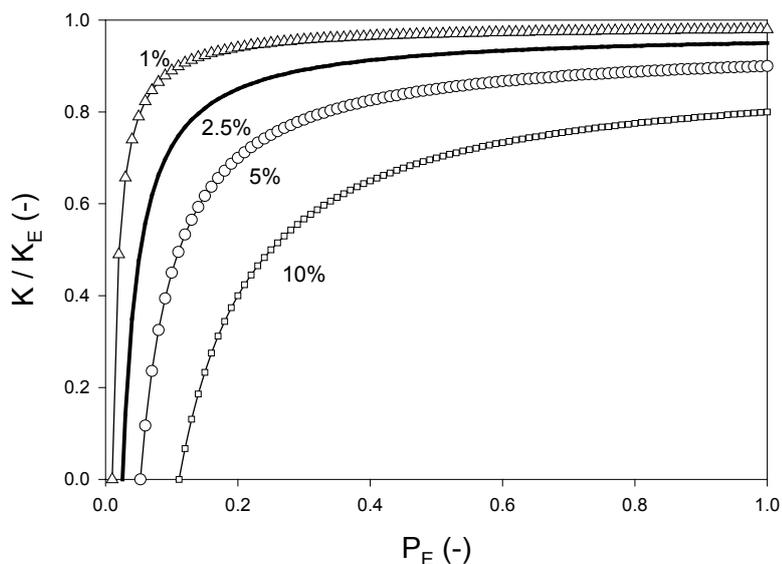


Figure 1
 Ratio of the true sorption coefficient divided by the measured sorption coefficient ($\Phi = K/K_E$) as a function of P_E calculated with Eqn 12 for fractions of the test substance lost (λ) of 1, 2½, 5 or 10% (i.e. $\phi = 0.99, 0.975, 0.95$ and 0.90 respectively).

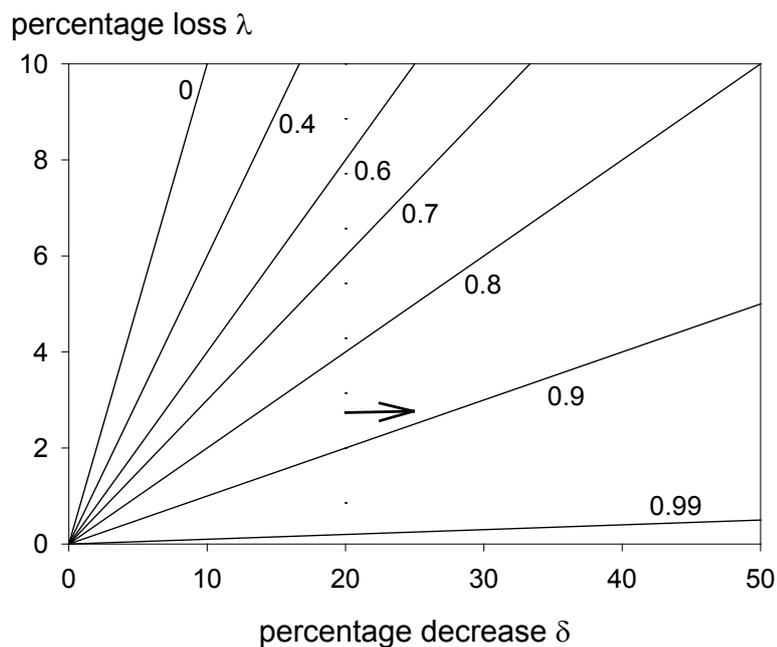


Figure 2
 Contour plot of the ratio between the true sorption coefficient divided by the measured sorption coefficient ($\Phi = K/K_E$) as a function of the fractional decrease in the liquid phase, δ , and the fraction of the test substance lost, λ . The solid lines are contour lines with values of Φ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

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 registration procedures.

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 compounds 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
Rhnen	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 describes the curvature of the Freundlich sorption isotherm:

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

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 very 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 ($1/n$) 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 $1/n$ should also be used (note that $1/n$ is sometimes also referred to as 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 $1/n$ -value. For models, which require the Freundlich adsorption coefficient, the exponent of the isotherm ($1/n$) is also required and values of this parameter are typically determined in each sorption experiment. If a number of $1/n$ have been determined (e.g. for a number of soils), the average value of $1/n$ should also be used (note that $1/n$ is sometimes also referred to as N). A default value of 0.9 is assumed if no information on the $1/n$ 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 then 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 to this recommendation firstly because it is inconsistent with the use of a default N value of 0.9 for the parent compound. 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 and of reliable studies we recommend to use $N = 0.9$ as a default value and to deviate only from this value if reliable measurements of N are available with an arithmetic mean value that differs statistically significantly from $N = 0.9$. So also when only one sorption point is available for a soil metabolite, 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:

- accept Freundlich exponents only from studies that included at least five different initial concentrations and in which the difference between the highest and the lowest initial concentration was at least a factor of 100 (this instruction for the measuring procedure is consistent with OECD 106, section 72, which states: 'Five test substance concentrations are used, covering preferably two orders of magnitude.', see OECD, 2000).
- additionally, do not accept measured Freundlich exponents if the correction of the sorption coefficient based on Eqn 18 exceeds 20% (so if the ratio $\Phi = K/K_E$ in Figure 2 is less than 0.8) or if P_E is less than 0.1; this is based on the argument that, if the sorption coefficient is considered unreliable, the curvature has to be unreliable as well.

This second 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 limits to the N values of sorption isotherms of a specific substance-soil combination. 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. 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 in the statistical test (N values for individual sorption isotherms have random errors in either direction and setting an upper limit will lead to such a bias).

3.4 Guidance for estimating sorption coefficients from soil column studies

When analysing dossiers of bentazone, mecoprop and mcpa, almost all batch sorption coefficients became zero after the correction based on Eqn 18. In the dossiers a number of soil column studies were available and we considered it appropriate to evaluate these hoping to obtain reliable non-zero values of the sorption coefficient. For that purpose, guidance was needed which is described below.

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

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

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 :

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

Equation 22 shows that a conservative (low) value of K is obtained for high values of θ and high values 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). Figure 3 shows K as a function of Z for a realistic value of W and these default values of θ and ρ . The figure shows that K becomes infinitely high when Z approaches zero. The consequence is that an error of 1 cm in the measured penetration depth will have a large effect at penetration depths shallower than 5-10 cm. So this method is mainly useful for penetration depths above 10 cm, so K values below 1 L/kg.

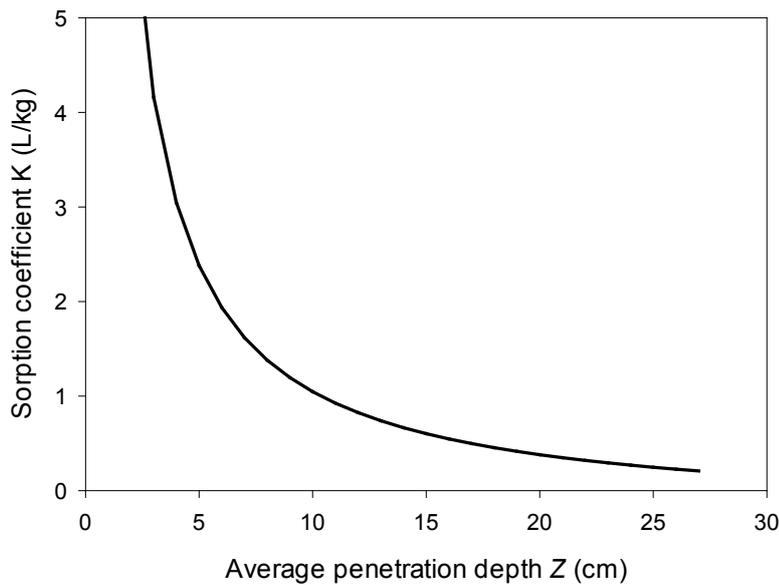


Figure 3

The sorption coefficient K as a function of the average penetration depth Z as calculated with Eqn 22 assuming $\theta = 0.43$, $\rho = 1.5 \text{ kg/L}$ and $W = 20 \text{ cm}$.

There are two possibilities for the outcome of a soil column experiment: (1) more than 50% of the dose has leached out of the column at the end of the experiment, (2) less than 50% of the dose has leached out of the column at the end of the experiment. In the first case, Z is set to the length of the column and W is set to the water layer necessary for leaching 50% of the dose out of the column. In the second case, Z is estimated from the measured concentration profile (see Mensink et al. ,2008, for detailed guidance for both cases).

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:

$$X = K c \quad (23)$$

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:

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

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

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

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

If all batch sorption lead to zero sorption coefficients after the correction based on Eqn 18, it may be appropriate to consider soil TLC studies if available because these may result in reliable non-zero values of the sorption coefficient. Therefore guidance for interpretation of soil TLC studies is described below.

The results of soil TLC studies are commonly expressed in terms of the factor R_F defined as:

$$R_F \equiv \frac{S}{W} \quad (26)$$

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_F is always between 0 and 1 (Helling, 1971; SCP, 2002). Usually the substance is located in a small dot at the end of the experiment. It is then justifiable to assume that S is approximately equal to the average distance over which the substance has moved. There are two measurement methods for S : the first is to measure the front of the dot at the end of the experiment and compare with the front at the start of the experiment and the second is to measure the centre of mass of the dot at the start and at the end of the experiment. We recommend to use the centre-of-mass approach (if possible) because this is more accurate.

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

$$R_F = \frac{\theta}{\theta + \rho K} \quad (27)$$

where θ is the volume fraction of water in the thin layer and ρ is the dry bulk density in this layer. Note that this R_F 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 :

$$K = \frac{\theta(1 - R_F)}{\rho R_F} \quad (28)$$

Figure 4 shows K as a function of R_f for $\theta = 0.6$ and $\rho = 1 \text{ kg/L}$. As described by SCP (2002) an absolute error of 0.05 in R_f is quite common. Figure 4 shows that this indicates that K values above 1 L/kg are very inaccurate.

