

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

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Brüssel, 22. September 2012

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Abstract

Volatilization of pesticides from soils under dry conditions (water content below the permanent wilting point) can be significantly influenced by sorption to hydrated mineral surfaces. This sorption process strongly depends on the water activity, expressed as equilibrium relative humidity in the pore space of the soil, and on the available surface area of the hydrated minerals.

In order to get a better understanding on the humidity state of the soil under dry condition, a systematic study on the water retention in dry soils was set up. The water vapour adsorption isotherm, that presents the water content as a function of the equilibrium relative humidity RH was measured for 18 soils with different soil textures. These data were used to calibrate a predictive model for the water sorption isotherm based on the clay content of the soil. In general dry soils typically can be found in warm areas where the temperatures can easily go up to 40 °C and also the temperature changes are quiet extreme. Therefore the temperature dependence of the water sorption isotherm was investigated exemplarily for nine soils. A significant temperature dependence of the water sorption isotherm was observed that varied only little between the studied soils.

Using the gained knowledge on water in soil under dry conditions the influence of different humidity regimes on the volatilization of two pesticides (trifluralin and triallate) was demonstrated with a bench-scale wind tunnel system under well controlled humidity conditions in the soil. In the beginning of the experiment the soil was equilibrated with the air phase containing a well known humidity. Thus, the water activity in the soil was known and homogeneous. The pesticides were applied by spraying an aqueous emulsion from using a commercial product. The pesticide concentration in the air was measured by trapping the volatilized pesticide on a sorption polymer and subsequent thermodesorption followed by GC/MSD analysis. In the experiment starting with very dry conditions, increasing the relative humidity in the adjacent air from 60 to 85% resulted in an up to eight times higher volatilization rate of the pesticides. An additional strong increase in volatilization (up to

three times higher) was caused by a simulated rain event, which eliminated all sorption sites associated to mineral surfaces. In agreement with this interpretation the comparison of two soils suggested that mineral surface area was the soil property that governs the volatilization under dry conditions while soil organic matter was the controlling variable under wet conditions. The experimental results show that humidity effects on pesticide volatilization can be interpreted via the mechanism of sorption to mineral surfaces under dry conditions.

Finally we wanted to combine the conceptual knowledge about sorption of organic compounds and the improved understanding on soil humidity under dry conditions. The mineral surfaces were integrated as an independent sorption compartment into a simple volatilization model. The model considers availability and contribution of the mineral surfaces as a function of their hydration status. For evaluation we tested the model on the volatilization data from the wind tunnel experiments and performed a sensitivity study to estimate the influence of the different parameters. The model captures the general trend of the volatilization in different humidity scenarios. The results reveal that it is essential to have high quality input data for sorption coefficient to the hydrated mineral surfaces, the available specific surface area, the penetration depth of the applied pesticide solution and the humidity conditions in the soil. The model approach presented here in combination with an improved description of the humidity conditions under dry conditions can be integrated into existing volatilization models that already work well for humid conditions but still lack the mechanistically based description of the volatilization process under dry conditions.

Zusammenfassung

Die Verflüchtigung von Pflanzenschutzmitteln unter trockenen Bedingungen im Boden (Wassergehalt des Bodens unterhalb des permanenten Welkepunktes) kann entscheidend durch die Sorption an hydratisierten Mineraloberflächen beeinflusst werden. Diese Sorption ist abhängig von der Wasseraktivität im Boden, die als relative Feuchte im Porenraum beschrieben werden kann und der verfügbaren Oberfläche der hydratisierten Mineraloberflächen.

Um ein besseres Verständnis der Rest-Feuchte im Boden unter trockenen Bedingungen zu erlangen, wurde zunächst eine systematische Studie zum Wasserrückhalt im Boden durchgeführt. Die Wasseradsorptionsisotherme, die den Wassergehalt im Boden in Abhängigkeit von der relativen Feuchte im Gleichgewicht beschreibt, wurde für 18 Böden unterschiedlicher Textur gemessen. Mit diesen Daten wurde, basierend auf dem Tongehalt der Böden, ein Vorhersagemodell für die Wasseradsorptionsisotherme kalibriert. Generell findet man trockene Böden in sehr warmen Klimaten, wo die Temperaturen an der Bodenoberfläche 40 °C und mehr erreichen und die Temperaturunterschiede zwischen Tag und Nacht extrem sein können. Die Temperaturabhängigkeit der Wasseradsorptionsisotherme wurde am Beispiel von neun Böden untersucht und eine signifikante Abhängigkeit festgestellt, die sich nur geringfügig zwischen den einzelnen Böden unterscheidet. Die Ergebnisse ermöglichen eine Temperaturkorrektur der Wasseradsorptionsisotherme für jeden beliebigen Boden zwischen 5 °C und 40 °C.

Im zweiten Teil der Studie wurde der Einfluss unterschiedlicher Feuchtezustände auf die Verflüchtigung von Pflanzenschutzmitteln (exemplarisch an den Herbiziden Triallate und Trifluralin) mit einem Windtunnelsystem im Labormaßstab unter gut kontrollierten Bedingungen im Boden demonstriert. Zu Beginn der einzelnen Experimente war der Boden im Gleichgewicht mit der relativen Feuchte im Luftstrom. Die Wasseraktivität im Boden wurde als homogen angenommen und konnte über die Wasseradsorptionsisotherme charakterisiert werden. Die Herbizide wurden in einer Wasseremulsion aus einem kommerziellen

Produkt auf den Boden gesprüht. Die Bestimmung der Herbizidkonzentration im Luftstrom des Tunnels erfolgte, indem ein Teil des Luftstroms über ein Sorptionsröhrchen geleitet und das Röhrchen im Anschluss durch Thermodesorption und GC/MSD analysiert wurde.

Die Versuche, die bei 60% relativer Feuchte in der Luft starteten, zeigten, dass eine Erhöhung der relativen Feuchte auf 85% zu einer acht Mal höheren Verflüchtigungsrate der eingesetzten Substanz führte. Ein zusätzlicher Anstieg der Verflüchtigung (bis zu drei Mal höher) wurde durch ein anschließend simuliertes Regenereignis verursacht, welches alle verfügbaren Sorptionsplätze der hydratisierten Mineraloberflächen eliminierte. Der Vergleich zwischen zwei unterschiedlichen Böden zeigte, dass die spezifische Bodenoberfläche unter trockenen Bedingungen und der organische Kohlenstoffgehalt unter feuchten Bedingungen entscheidend für die Verflüchtigung ist. Die experimentellen Ergebnisse bestätigen, dass der Feuchteeffekt auf die Verflüchtigung von Pflanzenschutzmitteln durch die Sorption der Chemikalien an die hydratisierten Mineralphasen erklärt werden kann.

Im letzten Teil der Arbeit sollte das konzeptionelle Wissen über die Sorption organischer Verbindungen im Boden mit dem verbesserten Verständnis über die Bodenfeuchte unter trockenen Bedingungen kombiniert werden. Dazu wurden die mineralischen Oberflächen als eigenständiges Sorptionskompartiment in ein einfaches Verflüchtigungsmodell integriert. Das Modell berücksichtigte den Beitrag der Mineraloberflächen und deren Verfügbarkeit in Abhängigkeit von deren Hydratisierungsstatus. Zur Evaluierung wurde das Modell mit den Daten der Verflüchtigungsversuche des Windtunnels getestet und eine Sensitivitätsstudie durchgeführt, um den Einfluss der verschiedenen Parameter einzuschätzen. Das Modell konnte den Trend der Verflüchtigung unter verschiedenen Feuchtezuständen gut erfassen. Die Ergebnisse zeigten, wie wichtig verlässliche Daten für den Sorptionskoeffizienten an die Mineralphasen, die Eindringtiefe der Applikationslösung, die verfügbare spezifische Oberfläche des Bodens und die Feuchtebedingungen im Boden sind. Das Modell kann in bereits existierende Verflüchtigungsmodelle, die bereits sehr gut Vorhersagen unter feuchten Bedingungen liefern, aber immer noch den mechanistischen Hintergrund unter trockenen Bedingungen vermissen lassen, integriert werden.

Preface

The present work was performed between December 2008 to May 2012 at the Helmholtz Centre for Environmental Research, Leipzig at the Department of Analytical Environmental Chemistry. The thesis was written in a cumulative form and is based on the following articles:

M. Schneider and K.-U. Goss: Prediction of the water sorption isotherm in air dry soils, *Geoderma*, VOL. 170, 64–69, 2012

M. Schneider and K.-U. Goss: Prediction of water retention curves for dry soils from an established pedo-transfer-function: Evaluation of the Webb Model, *Water Resources Research*, VOL. 48, W06603, 2012

M. Schneider and K.-U. Goss: The temperature dependence of the water retention curve for dry soils, *Water Resources Research*, VOL. 47, W03506, 2011

M. Schneider, S. Endo and K.-U. Goss: Volatilization of pesticides from the bare soil surface: evaluation of the humidity effect, *Journal of Environmental Quality*, VOL. 42, No. 3, 844-851, 2013,

M. Schneider and K.-U. Goss: Volatilization Modeling of Two Herbicides from Soil in a Wind Tunnel Experiment under Varying Humidity Conditions, *Environmental Science and Technology*, 46(22), 12527-33, 2012

Note that text passages and figures in the summary are partly taken from the original publication without further indication. The abstracts of the original publications were included at the end.

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Chapter 1

Summary: Volatilization of pesticides from the bare soil surface-evaluation of the humidity effect

1.1 Introduction

Worldwide pesticides play an important role in modern agriculture. Currently the amount of pesticides used in Germany account for up to 30000 t/year (federal ministry for agricultural and food). Because these compounds are directly released to the environment, their potential environmental fate is of major concern and an important point to investigate for risk assessment and registration processes.

The volatilization of pesticides immediately after their application can be a significant transport path for these chemicals. The volatilized and transported substance can affect human health (Lee et al., 2002), non-target plants (Follak and Hurle, 2003) and aquatic life (Johnson, 1986) or generally contribute to the contamination of the atmosphere (Bedos et al., 2002) and experiences long range transport (Shen and Wania, 2005). In addition the loss of the compound causes an economical disadvantage, because the volatilized amount cannot contribute to the desired effect and, thus, more pesticide has to be applied in the field (beside those, which are able to affect via the gas phase).

Various pesticides are applied directly to the bare soil surface to kill early weeds and competitors, e.g. Metolachlor (Gish et al., 2009). This study deals with the effect of humidity on the volatilization of pesticides from a bare soil surface and does of course also apply to the volatilization of any other organic chemicals from bare soil surfaces. Note that

there is also possible volatilization of pesticides directly from the small, sprayed droplets. This effect becomes most significant in case of spray drift, but is not discussed here.

Decades ago, numerous studies already investigated the factors influencing the volatilization of agrochemicals from the bare soil surface, e.g. Basile et al. (1986); Burkhard and Guth (1981); Petersen et al. (1995). These studies showed that one of the important factors is the sorption of the compound to the soil. Sorption to soil depends on the temperature, the agrochemical's properties and the soil properties. Based on these findings various models have been developed and tested to predict the volatilization of pesticides from the bare soil surface (e.g. Jury et al. (1983); Klein (1995); Bedos et al. (2009)).

