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Introduction

The air-soil exchange of organic chemicals is of considerable interest because (a) soils are key repositories for many organic contaminants subject to atmospheric deposition or direct emission¹ (b) persistent organic contaminants deposited in the past may be subject to re-volatilization from soils and translocation to other areas², and (c) the effect of primary emission reduction from anthropogenic sources on atmospheric levels may be mitigated by diffusive re-emission from soils and other environmental compartments³. In sum, air-soil exchange is believed to have important implications for the overall fate of many organic contaminants, even on a global scale¹. Environmental fate models addressing soil-air exchange have so far assumed that organic matter dominates the sorptive capacity of soil for organic chemicals, and commonly neglect adsorption to soil mineral matter. However, Goss et al. have recently shown that this assumption is not always correct in air-dry soils, even for non-polar organic chemicals⁴. Here, our aim is therefore to evaluate the potential impact of mineral matter adsorption on the air-soil exchange of organic chemicals. Specifically, we investigate the short-term variability that may occur for a-HCH in an arid soil subject to early morning dew.

Materials and Methods

It has been recognized that no single parameter is able to capture all the molecular interactions that determine the overall equilibrium partitioning of a given chemical between two phases⁵. For this reason, the research groups of Abraham, Goss and others have promoted the development and use of Poly-Parametric Linear Free Energy Relationships (PP-LFERs) to predict environmental phase partitioning (instead of Single-Parametric LFERs). We have previously shown how to use PP-LFERs in fugacity-based multimedia fate and transport models⁶. Here we implemented PP-LFERs for air-water partitioning⁷, water-organic carbon partitioning⁸ and air-mineral matter partitioning⁴ into CoZMo-POP, a non-steady-state, non-equilibrium multi-media fate model⁹. This model includes descriptions of advective transport (by leaching and run-off) and diffusive transport in the soil (within soil pores and by soil solids), as well as temperature dependent degradation rates⁹.

The temperature dependence of adsorption onto mineral matter adopts expressions published by Goss¹⁰-¹¹. The temperature dependence of air-water partitioning is estimated using the enthalpy of phase transfer between air and water⁹, whereas the temperature dependence of water-organic carbon partitioning is approximated with the help of the enthalpy of phase transfer between water and octanol. Finally, relative humidity (RH) of the gas phase in equilibrium with the surface is included as a new input parameter as RH has a significant impact on mineral matter adsorption (i.e. on the soil surface descriptors and on the specific surface area - SSA)⁴. The adsorption coefficients normalized to surface area decrease exponentially between 40% and 90% RH, due to a decrease in intermolecular interactions. Furthermore, the SSA available for vapor adsorption decreases dramatically when RH exceeds 90%. For this reason, mineral matter adsorption ceases to be of significance for RHs above 98%⁴.

In order to evaluate the short-term (diurnal) variability of air-soil exchange in response to changing RH and air/soil temperature, a hypothetical model scenario is defined representing a desert soil that experiences early morning dew and dries out during daytime¹². RH and T are assumed to vary sinusoidally with maxima in the early morning and early afternoon, respectively (Table 1). Table 1 lists some key model input parameters.

Table 1: Selected model input parameters.
The model was applied to a-HCH, an insecticide with an extensive global usage history. Physical-chemical properties (solute descriptors) were taken from Abraham et al., supplemented with additional data from the literature. The model was run for several years with constant atmospheric emissions until quasi steady-state conditions had been established.

**Results and Discussion**

Using fugacity nomenclature, the concentration \( (\text{mol m}^{-3}) \) is the product of a fugacity \( (\text{Pa}) \) and a fugacity capacity or Z-value \( (\text{mol m}^{-3} \text{ Pa}^{-1}) \). The Z-value for a bulk environmental compartment is derived additively from the Z-values for the individual sub-phases \( Z_X \) making up that compartment, weighted on a volume basis. As soil is composed of particulate organic carbon (POC), water, air, and mineral matter, its bulk fugacity capacity \( B_{Z_S} \) is derived using:

\[
B_{Z_S} = v_{POC} \cdot Z_{POC} + v_W \cdot Z_W + v_A \cdot Z_A + z_{MM} \cdot (\text{mol/m}^2\text{Pa}) \cdot \text{SSA}(\text{m}^2/\text{kg}) \cdot \rho_{MM}(\text{kg/m}^3)
\]

As the fugacity capacity for mineral matter adsorption is an interfacial z-value with units of \( \text{mol m}^{-2} \text{ Pa}^{-1} \) it needs to be weighted by the surface area in units of \( \text{m}^2/\text{m}^3 \), rather than a volume fraction \( v_X \) in units of \( \text{m}^3/\text{m}^3 \).