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 $\rho = 1.0 \text{ kg/L}$. 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.

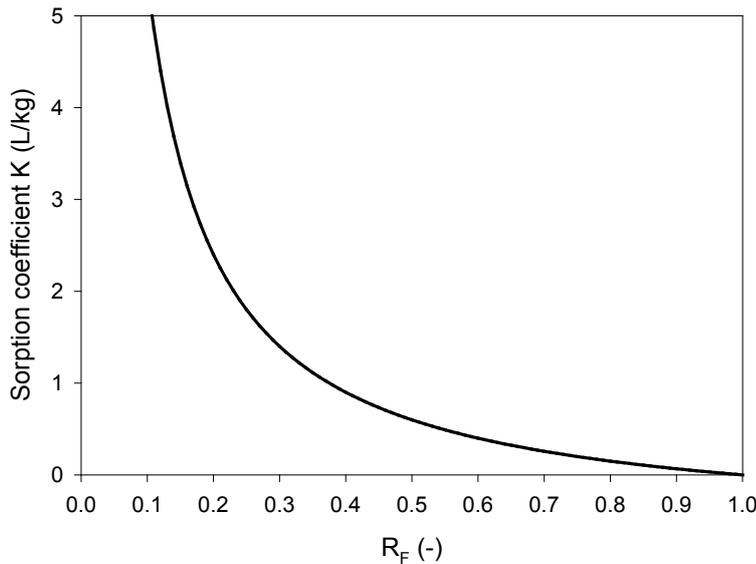


Figure 4

The sorption coefficient K as a function of the retention factor R_f as calculated with Eqn 28 assuming $\theta = 0.6$ and $\rho = 1 \text{ kg/L}$.

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_f is based on the average transport distance of the substance whereas the front is measured; so measured R_f 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 to the second argument of the SCP. However, we agree that soil TLC studies produce lower limits in view of the limited contact time.

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. By definition, no accurate Freundlich exponents will be available for such products. Therefore we recommend to use for TLC studies the default value of 0.9 for the Freundlich exponent using 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.

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

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 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:



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:

$$K_{eq} = \frac{[H^+][A^-]}{[HA]} \quad (30)$$

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):

$$K_{om,pH} = \frac{K_{om,acid} + K_{om,anion} \frac{M_{anion}}{M_{acid}} 10^{pH-pK_a-\Delta pH}}{1 + \frac{M_{anion}}{M_{acid}} 10^{pH-pK_a-\Delta pH}} \quad (31)$$

in which:

$K_{om,pH}$ the pH-dependent organic-matter/water sorption coefficient, $dm^3 kg^{-1}$

$K_{om,acid}$ the K_{om} for the weak acid, $dm^3 kg^{-1}$

$K_{om,anion}$ the K_{om} for the anion, $dm^3 kg^{-1}$

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 $500 dm^3/kg$, $K_{om,anion}$ is $5 dm^3/kg$ 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 $pH = 6$ ie 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.

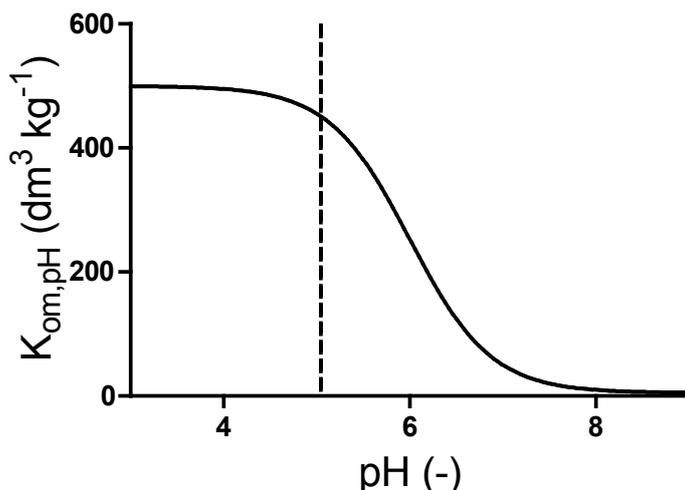


Figure 5

Example curve of the K_{om} as function of soil pH calculated with Eqn 31 for $K_{om,acid} = 500 \text{ dm}^3/\text{kg}$, $K_{om,anion} = 5 \text{ dm}^3/\text{kg}$, $M_{acid} = 200 \text{ g/mol}$, $M_{anion} = 199 \text{ g/mol}$, $pK_a = 5$ and $\Delta\text{pH} = +1$. The vertical line indicates $\text{pH} = 5$ (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 , $0.01 \text{ mol dm}^{-3} \text{ CaCl}_2$ solution and $1 \text{ mol dm}^{-3} \text{ KCl}$ solution for suspending the soil. The methods are referred to as $\text{pH}_{\text{H}_2\text{O}}$, $\text{pH}_{\text{CaCl}_2}$ 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 $\text{pH}_{\text{CaCl}_2}$ 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 CaCl₂ or KCl is expected to be lower than in a measurement with water. Comparing the CaCl₂ and KCl measurements, the pH in the KCl measurement is usually lower than the pH in the CaCl₂ 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 CaCl₂. 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 CaCl₂, 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 ^{uw}	81 ^{uw}	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} , $\text{pH}_{\text{CaCl}_2}$ and $\text{pH}_{\text{H}_2\text{O}}$ 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} , $\text{pH}_{\text{CaCl}_2}$ and $\text{pH}_{\text{H}_2\text{O}}$. Arguments for this decision are:

- description of the analysis method is not always complete, ie ratio or molarity is sometimes not stated;
- the soil:solution ratio is approximate for many samples, especially when fresh material was the starting point for the analysis;
- 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;
- 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:

$$\text{pH}_{\text{CaCl}_2} = 1.018 \text{pH}_{\text{H}_2\text{O}} - 0.660 \quad [32a]$$

$$\text{pH}_{\text{H}_2\text{O}} = 0.982 \text{pH}_{\text{CaCl}_2} + 0.648 \quad [32b]$$

$$\text{pH}_{\text{KCl}} = 1.109 \text{pH}_{\text{CaCl}_2} - 0.804 \quad [33a]$$

$$\text{pH}_{\text{CaCl}_2} = 0.902 \text{pH}_{\text{KCl}} + 0.725 \quad [33b]$$

$$\text{pH}_{\text{KCl}} = 1.163 \text{pH}_{\text{H}_2\text{O}} - 1.723 \quad [34a]$$

$$\text{pH}_{\text{H}_2\text{O}} = 0.860 \text{pH}_{\text{KCl}} + 1.482 \quad [34b]$$

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 $\text{pH}_{\text{CaCl}_2}$ results on the $\text{pH}_{\text{H}_2\text{O}}$ 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.

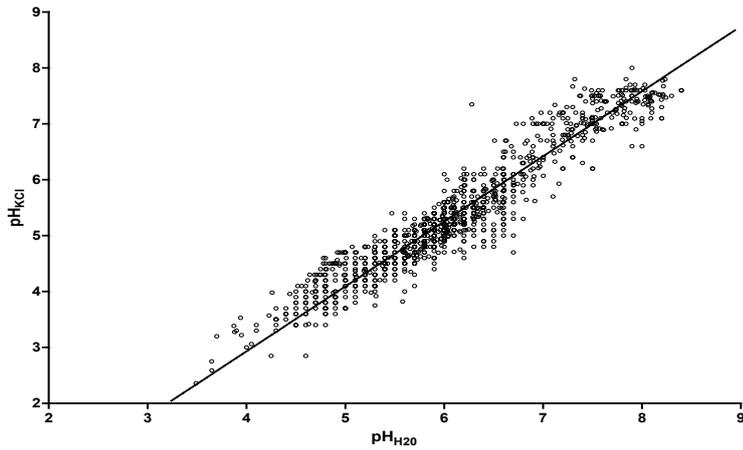


Figure 6

Orthogonal regression of $\text{pH}_{\text{H}_2\text{O}}$ 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.

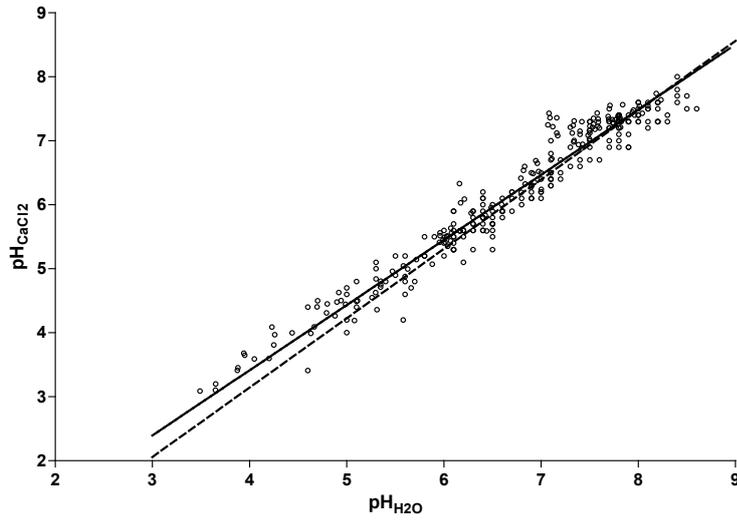


Figure 7

Orthogonal regression of $\text{pH}_{\text{H}_2\text{O}}$ versus $\text{pH}_{\text{CaCl}_2}$. 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.