In field and lab experiments, e.g. Spencer and Cliath (1974); Majewski et al. (1993); Bedos et al. (2002); Reichman et al. (2011), it had been observed that dry conditions at the soil surface strongly impair the volatilization process. Gish et al. (2009) observed a correlation of the volatilization for the pesticide metolachlor with the soil surface temperature when the soil was wet, but not when the soil was dry which presented a contrast to the principles that had been developed so far. This "humidity effect" is based on the mineral surfaces that become available as additional sorption sites for organic compounds under dry conditions. Overall the impact of soil humidity on volatilization in field experiments was observed, but further studies to refine the conceptual understanding was needed (Reichman et al., 2011). Numerical models to simulate volatilization of pesticides ignored this effect on the sorption of organic compounds to mineral surfaces for a long time (e.g. Jury et al. (1983); Yates (2006)). Recently, first attempts have been made to integrate sorption to the mineral surfaces in volatilization model (Garcia, 2010) but the current "state of the art in modeling" uses an arbitrarily chosen "fudge" factor in order to account for increased volatilization that occurs when the moisture content decreases below a certain value (Ferrari et al., 2005). However, in reality the humidity effect cannot be described by a factor that depends on the water content but it is also a function of the type of studied chemical and soil. Models for predictive purposes should rather be based on a conceptual and quantitative understanding, which has already been presented for sorption of organic compounds to minerals (Goss, 2004).

Such dry conditions frequently occur under the influence of direct solar radiation on the surface of bare soils. The deeper soil layers often stay humid but it is the soil surface where the pesticides remain just after application (e.g. see field studies performed in California, US (Reichman et al., 2011) and south of France (Bedos et al., 2006). In order to better assess and predict the relative importance of sorption of organic chemicals to

mineral surfaces for the volatilization process, it is necessary to know the hydration status of minerals and in general have a good understanding on the humidity conditions in dry soils. The relevant measure to describe the hydration status of mineral surfaces is the water activity rather than the water content in the soil (Goss, 2004). Water activity in a soil can be expressed as the equilibrium relative humidity in the adjacent air. Its dependence on the water content of the soil is described by the water vapor sorption isotherm. This characteristic soil water function describes the water retention in the soil and is not only useful to describe sorption to the mineral surfaces in soil, but also needed to better understand and assess water movement in the soil under dry conditions, e.g. for desertification or irrigation farming. In general the water retention is well described for soils under moist conditions (van Genuchten, 1980; Brooks and Corey, 1966) but these functions cannot be used to describe water retention under dry conditions.

To describe the influence of sorption of organic compounds under dry conditions on the volatilization process it is essential to have a high spatial resolution of the soil humidity under dry conditions. For practical reasons previous field studies are only able to report volatilization of pesticides as a function of the moisture content of the soil with a low spatial resolution (e.g. water content measured at 5 mm depth) and not directly at the soil surface (Gish et al., 2009; Reichman et al., 2011). Therefore, the so far performed volatilization studies with reported data on water content are not suitable to develop a conceptual understanding of the relationship between hydration of minerals and the volatilization of pesticides and cannot be used for quantitative modeling.

1.2 Objective of this study

The first objective of this study was to establish an experimental setup that can show the influence of dry conditions in soils on the volatilisation of pesticides with a high time resolution. To achieve defined humidity conditions we used a small wind tunnel setup with a soil layer of 5 mm where the soil was equilibrated with the air phase containing a well known humidity at the beginning of the experiment. Thus, the water activity in the soil was known and homogeneous. The pesticide concentration in the air was measured by trapping the volatilized pesticide on a sorption polymer and subsequent thermodesorption followed by GC/MSD analysis. Using this setup, we investigated the influence of humidity changes and soil type on the volatilization of two pesticides from the soil surface under dry conditions. The experimental results from this well-controlled system should allow a

mechanistically based quantitative modeling.

In order to get a better understanding on the humidity state of the soil under dry condition, a systematic study on the water retention in dry soils was set up. The water vapour adsorption isotherm, that presents the water content as a function of the equilibrium relative humidity RH was measured for 18 soils with different soil textures. These data were used to calibrate a predictive model for the water sorption isotherm based on the clay content of the soil. In general dry soils typically can be found in warm areas where the temperatures can easily go up to 40 °C and also the temperature changes are quite extreme. Therefore in addition the temperature dependence of the water sorption isotherm was investigated exemplarily for nine soils.

Finally we wanted to combine the conceptual knowledge about sorption of organic compounds and the improved understanding on soil humidity under dry conditions. The goal was to integrate the mineral surfaces as an independent sorption compartment into a volatilization model and consider their availability and contribution in dependence on their hydration status. For evaluation we tested the model on the volatilization data from the wind tunnel experiments and performed a sensitivity study to estimate the influence of the different parameters.

1.3 Soil humidity under dry conditions

The water retention curve (WRC) displays the water potential Ψ , i.e. the work that is needed to achieve water movement in the soil, against the water content of the soil. This characteristic soil function describes the water holding capacity of the soil, allows conclusions on the soil's hydrology (Scheffer and Schachtschabel, 1989) and is essential for modeling water transport in the soil. Under humid conditions (characterised by a continuous water phase in the soil) the van Genuchten approach (van Genuchten, 1980) is widely used to describe the WRC but it is not able to describe the WRC under dry conditions beyond log water potential 4.2 (Ross et al., 1991; Rossi and Nimmo, 1994). In dry soils the water phase is mostly discontinuous (Salager, 2006; Tuller and Or, 2005). At this state all mineral surfaces are still covered with several layers of water molecules that are strongly bound by van der Waals forces and H-bonds.

The WRC is equivalent to the water sorption isotherm (WSI) that displays the water content as a function of the equilibrium relative humidity in the soil's pore space, which can be used as a measure of the water activity in the soil. The water potential Ψ is directly

related to the relative humidity RH in the surrounding air, if equilibrium is achieved. This relationship is given by the Kelvin equation (Or and Wraight, 2000):

$$\Psi [cm] = \frac{R \cdot T \cdot \ln(RH)}{M_{H_2O} \cdot g} \quad (1)$$

where R is the universal gas constant, T is the temperature in K , M_{H_2O} is the molecular mass of water, and g is the constant of gravity. Via this equation the WSI and the WRC can be transformed into each other which is shown in Figure 1 for soils with different clay contents. The permanent wilting point PWP (log water potential of 4.2), at which all plants wilt without a chance of recovery, equals a relative humidity of 98.9%.

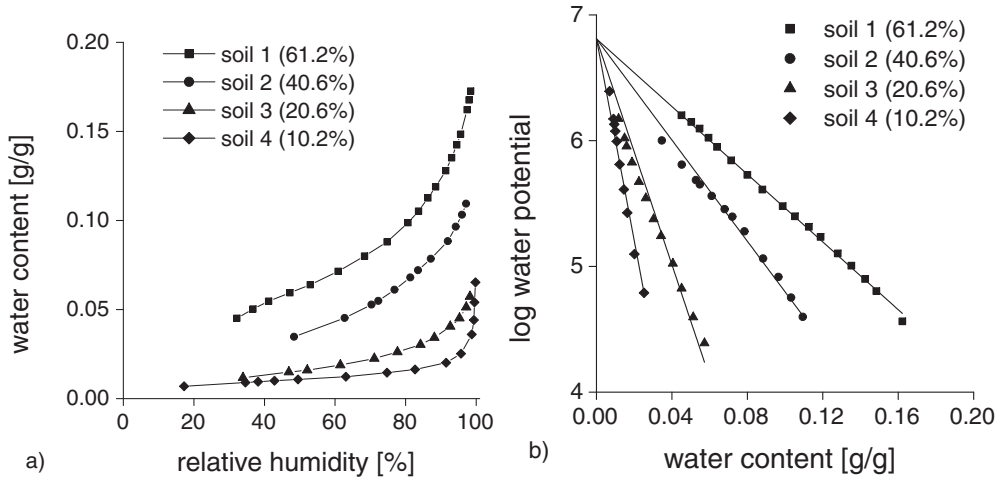


Figure 1: Water content versus relative humidity in the soil pore space (a) and the logarithmic water potential against the water content (b) for 4 soils (clay content of the soil set in brackets).

A pedo transfer function to predict the WSI

Campbell and Shiozawa (1992) proposed a linear relationship between the logarithm of the water potential and the degree of water saturation as a general function for describing the WRC under dry conditions (see Figure 1b). This linear function is defined by its two intersection points (end points) with the x-axis (water content) and the y-axis (log water potential). Based on a fixed endpoint at $\log(-\Psi)_{wc=0}$ Campbell et al. (1993) presented a correlation between the remaining endpoint on the x-axis and the clay content of the soil. Thus, this approach aims to predict the WRC in the dry region simply based on the clay content of soils. An empirical correlation between clay content and water retention

by Campbell et al. (1993) was derived from experimental data for only eight soils covering a clay content range from 5% to 45% (seven soils with clay fraction less than 35%) and excluding one outlier. Given the practical importance of such a prediction tool we set out to calibrate and validate a revised pedotransfer function based on a more diverse set of soils and pure clay minerals. To this end we measured water sorption isotherms for 18 soils (clay content between 2% and 61%) with relative humidity sensor as described by Goss and Madliger (2007). In addition WRC data for the dry region from the literature were considered for evaluation (Campbell and Shiozawa, 1992; Lu et al., 2008; Montes et al., 2003).

The empirical linear relationship between the water content wc and the base-ten logarithm of the negative water potential $\log(-\Psi)$ as proposed by Campbell and Shiozawa (1992) fits most of the data well. From the 18 soils we characterized the fitted log linear equations by their slope SL and their endpoint $\log(-\Psi)_{wc=0}$ at zero water content on the log water potential axis.

$$\log(-\Psi) = SL \cdot wc + \log(-\Psi)_{wc=0} \quad (2)$$

The use of a revised endpoint at $\log(-\Psi)_{wc=0} = 6.8$ at "zero" water content, that can be derived theoretically from the conditions under which the soil is dried in the lab, did improve the prediction as compared to the endpoint that has been used in the literature before. The slope SL remains the only variable that defines the log linear relationship of the WRC in the dry region. As seen in Figure 1b the slope becomes shallower with increasing clay content of the soils and the inverse $1/SL$ shows a very strong linear correlation with the clay content and can therefore be used for creating a pedotransfer function (PTF). The PTF for the slope, SL , was calibrated using the data of 18 soils measured in this study that covers a wide range of clay contents. The resulting PTF is:

$$\frac{1}{SL} = -0.19SL \cdot [clayfraction] - 0.003 \quad (3)$$

$$(n = 18, r^2 = 0.96)$$

The clay content of a soil is the dominant factor in determining water sorption in the dry region of the WRC. All other influences are represented by the intercept which has only a small value here.