Figure 1 shows the variability of the bulk soil Z-value when diurnal variability of RH (Fig. 1A) and diurnal variability of both RH and T (Fig. 1B) are considered. It is evident that (i) \( B_{Z_S} \) for soil is generally controlled by adsorption to mineral matter (red lines in Fig 1) and to a lesser extent sorption to POC (data not shown). A notable exception occurs when RH is at its peak in the early morning hours, and SSA is significantly reduced. (ii) From the pronounced peak of \( B_{Z_S} \) during the late afternoon, when the soil is driest (blue lines in Fig 1), we can conclude that the diurnal change in RH exhibits a more significant influence on the diurnal variability of \( B_{Z_S} \) than diurnal temperature change. (iii) The relative decrease in the peak value for \( B_{Z_S} \) (Fig 1B as compared to Fig 1A) is caused by elevated temperatures during the early evening, reducing the adsorptive capacity of mineral matter.

![Figure 1. Diurnal variability of bulk Z of a-HCH in surface soil (BZS - left y-axis) when diurnal variability of RH (A) as well as T (B) is considered. Also presented (right y-axis) are the relative contributions of the weighted Z-value terms for mineral matter (MM). MM and POC are the soil phases that dominate BZS for a-HCH.](image-url)
When contamination levels in adjacent compartments are expressed in terms of fugacity, the levels can be compared directly, and the chemical flux direction can be predicted from the fugacity fraction (FF). In the case of air-soil equilibrium, FF is defined as \( f_A / (f_A + f_S) \). Equilibrium is suggested by a value of 0.5, and deviations from equilibrium in either direction are depicted on the same scale. In the context of air-surface exchange, a FF of larger than 0.5 implies net atmospheric deposition and a value below 0.5 implies net volatilization. In Figure 2, we present the diurnal change of FF (A) and air-soil exchange (B) for the two model scenarios (with and without diurnal change of temperature).

Figure 2. Diurnal variability of the fugacity fraction (A) and air-soil exchange (B) at constant and variable temperatures. The air-soil exchange is scaled according to the maximum value of atmospheric deposition.

We note that the fugacity fraction fluctuates significantly over a 24 hour period (Fig 2A). The fugacity fraction is at a minimum in the early morning, reflecting the lack of mineral adsorption sites at elevated RH during this time. When the temperature is assumed to be constant (green markers), a short period of net volatilization is predicted. The lack of such a situation for variable temperature can be attributed to the enhanced sorbing capacity of soil POC and MM at low nighttime temperatures. Finally, it should be mentioned that the predicted volatilization flux exhibits a much more significant diurnal variation than the deposition flux. In other words, the diurnal fluctuations in Figure 2B are controlled by differences in the soil fugacity, which in turn is significantly affected by fluctuations in RH.

These preliminary model simulations confirm that adsorption to mineral matter may dominate the sorption of even non-polar chemicals to dry soils with low organic matter content\(^4\), and indicates that this process needs to be considered when seeking to understand and quantify air-soil exchange processes of organic chemicals in arid regions. Because of the strong sensitivity of mineral matter adsorption to relative humidity, dramatic and sudden changes in air-soil exchange behavior (e.g. air-soil equilibrium and flux direction) of organic chemicals may result from changes in RH brought about by low nighttime temperatures\(^12\), water vapor condensation, or precipitation. The effect of variable RH on the soil sorptive capacity may often be as, if not more important than, the effect of variable temperature. Future work will include additional chemicals as well as environmental conditions to expand on the potential role of mineral matter adsorption on air-soil exchange and the overall environmental fate of organic chemicals.

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References


