

Application of a multimedia activity model for evaluating the fate of persistent mobile organic chemicals in soil: The influence of media-specific volume fractions

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Introduction

- In recent years there has been increasing interest to screen and prioritize chemicals used in commerce with respect to their potential to contaminate drinking water sources.
- The German Environment Agency (Umweltbundesamt – UBA) has proposed screening criteria to identify chemicals that may pose hazards to drinking water. The hazard criteria aim to prioritize chemicals that are persistent, mobile and toxic (PMT) or very persistent and very mobile (vPvM).
- The development and application of exposure assessment tools would thus support prioritization activities.
- This study summarizes the development of a multimedia environmental fate and transport model, which supports the exposure assessment of persistent mobile organic chemicals (PMOCs) under a variety of scenarios, including under steady-state, equilibrium and non-steady-state and non-equilibrium conditions.
- The developed model includes multilayer soil and aquifer compartments (unsaturated and saturated) (Figure 1), which is used to enable a screening level estimate of exposure to PMOCs.

Model summary

- Multimedia fugacity-based model with multilayer soil compartment segmented between 19 unsaturated soil layers and 1 saturated soil layer linked to freshwater sediment compartment.
- Chemical flux between surface water and saturated soil is assumed to occur via advection, with water flow described by Darcy's Law. The rate and direction of transfer between surface water and saturated soil is controlled by the hydraulic gradient and moderated by the hydraulic conductivity of the porous medium.
- The partitioning of chemicals between the various environmental media strongly influences the rates of transport, which is described using a fugacity-based approach. Fugacity (f) can conceptually be understood as the 'escaping tendency' of a chemical, which has units of pressure (Pa).
- An important challenge for chemicals screened as possible PMOCs, is that they may have negligible partial pressures, as might be the case for the charged species of an ionizable organic chemical. Since ions do not volatilize, and therefore do not exert a partial pressure or fugacity, the development of an activity-based approach, consistent with the model developed by Trapp et al. (2010), has been adopted here.
- Here, we present the results from a Level 1 calculation, which assumes an environmental system that is at steady-state and equilibrium.
 - A Level 1 calculation can be informative, in that it provides an assessment of the relative influence of changes in physicochemical properties, such as the acid-dissociation constant (pK_a) of a chemical, relative to an environmental pH, may have on the distribution and fate of a chemical.
 - The Level 1 calculation is mathematically simple, requiring only a definition of the environmental system (i.e. volumes and compositions of each of the compartments) and an estimate of the total mass of chemical emitted into the system, in order to derive predicted activities and concentrations in each environmental compartment.
- When considering that the mixing depth of agricultural soil defined in the EU Technical Guidance Document (TGD) is 0.2m, the depth of each of the 19 unsaturated soil layers can be initially set at 1.053cm (resulting in an unsaturated soil zone depth of 20cm), which thus enables a direct comparison with output obtained from the TGD default setting for the unsaturated soil zone. To explore the relative differences in the mass fraction of chemicals between the unsaturated and saturated soil zones, we have assumed each zone to have a depth of 20cm, defined here strictly to enable a direct comparison for illustrative purposes.
- A useful approach for understanding the role of physicochemical properties in multimedia environments is to assess how a suite of hypothetical chemicals with varying partitioning properties distribute between each of the environmental compartments at equilibrium. Using a graphical approach, the chemical mass fraction in air, water, sediment, soil and the saturated zone from the Level 1 calculation are plotted over different combinations of partition coefficient (e.g. the octanol-water partition coefficient (K_{ow}) versus the air-water partition coefficient (K_{aw})). This approach can also investigate how differences in pK_a , relative to a defined environmental pH influence the relative distributions. Illustrative calculations for hypothetical chemicals (all with molecular weight of 100 g mol⁻¹) over a chemical space covering the region between $-5 < \log K_{ow} < 8$ and $-10 < \log K_{aw} < 3$ with a step of 1 log₁₀ unit, while also holding the pK_a at 4, 7, and 9 for both organic acids and organic bases.

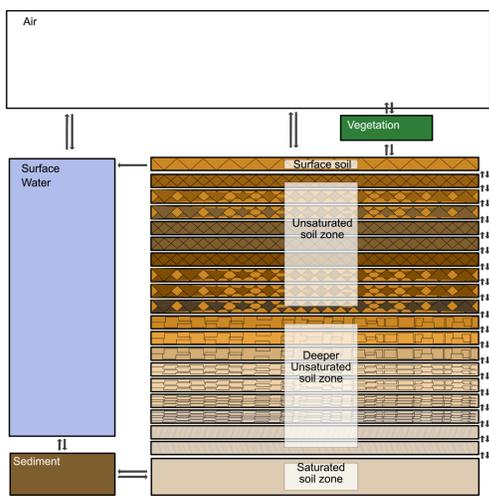


Figure 1: Conceptual illustration of model compartments and structure.