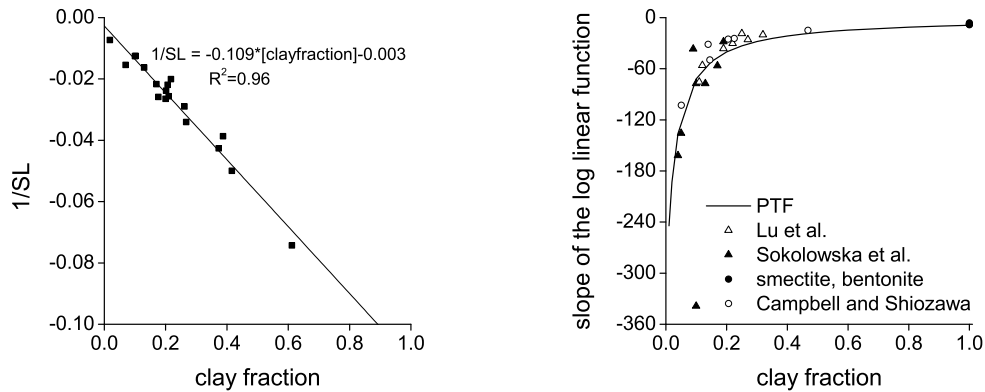


Figure 2: a) Linear relationship between the inverse of the slope of the log linear function ($1/SL$) and the clay fraction of the 18 soils used for calibration of the pedotransfer function. b) Fitted slopes of the log linear function for the water retention data of 22 soils and 3 pure clays from the literature and the slope predicted from the pedotransfer function (continuous line).

The literature data for water sorption isotherms from Montes et al. (2003) and Likos and Lu (2002) and the water retention curve data by Lu et al. (2008) which all had not been used for calibration of the PTF were used for validation purposes (see Figure 2b). As already observed for the calibration data set the predictions for soils with lower clay content do not fit the data so well.

The soils used for calibration of the PTF are all from Europe and are dominated by 2:1 clay minerals. In addition we also measured the WRC for a pure kaolinite, a 1:1 clay mineral, from Fluka (Sigmar Aldrich). The prediction of the WRC largely overestimates the water retention capacity of pure kaolinite. This is plausible because 2:1 clay minerals are able to swell and thus possess sorption sites in the inner layers that are not present in kaolinite. In addition the WRC data for soils containing kaolinite are not well described using a log linear function. Therefore we conclude that the PTF presented here and elsewhere is only valid for soils containing 2:1 clay minerals as the dominant clay type.

Prediction of the WRC via the Webb approach

For modeling purposes it is highly desirable to describe the WRC for the complete moisture regime with a function that exhibits a smooth transition between the dry and the moist region, i.e. the two different functions for the dry and moist regions should have the same first derivative at the connecting point.

Different models have been presented that "connect" the established WRC models for the

humid region with the log linear description under dry conditions proposed by Campbell and Shiozawa (1992), e.g. Rossi and Nimmo (1994); Fayer and Simmons (1995); Khlosi et al. (2006); Webb (2000). These models are designed to show a smooth transition between the dry and the moist region. Lu et al. (2008) tested various models on a data set of eight soils containing measurements for the whole humidity range and documented good results for all models with the Webb model being slightly superior.

All these literature works have in common that they are based on fitting some existing data of the WRC in order to then predict the WRC on the whole humidity range. Here we are interested in evaluating a method that does not require any experimental data for calibration but that is simply based on an existing, well established pedo transfer function for the moist range of the WRC in combination with a fixed endpoint of the dry end of the WRC.

The approach we use here is based on the work of Webb (2000). Webb (2000) extends the WRC from the moist range to the dry range as a continuous transition without the need for fitting any experimental data. This approach can be applied to the van Genuchten model (van Genuchten, 1980) as well as to the Brooks-Corey equation (Brooks and Corey, 1966). The idea behind the Webb approach is to define a so called matching point that connects the van Genuchten or Brooks and Corey function with the log linear function of the dry range that has been proposed by Campbell (see Figure 3). The matching point is a point on the van Genuchten curve that is chosen such that its tangent goes directly through the endpoint $\log(-\Psi)_{wc=0}$ at "zero" water content at the dry end of the WRC. The liquid saturation at the matching point Θ_{mp} can be calculated by a few iteration steps. Thus the tangent (first derivative of the van Genuchten curve) at the matching point represents the Campbell function for the dry part of the WRC and at the same time provides a smooth transition to the van Genuchten or the Brooks-Corey function.

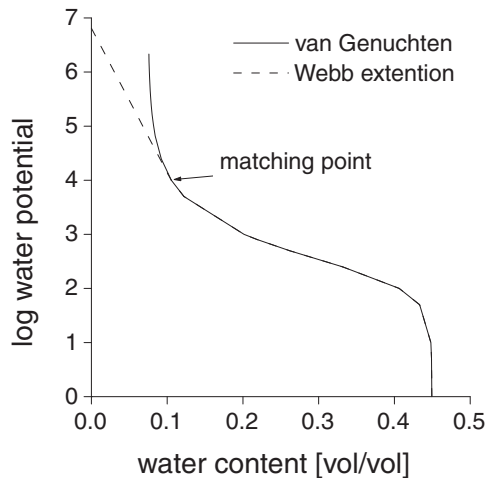


Figure 3: Van Genuchten curve and the linear Webb extension starting from the matching point.

With this approach Webb (2000) was able to fit data from saturation to oven dryness measured by Campbell and Shiozawa for 6 soils. Lu et al. (2008) confirmed this approach with water retention data for eight other soils. In both cases, Webb (2000) and Lu et al. (2008) used a van Genuchten model that had been fitted to existing experimental data from the WRC in the moist range. However, it should also be possible to predict the van Genuchten curve from existing pedo transfer functions and then use the Webb approach to further predict the dry part of the WRC. Thus the WRC for the complete humidity range would be estimated from texture data. This is what we want to evaluate here, based on the data set we used to calibrate the pedo transfer function, that is larger (additional 18 soils) and more diverse than what has previously been used for evaluating the original Webb approach. As an endpoint at zero water content we used the revised value of $\log(-\Psi)_{wc=0} = 6.8$ as used for calibrating the pedo transfer function. The program Rosetta, version 1.2 (Schaap et al., 2001) was downloaded from the US Salinity Laboratory webpage and used to predict the van Genuchten parameters from the texture data.

In dry soils the WRC is actually expected to be independent from the pore structure because the water is retained only by adsorption to the mineral surfaces and not by pore filling/drainage processes. Therefore, the WRC in the dry range should be independent of the actual bulk density during the experiment. However, in order to transform the gravimetric water content (typically reported for the dry part of the WRC) into the volumetric water content (typically reported for the humid region) a value for the bulk density had to be chosen. The bulk density was not known for most of our soils. Therefore we estimated

the bulk density ρ_{bd} from the saturated water content θ_S given by Rosetta and a particle density ρ_{pd} of 2.65 g/cm^3 (compare soil bulk density calculator on pedosphere.com based on Saxton et al. (1986)):

$$\rho_{bd} = (1 - \theta_S) \cdot \rho_{pd} \quad (4)$$

Figure 4 presents the prediction of the log linear function using the Webb model exemplarily for six soils measured in this study.

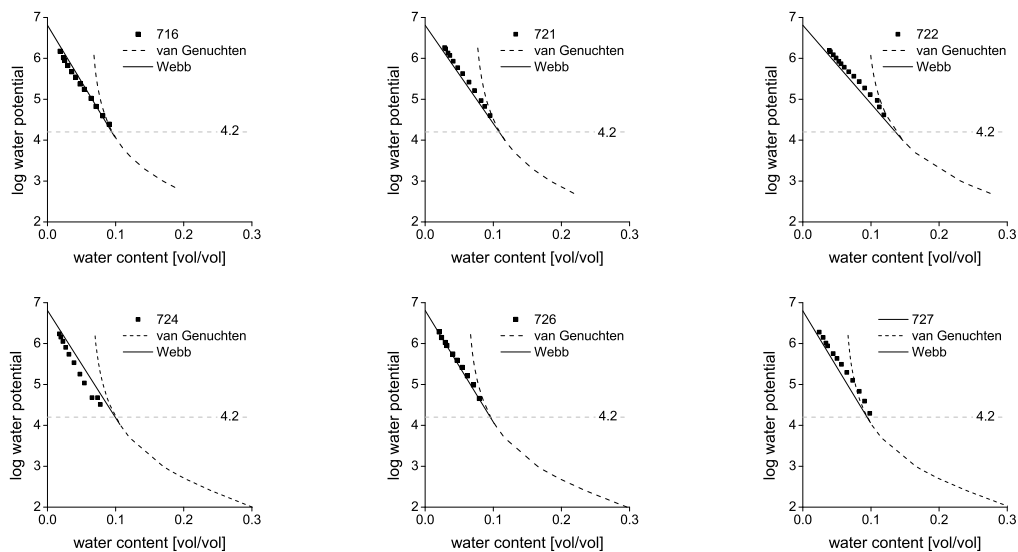


Figure 4: Predicted van Genuchten curve by Rosetta, measured WRC data within the dry region, and our prediction of the log linear function using the Webb model exemplarily for six soils measured in this study.

The results achieved using the Webb approach and the predicted van Genuchten parameter are almost as good as the pedo transfer function that had been calibrated on just these experimental data for predicting the log linear function under dry conditions only, and not the complete WRC. For soils with low clay content the approach presented here provides even better predictions. We assume that the occasionally inferior performance is more likely due to uncertainties in the texture data rather than due to conceptual shortcomings. Therefore if the actual bulk density or additional data of the WRC within the moist region are known, they should be included into the prediction of the van Genuchten parameters to improve the results. Still the prediction from texture data alone works well.

Temperature dependence of the WRC under dry conditions

In general the temperature effect on any adsorption equilibrium (including the adsorption of water on mineral surfaces) is quantified by the enthalpy of adsorption ΔH_{ads} . ΔH_{ads} is the heat that is absorbed when one mole of the compound is transferred from the surface into the gas phase. This ΔH_{ads} represents the interaction energy of the sorbate molecules with the sorbing surface and depends on the sorbate molecule (here: water), the sorbing surface and the temperature. Under dry conditions ΔH_{ads} for water may depend on the specific minerals and thus the type of soil considered. Therefore, it is important to examine the variability of ΔH_{ads} (thus temperature dependence of WRCs) across various soils. The influence of temperature on sorption equilibrium is described by the van't Hoff equation with enthalpy as the characteristic parameter:

$$\ln \left(\frac{K_2}{K_1} \right) = \frac{\Delta H_{\text{ads}}}{R} \cdot \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (5)$$

K is the adsorption coefficient (defined as mass of sorbate per mass of sorbent over the sorbate's partial pressure in the gas phase) at a given absolute temperature T .

For nine soils the WSI was measured using the method by Goss and Madliger (2007) at four different temperatures (5, 20, 30 and 40 °C). In addition literature data for a Haplic Acrisol from Tanzania with a high content of kaolinite were considered in the discussion below (Goss and Madliger, 2007).