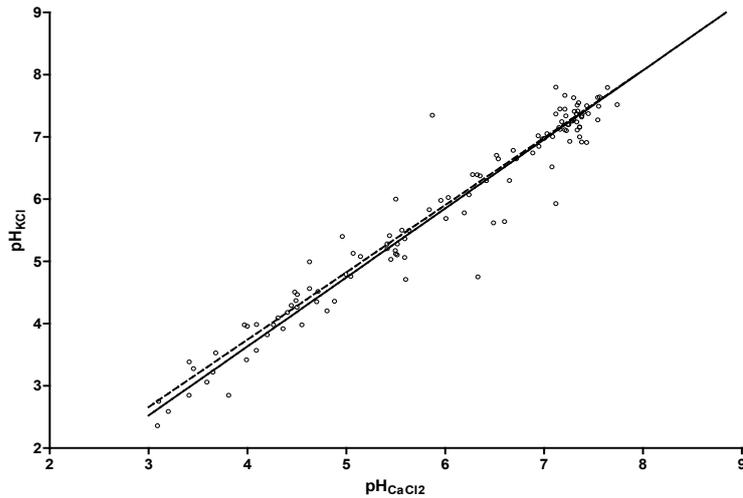


Figure 8

Orthogonal regression of pH_{CaCl_2} 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_{H_2O} 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 $pH_{KCl} - pH_{CaCl_2}$ 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:

$$pH_{KCl} = 1.08 pH_{CaCl_2} - 0.59 \quad (35a)$$

$$pH_{CaCl_2} = 0.92 pH_{KCl} + 0.54 \quad (35b)$$

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_{CaCl_2} and pH_{H_2O} for soils originating from the south-eastern USA. Using ordinary linear regression, they found the regression line ($R^2 = 0.9088$):

$$pH_{H_2O} = 0.92 pH_{CaCl_2} + 1.10 \quad (36)$$

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 $\log(\text{CaCl}_2)$ 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 $\text{pH}_{\text{H}_2\text{O}}$ and pH_{KCl} from Eqn 34b:

$$\text{pH}_{\text{H}_2\text{O}} - \text{pH}_{\text{KCl}} = + 1.482 - 0.140 \text{pH}_{\text{KCl}} \quad (37)$$

Similarly we can calculate the difference between $\text{pH}_{\text{CaCl}_2}$ and pH_{KCl} from Eqn 33b:

$$\text{pH}_{\text{CaCl}_2} - \text{pH}_{\text{KCl}} = + 0.725 - 0.098 \text{pH}_{\text{KCl}} \quad (38)$$

The difference between $\text{pH}_{\text{CaCl}_2}$ and $\text{pH}_{\text{H}_2\text{O}}$ can be calculated from Eqn 32b:

$$\text{pH}_{\text{H}_2\text{O}} - \text{pH}_{\text{CaCl}_2} = + 0.648 - 0.018 \text{pH}_{\text{CaCl}_2} \quad (39)$$

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:

$$\text{pH}_{\text{H}_2\text{O}} - \text{pH}_{\text{CaCl}_2} = + 0.635 - 0.0162 \text{pH}_{\text{KCl}} \quad (40)$$

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 $\text{pH}_{\text{H}_2\text{O}}$ and pH_{KCl} decreases from about 1.0 at $\text{pH}_{\text{KCl}} = 3.5$ to about 0.4 at $\text{pH}_{\text{KCl}} = 7.5$. The average difference $\text{pH}_{\text{H}_2\text{O}} - \text{pH}_{\text{KCl}}$ over this range is 0.7. The figure shows also that the difference between $\text{pH}_{\text{CaCl}_2}$ and pH_{KCl} decreases from about 0.4 at $\text{pH}_{\text{KCl}} = 3.5$ to about 0 at $\text{pH}_{\text{KCl}} = 7.5$. The average difference $\text{pH}_{\text{CaCl}_2} - \text{pH}_{\text{KCl}}$ over this range is 0.2. Figure 10 shows also that the difference $\text{pH}_{\text{H}_2\text{O}} - \text{pH}_{\text{CaCl}_2}$ does only vary slightly between $\text{pH}_{\text{KCl}} = 3.5$ and $\text{pH}_{\text{KCl}} = 7.5$. The average difference over this range is 0.5. These average differences are summarized in Table 4.

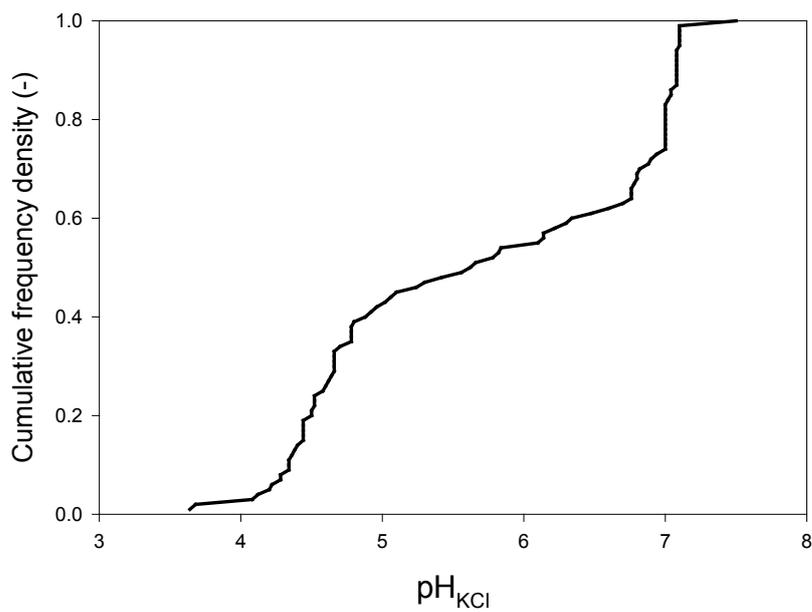


Figure 9
 Cumulative frequency density of pH_{KCl} of Dutch arable soils based on the GeoPEARL database (personal communication R. Kruijine, 2010).

pH difference

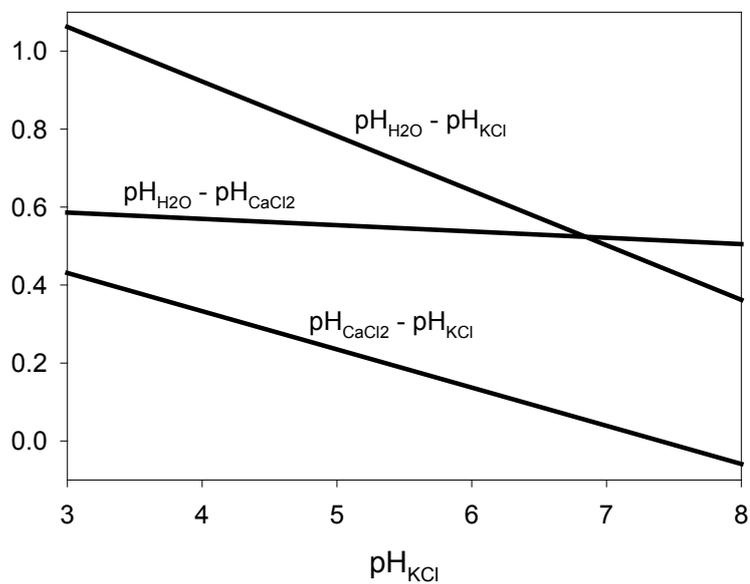


Figure 10
 Differences between the three pH measurement methods as a function of pH_{KCl} as calculated with Eqns 37, 38 and 40.

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
$pH_{H_2O} - pH_{KCl}$	0.7
$pH_{H_2O} - pH_{CaCl_2}$	0.5
$pH_{CaCl_2} - pH_{KCl}$	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 should be easy to use also for 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 if the pK_a of the substance is between 2 and 8. 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.

If the pK_a of a substance is between 2 and 8, the data handling has to follow the next 6 steps:

1. Evaluate the quality of the individual sorption data and exclude all data that are considered to have insufficient quality from further analyses. Continue only if at least four K_{om} values are left.
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_{H_2O} 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 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 and upper/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.
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 influence the curve because a default correction for the recovery was made. If this is the case, the data pair should be discarded.

After following this data handling procedure, we recommend to use the flow chart in Figure 11 to obtain the sorption parameters. 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. The next step is to check whether the range of pH values is at least 3. We consider this as a minimum to estimate the 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 fixed⁶ 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 software package successfully terminates the fitting procedure), plot the fitted line along with the measurements 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.

⁶ 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.

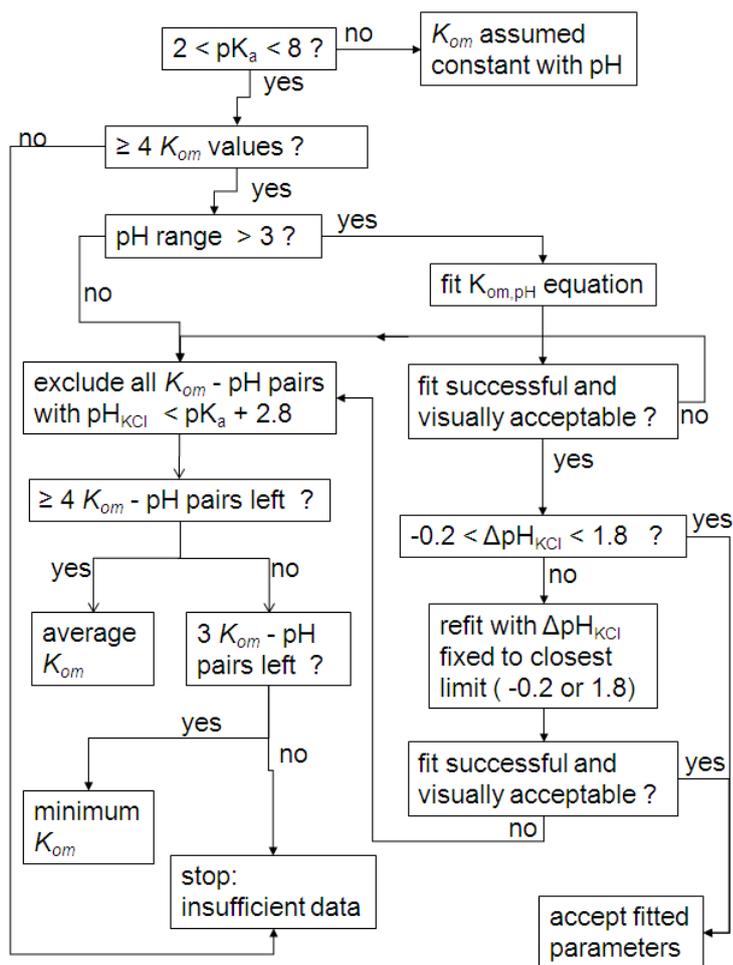


Figure 11

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).