Summary of key equations

Organic carbon-water partition coefficient (K_{oc}) (Trapp et al. (2010))

For non-ionizable organic chemicals:

$$\log K_{oc} = 0.54 \log K_{ow}$$

For monoprotic acids:

$$K_{oc} = \alpha_1 10^{0.54 \log K_{ow,n} + 1.11} + \alpha_2 10^{0.11 \log K_{ow,n} + 1.54}$$

For monoprotic bases:

$$K_{oc} = \alpha_1 10^{0.37 \log K_{ow,n} + 1.71} + \alpha_2 10^{0.65 \log K_{ow,n} + 0.14}$$

The total mass of chemical in the system (m_t) is the product of the sums of the concentrations (C) and volumes (V) of each environmental compartment, I (Gouin et al. (2000)):

$$m_t = \sum C_i V_i$$

The mass fraction of chemical in each compartment (F_i) can be simply obtained as:

$$F_i = \frac{m_i}{m_t}$$

where, m_i is the mass of chemical in each individual compartment at equilibrium.

Results

FIGURE 2 summarizes results for neutral non-polar organic chemicals. Results suggest that the mass distribution of highly volatile neutral organic chemicals will be predominately in the air.

- Specifically for chemicals with $\log K_{ow} > -3.5$ and $\log K_{aw} < 2$, whereas for chemicals with $\log K_{ow} < 2$, the mass distribution in the air (Fig. 2a) is influenced by the log octanol-air partition coefficient (K_{ow}), with chemicals having a $\log K_{ow} < 6$ predicted to be predominately in the air.
- Conversely, the mass distribution of chemicals in the unsaturated soil (Fig. 2b) is >50% for chemicals with $\log K_{ow} > 2$ and $\log K_{aw} > 6$.
- The remaining distribution for chemicals with $\log K_{ow} < 2$ and $\log K_{aw} < -3.5$ tends to increase in both surface water (Fig. 2c) and in the saturated zone (Fig. 2d) (i.e. the lower left corner of the chemical space plots), with approximately 45% and 35% of chemical predicted in surface and groundwater, respectively.
- The observation that the predicted mass in surface-water is greater than in the saturated zone is intuitive and is influenced by the bulk activity capacity of the surface water compartment, which is 0.9 m³m⁻³, whereas that of the saturated zone is =0.4 m³m⁻³.
- It is notable that the bulk activity capacity, which is the sum of the activity capacities of all the individual phases of the soil, such as air, water and the soil solids, is influenced by the relative volume fraction of each phase in an environmental compartment.
- Thus, the reason, that the bulk activity capacity of the saturated zone is less than surface waters is because the volume fraction of water in the saturated zone is assumed to be about 0.4 but is unity in the surface water.
- Curiously, if the volume fraction of water in the saturated zone were to increase to 0.6, the mass fraction of chemical in the saturated zone would increase to 45%, whereas the mass fraction in surface water would decrease to 35%.
- Consequently, for chemicals with physicochemical properties that fall in the lower left corner of the chemical space plots (i.e. potential PMOCs), the activity capacity will be strongly influenced by the relative fraction of water in a specific compartment.

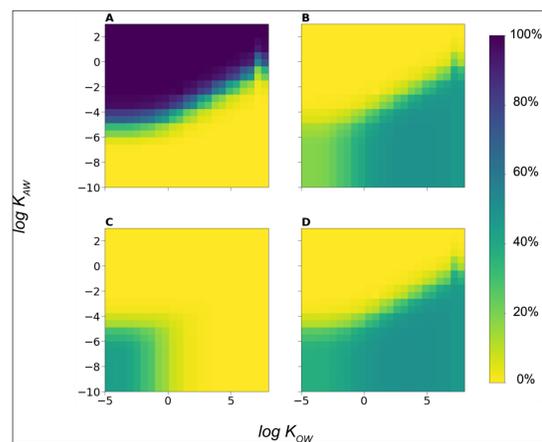


Figure 2: Illustrative summary of the mass distribution of neutral organic chemicals with varying partitioning properties of $\log K_{ow}$ and $\log K_{aw}$ in A: air, B: unsaturated soil, C: surface water, D: saturated soil.