Figure 5a shows the WSI of soil number 716 at different temperatures. RH is the water activity scale and thus uses pure water (i.e. 100% RH) at the given temperature as a reference. Hence, curves for different temperatures only deviate from each other if ΔH_{ads} of water on the soil differs from ΔH_{cond} of water into its own pure phase. In the region $>90\%$ RH the curves for the different temperatures superpose each other. This is reasonable because the thick multilayer water film on minerals at $>90\%$ RH resembles pure water and thus the interaction energy of a water molecule adsorbing on such a multilayer water film is similar to adsorption on a pure water surface (i.e. condensation). With decreasing RH, though, the temperature dependence becomes more and more visible due to the additional interactions that water undergoes with the minerals when the adsorbed water film becomes thinner. These additional interactions grow stronger at lower RH because of the decreasing water film thickness on the mineral surface, i.e. the divergence of the curves measured at different temperature increases with decreasing water content.

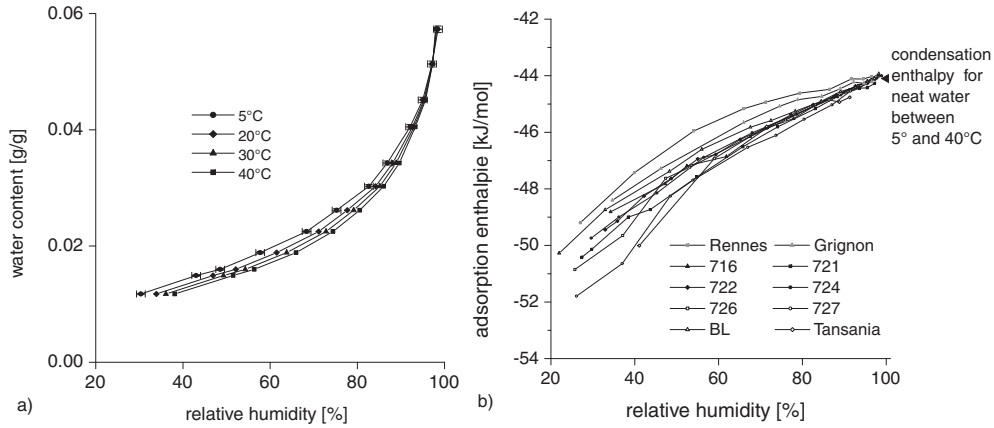


Figure 5: Water retention curves at 5, 20, 30 and 40 °C exemplarily for soil number 716 (a). ΔH_{ads} calculated from sorption isotherms at 5 and 20 °C for ten soils plotted against the average relative humidity (b).

In the following evaluation step we used the van't Hoff equation (eq. 5) to derive ΔH_{cond} for 10 soils from the water adsorption isotherms at 5 and 40 °C. The results are presented in Figure 5b and show the expected features:

- At RH close to 100%, ΔH_{ads} on all soils is identical to the ΔH_{cond} of water (also shown by Goss and Madliger (2007)).
- With decreasing water activity and thus decreasing water content the absolute ΔH_{ads} values increase above that of ΔH_{cond} . This effect was also shown for lepidocrocite (γ -FeOOH) by Majzlan et al. (2006).
- The ΔH_{ads} values for the different soils become more scattered due to their different mineral composition.

The observed scatter between different soils is quite small: the ΔH_{ads} -values of the various soils below 50% RH (a value that is rarely exceeded even in dry soils). It is noteworthy that even a soil from Tansania rich in kaolinite does not deviate from the other soils. This goes along with the finding of Likos and Lu (2002). They estimated water adsorption isotherms for kaolinite-smectite mixtures without finding any trend in the heat of adsorption. Therefore, for practical purposes the average values calculated from the data in Figure 5b can represent all soils studied and may serve as a good approximation of the actual ΔH_{ads} values for other types of soils. What remains is a significant influence of the equilibrium RH (as a parameter that represents the thickness of the adsorbed water film) on ΔH_{ads} for all soils. An average ΔH_{ads} as a function of RH calculated from the temperature interval from 5 to 40 °C is given by the following logarithmic equation:

$$\Delta H_{\text{ads}} [kJ/mol] = -4.9 \cdot \ln RH + 66.5 \quad (6)$$

$$(r^2 = 0.59, SD = 0.4)$$

The average values of ΔH_{ads} determined from this equation can serve as a good approximation for other soils without generating a substantial error and thus can allow a temperature correction for WRC data under dry conditions.

1.4 Sorption of organic chemicals in soils

Possible sorption compartments of organic compounds in soils are the soil water phase, the organic phase (humic matter) and the hydrated mineral surfaces. The equilibrium distribution of the compound between these phases depends on the contribution of each compartment to the equilibrium sorption coefficient:

$$K_{\text{soil/air}} = \frac{K_{\text{water/air}} \cdot \theta}{\rho_{\text{H}_2\text{O}}} + K_{\text{OC}} \cdot f + K_{\text{min/air}} \cdot SSA \quad (7)$$

where $K_{\text{water/air}} [m_{\text{air}}^3/m_{\text{water}}^3]$ is the water-air partitioning constant, θ the gravimetric water content [$g_{\text{water}}/g_{\text{dry soil}}$], δ the density of water [kg/m^3], $K_{\text{OC/air}} [m_{\text{air}}^3/kg_{\text{OC}}]$ the partitioning coefficient of the compound into the organic phase, $f_{\text{OC}} [kg_{\text{OC}}/kg_{\text{dry soil}}]$ the gravimetric organic carbon content of the soil, $K_{\text{min/air}} [m_{\text{air}}^3/m_{\text{min}}^2]$ is the partitioning coefficient between the hydrated mineral surfaces and air and their available specific surfaces area SSA in [m^2/kg_{soil}].

All three compartments show different sensitivities to the soil moisture. Under dry conditions the water phase will only have a small contribution to the overall sorption, because of the small water solubility of pesticides. The sorption of organic compounds to humic matter is largely independent of the soil moisture (Niederer et al., 2006). For the mineral surfaces the sorption coefficient and the SSA directly depend on the hydration status of the mineral surfaces, which is best described by the water activity, expressed as equilibrium relative humidity RH in the pore space of the soil (see above).

Below the PWP (log water potential 4.2) even small pores in the soil are not filled with water, although all mineral surfaces are covered with a water film of several molecular layers. Due to the high affinity of water molecules for hydrophilic surfaces these water layers prevent the sorption of organic molecules directly at the mineral surfaces but adsorption on

top of this water layer takes place Goss (2004). The thickness of this water layer strongly influences the strength of the sorption of the organic compound to the hydrated mineral surfaces, expressed by the sorption coefficient $K_{\text{min/air}}$. Above 90% RH the water film is so thick, that almost no molecular interaction between the compound and the minerals occur and the sorption can be considered as identical to the sorption on a neat water surface ($K_{\text{min/air}}=K_{\text{water surface/air}}$). With decreasing RH, the thickness of the water layer reduces and the distance between the molecules and the mineral surfaces decreases. As a result the interactions with the mineral surface become more and more important and the overall sorption coefficients $K_{\text{min/air}}$ increase exponentially.

Besides the sorption coefficient $K_{\text{min/air}}$ also the available surface area of the hydrated mineral surface depends on the relative humidity in the soil. Below about 95% RH the water films on the minerals do not form a meniscus and the surface area of the hydrated minerals equals the maximum specific surface area of the dry soil (SSA_{soil}). In this way a soil, containing a high amount of clay, can provide a significant contribution to the overall sorption. For $\text{RH} > 95\%$ the water films on the mineral surfaces rapidly grow thicker, start to get connected and the very small pores, which are responsible for the high surface area of the water film, finally get filled with water. Thus the total surface area of the water surface decreases dramatically until it becomes negligible close to 100% RH.

1.5 Volatilization experiments

Experimental set up

A bench scale wind tunnel system was set up to measure the volatilization from the bare soil surface under controlled humidity and constant temperature conditions (22 °C). The tunnel was made of a glass tube with a diameter of 3 mm and a length of 40 mm (Figure 6). The soil was filled into a tray made from aluminum that had an indentation of 2 x 15 cm and 0.5 cm depth to fill in the soil. Pressurized air was used to create an air stream through the tunnel after passing an active carbon filter system and a humidifier. The air flow of 17 l/min corresponded to a wind speed of 0.8 m/s. The soil water content was controlled via the air humidity (i.e., equilibrium between air and soil in the beginning of the experiment) by a water-filled, temperature-controlled washing bottle upstream of the tunnel. In addition the experimental set up contained the possibility of simulating a rain event.

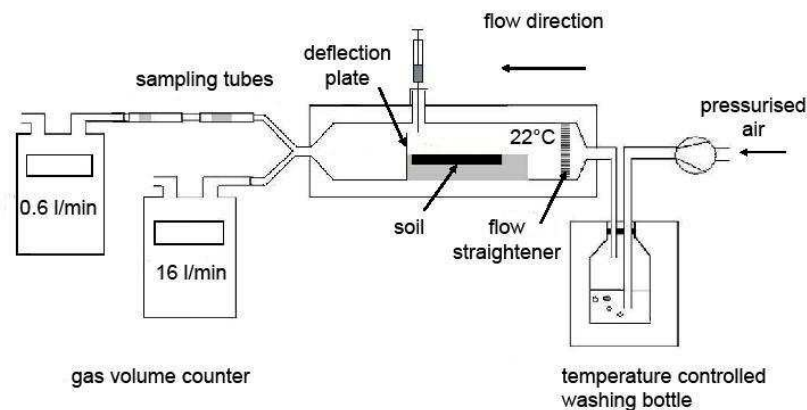


Figure 6: Experimental set up of the wind tunnel system used for the volatilization study.

At the end of the tunnel an aliquot of the total flow was sampled via a glass tube filled with ca. 150 mg of the polymer sorbent Tenax TA (Supelco, 80/100 mesh). Before use, the sampling tubes were conditioned for 20 min with a helium flow of 50 ml/min at 300 °C (compare Briand et al. (2002)). To quantify the amount of compounds on the Tenax tube a thermodesorption unit TDAS 2000 (Chromtech, Idstein, Germany) was used in combination with a GC/MSD (GC 7890A and MSD 5975C, Agilent Technologies). Before desorption, the sample tubes were flushed with a helium flow for one minute to exchange the air to inert gas. Successively, the tubes were desorbed for 10 min at 300 °C with a helium flow of 50 ml/min. The desorbed analyte was trapped at -30 °C in the liner of the PTV injector. To desorb the analyte from the liner, the injector was heated up rapidly to 270 °C and the analyte was flushed to the column and focused again at 40 °C. The following conditions were used for GC/MS analysis: The oven with the column (HP-5ms, 30 m \times 0.25 mm i.d., 0.25 μ m coating thickness, Agilent Technologies) was heated up with a rate of 15 °C/min from 40 to 220 °C and then further with a rate of 30 °C/min to 250 °C (hold for 1 min). The column flow (helium) was 1.5 ml/min. The temperature of the transfer line was 270 °C. The mass spectrometer was operated in the SIM mode, monitoring the ions $[m/z]$ 264, 306 and 335 for trifluralin and 86, 128 and 268 for triallate. For calibration Tenax tubes were spiked with 2 - 10 μ l of different standard concentrations

of triallate or trifluralin in acetone. The acetone was volatilised with a nitrogen flow and the calibration tubes were closed immediately with teflon-lined caps and analyzed. The applied method had a standard deviation of 9% for both pesticides calculated from five replicate measurements.