So for that purpose we have to define the acceptable range of ΔpH . Bolt and Bruggenwert (1976) mention a value of 1 pH unit for the surface acidity effect, ie the pH at the surface is 1 pH unit lower than in the bulk solution. Nicolls and Evans (1991) report a value of 1.8 for this. Schachtschabel et al. (1989) report a range of surface charge values; the average surface charge being higher for illite and vermiculite clays. According to their values, the theoretical surface acidity effect could be around 3 pH units for very heavy clay soils, so somewhat higher than the value reported by Nicolls and Evans. In general, however, it is to be expected that the surface acidity effect is lower and more close to the value reported by Bolt and Bruggenwert for agricultural soils. The main reasons for this are the shielding effect of compounds sorbed to the surface, the fact that soils do not consist of pure clays and the abundant presence of other cations than H^+ in the diffuse double layer. 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 Eigenraam (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. Based on these arguments, we conclude that a range of ΔpH of 2 pH-units is acceptable.

As mentioned earlier, Bolt and Bruggenwert (1976) state that $\Delta\text{pH} = 1$ is typical for temperate agricultural soils, when measured in a 0.01 normal salt solution. An acceptable range in ΔpH -values would then be 0 - 2 for the $\text{pH}_{\text{CaCl}_2}$ 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, ie 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 $\text{KCl} < \text{CaCl}_2 < \text{H}_2\text{O}$, 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 $\text{pH}_{\text{CaCl}_2}$ series or a $\text{pH}_{\text{H}_2\text{O}}$ series. This is illustrated with Figure 12 which shows an example of $K_{\text{om,pH}}$ as a function of pH for the three measurement methods.

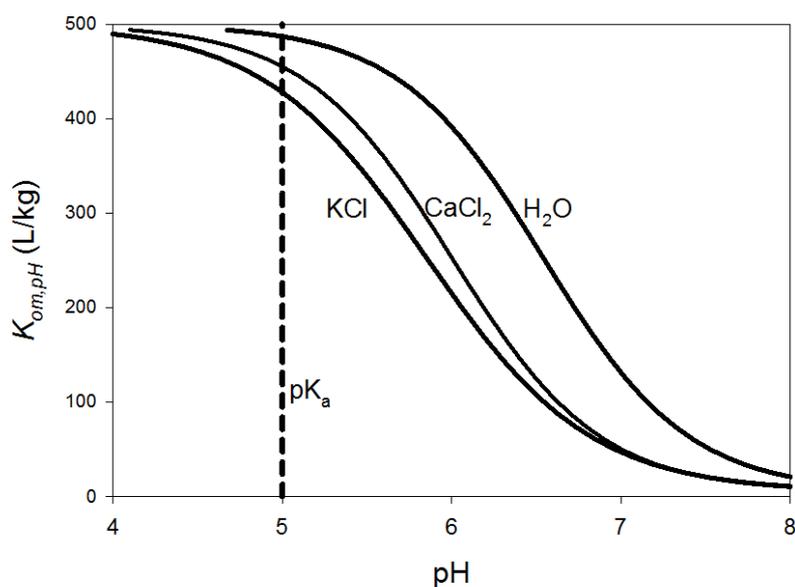


Figure 12

Example of a relationship between $K_{\text{om,pH}}$ and pH for the three different pH-measurement methods.

The line for CaCl_2 was calculated with Eqn 31 for $K_{\text{om,acid}} = 500 \text{ dm}^3/\text{kg}$, $K_{\text{om,anion}} = 5 \text{ dm}^3/\text{kg}$, $M_{\text{acid}} = 200 \text{ g/mol}$,

$M_{\text{anion}} = 199 \text{ g/mol}$, $\text{pK}_a = 5$ and $\Delta\text{pH} = +1$. 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 acceptable range for $\Delta\text{pH}_{\text{CaCl}_2} = 0 - 2$, the acceptable range for $\Delta\text{pH}_{\text{H}_2\text{O}}$ is 0.5 - 2.5, and the acceptable range for $\Delta\text{pH}_{\text{KCl}}$ is -0.2 - 1.8. In Figure 11, we assume 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 $\Delta\text{pH}_{\text{KCl}}$ is replaced by the ranges of $\Delta\text{pH}_{\text{H}_2\text{O}}$ or $\Delta\text{pH}_{\text{CaCl}_2}$.

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 $\Delta\text{pH}_{\text{KCl}}$ was below -0.2 or +1.8 if the fitted $\Delta\text{pH}_{\text{KCl}}$ was above 1.8) and Eqn 31 fitted again. Then it is again checked whether the fit was successful and visually acceptable.

We now consider the left branch 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 4 K_{om} -pH pairs with pH_{KCl} above $\text{pK}_a + 2.8$. This is based on the

requirement that $\text{pH}_{\text{CaCl}_2} > \text{pK}_a + 3$ which implies that $\text{pH}_{\text{KCl}} > \text{pK}_a + 2.8$ (Table 4). If this is the case, the average K_{om} of these pairs can be used to estimate the $K_{om,anion}$ as a conservative result.

The background of the criterion $\text{pH}_{\text{CaCl}_2} > \text{pK}_a + 3$ 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 $\text{pH}_{\text{CaCl}_2} = 8$ (ie $\text{pH}_{\text{CaCl}_2} = \text{pK}_a + 3$) the K_{om} is very close to that of the anion. Following the same reasoning, for $\text{pH}_{\text{H}_2\text{O}}$ the criterion becomes $\text{pH}_{\text{H}_2\text{O}} > \text{pK}_a + 3.5$.

If there are no 4 such K_{om} -pH pairs, it is tested in Figure 11 whether there are at least 3 such pairs. If yes, the minimum of these three is used to estimate the $K_{om,anion}$ as a conservative result. If less than 3 pairs are available, the data are considered insufficient to estimate 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 $\text{pH}_{\text{H}_2\text{O}}$ 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 $\text{pH}_{\text{H}_2\text{O}}$ value to either a $\text{pH}_{\text{CaCl}_2}$ 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 $\text{pH}_{\text{CaCl}_2}$ and pH_{KCl} values are always lower than $\text{pH}_{\text{H}_2\text{O}}$ 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 $K_{om,pH}$, ie 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 $\text{pH}_{\text{H}_2\text{O}}$ will be further illustrated by the example in Section 3.6.4.

The selection of the acceptable range of $\Delta\text{pH}_{\text{KCl}}$ 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 $\Delta\text{pH}_{\text{KCl}} = 1.8$ there may be a significant contribution of the weak acid between $\text{pH}_{\text{KCl}} = 4$ and $\text{pH}_{\text{KCl}} = 5$. 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.

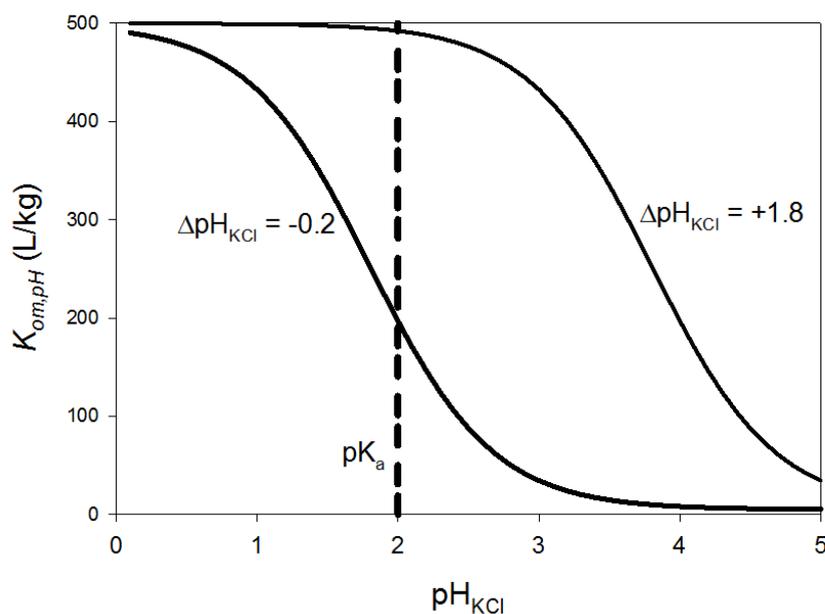


Figure 13

Relationship between $K_{om,pH}$ and pH_{KCl} calculated with Eqn 31 for $K_{om,acid} = 500 \text{ dm}^3/\text{kg}$, $K_{om,anion} = 5 \text{ dm}^3/\text{kg}$, $M_{acid} = 200 \text{ g/mol}$, $M_{anion} = 199 \text{ g/mol}$, $pK_a = 2$ 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_{H_2O} 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 $500 \text{ dm}^3 \text{ kg}^{-1}$, a $K_{om,anion}$ of $5 \text{ dm}^3 \text{ kg}^{-1}$ 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.

