Total and soil pore water concentration of pesticides in OECD artificial soil with different organic matter content

Penning, H.[1*]; Gottesbüren, B. [1]; Krieg, W.[2]

[1] Environmental Fate, [2] Ecotoxicology; Crop Protection, BASF SE, Limburgerhof, Germany

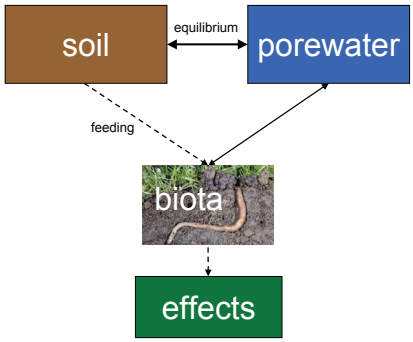
[*] holger.penning@basf.com

Introduction

The total concentration (TC) of a pesticide in soil has been used as generic exposure level in the terrestrial risk assessment. Recently, pore water concentration (PWC) was proposed to be an additional or even more relevant exposure metric than TC in soil (EFSA PPR, 2009). Determination of both, TC and PWC, may furthermore be used to better understand the effect of residence time ("ageing") of pesticides on sorption and its influence on bioavailability to exhibit toxic effects. Yet, today analytical experience on the quantification of pore water concentration as well as on how sample storage may influence the results in the OECD artificial soil (~5% peat, 20% kaoline, 75% quartz sand, adjusted to pH 6) used in terrestrial ecotoxicological experiments is lacking.

Objectives

- to investigate whether pesticide-spiked soils can be stored frozen for certain time periods without changing the sorption properties of the pesticide
- to investigate whether porewater is a more suitable metric than total concentration to assess toxicity to earthworms
- to show how PWC and TC data can be used to better understand implications of ageing of pesticides in soil on environmental behaviour and ecotoxicological effects



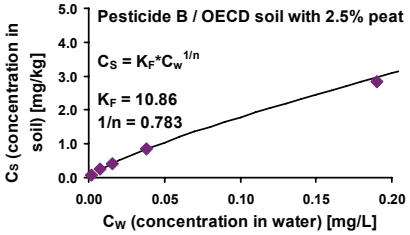
Porewater vs. total concentration to assess ecotoxicological effects

Earthworm exposure studies were conducted in OECD artificial soils with three levels of organic matter content (2.5, 5, and 10% peat) and at five test concentrations. Pesticide A (acutely toxic) was tested in a 14-day test, while pesticide B (chronically toxic) was tested in a 56-day reproduction test.

Ecotoxicological effect levels (LC50 for acute and LC10 for chronic study) were determined in the metric "mg/kg". As PWC usually cannot directly be measured due to the small water volume in soil, we determined PWC in three steps as described below.

Method: Determination of porewater concentrations:

Step 1: Freundlich sorption isotherm



Step 2: Measurement of concentration and water content in a specific sample

yields:

m_{eq}: mass of pesticide in sorption equilibirum (= total mass for fresh residues)

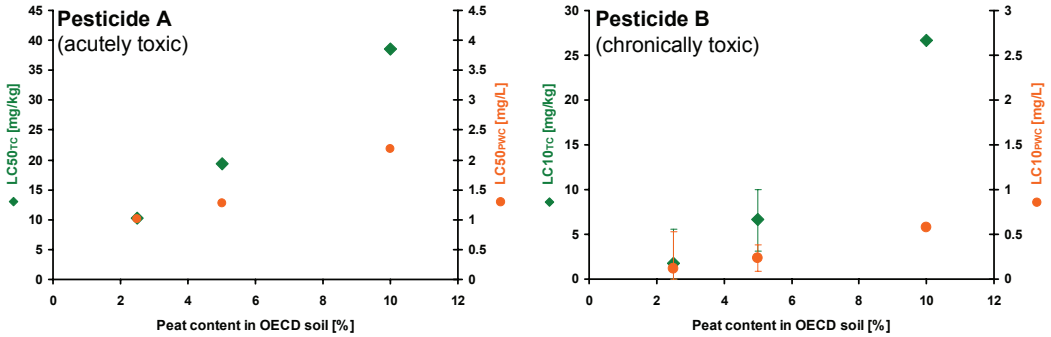
m_s: dry mass of soil sample

V_w: water volume in the sample

Step 3: With parameters determined in step 1 (K_F; 1/n) and step 2 (m_s; m_{eq};V_w), PWC (C_W) is determined by numerical solution of the following equation for sorbed mass of pesticide to soil in equilibrium (m_{eq-s}):

$$\underbrace{\frac{m_{eq-s}}{m_s}}_{C_S} = K_F \underbrace{\frac{m_{eq} - m_{eq-s}}{V_W}^{\frac{1}{n}}}_{C_W}$$

Results: Influence of peat content on effect levels related to TC and PWC :



Conclusion:

Acute (LC50) and chronic (LC10) effect levels related to TC and to PWC of earthworm exposure studies demonstrate that endpoints related to the **metric PWC** are clearly **less dependent on the organic matter content** of the artificial soil than levels related to the metric TC. This indicates that toxic effects are primarily related to the metric porewater.

Error bars (only shown for Pesticide B) are 95% confidence intervals of exposure studies (for calculation of PWC, error values were propagated through calculations).

Decreasing bioavailability of pesticides in OECD artificial soil over time

TC and PWC data for different time points allow better understanding of long-term changes of sorption in in the OECD artificial soil (~5% peat, 20% kaoline, 75% quartz sand, adjusted to pH 6) and therefore changing bioavailability over time. By desorption of pesticides from aged soil with 0.01 M $CaCl_2$ for 24 h (measurement of C_W) and applying the earlier determined Freundlich sorption isotherm parameters, the total pool of molecules available for fast sorption processes is calculated (m_{eq}) and then PWC is calculated as described in Step 3 (above):

$$m_{eq} = m_{eq-S} + m_{eq-W} = m_s K_F C_W^{\frac{1}{n}} + V_W C_W$$

This approach assumes that only molecules that equilibrate with the $CaCl_2$ solution within 24 h contribute to the PWC in the soil.

Apparent K_{oc} is:

$$K_{OC-app} = \frac{\frac{m_{total} - m_{eq-W}}{m_S}}{C_W f_{oc}}$$

with m_{total}: total mass in soil
f_{OC}: fraction of organic carbon

Results: Pore water concentrations decreased in average by 19% for Pesticide A in 14 days and 46% for Pesticide B in 56 days, while no significant change of TC was observed. Hence, the apparent K_{OC}-values (desorption) increased from 728 to 1268 L/kg within 14 days for pesticide A and from 3162 to 5843 L/kg within 56 days for pesticide B.

Conclusion: **Decline of pore water concentrations and likely ecotoxic effects by long-term sorption or "ageing" of pesticides** during their residence time in soil.

Storage stability of sorption properties at < -18°C

To investigate the effect of soil storage (at <-18 °C) on sorption, OECD artificial soils with three levels of organic matter content (2.5, 5, and 10% peat) were spiked with pesticide A and B (K_{oc} = 500-5000). Samples were analysed for residues, which can be desorbed by 0.01 M $CaCl_2$ solution at the day of spiking the soil (not-frozen) and after one, two, and three months of frozen storage (<-18°C). TC in soil was also measured by extraction with organic solvents to confirm stability of the overall amount of pesticide present in the soil. For the two pesticides tested, deep-freezing and thawing of soil samples did not change the amount of pesticide extractable by $CaCl_2$ desorption.

Conclusion: Freezing of OECD artificial soil samples up to three months did not alter sorption of the two tested pesticides.