The soil was ground with a mortar and sieved to 1 mm before it was filled into the aluminum tray. We used two soils with different clay and organic carbon contents (Table 1). Soil BL was from the city Bad Lauchstädt, Germany (21% clay and 2.1% organic carbon content). Soil 6S was a standard soil from the Agricultural Investigation and Research Institute (LUFÄ, North Rhine-Westphalia, 42% clay and 1.6% organic carbon content).

Table 1: Soil properties of the soil used in this study.

	Bad Lauchstädt (BL)	6S LUFÄ (6S)
clay [%]	21	42
silt [%]	68	55
sand [%]	11	3
org. C [%]	2.1	1.6
<i>SSA</i> [m^2/g]	18.3	37.6

For the volatilization experiments the herbicides trifluralin and triallate were used. They are both pre-emergent pesticides that are usually applied to the bare soil surface. The volatilization from the soil surface is a relevant process for these compounds, as already shown in field and lab experiments (Spencer and Cliath, 1974; Majewski et al., 1993; Pattey et al., 1995; Grover et al., 1988). Indeed, for agricultural use it is strongly recommended to incorporate trifluralin into the soil directly after application to minimize the losses through volatilization. For both pesticides we used commercial products comprised of pesticide-formulation mixtures. Trifluralin was provided as an emulsifiable concentrate (480 g/l active ingredient) from Omya Agro (Switzerland). Triallate was delivered by the company Gowan (UK) as Avadex EC (480 g/l active ingredient). To create the application solution 75 μ l of commercial product was diluted in 25 μ l milli-Q water (for some experiments triallate and trifluralin were combined within one application solution, then 75 μ l of each commercial product was used). The application of the pesticide solution was done with an aerosol can that is typically used to spray plates for thin layer chromatography. The final application rates are comparable to field application rates recommended by the producer. Before applying the pesticide, the soil was equilibrated for two days within an air stream

of a specified relative humidity to create the starting condition. The following air humidity regimes were applied during the experiments:

Regime I) constant 60% RH: For a reference experiment the application solution was sprayed on a very dry soil surface. The RH in the air flow was equal to 60% RH. This condition was kept constant for the duration of the experiment (about 25 hours).

Regime II) constant 90% RH: The RH in the air flow was equal to 90% RH and this condition was kept constant for the duration of the experiment (about 25 hours).

Regime III) 60% RH, after 2 hours increased up to 85% RH, after 6 hours rain event: The experiment started with the same RH conditions as under humidity regime I and then the air flow RH was increased to 85%. After 6 hours a rain event of 0.5 to 0.7 mm was simulated. Along with the rain event the RH in the inflowing air stayed at 85%.

Experimental results

In order to account for different application rates of the compounds in different experiments the measured volatilization rate [$kg/(ha \cdot d)$] was divided by the application rate [kg/ha] and plotted against time. Figure 7 shows the results for triallate under the humidity regimes of 60 and 90% RH for the soil BL. Note that 60% RH corresponds to a water content of 0.023 g/g and 90% RH to 0.045 g/g respectively for soil BL.

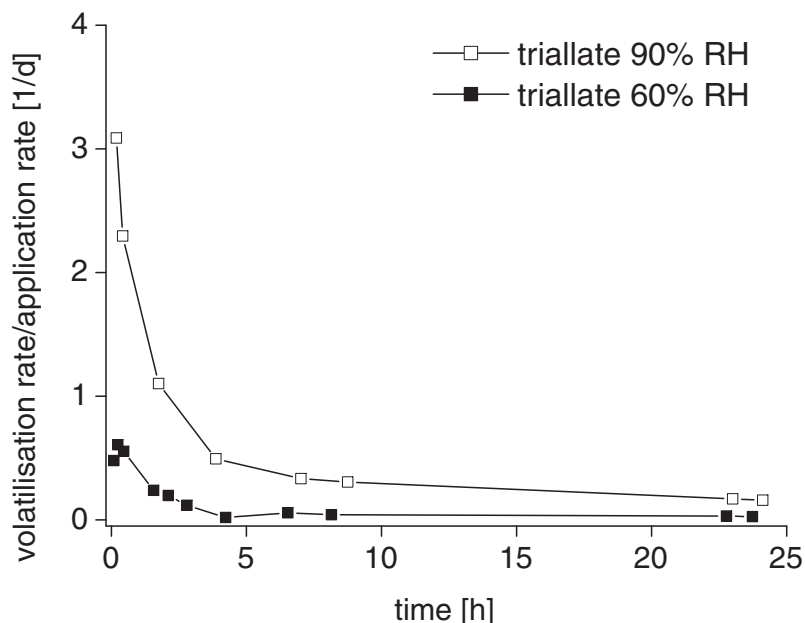


Figure 7: Volatilization rate divided by the application rate for triallate under different humidity regimes from soil BL. Each data point represents the value at the midpoint of the sampling time period.

Triallate shows significantly lower volatilization at 60 % RH than at 90% RH. This result agrees with our understanding of the equilibrium partitioning of organic chemicals under such dry conditions. At 60 and 90 % RH the volatilization of both pesticides decreases rapidly within the first 3 hours. Later the volatilization rates decrease only gradually (at 90% RH) or even level out (at 60% RH). This volatilization behavior can be explained as follows. Before the application of pesticides, the humidity in the soil is in equilibrium with the relative humidity in the air stream. Application of the aqueous emulsion on the soil surface increases the soil moisture content above the equilibrium condition. Initially this reduces the sorption of the pesticide molecules to the mineral surfaces and leads to higher volatilization rates. The amount of water applied during spraying (average 0.06 mm) evaporates quickly though after the application. This was confirmed in a separate experiment using pure water as application solution and measuring RH in the air flow at the end of the tunnel. Directly after the application the air flow RH of initially 60% increased by 5 percentage points above starting conditions and dropped back to the initial value within 30 min. The evaporation of the excess water from the application solution goes along with an increase of the sorption of the pesticide to the mineral surfaces and thus the volatilization rate decreases.

In equilibrium with 60% RH only a small fraction of the originally applied amount of triallate is lost by volatilization (ca. 6% within 24 hours). Thus a practically constant concentration gradient develops between the soil air and the incoming air which results in a constant volatilization rate from 4 to 24 hours after application. The generally higher volatilization under 90% RH is caused by the strong humidity dependence of the equilibrium sorption to the mineral surfaces under dry conditions. At 90% RH the depletion in the soil must have diminished the volatilization itself by decreasing the concentration gradient between soil and air. This can explain the continuous volatilization decrease between 4 and 24 hours. The data for trifluralin are not presented here but show the same features as triallate.

In the next experiment we increased the humidity in the air from 60 to 85% after 2 hours and simulated a rain event of around 0.5 mm after 6 hours. The results for triallate for the two different soil types are presented in Figure 8. The volatilization rate of triallate shows the same time trend for both soils. In the beginning of the experiment the volatilization rates for soil BL are within the same range as under constant 60% RH. For both soils the increase of the relative humidity up to 85% results in an increase of the volatilization rate. Within two hours after the humidity increase, the volatilization rate reaches a maximum and then decreases again.

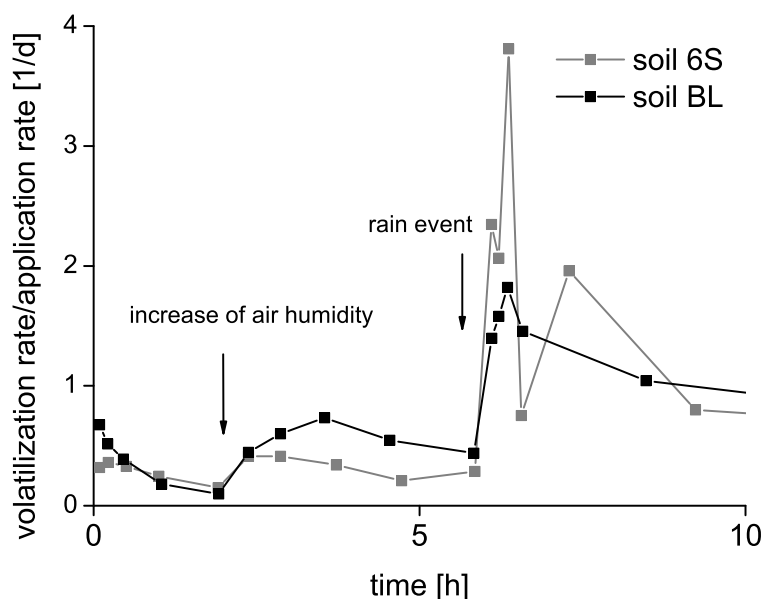


Figure 8: Volatilization rate divided by the application rate for triallate applied as an aqueous solution of Avadex EC to the soils BL and 6S under humidity regime III: increase of air humidity and simulated rain event.

The observed changes in volatilization agree with the humidity-dependent sorption mechanisms presented in the theory section. The increase of relative humidity up to 85% in the incoming air stream leads to a humidification of the soil. Additional water molecules sorb to the hydrated mineral surfaces, the thickness of the water layer increases and the sorption of the pesticide molecules decreases. The maximum volatilization rate is only reached after two hours most likely due to the kinetics of the moistening process. After reaching the maximum the volatilization decreases due to the significant depletion of the pesticide within the soil.

The abrupt rain event fills the pores of the upper soil with water. This immediately decreases the surface area of the water film on the mineral surfaces. The water surface area becomes so small that its contribution to the total sorption capacity can be neglected at this point. Under these conditions close to water saturation only the organic carbon and the bulk water phase remain as possible sorption compartments and thus the total sorption capacity decreases. This results in an immediate increase of the volatilization rate. The following decrease in the volatilization can be explained by various processes: depletion of the chemical in the soil, transport of the chemical from the upper soil layer downwards

into the soil with the infiltrating water and the subsequent drying of the soil surface due to a relative humidity in the air stream of 85%. The massive change in volatilization under changing humidity states strongly indicates the predominance of mineral sorption under dry conditions, as explained in the theory section.

Soil BL tends to show a higher volatilization rate under dry conditions (85% RH) while it is slightly higher for soil 6S under wet conditions (after the rain event). Soil 6S has a higher specific surface area due to its higher clay content. As discussed in the theory section, a higher specific surface area of the soil corresponds to a higher surface area of the adsorbed water film under dry conditions and thus a higher sorption capacity. This can explain the lower volatilization rates for soil 6S than for soil BL at 85% RH. In contrast, the surface area is not the controlling factor after the rain event, because the rain event quickly fills the pores in the soil with water, the surface area of the water films on the minerals decreases, and organic carbon starts to dominate the soil sorption properties. As a consequence 6S shows a higher volatilization rate due to its lower organic carbon content.