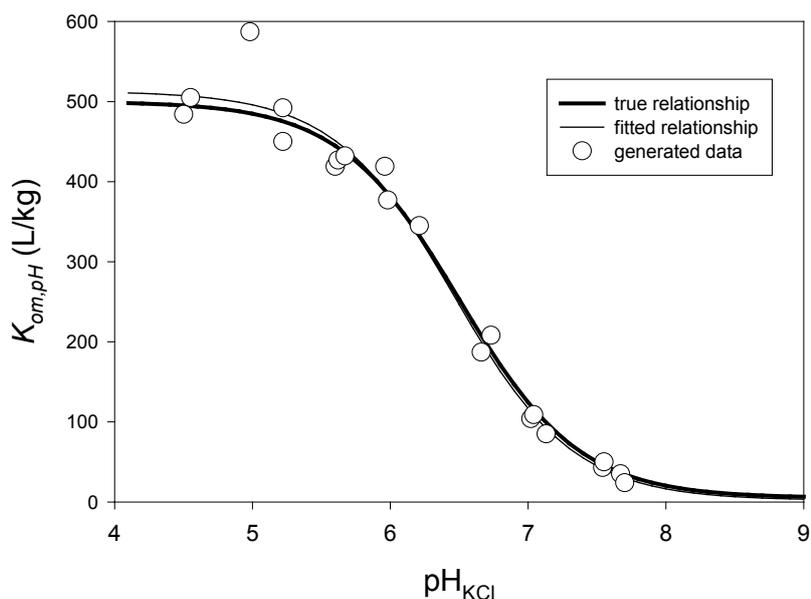


Figure 14

$K_{om,pH}$ as a function of pH. The thick solid line was calculated with Eqn 31 for $K_{om,acid} = 500 \text{ dm}^3/\text{kg}$, $K_{om,anion} = 5 \text{ dm}^3/\text{kg}$, $M_{acid} = 200 \text{ g/mol}$, $M_{anion} = 199 \text{ g/mol}$, $pK_a = 6$ and $\Delta pH = +0.5$. 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 $500 \text{ dm}^3 \text{ kg}^{-1}$). The fitted $K_{om,anion}$ was $2 \text{ dm}^3 \text{ kg}^{-1}$, so somewhat lower than the true value of $5 \text{ dm}^3 \text{ kg}^{-1}$. The fitted ΔpH was 0.46 which is close to the true value of 0.5.

In order to illustrate that use of pH_{H_2O} 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_{H_2O} 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_{H_2O} as the default measurement method is conservative: the line for dataset B is below that for dataset A.

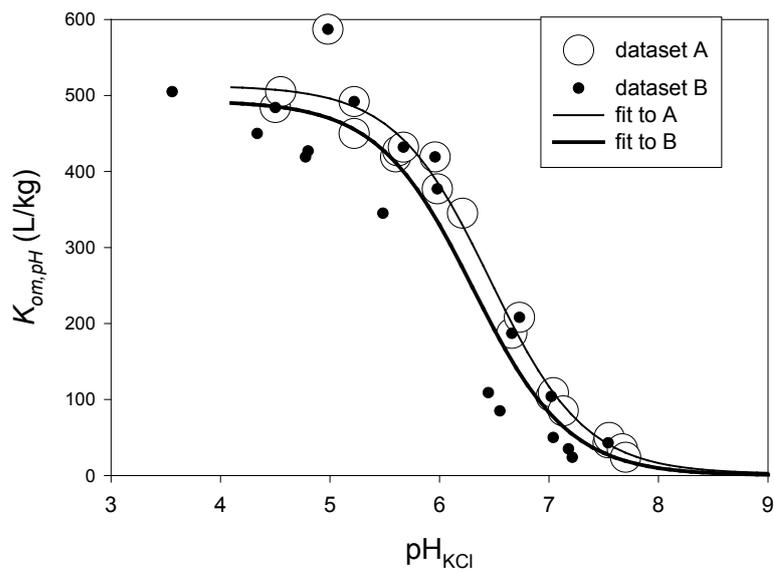


Figure 15
 Datasets A and B and their fits to the relationship between $K_{om,pH}$ and pH of Eqn 31.
 See Table 6 for parameter values of the fitted lines.

Table 5

Two hypothetical example data sets. Dataset A was generated using Eqn 31 with $K_{om,acid} = 500 \text{ dm}^3/\text{kg}$, $K_{om,anion} = 5 \text{ dm}^3/\text{kg}$, $M_{acid} = 200 \text{ g/mol}$, $M_{anion} = 199 \text{ g/mol}$, $pK_a = 6$ and $\Delta pH = +0.5$ 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_{H_2O} .

Dataset A		Dataset B		
pH_{KCl}	$K_{om} (\text{dm}^3 \text{ kg}^{-1})$	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: $K_{om,acid} = 500 \text{ L/kg}$, $K_{om,anion} = 5 \text{ L/kg}$ and $\Delta pH_{KCl} = 0.5$.

Fitted parameter	Dataset	Best fit value	Standard error	95% confidence interval
$K_{om,acid} (\text{L/kg})$	A	513	13	485-540
	B	493	25	440-546
$K_{om,anion} (\text{L/kg})$	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 sorption coefficient depends 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:

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

where:

$K_{F,eq}$ ($m^3 \text{ kg}^{-1}$) is the overall Freundlich sorption coefficient,

$K_{F,eq,0}$ ($m^3 \text{ kg}^{-1}$) 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,

$K_{om,eq}$ ($m^3 \text{ kg}^{-1}$) 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 $K_{clay,eq}$ ($m^3 \text{ kg}^{-1}$) are the coefficients for sorption to sand, silt and clay, respectively,

c_{sox} (mmol kg^{-1}) is the soil content of sesqui-oxides and

$K_{sox,eq}$ ($m^3 \text{ mmol}^{-1}$) 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 to 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

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. The guidance in Section 3.2.3 implies that each K_{om} value derived from a batch study has to be corrected. So the further assessment is based on the 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). We recommend as a base line to calculate the arithmetic⁷ mean of all corrected values and use this mean in the leaching calculations.

However, 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.

⁷ We are aware that EFSA (2011) suggested to use a geomean of the relevant K_{om} values instead of an arithmetic mean for the exposure assessment of soil organisms. We have the impression that this was mainly based on the use of the geomean K_{om} when deriving the soil exposure scenarios (considering both a stochastic K_{om} and *DegT50*) and the need for consistency between the scenario development and the assessment using dossier data. The assessment of the 90th percentile leaching concentration in GeoPEARL did not consider stochastic uncertainty in the K_{om} so this consistency is not an argument for the Dutch leaching assessment procedure. Moreover, EFSA (2011) has only the status of a guidance proposal for soil exposure assessment. Therefore we stick to the convention of using the arithmetic average (Anonymous, 2011) until consolidated guidance has become available at the EU level.

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 for calculation
A	20	>16		16
B	18	>12		12
C	14	>0	6	6
D	30	>0		0
E			8	8
arithmetic mean				8

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).

Let us next consider the example in Figure 16 (where corrections are based on the default 10% loss). The first point is that the result of soil nr. 4 is discarded because the range of uncertainty is too wide and the measurement has therefore no added value. For soil nr. 8 we recommend to test whether zero is part of the 95% confidence interval of the remaining measurements; if yes, then include this zero value and if no, then exclude (in this particular case soil nr. 8 would be included because adding soil nr. 7 leads to a 95% confidence interval that includes very probably zero). The argument for this is that the corrected value is a lower limit if based on the default 10% loss and that therefore a lower limit outside the range of the other values has no added value.

If corrections would be 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 nr. 6 for which we do not recommend any statistical testing. In the case of Figure 16, thus at the end only soil nr. 4 would be excluded and the value selected for calculation is the arithmetic mean of the closed symbols of all soils except nr. 4, resulting in a K_{om} of 8 L/kg.

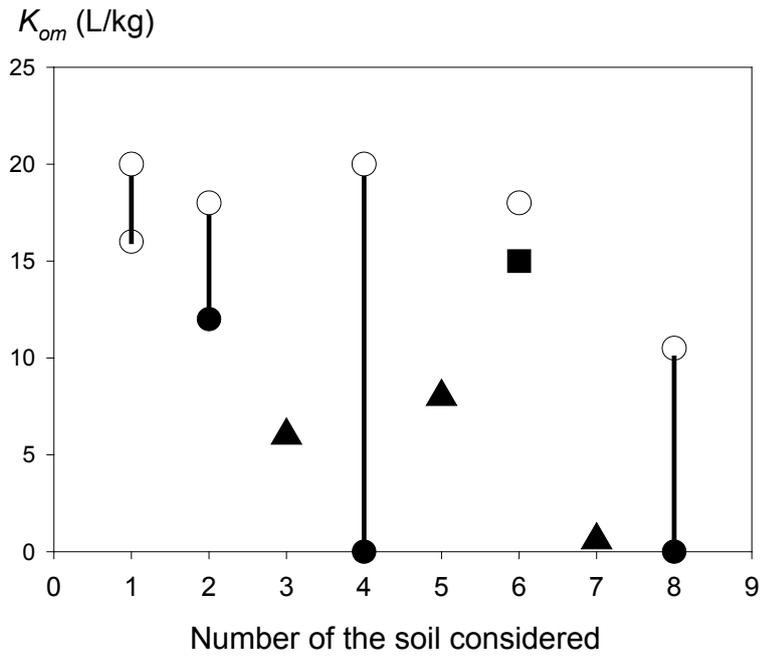


Figure 16

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 nr. 6 is a batch value that is corrected based on measured recovery in the study; the triangles for soils nrs. 3, 5 and 7 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 test whether this mean differs significantly (using t-test at 5% level) from 0.9 as described in Section 3.4.

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 PPP areic masses 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 cm²: 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).

Say that m = content of plant protection product in soil (mg/kg). The following procedure for estimating total amount in soil from concentration profiles is proposed as long as it is expected that >50% of the plant protection product present in the soil at the sampling time is still in the top sampled layer:

1. As long as no rain has fallen, and no tillage or ploughing took place, include only top layer in calculation.
2. In case $LOD < m < LOQ$, assume $m = 0.5 (LOQ + LOD)$. This is the same procedure as proposed by FOCUS (2006; p. 73). If only LOQ is given, we suggest to use $LOQ = 3 LOD$ (ENV-ISO, 1998).
3. When going from top layer to deeper layers, and assuming that m remains below LOD after first layer with $m < LOD$:
assume $m = 0.5 LOD$ for first layer with $m < LOD$ and assume $m = 0$ for deeper layers unless penetration depth calculations (see Eqn 43 later in this section) indicate that penetration into first layer with $m < LOD$ is unlikely (ie if penetration depth is less than half the thickness of the first layer); in this unless-case assume $m = 0$ for first layer with $m < LOD$.
If only LOQ is given and results are stating $m < LOQ$, then assume: (i) $m = 2/3 LOQ$ for the first layer with $m < LOQ$, (ii) $m = 1/6 LOQ$ for the second layer with $m < LOQ$ and (iii) $m = 0$ for deeper layers unless penetration depth calculations (see Eqn 43 later in this section) indicate that penetration into first layer with $m < LOQ$ is unlikely (ie if penetration depth is less than half the thickness of the layer above); in this unless-case assume $m = 0$ for first layer with $m < LOQ$.
In case of very mobile plant protection products, a more strict procedure is necessary (see below).
4. When going from top layer to deeper layers, and assuming that m first decreases below LOD and then increases again above LOD: assume $m = LOD$ for all intermediate layers with $m < LOD$; assume $m = 0.5 LOD$ for first layer below in which m remains below LOD and assume $m = 0$ for deeper layers.
If only LOQ is given and m first decreases below LOQ and then increases above LOQ again: assume $m = LOQ$ for all intermediate layers with $m < LOQ$; assume $m = 2/3 LOQ$ for first layer of the toe of the

concentration profile in which m remains below LOQ, assume $m = 1/6$ LOQ for the second layer and $m = 0$ for deeper layers.