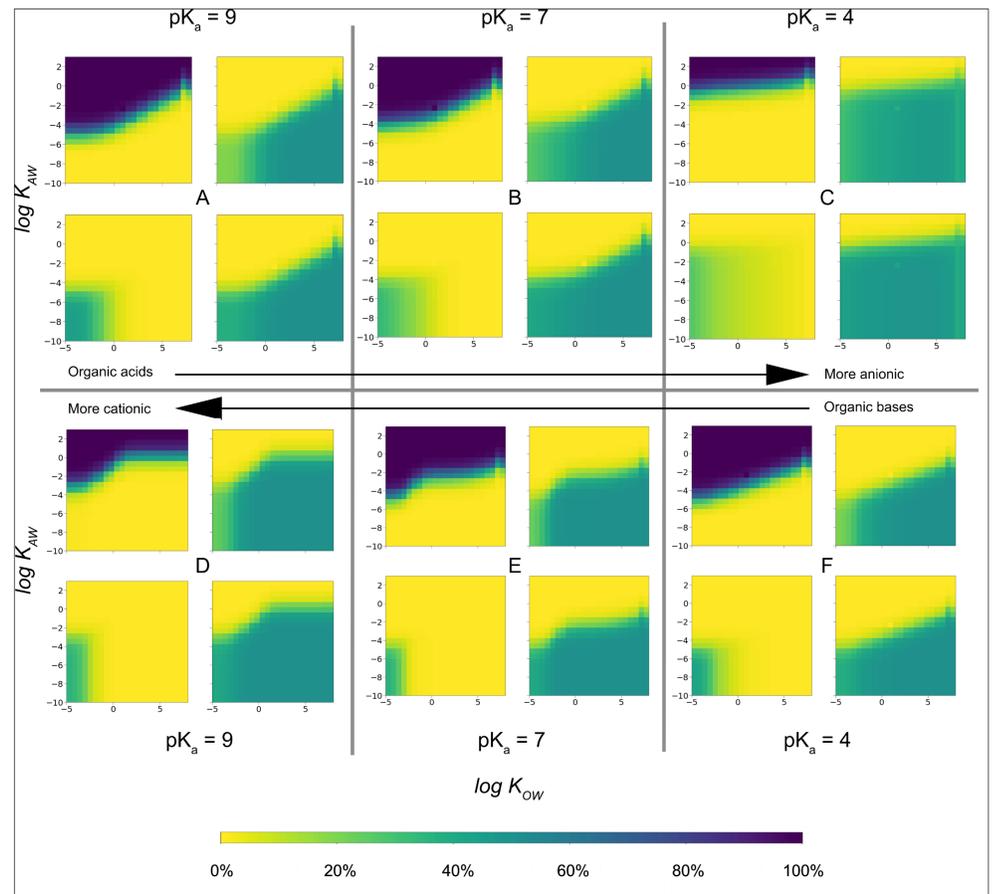


Figure 3: Illustrative summary of the mass distribution of ionisable organic chemicals with varying partitioning properties of $\log K_{ow}$ and $\log K_{aw}$ and pK_a for organic acids (Top panel) and organic bases (Bottom panel). For each of the four plots presented for each individual pK_a , the results presented summarize the mass distribution for air (top left), unsaturated soil (top right), surface water (bottom left) and saturated soil (bottom right).

FIGURE 3

- It is notable that the results of Figure 3A and 3F are consistent with those shown in Figure 2 for neutral organics. This is because >99% of organic acids and bases that might fall in the chemical space presented in Figures 3A and 3F, respectively, are in the neutral form, which is determined based on the difference between pK_a and the assumed pH of the environmental system.
- A small difference in the mass distribution of chemicals with $\log K_{ow}$ between -2 and 0, however, can be seen between the largely neutral organic acids and bases, with a slightly higher mass distribution predicted for the neutral organic bases in the unsaturated compartment than for the neutral organic acids. This difference in mass distribution is attributed to small differences in the K_{ow} -based regressions shown used for estimating K_{oc} between Figures 2 and 3 for the neutral species of the chemicals.
- As the ionised form of both organic acids and bases increases, differences in the mass distribution can be observed.
- Specifically, for the organic acids there is a pronounced increase in the mass distribution of chemicals in both the unsaturated and saturated zones with $\log K_{aw} < 0$, particularly for organic acids with $pK_a \leq 4$ (Fig. 3C), or when the anionic form of the chemical is >99% in the saturated zone.
- In the case of organic bases, a similar trend is observed (Fig. 3D). However, as the cationic form of the chemical is >99%, the predicted mass fraction in the unsaturated compartment is greater than in the saturated zone. This is attributed to a greater fraction of the charged species being sorbed to the solid phase fraction.
- Consequently, it can again be observed that differences regarding assumptions pertaining to the volume fractions of air, water and solids influence the distribution of chemicals, particularly between the unsaturated and saturated compartments of the model environment.