1.6 Modeling of the volatilisation of pesticides under dry conditions

So far the efforts to introduce above described "humidity effect" into established volatilization models did not explicitly consider the hydrated mineral surfaces as an independent sorption compartment. Wolters et al. (2004) and Ferrari et al. (2005) introduced a factor that depends on the volumetric water content into the pesticide fate model PELMO in order to account for the increase of sorption under conditions drier than the permanent wilting point (PWP). This dimensionless factor, that increases the sorption coefficient, depends on the so-called maximum possible increase of soil sorption, when the soil is "air dry". For the investigated compounds from their study Wolters et al. (2004) arbitrarily set the possible maximum value for this factor to 100. This modeling approach did account for the humidity effect they had seen in their study and thus provides an improvement compared to models that do not consider the humidity effect at all. However, this approach does not correctly describe the underlying processes and cannot be expected to work in other scenarios (e.g. different compounds or soils). The maximum increase of sorption under dry conditions depends on the number of sorption sites at the hydrated mineral surfaces and the properties of the investigated compound. For soils low in organic carbon

and with a large specific surface area this disagreement would be even larger than for those soils tested here.

Model Description

To model the volatilization experiments we used a simple transport model similar to that from Jury et al. (1983). The contaminated soil compartment is considered as well mixed and vertically and horizontally homogenous. Transport through the adjacent laminar layer in the gas phase is considered to be the kinetically controlling step. The mass transport of the pesticide from the soil surface into the air is calculated with following equation:

$$F = \frac{D_{\text{air}} \cdot A}{x} (C_{\text{soil air}} - C_{\text{air flow}}) \quad (8)$$

where F is the volatilisation rate, D_{air} is the diffusion coefficient of the compound in air, x the thickness of the laminar boundary layer, A the surface area of the soil, $C_{\text{air flow}}$ the concentration in the entering air flow, $C_{\text{soil air}}$ the concentration in the air within the contaminated soil. The soil air concentration $C_{\text{soil air}}$ is calculated from the equilibrium partitioning of the compound between the different phases in the soil (water, air, organic matter, mineral surfaces). We assume immediate partitioning equilibrium between the different sorption compartments directly after application. The following equations consider the partitioning into the air, water and organic phase and to the hydrated mineral surfaces:

$$C_{\text{soil air}} = \frac{f_{\text{air}} \cdot m_{\text{total}}}{V_{\text{air}}} = \frac{f_{\text{air}} \cdot m_{\text{total}}}{A_{\text{soil}} \cdot d \cdot \theta_{\text{air}}} \quad (9a)$$

$$\frac{1}{f_{\text{air}}} = 1 + \frac{\theta_{\text{water}}}{\theta_{\text{air}} \cdot K_{\text{air/water}}} + \frac{K_{\text{OC/water}} \cdot f_{\text{OC}} \cdot \rho}{K_{\text{air/water}} \cdot \theta_{\text{air}}} + K_{\text{min/air}} \cdot SSA \cdot \frac{\rho}{\theta_{\text{air}}} \quad (9b)$$

f_{air}	$[-]$	fraction of the compound in the soil air
V_{air}	$[m^3]$	soil air volume within the penetration depth
d	$[m]$	penetration depth of the pesticide solution
θ_{water}	$[kg_{\text{water}}/kg_{\text{dry soil}}]$	water content of the soil
θ_{air}	$[m_{\text{air}}^3/m_{\text{bulk soil}}^3]$	air content of the soil
$K_{\text{air/water}}$	$[m_{\text{water}}^3/m_{\text{air}}^3]$	air/water partitioning coefficient of the pesticide
ρ	$[kg_{\text{soil}}/m_{\text{bulk soil}}^3]$	soil bulk density
$K_{\text{OC/water}}$	$[m_{\text{water}}^3/kg_{\text{OC}}]$	organic carbon/water partitioning coefficient of the pesticide
$K_{\text{min/air}}$	$[m_{\text{air}}^3/m_{\text{min}}^2]$	sorption coefficient air/hydrated mineral surfaces of the pesticide
SSA	$[m^2/kg_{\text{soil}}]$	surface area of the mineral surfaces available for sorption

The top view surface area ($2 \times 15 \text{ cm}^2$) was used as surface area A in the calculation. The Diffusion coefficient of the compound in the air D_{air} was calculated using the method of Fuller, Schettler and Giddings (Lyman et al., 1990). The concentration of the pesticide in the incoming air was assumed to be zero. The thickness of the laminar boundary layer x was estimated by measuring the volatilization of water from the moist soil surface.

The initial penetration depth of the applied pesticide solution into the soil has a direct influence on the concentration in the soil and therefore on the concentration gradient between the soil air and the atmosphere. Simulating an application procedure to a dry soil surface (60% RH) with a water solution we observed a color change of the dry soil surface that reached to about 1 mm in depth with a rather sharp borderline. We assume that this depth of 1 mm is identical with the penetration depth and that almost none of the applied pesticide solution penetrated any deeper into the soil because of the very small hydraulic conductivity that is observed for soil under dry conditions (Lebeau and Konrad, 2010; Zhang, 2011). As a result we also neglected any further downward transport of the pesticides in modeling of the remainder of the experiment.

As mentioned above the water activity in the soil expressed as equilibrium relative humidity is a key parameter for the description of sorption to mineral surfaces. It can be derived from the water content if the water sorption isotherm (WSI) is known. For the modeling the WSIs for the respective soils were calculated from the clay content via the pedo transfer function described above.

Before the application of the pesticide solution the soil humidity was in equilibrium with the constant air flow RH. The water content was constant within the whole soil and can be extracted from the WSI. As a result 60% RH equals 0.23 g/g, 90% RH equals 0.45 g/g

for soil BL. Directly after application the equilibrium between the relative humidity in the air flow and the soil water content is disturbed by the water from the application solution that increases the water content within the upper soil layer. This amount of water is evaporated within a short time frame so that the soil goes back to its original equilibrium state. Evaporation of the water from the sprayed formulation is described in a simple way in the model (see annex). After its volatilization a constant water activity is assumed for the soil under constant RH conditions (humidity regime I and II).

Under humidity regime III the determination of the water activity in the soil is not as simple as under constant conditions. In Figure 9 we plotted the water content and the corresponding relative humidity against time to illustrate the different humidity states within the experiment. The time points for which the water content was known are marked in the figure (black squares). Between these points the water content had to be interpolated. We did not put much emphasis on optimizing this interpolation because the major features of the time curve of the moisture related parameters are already presented by the well defined points 1-5 in Figure 9.

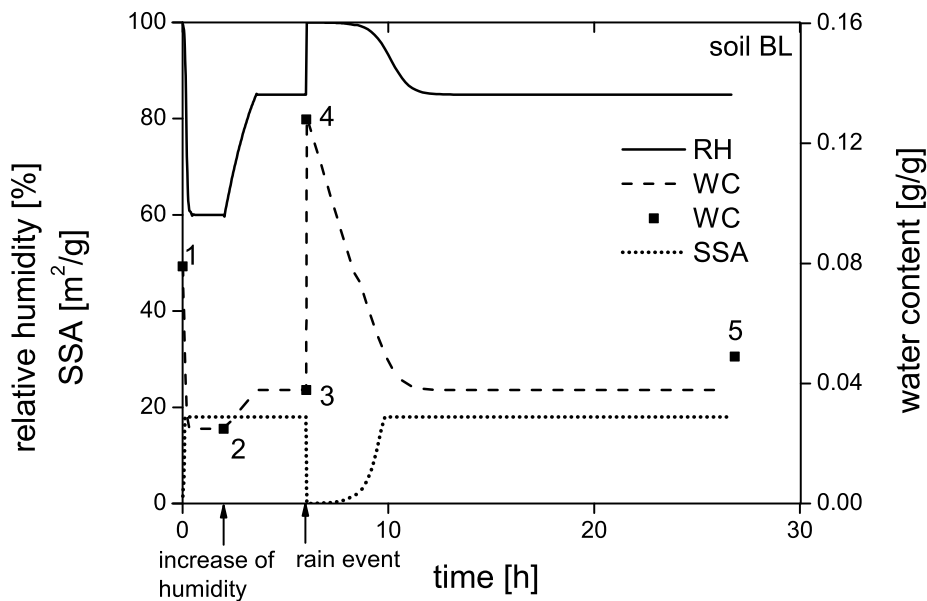


Figure 9: Water content, relative humidity and specific surface area of the hydrated mineral surfaces in the top soil layer (1mm) in moisture regime III for soil BL. At points 1-5 the water content is well known due to the experimental procedure (e.g. addition of a specified amount of water or equilibration with a specified humidity) and our knowledge of the WSI.

Figure 9 also shows the resulting specific surface area that is available for adsorption of pesticides. The specific surface area was calculated based on the following assumptions: Under dry conditions ($RH < 95\%$) the hydrated mineral surface area available for sorption of organic compounds, SSA , equals the specific surface area of the oven-dry soil, SSA_{soil} :

$$RH < 95 \% : SSA = SSA_{\text{soil}} \quad (10a)$$

Under moist conditions (100% RH) the available surface area of the hydrated mineral surface SSA is zero. Between 95% and 100% RH, we chose a linear interpolation between the maximum value of SSA_{soil} and zero (Garcia, 2010):

$$95 \% > RH < 100 \% : -\frac{SSA_{\text{soil}}}{100\% - 95\%} \cdot RH + \frac{SSA_{\text{soil}}}{100\% - 95\%} \cdot 100\% \quad (10b)$$

The sorption coefficient to the mineral surfaces, $K_{\text{min/air}}$, as a function of relative humidity is a key parameter within the prediction of the volatilization of pesticides under dry conditions in the soil. Goss (2004) presented a pp-LFER model to predict $K_{\text{min/air}}$. The pesticides studied here do not fall into the application domain of this model though, because they contain several functional groups that may not all lie in the sorption plane of the compound (Goss, 2004). However, from this earlier work an empirical correlation can be derived that allows for prediction of the slope of the exponential relationship of the sorption coefficient with RH for any compound Goss et al. (2003). The predicted slope of the exponential RH relationship combined with a single value for $K_{\text{min/air}}$ at any relevant RH provides the input information needed for modeling. In order to obtain this $K_{\text{min/air}}$ -value we fitted the volatilization model to the quasi steady-state situation at 60% RH from the experimental data using the solver method in Excel. We stress that besides this one value no other fitting to the volatilization data was used in the model results presented below.

Model Results

Figure 10 presents the experimental data and the model results for volatilisation of triallate under constant humidity conditions from the soil BL. Over the whole time period the generally lower volatilization under 60% RH compared to 90% RH is quantitatively predicted by the model. Under both humidity conditions the elevated volatilization directly after application is reproduced by the model, but in the following (until 5 hours the model shows too quick a decrease in the volatilization rate. Possible reasons for that may be that the model overestimates the evaporation rate of the water from the initially applied pesticide

solution and the assumption of immediate sorption equilibrium of the compound may also not hold.