Based on the above procedure, values of 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:

$$A = \int \rho m dx \quad (42)$$

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 $1.5 \text{ kg}/\text{L}$ 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.

Table 8 shows an example of this calculation procedure.

Table 8

Illustration of calculation procedure of total PPP mass from measured course of PPP content with depth in a field persistence study. It was assumed that the dry soil bulk density is $1.5 \text{ kg}/\text{L}$ for all layers.

Depth of soil layers	Measured content (mg/kg)	Content used in calculation (mg/kg)	Areic mass (kg/ha)
0-10 cm	0.60	0.60	0.900
10-20 cm	0.06	0.06	0.090
20-40 cm	< LOQ = 0.010	0.006	0.018
40-70 cm	< LOD = 0.002	0.001	0.005
70-100 cm	< LOD = 0.002	0	0.000
Sum of all layers			1.013

In the above procedure it is assumed that the PPP concentration decreases continuously with soil depth. This assumption is not valid anymore if the concentration in the top sampled layer is not the maximum concentration. If then m is below the e.g. LOD, there is no reasonable certainty that it is zero even if all shallower layers are below the LOD. So it is necessary to estimate the depth over which the plant protection product may have penetrated into soil, i.e. the toe of the front. We propose 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 the equation for the average penetration depth of plant protection product in soil assuming chromatographical transport theory and piston flow:

$$X_p = \frac{R}{\theta + \rho OM K_{OM}} \quad (43)$$

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)

It is recommended to estimate the volume fraction of water at field capacity from FOCUS (2000, p. 90) and to set the dry bulk density at 1.3 kg/L if it was not measured in the field experiment. This 1.3 kg/L is the average value of the top layers of the soil profiles of the nine FOCUS groundwater scenarios (FOCUS, 2000). If the dry bulk density was measured, then the measured value should be used.

Eqn 43 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. Further simulations with FOCUS scenarios are recommended to support or refine this approach. Eqn 43 should be seen as a first version of a metamodel for the 90% penetration depth. We recommend to test this proposal against a number of simulations with FOCUS groundwater scenarios. This testing is beyond the scope of this report.

So if the 90% penetration depth as estimated with Eqn 43 is located deeper than the bottom of the top sampled layer, the above procedure is applied but with the following additional rules for the toe of the concentration profile (in between brackets the assumptions when only LOQ is reported):

5. If $m < LOD$ and bottom of a sampling layer less than 90% penetration depth, then assume $m = LOD$ (if $m < LOQ$ then assume $m = LOQ$).
6. For first sampled layer deeper whose bottom is deeper than 90% penetration depth assume $m = 0.5 LOD$ if $m < LOD$ in this layer (assume $m = 1/2 LOQ$ if $m < LOQ$).
7. For second sampled layer whose bottom is deeper than 90% penetration depth and for deeper sampled layers assume $m = 0$ if $m < LOD$ (assume $m = 1/6 LOQ$ if $m < LOQ$ for second layer and $m = 0$ for deeper layers).

If the 90% penetration depth as estimated with Eqn 43 is located deeper than the bottom of the top sampled layer, the procedure of points 1-4 is applied but with the following additional rules for the concentrations in top layers that are below LOD and thus are in the tail of the concentration profile (in between brackets the assumptions when only LOQ is reported):

8. for the deepest layer of these top layers with $m < LOD$, assume $m = LOD$ (if $m < LOQ$ then assume $m = LOQ$).
9. for the one but deepest layer of these top layers with $m < LOD$, assume $m = 0.5 LOD$ (assume $m = 1/2 LOQ$ if $m < LOQ$).
10. for the second but deepest layer of these top layers with $m < LOD$, assume $m = 0$ (assume $m = 1/6 LOQ$ if $m < LOQ$ for second layer and $m = 0$ for layers above).

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.

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 to 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

However for the majority of the field experiments, 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 Appendix 2). 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 Appendix 2 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 notifier performs a statistical analysis of the accuracy of the *DegT50* value (following a procedure similar to Appendix 2 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, the 90th percentile of the *DegT50* should 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 unweighted 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 done 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 compounds 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:

$$DegT50_{plot} = DegT50_r + f_{om}(m_{om} - m_{om,r}) + f_{clay}(m_{clay} - m_{clay,r}) + f_{pH}(pH - pH_r) \quad (44)$$

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 44 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 44 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 44 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 44.

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 geometric mean 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).

5 Guidance proposals on further aspects of the leaching assessment

5.1 Guidance for the simulation error of lysimeter experiments

5.1.1 Introduction

The next sections clarify a few aspects of the guidance for assessment of lysimeter studies developed by Verschoor et al. (2001). This guidance differs from that proposed by FOCUS (2009). So the guidance of FOCUS (2009) will supersede that by Verschoor et al. (2001) and the next sections are only relevant as long as this has not yet happened.

The guidance of FOCUS (2009) is based on the principle that a lysimeter study is used to estimate the $DegT50$ in the top soil using inverse modelling. However, this guidance has been formulated only at a general level and has not been tested in a few case studies. Therefore we recommend applying this guidance to a few lysimeters studies from regulatory dossiers and, based on this, developing more detailed guidance.

The first aspect of clarification of the guidance by Verschoor et al. (2001) is that the assessment is only based on the simulation error; so the qualitative judgement as described in Table 3 on p. 19 of Verschoor et al. (2001) is of no use for the assessment. See next sections for the other aspects.

5.1.2 Acceptable combinations of laboratory and field $DegT50$ values when calculating the simulation error

Simulation errors (SE) of lysimeter studies can be estimated on the basis of a site-specific K_{om} or a worst-case case K_{om} from available labstudies. For the $DegT50$ the following options are available:

- A. site-specific lab $DegT50$, so lab studies for $DegT50$ with soil from the lysimeter;
- B. worst-case $DegT50$ from lab studies in dossier;
- C. worst-case $DegT50$ from field studies in dossier.

Note that the option 'site-specific field $DegT50$ ' is not included because this is in practice technically difficult to achieve.

PEC calculations for groundwater can be calculated on the basis of the following parameter combinations:

- A. average K_{om} from labstudies in dossier and average $DegT50$ from lab studies in dossier;
- B. average K_{om} from labstudies in dossier and average $DegT50$ from field studies in dossier.

The acceptable combinations of the $DegT50$ estimates are listed in Table 9. The background is consistency in the risk assessment procedure: a lysimeter study is triggered by a PEC calculation and thus has to demonstrate that the model overestimates leaching when using the assumptions underlying these PEC calculations. E.g. when the PEC is based on the average $DegT50$ from field studies, then the SE cannot be based on site-specific lab study because the advantage of the lower $DegT50$ is already accounted for in the risk assessment. It is of course inappropriate to account for the same advantage twice.

This can also be understood by considering the equation for adjusting results of GeoPEARL calculations on the basis of lysimeter measurements:

$$C_{adj} = \frac{C_{GeoPEARL}}{\left(\frac{C_{lysimeter}}{M_{lysimeter}} \right)} \quad (45)$$

where C_{adj} is the calculated adjusted concentration used in decision making, $C_{GeoPEARL}$ is the concentration calculated with GeoPEARL, $C_{lysimeter}$ is the calculated concentration for the lysimeter and $M_{lysimeter}$ is the measured concentration for the lysimeter. Use of Eqn 45 implies that the procedures for calculating $C_{GeoPEARL}$ and $C_{lysimeter}$ should be consistent. E.g. if the GeoPEARL calculation is based on field degradation rates, then also the subsequent lysimeter evaluation should be based on field degradation rates.

Table 9

Overview of possible combinations of using results of soil degradation rate studies in the procedure of calculating the simulation error in lysimeter experiments.

PEC calculation groundwater based on average <i>DegT50</i> from	Estimation of simulation error from lysimeter study with <i>DegT50</i>		
	site-specific lab study	worst-case lab study	worst-case field study
lab studies	yes	yes	yes but not relevant
field studies	no	no	yes

5.1.3 Estimation of the adjustment factor for lysimeter studies

5.1.3.1 Description of general procedure

In the decision tree for the evaluation of leaching of plant protection products, an adjustment factor is used to account for uncertainty in leaching as observed in leaching experiments (see Eqn 5-1). The adjustment factor is defined as the lower limit of the confidence interval for the average simulation error (SE), obtained via the procedure described below.

For one substance in different situations the simulation error (see text above or Verschoor et al., 2001) may differ an order of magnitude. Considering this large variation in simulation errors for one substance, a decision based on one simulation error is highly uncertain. For this reason the lower limit of the confidence interval of the average simulation error is used as the adjustment factor.

