

Perspectives of a new degradation rate concept for regulatory leaching assessment of pesticides at EU level

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1. Introduction

In the past decade, the risk assessment of pesticide leaching to groundwater in the EU, has mostly been based on CDE-type models [1]. Around 1990 sensitivity analyses of such CDE models demonstrated that pesticide leaching is very sensitive to the Freundlich sorption isotherm parameters, ie the Freundlich coefficient and Freundlich exponent [2]. The quality of measured Freundlich coefficients is a subject of scientific debate if the measured decline of the concentration in the liquid phase is less than 20% in the sorption experiment according to the OECD 106 guideline [3]. But even when the decline is 20%, the quality may be questioned. Eg if there is 20% decline in the experiment and if there is 3% degradation during the experiment, the OECD instructions may lead to an overestimation of the Freundlich coefficient by 30%. For the Freundlich exponent, quality criteria have even not been developed so far. The sensitivity may be illustrated with the following example. The leaching was calculated for a pesticide with a half-life of 20 d in top soil for the FOCUS Hamburg EU leaching scenario. The pesticide was applied in winter cereals just before emergence. Calculations were made for values of the organic-matter/water distribution coefficient, K_{om} , ranging from 0 to 100 L/kg. At $K_{om} = 0$ the leaching concentration was in the order of 10 µg/L and at $K_{om} = 100$ L/kg it was in the order of 10^{-5} µg/L. The relationship between leaching concentration and K_{om} showed that decreasing the K_{om} value by 30% may increase the leaching concentration by about a factor 10. This combination of large sensitivity to sorption parameters and no agreed procedure to produce high quality sorption parameter values is undesirable.

2. Change of sensitivity to sorption parameters when degradation rate is assumed proportional to the concentration in the liquid phase

In the CDE-type models used so far in the EU leaching assessment, the degradation rate of pesticides is assumed to be proportional to the concentration in total soil. A recent analysis showed that the sensitivity to the Freundlich isotherm parameters disappears almost completely for multi-year European leaching scenarios if it is assumed that the degradation rate of the pesticide is proportional to the concentration in the liquid phase [4].

The loss of sensitivity to the sorption parameters is caused by two counteracting effects of sorption: (1) the higher the sorption, the slower the overall degradation rate in a soil layer will be, and (2) the higher the sorption, the longer the residence time of the substance in a soil layer will be. These effects tend to compensate each other with respect to leaching, thus leading to low sensitivity to sorption parameters. Beltman et al. [4] developed the analytical solution for the fraction of the dose leached for a homogeneous soil column, linear sorption isotherm and constant water flow. They found that this fraction, F , is described by:

$$F = \exp \left[-\frac{L}{2L_d} \left(\sqrt{1 + 4 \frac{kL_d}{v}} - 1 \right) \right] \quad (1)$$

where L is the leaching depth (m), L_d is the dispersion length (m), k is the degradation rate coefficient in the liquid phase, and v is the pore water velocity (m/d). Surprisingly this equation does not contain any sorption parameters. Obviously these two counteracting effects compensate each other exactly for such a simplified system. Beltman et al. [4] made also numerical calculations for a homogeneous soil column and constant water flow but with a Freundlich isotherm instead of a linear isotherm and with combinations of equilibrium and kinetic sorption sites. For all calculations Eqn 1 appeared to predict the fraction leached very well.

So switching to the concept of a degradation rate that is proportional to the concentration in the liquid phase is perhaps a solution for the problem of the large sensitivity to the sorption parameters. In this approach the degradation half-life of the pesticide in the liquid phase (defined as $\ln 2 / k$) is the single key substance parameter for the leaching assessment.

