Volatilization of pesticides from the bare soil surface - modelling of the humidity effect

Martina Schneider and Kai-Uwe Goss

Helmholtz Centre for Environmental Research, Department Analytical Environmental Chemistry
Volatilization of pesticides

- chemical properties
- temperature
- soil moisture
- soil properties
Field study

Moist soil => temperature and volatilization are correlated

Dry soil => temperature and volatilization are **inversely** correlated

Gish et al, 2009, Atmospheric Pollutants and Trace Gases
Outline

a) mechanistic explanation of the humidity effect

b) quantitative modelling of the humidity effect

c) practical implications
Soil humidity and sorption under dry conditions

Decreasing moisture in soil

- exponential increase of sorption to hydrated mineral surfaces
- surface area of hydrated minerals becomes available
- sorption in OC and water

Sorption of organic compounds in soil (typical scenario)

- sorption to organic carbon
- sorption to soil water phase
- sorption to hydrated mineral surfaces

\[ K_{\text{soil/air}} = K_{\text{min/air}} \cdot \text{SSA} \]
Quantitative modelling of the humidity effect

What do we need?

- knowledge on the quantitative prediction of the humidity effect on sorption coefficients to hydrated minerals
  (Goss et al., 2004, ES&T and others)

- knowledge on the prediction of the water sorption isotherm under dry conditions

- a kinetic volatilization model

- validation data from experiments with well-controlled humidity conditions
Wind tunnel experiments

... with 2 pesticides, 2 soils and different humidity regimes

Pesticide: Triallate (Gowan Company: Avadex EC)

Soil: Bad Lauchstädt (BL) SSA 18 m²/kg
C_{org} 2.1%
Model assumptions

\[
\text{volatilization rate} = \frac{F}{A} = D_{\text{diff}} \left( \frac{C_{\text{soil}} - C_{\text{air}}}{x} \right)
\]

\( C_{\text{air}} \) assumed to be zero

Calibration of the laminar boundary layer \( x \) by water evaporation

Experiment (\( x = 2 \text{ mm} \))

Penetration depth of the pesticide solution in dry soil: 1 mm
Volatileization of Triallate (soil BL)

Schneider and Goss, ES&T, 2012

60% 85% rh
Temperature dependence

Schneider and Goss, ES&T, 2012
Conclusion

We do have a good mechanistic and quantitative understanding of the humidity effect that can be included in pesticide fate models

Remaining challenge for good modelling:

- knowledge of water movement in soil under dry conditions
Practical implications

- Spraying pesticides to dry (rather than wet) soil surfaces will not necessarily help to reduce volatilisation losses. In fact, the losses are only postponed to the next rain event …

- …unless the pesticides are incorporated before the next rain

- Infiltration depth of the sprayed solution is also very influential for volatilization. A better understanding might further help to reduce losses.
questions
For more information…

M. Schneider, S. Endo and K.-U. Goss, *Volatileization of pesticides from the bare soil surface: evaluation of the humidity effect*, Journal of Environmental Quality, 2013, 42, 844-851

Humidity regime III (soil BL and 6S)

S6: SSA 36 m²/kg,
Corg: 1.6%

BL: SSA 18 m²/kg,
Corg: 2.1%

60%  85% rH

volatilization rate/application rate [1/d]

time [h]
Calculation of the soil air concentration

\[ c_{\text{soil/air}} = \frac{f_{\text{air}} \cdot m_{\text{total}}}{V_{\text{air}}} \]

**equilibrium partitioning**

\[
\frac{1}{f_{\text{air}}} = 1 + \frac{\Theta_{\text{water}}}{\Theta_{\text{air}} \cdot K_{\text{air/water}}} + \frac{K_{\text{OC/water}}}{K_{\text{air/water}}} \cdot f_{\text{OC}} \cdot \frac{\rho}{\Theta_{\text{air}}} + K_{\text{min/air}} \cdot \text{SSA} \cdot \frac{\rho}{\Theta_{\text{air}}}
\]

- **water phase**
- **organic phase**
- **hydrated mineral surfaces**

\[ K_{\text{min/air}}, \text{SSA} = f(\text{RH}) \]
Sensitivity study

- Organic carbon content [%]
- Volatilization rate [mg/m²h]
- Time [h]

- Application rate [mg/m²]
- Volatilization rate [mg/m²h]
- Time [h]

- Specific Surface Area [m²/g]
- Volatilization rate [mg/m²h]
- Time [h]

- Penetration depth [cm]
- Volatilization rate [mg/m²h]
- Time [h]
Advise for field practice

Schneider and Goss, ES&T, 2012
Humidity regime I and II (soil BL)

Schneider and Goss, ES&T, 2012
Humidity regime III

- Relative humidity [%]
- SSA min [m²/g]
- Water content [g/g]

Graph showing:
- RH (relative humidity)
- WC (water content)
- SSA (soil bulk density)

Key points:
1. Increase of humidity
2. Rain event
3. Time [h]

Legend:
- Soil BL
- Water content [g/g]