The simulation error is likely to be log-normally distributed because it can increase without bound, but is confined to a finite value at the lower limit (= 0). Therefore, the procedure starts with a log-transformation of the observed simulation errors (we will use natural logarithms here). The natural logarithm of the simulation error probability distribution will yield a normal distribution curve. In practice, the number of simulation errors will be limited, so a t-distribution will apply. After transformation, the arithmetic mean and the standard deviation of the transformed data are calculated. The lower limit of the confidence interval for the transformed data is now determined according to:

$$SE_{tr, ll} = \overline{SE}_{tr} - t_{prob} \cdot \frac{SD_{tr}}{\sqrt{n}} \quad (46)$$

with:

- $SE_{tr, ll}$ the lower limit of the confidence interval of the transformed simulation errors
 \overline{SE}_{tr} the arithmetic mean of the transformed simulation errors
 t_{prob} the t-distribution probability factor
 SD_{tr} the standard deviation of the transformed simulation errors
 n the number of experiments (the number of degrees of freedom is n minus one)

As we are concerned about over-correction, only the lower limit of the confidence interval is of interest. Therefore, we can apply single-sided statistics. Up till now, there is little experience in using the adjustment factor and thus in choosing the probability factor. For the moment, it seems reasonable to use a 75% confidence limit ($\alpha = 0.25$).

The adjustment factor is obtained through back-transformation:

$$f_{adj} = \exp(SE_{tr, ll}) \quad (47)$$

The procedure described above can be followed if more than one field or lysimeter experiment is performed. If there is only one experiment, there are no degrees of freedom left and the adjustment factor cannot be determined according to the formula. If only one experiment is available, the adjustment factor is calculated using essentially the formulae above assuming a variation coefficient of 75% for the population of transformed simulation errors. This procedure might be updated after having gained more experience with the procedure.

Let us consider the following example.

Suppose we have three lysimeter experiments with simulation errors of respectively 2, 7, and 20 (geometric mean = 6.55). Following the procedure, we obtain: $\ln(SE) = 0.69, 1.94$ and 3.00 ; mean = 1.88 and standard deviation = 1.15. As we have two degrees of freedom, the single sided t-probability factor ($\alpha = 0.25$) is 0.816. $SE_{tr, ll} = 1.88 - 0.816 \cdot 1.15 / (\sqrt{3}) = 1.34$ and $f_{adj} = \exp(1.34) = 3.81$.

t-values (one-sided, $\alpha=0.25$)

df	1	2	3	4	5	6	7	8	9	10
t-prob	1.000	0.816	0.765	0.741	0.727	0.718	0.711	0.706	0.703	0.700

5.1.3.2 Procedure for a single lysimeter experiment

Luttik and Aldenberg (1997) examined extrapolation factors for small samples of, in their case, toxicity values. Assuming a log-logistic distribution of the toxicity values, they derived the following equation for the hazardous dose (5th percentile):

$$\ln(HD5) = \bar{x} - 1.62\sigma \quad (48)$$

where:

- HD5 the 5th percentile of the distribution of the hazardous dose
 \bar{x} the mean of logtransformed toxicity values (in our case the mean of the logtransformed simulation errors)
 σ the standard deviation of the logtransformed toxicity values
(If a log-normal distribution would have been assumed, the constant (1.62) would have been 1.64).

The formula can also be applied when the sample size is small (including one) if the standard deviation is known, for instance from experiments in the past or data in literature. The lower confidence limit of the 95% confidence interval of the HD5 is obtained from (Luttik and Aldenberg, 1997):

$$\ln(HD5) = \bar{x} - 1.62\sigma - 1.64\sigma / \sqrt{n} \quad (49)$$

with:

- n the number of values in the sample

The equations of Luttik and Aldenberg (1997) are a specific case of the more general approach given by Aldenberg and Slob (1991). Again assuming a logistic distribution, characterised by the probability density function $f(x)$ and the cumulative distribution function $F(x)$

$$f(x) = \frac{1}{\beta} \cdot \frac{\exp(-(x-\alpha)/\beta)}{(1 + \exp(-(x-\alpha)/\beta))^2} \quad (50)$$

$$F(x) = \frac{1}{1 + \exp(-(x-\alpha)/\beta)} \quad (51)$$

in which the α and β parameters determine position and shape of the distribution. Note that the α parameter here has a meaning which is different from the meaning in the report on the decision tree.

α is equal to the average of the distribution and the standard deviation (σ) is calculated from:

$$\sigma = \frac{\pi}{\sqrt{3}} \cdot \beta \quad (52)$$

The lower limit of a confidence interval is obtained from:

$$ll_p = \alpha - \beta \cdot \ln\left(\frac{100-p}{p}\right) \quad (53)$$

where:

- // the lower limit of the confidence interval
 p the given or required level of accuracy

After substitution of α and β :

$$l_p = \mu - \frac{\sqrt{3}}{\pi} \cdot \sigma \cdot \ln\left(\frac{100-p}{p}\right) \quad (54)$$

Assuming a similar distribution for simulation errors of the leaching calculation, this equation can be used to calculate the adjustment factor if only one simulation error is available. For the assumed coefficient of variation of 75% (of logtransformed values) and the required level of accuracy of 25% ($p = 25$) the equation becomes:

$$l_{25} = \bar{x} - 0.4543 \cdot \bar{x} = 0.5457 \cdot \bar{x} \quad (55)$$

and the adjustment factor for a single lysimeter experiment thus reads:

$$f_{adj} = \exp(0.5457 \cdot SE) = SE^{0.5457} \quad (56)$$

Table 10 gives numerical examples of calculated adjustment factors for sets of simulation errors.

Table 10

Calculated adjustment factor sets of simulation errors.

No. of experiments	Values of the simulation error (SE) for individual experiments	Geomean of SE	f_{adj}
3	2, 7, 20	6.55	3.81
2	2, 7	3.74	2
2	2, 20	6.32	2
2	7, 20	11.8	7
1	2	2	1.46
1	7	7	2.89
1	20	20	5.13

So, if you have one lysimeter experiment for which a simulation error of 20 is obtained, the adjustment factor to be used in the evaluation procedure is 5.13. If two values for the simulation error are available, then the adjustment factor equals the lower value of the two simulation errors.

5.2 Leaching assessment for ridged potato fields

Studies with PPP leaching in Dutch ridged potato fields have shown that leaching for such tillage systems may be considerably higher than leaching in tillage systems with flat soils (Smelt et al., 1981; Leistra and Boesten, 2010). This implies that the current Dutch leaching assessment based on PEARL and GeoPEARL scenarios for flat soils is likely to be not conservative enough.

If field studies with lysimeter experiments would be available, it is possible to derive a simulation error from these data by calculations with PEARL for a flat soil.

If this would result in a value of C_{adj} that is lower than $C_{GeoPEARL}$ then this seems a defensible approach. However, it is more likely that it is the other way round because the ridged system is expected to lead to more leaching.

This is then an anomaly in the tiered system: the higher tier leads to more leaching. Such an anomaly is of course undesirable.

So the conclusion is that the current Dutch leaching assessment procedure is not conservative enough for tillage systems with ridges and furrows. Therefore we recommend to consider development of a separate assessment procedure for such systems.

5.3 Handling of deposition of plant protection products onto the crop and subsequent wash-off to soil

In the Netherlands, crop interception was introduced in the leaching assessment in the eighties. Following recommendations from the USES model (Linders et al., 2002), the PPP dose was split between interception by the crop, deposition onto the soil and 10% loss during application (CTB, 2003, 2006). The fraction intercepted by the crop was assumed never to reach the soil. The same assumption was made in the FOCUS Groundwater scenarios in 2001.

In the FOCUS Surface Water scenarios (FOCUS, 2003) a different approach was followed for Step 3 scenarios: behaviour of intercepted plant protection product on the plant surface was modelled by PRZM and MACRO. A default value for degradation half-lives on the plant surface (10 d) was provided. For the wash-off factor a regression equation was provided that relates it to the water solubility of the plant protection product (see p. 202 of FOCUS, 2003). This guidance on the wash-off factor has been criticised by Leistra (2005): measured wash-off for plant protection products with a low solubility is usually much more than predicted by the FOCUS regression equation.

Estimation of crop interception values has been harmonised at EU level: values from the 2002 generic guidance document of the FOCUS groundwater scenarios can be used. It is scientifically not defensible to assume that none of the PPP molecules intercepted by a crop will reach the soil surface. So in the current Dutch decision tree, crop interception is handled in a non-conservative way without any justification whereas FOCUS (2003) follows a more realistic approach.

EFSA (2011) proposed to include plant processes using the FOCUS-2002 interception percentages for all crops (except for cereals for which EFSA, 2011, proposes new values). Furthermore EFSA (2011) proposed a default half-life for decline of dislodgeable residue on the plants of ten days and a default wash-off factor of 0.1 mm^{-1} . We recommend to follow this proposed guidance both for Tier 1 and Tier 2 of the Dutch leaching assessment procedure.

Both PEARL and GeoPEARL can handle interception by the crop (using the option of a user-specified interception percentage) and subsequent dissipation at the plant surface and wash-off to the soil. This implies that the PEARL option 'interception calculated by model' should not be used in Dutch leaching risk assessments.

5.4 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 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 compound
- 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 at least two sequential time points, accounts for more than 5% of the amount of active substance added, or 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 $\mu\text{g/L}$ (Boesten and Van der Linden, 1991). So this 10% trigger does not lead to protection of groundwater at a level of 0.1 $\mu\text{g/L}$.

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.

5.5 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 arithmetic mean 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).

5.6 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, ie 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 *DegT50* values and the arithmetic mean of 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_{CaCl_2} (see Table 11 for these ranges).

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 12 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 11.

Table 11

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 12

Properties of arable soils in four regions of the Netherlands taken from Reijneveld et al. (2009). Values shown are averages and standard deviations (\pm) 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 \pm 7	7.4 \pm 0.3	13 \pm 6	2.2 \pm 1.0
Marine clay, west-central	11, 13, 38, 82, 83	1984/1985			20	
		1999/2000			23	
		2003	22 \pm 10	7.4 \pm 0.2	17 \pm 9	2.9 \pm 1.6
Reclaimed peat, north-east	78, 94-96	1984/1985			63	
		1999/2000			64	
		2003	<8	4.9 \pm 0.3	59 \pm 29	10.2 \pm 5.0
Loess, south	61-64	1984/1985			14	
		1999/2000			14	
		2003	14 \pm 2	6.6 \pm 0.6	14 \pm 4	2.4 \pm 0.7

5.7 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 eg not include the following uses:

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

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 5.4), (ii) we described new criteria for Tier 1 (see Section 5.5), and (iii) we recommend to follow guidance developed by EFSA (2011) for deposition on the crop and subsequent wash-off (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 (based on a recent EFSA opinion) 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 improvements 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 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.