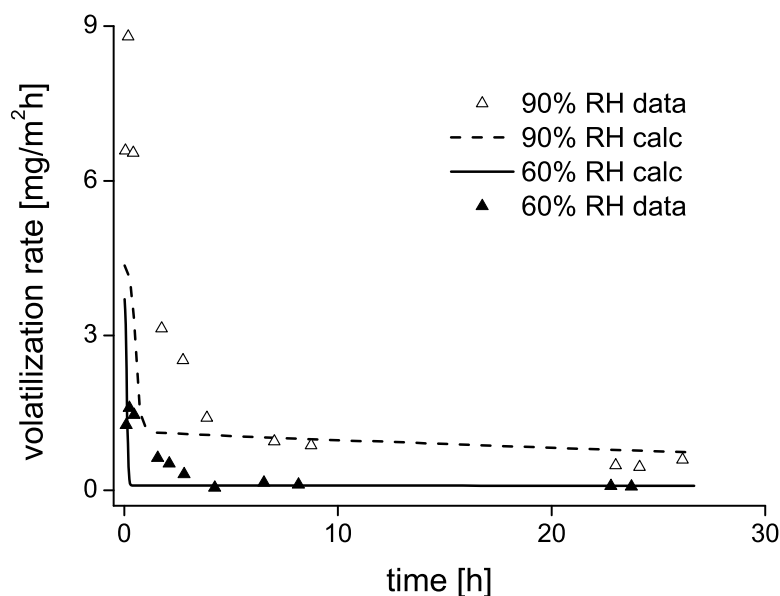


Figure 10: Measured and predicted triallate volatilization rates after spray application to soil BL under constant humidity conditions at 60 and 90% RH.

After 5 hours at 60% RH the volatilization reaches a quasi steady state; the volatilized amount is small compared to the total amount in the soil so that the concentration gradient does not change substantially over the next 20 hours. A similar explanation applies at 90% RH although here the higher volatilization rate results in a slight depletion of triallate which, in turn, leads to a small but observable decrease in the volatilization rates. The characteristic trends of the data at 60 and 90% RH are both adequately presented by the model predictions. The model results for volatilization of triallate under humidity regime III for both soils are presented in Figure 11. The increase of volatilization after increasing the relative humidity is qualitatively well presented but for both soils and both humidification steps (increase of RH and simulated rain event) the maximum observed volatilization rate is not reached by the model.

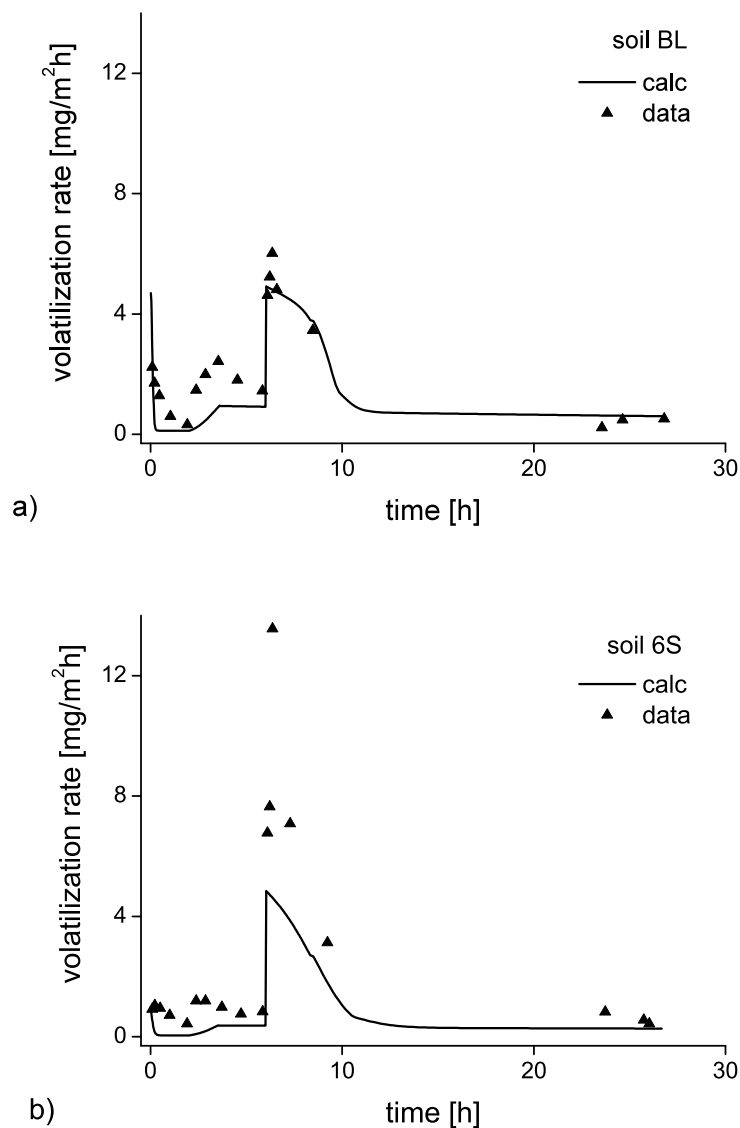


Figure 11: Measured and predicted volatilization rates of triallate after spray application to soil BL (a) and 6S (b) under humidity conditions III (60 to 85%, rain event).

An important reason for this is the simplified assumption of instantaneous re-equilibration of the partition system after the externally applied humidity changes. According to the model a change of the humidity state results in an instantaneous reallocation of the compound between the different sorption compartments according to the changes in $K_{\text{min/air}}$ and the available SSA . But in reality, compound molecules desorbed from the hydrated minerals will need to pass the air phase and diffuse into the humic matter in order achieve

the new equilibrium partitioning. Thereby in reality the concentration in the soil air will temporarily increase above the concentration estimated from the equilibrium distribution and the overall volatilization rate increases above the maximum calculated value.

Along with the rain event the pores in the soil get filled with water, the available surface area of the hydrated minerals decreases dramatically and a maximum in the volatilization rate is observed in the experiments. This is correctly simulated by the model. The model also correctly accounts for the subsequent decrease of the volatilization rate. In the model this effect results from two processes; a) depletion of the chemical reservoir in the soil and b) the drying of the soil surface due to a relative humidity in the air stream of 85% so that additional sorption sites at the hydrated mineral surfaces become available again. In reality the volatilization decrease could also be partly caused by the dislocation of the compound into the soil profile after the rain event, which was not considered in the model. Comparing the results for the different soils, the model shows a higher volatilization rate under dry conditions for soil BL, which reflects its lower specific surface area compared to soil 6S. The underestimation of the volatilization directly after the rain is even larger for soil 6S. This is consistent with the fact that the model does not consider increased losses to the gas phase during the reallocation of the compound by establishing a new equilibrium conditions (under 85% RH only 10% of the total amount of triallate are estimated to be absorbed in the organic carbon of soil 6S, so a larger amount of the compound needs to be reallocated).

Sensitivity study

In an additional sensitivity study we used the model to show the influences of various input parameters organic carbon content f_{OC} , application rate (respectively m_{total}), SSA_{soil} and the penetration depth of the applied formulation on the volatilisation under humidity regime III. For that purpose we calculated the volatilization rate of triallate from soil BL under humidity regime III while increasing and decreasing each parameter by 30% and keeping the rest of the parameters unchanged. Note that SSA highly correlates with the clay content of the soil (Sokolowska et al., 2002). Therefore the clay content that influences the shape of the WSI was changed accordingly.

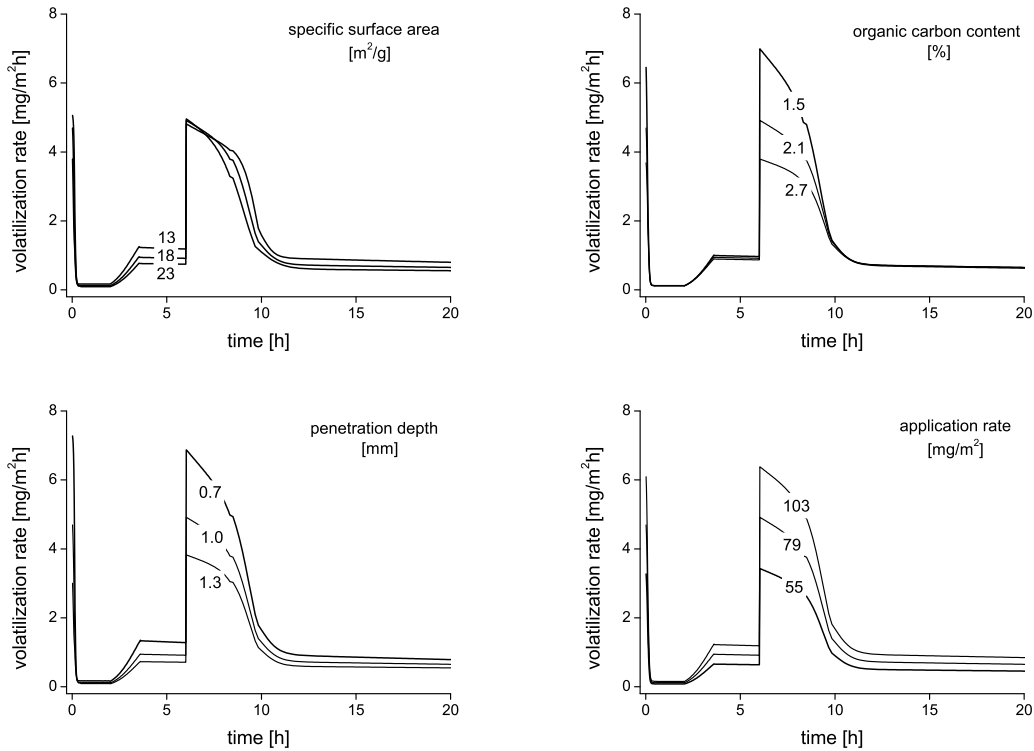


Figure 12: Sensitivity study for the volatilization under humidity regime III for the parameters org. carbon, application rate, SSA and the penetration depth.

The penetration depth and the application rate proportionally influence the volatilization rate over the whole humidity range. As expected the influence of SSA_{soil} and the organic carbon is only visible under specific humidity conditions. According to theory the influence of SSA_{soil} only shows under dry conditions. The specific surface area of the soil directly influences the maximum number of sorption sites on the hydrated mineral surfaces that are available under dry conditions and dominate the volatilization. A variation in the organic carbon content affects the volatilization over the whole humidity range. However it becomes visible only under humid conditions, where sorption to organic carbon dominates the overall sorption process.