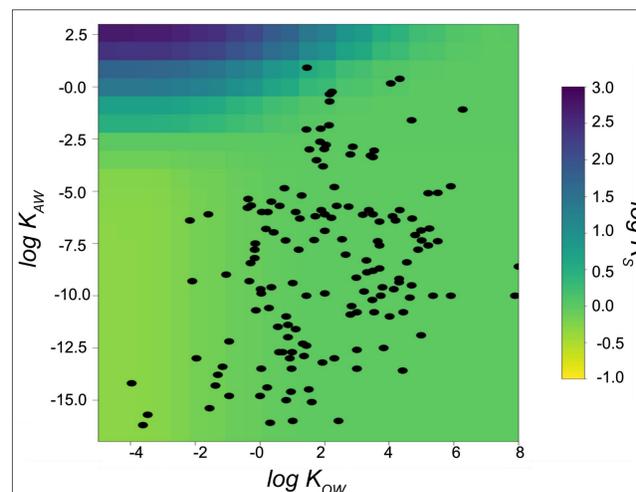


Figure 4: Summary of the ratio of bulk concentration in the unsaturated soil and saturated soil (R_s). Results are shown as a logarithmic scale. Where the $\log R_s$ is <1 the bulk concentration in the saturated soil is greater than the unsaturated soil (lower left corner).

FIGURE 4

- When considering the results from Figures 2 and 3 differences in the mass distribution between the unsaturated and saturated subsurface compartments can occur, relative to differences in the physicochemical properties of an organic chemical.
- This is an important observation, because it helps to evaluate whether the predicted pore water concentration in an agricultural soil represents a "worst case" proxy for the PEC for groundwater, i.e., a surrogate for (untreated) drinking water exposure for PMOCs, as used in the TGD.
- The worst-case scenario argument can be evaluated by simply deriving the ratio of the bulk concentration in the unsaturated compartment to that in the saturated zone.
- Where the ratio (R_s) derived is > 1 , the predicted bulk concentration in the unsaturated zone is greater than that in the saturated zone, which would support the steady-state worst case assumption.
- When $R_s < 1$ the bulk concentration in the saturated zone is higher than in the unsaturated zone, implying that the unsaturated soil porewater concentration (with a water volume fraction of 0.2), would be inconsistent with the steady-state worst case assumption.
- Figure 4 illustrates R_s for neutral organic chemicals over a range of physicochemical properties.
- Chemicals with a $\log K_{ow} < 0$ have bulk concentrations in the saturated zone that are greater than those in the unsaturated zone, particularly for chemicals with $\log K_{ow} < 0$.
- Consequently, for this region of chemical space, it may not be appropriate to assume that the steady-state unsaturated soil pore water concentration represents the worst-case exposure scenario.
- For illustrative purposes figure 4 includes 150/173 High-Priority Category A persistent, mobile and toxic (PMT) and very persistent and very mobile (vPvM) chemicals identified by Arp et al. (2023).

Conclusion

- The results presented here summarize output from Level 1 assumptions, which provide an initial opportunity to evaluate the sensitivity of the model parameterization using a chemical space approach, particularly with respect to chemicals that may be identified as PMOCs.
- This has shown that the key parameters influencing the mass distribution of chemicals in the Level 1 model environment relate to the volume fractions of air, water and solids in both the unsaturated and saturated zones.
- The observation applies to both neutral organics and to the ionised fraction of organic acids and bases, for which assumptions about partitioning behaviour of anions and cations represent an additional complicating factor.
- Future research should consider how differences in the physicochemical properties of organic chemicals influence their intermedia mass transfer and advective flows as well evaluating model performance against specific chemicals identified as PMOCs using site-specific examples.
- It is anticipated that the model presented here will represent a valuable tool, that can be used in combination with other exposure models to estimate the potential (i.e., based on a unit emission rate) or actual (i.e., based on the actual emission rate) drinking water exposure to PMOCs, especially within a tiered exposure assessment approach.

Acknowledgements

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