3. Hurdles to be taken for introduction of new degradation rate concept in regulatory leaching assessment

There are in principle three hurdles to be taken before this approach can be implemented in the leaching assessment at EU level. The first hurdle is that a change is needed in the measurement procedure of the half-life. In the current leaching assessment procedure at EU level, degradation rate measurements are available for four soils and sorption measurements with four other soils. Such measurements are not suitable for estimating the half-life in the liquid phase. To measure this half-life, degradation rate measurements are needed in which also the partitioning over solid and liquid phase is followed over the course of the experiment by extractions with an aqueous solution of CaCl_2 . This is only a limited additional experimental effort which is currently already done in part of studies to be able to estimate parameters for long-term sorption kinetics.

The second hurdle is the change in the parameters describing the relationships between degradation rate coefficient on the one hand and (i) soil depth, (ii) soil temperature and (iii) soil moisture on the other hand (the degradation will usually decrease with soil depth, increase with increasing temperature and increase with increasing soil moisture content). These parameters need to be re-estimated because the definition of the new half-life differs from that of the old half-life. If we assume for simplicity a linear sorption isotherm then the relationship between the two half-lives is described by:

$$DegT50_{liq} = \frac{DegT50_{total}}{1 + \left(\frac{f_{om} K_{om}}{W} \right)} \quad (2)$$

where $DegT50_{liq}$ is the half-life in the liquid phase (d), $DegT50_{total}$ is the half-life in total soil (d), f_{om} is the mass fraction of organic matter of the soil (-), K_{om} is the organic-matter/water distribution coefficient (L/kg) and W is the water content defined as volume of water per mass of dry soil (L/kg). As could be expected, the two half-lives are equal if f_{om} or K_{om} are zero, so if there is no sorption.

The current relationship between degradation rate and soil depth is based on degradation measurements with the same pesticide using different soil layers from the same soil profile incubated at the same temperature and the same moisture potential ('field capacity'). So the quotient f_{om} / W differs between these measurements for the different soil layers. Therefore the measured depth-dependency of $DegT50_{liq}$ will differ from that of $DegT50_{total}$. Probably the variation in f_{om} within a soil profile will in most cases be stronger than the variation in water content at field capacity. Then the $DegT50_{liq}$ will increase stronger with depth than the $DegT50_{total}$ according to Eqn 2 (leading to more leaching).

The current relationship between degradation rate and soil temperature is based on measurements with a top soil at the same water content but at different temperatures. The K_{om} is then the only variable in the quotient $f_{om} K_{om} / W$ in Eqn 2. Usually the K_{om} will decrease somewhat with temperature. Eqn 2 implies then that the $DegT50_{liq}$ will decrease less with increasing temperature than the $DegT50_{total}$ (so lower Arrhenius activation energy which will lead usually to less leaching). The current relationship between degradation rate and soil moisture is based on measurements with a top soil at the same soil temperature but at different water contents. W is then the only variable in the quotient $f_{om} K_{om} / W$ in Eqn 2. As a consequence the $DegT50_{liq}$ will increase less with decreasing water content than the $DegT50_{total}$ (leading to less leaching).

So the direction of the net effect of the changes in the three relationships on the leaching is difficult to predict: both an increase or a decrease of the leaching concentration is possible.

The third hurdle is that the scenario selection procedure for the FOCUS groundwater scenarios needs to be redone because the organic matter content of the soil profile played an important role in the selection of these scenarios [1]. This selection procedure is probably not defensible anymore when the new degradation rate concept is used.

4. References

- [1] FOCUS. 2000. FOCUS groundwater scenarios in the EU review of active substances. Report of the FOCUS Groundwater Scenarios Workgroup, EC Document Reference Sanco/321/2000 rev.2, 202 pp.
- [2] OECD. 2000. OECD guideline for the testing of chemicals. Adsorption-desorption using a batch equilibrium method. OECD guideline 106. OECD, Paris.
- [3] Boesten JJTI. 1991. Sensitivity analysis of a mathematical model for pesticide leaching to groundwater. Pestic. Sci. 31: 375-388.
- [4] Beltman WHJ, Boesten JJTI, van der Zee SEATM. 2008. Spatial moment analysis of transport of nonlinearly adsorbing pesticides using analytical approximations. Water Resources Research 44, W05417, doi:10.1029/2007WR006436.