1.7 Conclusion and Outlook

Volatilization of pesticides from soils under dry conditions (water content below the permanent wilting point) can be significantly influenced by sorption to hydrated mineral surfaces. The wind tunnel experiments confirm that the sorption of pesticides to the mineral surfaces

strongly depends on their hydration status. Under dry conditions already small changes in the water content which come about by changes in the relative humidity in the air can have great effects on the sorption to the mineral surfaces and therefore on the volatilization rate. In addition, sorption to hydrated mineral surfaces depends on the available number of sorption sites and as a result a soil with a higher specific surface area shows a lower volatilization. The filling of the soil pores with water (e.g. during a rain event) strongly decreases the available surface area and the total sorption to hydrated mineral surfaces becomes negligible. The general effect of humidity on the mineral sorption was already shown for a diverse set of dozens of organic compounds for different minerals (Goss, 2004) under equilibrium sorption conditions. Thus we expect the volatilization behavior observed in this study to principally hold for other pesticides and soils as well.

The presented model was able to correctly predict volatilization rates of two pesticides on two soils under varying humidity conditions by considering mineral surfaces as an independent sorption compartment. The key factor for improving the volatilization model was to incorporate and parameterize the sorption to hydrated mineral surfaces and its dependence on the humidity state of the soil. This model approach, in combination with an improved description of the WSI under dry conditions, can be integrated into existing volatilization models that already work well for humid conditions but still lack the mechanistically based description of the volatilization process under dry conditions.

In addition to the appropriate mechanistic approach the results reveal that it is essential to have high quality input data for $K_{\text{min/air}}$, the available specific surface area SSA , the penetration depth of the applied pesticide solution and the humidity conditions in the soil. The simple estimation of the humidity dependence of SSA and $K_{\text{min/air}}$ that we proposed here should work in other cases as well. However, there still is the need for a reliable predictive method of $K_{\text{min/air}}$ for a reference humidity. The rather accurate information on the humidity state of the soil that we could extract here from the well defined wind tunnel experiments might be very difficult to get at in a field situation. Only recently tools are beginning to be developed that allow the prediction of the water activity and the hydraulic conductivity in soils under dry conditions (Lebeau and Konrad, 2010; Zhang, 2011).

In general the results of this study (experiments and presented model approach) can be used to improve the assessment of the volatilization of pesticides under dry conditions. As a practical consequence, spraying of the pesticide on a dry soil surface would minimize the initial loss. However a subsequent incorporation into the soil before the next rain event would be needed to avoid the loss that is initiated by humidifying the dry soil surface.

This combination could be the optimal strategy for lowest volatilization losses in the field.

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Chapter 2

Abstracts of the original publications

Prediction of the water adsorption isotherm in air dry soils

Martina Schneider and Kai-Uwe Goss

Geoderma, VOL. 170, 64–69, 2012

doi:10.1016/j.geoderma.2011.10.008

Abstract

Within this work we present a revised pedotransfer function (PTF) that predicts water sorption isotherms for dry soils based on the clay content of the soils. When the water sorption isotherm is plotted as a water retention curve (log water potential plotted against the water content) it typically results in a log linear function as described by Campbell and Shiozawa (1992). The linear function is defined by its slope and a fixed endpoint at zero water content. The reciprocal of the slope shows a strong correlation with the clay fraction. For the calibration of a PTF we measured water sorption data for 18 soils with clay contents from 2 % to 61 %. The final predictions of the water sorption isotherms from the clay mass fraction were very good if the clay content was higher than 7 %. The use of a revised theoretical endpoint at the dry end of the WRC did improve the prediction as compared to the endpoint that has been used in the literature before. In addition literature data for 22 soils and 3 pure clay minerals were used for validation. The good performance only occurred if the clay fraction was dominated by 2:1 clay minerals. The water retention isotherm of soils rich in the 1:1 clay mineral kaolinite could not be predicted by this approach; the actual water content was strongly over-predicted and the water retention curve did not follow a log linear relationship.

Prediction of water retention curves for dry soils from an established pedo-transfer-function: Evaluation of the Webb Model

Martina Schneider and Kai-Uwe Goss

Water Resources Research, VOL. 48, W06603, 2012

doi:10.1029/2011WR011049

Abstract

The van Genuchten curve, and its prediction by various pedotransfer functions, has long been an established method to describe the water retention curve (WRC) in soils, but it cannot be used to describe water retention under conditions dryer than the wilting point. Water retention under dry conditions follows a log linear function, which does not agree with the extrapolated van Genuchten curve. As a remedy Webb (2000) proposed an approach that predicts this linear function for the dry range with a smooth transition to the van Genuchten curve that has been fitted to experimental data for the moist range. In this work we present the prediction of water retention curves for 31 soils under dry conditions using the approach presented by Webb. In addition to the larger number of soils that we use for evaluation we deviate from the original Webb approach in two ways: (a) we use predicted (Rosetta) rather than fitted van Genuchten curves and (b) we use a corrected endpoint at zero water content. The outcome reveals good results for the prediction of water retention curves for the dry region and provides a smooth transition between the moist and the dry region of the water retention curve. Occasional inferior performance for some data is likely due to uncertainties in the texture data or in the choice of the right bulk density rather than due to conceptual shortcomings of the Webb approach. This work shows that the WRC for the whole humidity range, from oven dryness to full saturation, can be described by two functions with a smooth transition whose parameters can all be predicted by Rosetta without the need of experimental information.

Temperature dependence of the water retention curve for dry soils

Martina Schneider and Kai-Uwe Goss

Water Resources Research, VOL. 47, W03506, 2011

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Abstract

Water retention curves (WRCs) are equivalent to water adsorption isotherms that display the soil water content as a function of water activity in the pore space. The use of water activity implies that pure (unbound) water at the given temperature is considered as reference state. In this study we measured the temperature dependence of WRCs for nine European soils under dry conditions (i.e. water activity < 90 %RH, matrix tension < -1.5 MPa). The results show a significant temperature dependence of the WRCs. The absolute value of the adsorption enthalpy of water, ΔH_{ads} , which reflects this temperature dependence, increased with decreasing water content and thus deviated from the condensation enthalpy of a pure (unbound) water phase, ΔH_{cond} . These results are explained by the following facts: under increasingly drier conditions the interactions between water molecules and the mineral surfaces become more and more dominant because the sorbed water film becomes very thin. These interactions between water and minerals are stronger than those between pure water molecules. The observed temperature dependence of WRCs varied only little between the studied soils. Therefore, the average equation, $\Delta H_{\text{ads}} [kJ/mol] = 4.9 \cdot \ln RH - 66.5$, derived from our experimental data may serve as a good approximation of ΔH_{ads} for soils in general and thus allow the temperature extrapolation of WRCs (in the dry region down to 30 %RH) between 5 °C and 40 °C without the need for additional experimental information.

Volatilization of pesticides from the bare soil surface: evaluation of the humidity effect

Martina Schneider, Satoshi Endo and Kai-Uwe Goss

Journal of Environmental Quality, VOL. 42, No. 3, p. 844-851, 2013

doi: 10.2134/jeq2012.0320

Abstract

Volatilization of pesticides from soils under dry conditions (water content below the permanent wilting point) can be significantly influenced by sorption to hydrated mineral surfaces. This sorption process strongly depends on the water activity, expressed as equilibrium relative humidity in the pore space of the soil, and on the available surface area of the hydrated minerals. In this study, the influence of different humidity regimes on the volatilization of two pesticides (trifluralin and triallate) was demonstrated with a bench-scale wind tunnel system that allowed the establishment of well controlled humidity conditions within the soil. In the experiment starting with very dry conditions, increasing the relative humidity in the adjacent air from 60 to 85 % resulted in an up to 8 times higher volatilization rate of the pesticides. An additional strong increase in volatilization (up to 3 times higher) was caused by a simulated rain event, which eliminates all sorption sites associated to mineral surfaces. In agreement with this interpretation the comparison of two soils suggested that mineral surface area was the soil property that governs the volatilization under dry conditions while soil organic matter was the controlling variable under wet conditions. In contrast to expectations, the use of a novel encapsulated suspension for triallate showed the same humidity effects and no substantially lower volatilization rates in comparison to the regular formulation. This study demonstrated that humidity effects on pesticide volatilization can be interpreted via the mechanism of sorption to mineral surfaces under dry conditions.

Volatilization Modeling of Two Herbicides from Soil in a Wind Tunnel Experiment under Varying Humidity Conditions

Martina Schneider and Kai-Uwe Goss

Environmental Science and Technology, 46(22), p. 12527-33, 2012

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Abstract

Volatilization of pesticides from the bare soil surface is drastically reduced when the soil is under dry conditions (i.e., water content lower than the permanent wilting point). This effect is caused by the hydrated mineral surfaces that become available as additional sorption sites under dry conditions. However, established volatilization models do not explicitly consider the hydrated mineral surfaces as an independent sorption compartment and cannot correctly cover the moisture effect on volatilization. Here we integrated the existing mechanistic understanding of sorption of organic compounds to mineral surfaces and its dependence on the hydration status into a simple volatilization model. The resulting model was tested with reported experimental data for two herbicides from a wind tunnel experiment under various well-defined humidity conditions. The required equilibrium sorption coefficients of triallate and trifluralin to the mineral surfaces, $K_{\text{min/air}}$, at 60 % relative humidity were fitted to experimental data and extrapolated to other humidity conditions. The model captures the general trend of the volatilization in different humidity scenarios. The results reveal that it is essential to have high quality input data for $K_{\text{min/air}}$, the available specific surface area (SSA), the penetration depth of the applied pesticide solution, and the humidity conditions in the soil. The model approach presented here in combination with an improved description of the humidity conditions under dry conditions can be integrated into existing volatilization models that already work well for humid conditions but still lack the mechanistically based description of the volatilization process under dry conditions.

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Publication List

Publications

- 2013 M. Schneider, S. Endo and K.-U. Goss: *Volatilization of pesticides from the bare soil surface: evaluation of the humidity effect*, Journal of Environmental Quality
- 2012 M. Schneider and K.-U. Goss: *Volatilization Modeling of Two Herbicides from Soil in a Wind Tunnel Experiment under Varying Humidity Conditions*, Environmental Science and Technology
- 2012 M. Schneider and K.-U. Goss: *Prediction of water retention curves for dry soils from an established pedo-transfer-function: Evaluation of the Webb Model*, Water Resources Research
- 2012 M. Schneider and K.-U. Goss: *Prediction of the water sorption isotherm in air dry soils*, Geoderma
- 2011 M. Schneider and K.-U. Goss: *The temperature dependence of the water retention curve for dry soils*, Water Resources Research
- 2009 M. Schneider and K.-U. Goss: *Systematic Investigation of the Sorption Properties of Tenax TA, Chromosorb 106, Porapak N and Carboxpak F*, Analytical Chemistry

Conference contributions

- 2011 M. Schneider and K.-U. Goss: *Prediction of the water retention curve in dry soils*, oral presentation, EGU Vienna
- 2010 M. Schneider and K.-U. Goss: *Influence of the soil moisture on the volatilisation of pesticides from the bare soil surface* (in german), oral presentation, SETAC Dessau
- 2007 M. Schneider, E. Klingelmann, H. Stoffregen, D. Schenke, W. Pestemer, G. Wessolek: *Leaching von Glyphosat auf teilversiegelten Flaechen- experimentelle Ergebnisse und Modellierung mit HYDRUS1D*, poster presentation, SETAC Leipzig

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