In batch adsorption studies the sorption coefficient is derived from the decrease in the concentration in the liquid phase after mixing the soil and the water containing the substance. If the sorption coefficient is low, it is almost impossible to measure this coefficient in batch studies with an appropriate accuracy because this decrease in the concentration may become as low as e.g 5%.

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 CaCl₂ and in 0.1 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.

7.2 Recommendations

To avoid systematic overestimation of the sorption coefficient, 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.

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 compounds, 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. 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. The mean 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, (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 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 this study are not available, we recommend to use as a default value a Freundlich exponent of $N = 0.9$ and to deviate only from this value if reliable measurements of N are available with an arithmetic mean value that differs statistically significantly from $N = 0.9$.

We recommend to consider an N value reliable only if it is based on at least five 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.

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 0.1 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.

In view of the complexity and the preliminary nature of the proposed guidance for assessment of pH-dependent K_{om} values, we recommend to apply this guidance to the sorption of bentazone, MCPA and mecoprop and to revise the guidance thereafter.

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. We recommend further that such a fit 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.

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 our guidance proposals.

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). Because of the complexity of this guidance we recommend testing and improving the guidance proposal by applying it to a number of datasets. As part of this guidance we proposed a simple equation for estimating the 90% penetration depth at the sampling time considered. We recommend to test this simple equation against a number of simulations with FOCUS groundwater scenarios.

Field studies with ridged potato fields indicate that leaching for full-field spray applications in such tillage systems may be considerably higher than for spray applications to crops grown on flat fields. Therefore we recommend to consider development of a separate leaching assessment procedure for such crop-tillage systems.

FOCUS (2009) developed guidance for evaluating lysimeter studies. This guidance is based on the principle that a lysimeter study is used to estimate the *DegT50* in the top soil using inverse modelling. However, this guidance has been formulated only at a general level and has not been tested in a few case studies. Therefore we recommend applying this guidance to a few lysimeters studies from regulatory dossiers and, based on this, developing more detailed guidance.

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.

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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°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

Appendix 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 (<i>n</i>) when occurring at one abstraction
bentazone	Ten abstractions	
bromacil	Six abstractions	
chlorbromuron	Boerhaar	max 0.14 µg/L, <i>n</i> = 4, 1995
dichlobenil	Lith	max 0.23 µg/L, <i>n</i> = 4, 1993
dichlorprop (2,4-DP)	Hengelo (Overijssel)	max 0.12 µg/L, <i>n</i> = 12, 1992
dikegulac-sodium	Leersum	max 0.21 µg/L, <i>n</i> = 3, 1995/1996/1998
	Groenekan	max 0.43 µg/L, <i>n</i> = 9, 1995/1996/ 1998-2004
diuron	Bilthoven	max 0.13 µg/L, <i>n</i> = 9, 1999
DNOC	Bergen	max 0.15 µg/L, <i>n</i> = 4, 2002
(2-methyl-4,6-dinitrofenol)		
ethylenethiourea (ETU)	Noordwijk	Six records instead of one in file for 1991, giving different concentrations. min 0.2 µg/L
MCPA	Almelo-Wierden	<i>n</i> > 10, 1997
(4-chloro-2-methylphenoxy acetic acid)	Hengelo (Overijssel)	<i>n</i> > 10, 1999
mecoprop (MCP)	Four abstractions	
metobromuron	Zutphen - Vierakker	max 0.12 µg/L, <i>n</i> = 6, 1998
metoxuron	Espelo	max 0.19 µg/L, <i>n</i> = 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, <i>n</i> = 1	No active ingredient
1-(4-isopropylphenyl)urea	Beegden, 2001 0.17 µg/L, <i>n</i> = 1 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, <i>n</i> = 12	No active ingredient
2,6-dichlorobenzamide (BAM)	Holten, 1995 max 0.12 µg/L, <i>n</i> = 12, Eight abstractions	Metabolite evaluated as human toxicological not relevant (European Commission, 2003)
aldrin	Eindhoven, Aalsterweg 2000 1 µg/L, <i>n</i> = 1	Only one positive
ametryn	Manderveen, 2000 min 0.02, max 0.39, avg 0.14 µg/L, <i>n</i> = 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, <i>n</i> = 1	Only one positive
beta-endosulfan	Velddriel, 1995 0.14 µg/L, <i>n</i> = 1	Only one positive
Heptachlor epoxide	Eindhoven, Aalsterweg 1999 8 µg/L, <i>n</i> = 1	Only one positive
MCPB (4-(4-chloro-2-methylphenoxy)butanoic acid)	Helmond, 2001 0.27 µg/L, <i>n</i> = 1	According to the Waterleidingbesluit (2001) the standard for aldrin, dieldrin, heptachloor and heptachloorepoxide is 0.030 µg/L Only one positive
monuron	Six abstractions	Known artefact (Bannink, Personal communication, 2008)) 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, <i>n</i> = 3	Third measurement <0.1 µg/L, hence, only one positive

References Appendix 1

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Appendix 2 The pH measurements used in Section 3.6 to establish quantitative relationships between pH_{KCl} , $\text{pH}_{\text{CaCl}_2}$ and $\text{pH}_{\text{H}_2\text{O}}$

Table A2-1

Data pairs of $\text{pH}_{\text{H}_2\text{O}}$ and $\text{pH}_{\text{CaCl}_2}$. Reference numbers in first column indicate the data source described in Table 3.

Reference nr.	$\text{pH}_{\text{H}_2\text{O}}$	$\text{pH}_{\text{CaCl}_2}$
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

Reference nr.	$\text{pH}_{\text{H}_2\text{O}}$	$\text{pH}_{\text{CaCl}_2}$
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

Reference nr.	$\text{pH}_{\text{H}_2\text{O}}$	$\text{pH}_{\text{CaCl}_2}$
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

Reference nr.	pH _{H2O}	pH _{CaCl2}
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
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

Reference nr.	pH _{H2O}	pH _{CaCl2}
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

Reference nr.	pH _{H2O}	pH _{CaCl2}
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

Reference nr.	pH _{H2O}	pH _{CaCl2}
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
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 A2-2

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

Reference nr.	pH_{CaCl2}	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

Reference nr.	pH_{CaCl2}	pH_{KCl}
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

Reference nr.	pH_{CaCl2}	pH_{KCl}
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 A2-3

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_{H_2O}	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

Reference nr.	pH_{H_2O}	pH_{KCl}
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	4.7	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

Reference nr.	pH_{H_2O}	pH_{KCl}
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	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

Reference nr.	pH _{H2O}	pH _{KCl}
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
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	4.2
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

Reference nr.	pH _{H2O}	pH _{KCl}
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	4.3
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	4.9
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

Reference nr.	pH _{H2O}	pH _{KCl}
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	4.8
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

Reference nr.	pH _{H2O}	pH _{KCl}
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
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

Reference nr.	pH _{H2O}	pH _{KCl}
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

Reference nr.	pH _{H2O}	pH _{KCl}
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

Reference nr.	pH _{H2O}	pH _{KCl}
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
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

Reference nr.	pH _{H2O}	pH _{KCl}
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

Reference nr.	pH _{H2O}	pH _{KCl}
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

Reference nr.	pH _{H2O}	pH _{KCl}
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
7	5.01	4.6
7	5.07	4.8
7	5.1	3.8

Reference nr.	pH _{H2O}	pH _{KCl}
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	4.7
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

Reference nr.	pH _{H2O}	pH _{KCl}
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

Reference nr.	pH _{H2O}	pH _{KCl}
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

Reference nr.	pH _{H2O}	pH _{KCl}
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
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

Reference nr.	pH _{H2O}	pH _{KCl}
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

Reference nr.	pH _{H2O}	pH _{KCl}
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

Reference nr.	pH _{H2O}	pH _{KCl}
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
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

Appendix 3 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:

$$\mu = \ln\left(\frac{F}{\sqrt{1 + CV^2}}\right) \quad (\text{A3-1})$$

$$\sigma = \sqrt{\ln(1 + CV^2)} \quad (\text{A3-2})$$

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 A3-1 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 A3-1 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 A3-1 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 A3-1 (e.g. the value for five sampling times and 20 samples was about 13% compared to about 20% in Figure A3-1).

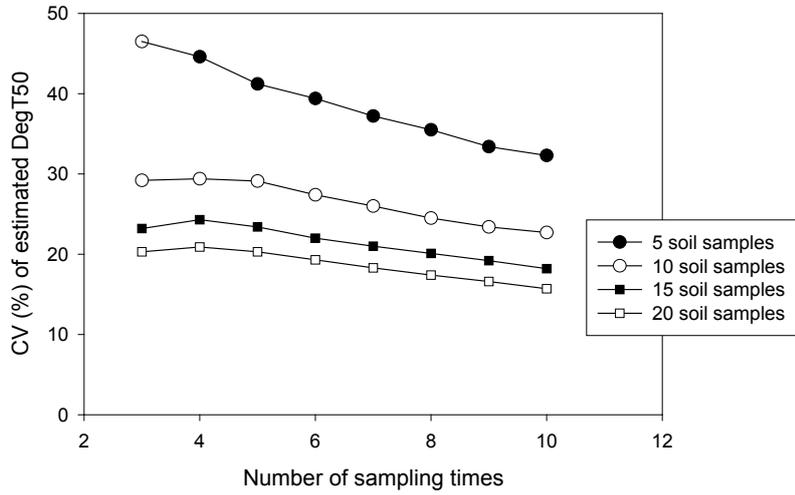


Figure A3-1

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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