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Are airborne organic pollutants subject to a "forest filter effect"?

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Question 1

Our interpretation of the forest filter effect (FFE) is that the FFE includes two elements, (i) a reduced concentration in the air and (ii) an increased concentration in the vegetation-covered soil. For DDT as a test chemical in a five-compartment box model, we find both elements but they do not always occur in combination. The occurrence and magnitude of the concentration changes depend on a variety of environmental parameters, substance properties, and their interplay. There are also parameter combinations for which a slight increase of the atmospheric concentration is observed (shielding effect). Accordingly, vegetation can alter the mass balance of POPs-type chemicals significantly. Vegetation provides an additional sink and/or an additional, efficient pathway for mass transfer from the air to the ground. Generally, the influence of vegetation is more pronounced in regional models with large areas covered by vegetation than in global models.

As Wania and McLachlan (2001) point out in their modeling study on the FFE, degradation is an important factor influencing the FFE. Here, we focus on the effect of degradation in air and vegetation on the occurrence and extent of the FFE. We use a five-compartment model consisting of tropospheric air, surface ocean, vegetation, vegetation-covered soil, and bare soil to compare the steady-state results from this model (henceforth called "*VegeZoMo*") with results from a model without vegetation and the vegetation-covered soil included into the bare soil compartment (henceforth called "*NoVegeZoMo*"). All processes not affected by vegetation are identical in both models. 25% of the surface of the model system are covered by vegetation, 71% by seawater and 4% by bare soil (global averages). The vegetation is described by parameters for foliage–air partitioning, gaseous and particle deposition, leaf fall etc. as reported by Riederer (1990), Horstmann and McLachlan (1998). Values for grassland and deciduous and coniferous forests are combined in a global average.

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Question 2

We use the following DDT properties as the base case for model calculations with varying degradation rate constants in air and vegetation (variation of the degradation rate constants in soils or water does not influence the vegetation effect significantly): $k_s = 2.16 \cdot 10^{-4}$ d^{-1}, $k_w = 3.88 \cdot 10^{-3}$ d^{-1}, $k_a = 1.72 \cdot 10^{-1}$ d^{-1} (Howard et al., 1991), log $K_{AW} = -2.94$, log $K_{OW} = 5.98$ (Mackay et al., 1985). The base case of the degradation rate constant in vegetation, k_{veg}, is an average value of $1.72 \cdot 10^{-1}$ d^{-1} (Mackay et al. 1997; Garrison et al. 2000).

The influence of vegetation is expressed in terms of quotients of the steady-state concentrations in *VegeZoMo* divided by concentrations in *NoVegeZoMo*. In all calculations, DDT is released to the air.

First, k_{veg} is varied from $1.0 \cdot 10^{-4}$ d^{-1} to 1.0 d^{-1} with all other parameters as in the base case. Figure 1 shows the ratio of the concentrations in air in the two models. For $k_{veg} \leq 1.0 \cdot 10^{-3}$ d^{-1}, values slightly above one are obtained. This indicates a higher concentration in air in *VegeZoMo* compared to *NoVegeZoMo* and represents the shielding effect: the foliage shields the underlying vegetation-covered soil against deposition from the air. The very slow degradation in vegetation combined with the strong diffusive coupling between the canopy and air compartments leads to this effect. Degradation in the vegetation accounts for 0.2% of the total vegetation outflow, revolatilization into the air for 96.5%, and leaf fall for 3.3%. The slope of the concentration ratio is steepest in the range $1.0 \cdot 10^{-3} < k_{veg} < 1.0$ d^{-1}; increasing the degradation rate constant in vegetation over this range reduces the air concentration by 11%.

Figure 2 shows the variation of k_a from $1.72 \cdot 10^{-3}$ d^{-1} to $1.72 \cdot 10^{1}$ d^{-1}. The slower the degradation in air, the stronger the filter effect. The minimum air concentration quotient is 0.44. The concentration reduction in the air at low k_a is due to the efficient transfer into the foliage with subsequent removal by degradation in the foliage (and leaf fall): at $k_{veg} = 0.172$ d^{-1}, 78% of the mass in the foliage is removed by degradation and 1% by leaf fall; 21% of the total outflow from the foliage volatilizes back into the air.

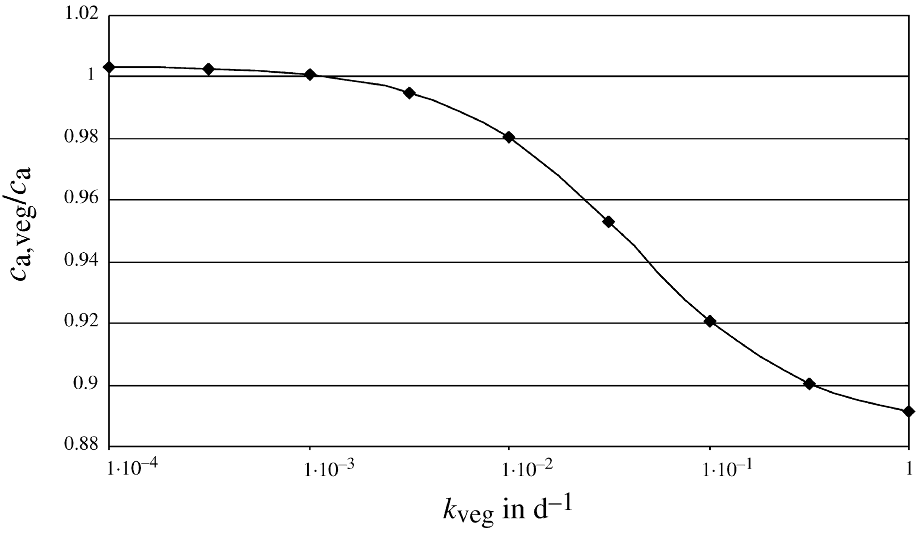

Fig. 1. Ratio of the concentrations in air in *VegeZoMo* and *NoVegeZoMo* vs. degradation rate constant in vegetation, k_{veg}. $k_a = 1.72 \cdot 10^{-1}$ d^{-1}

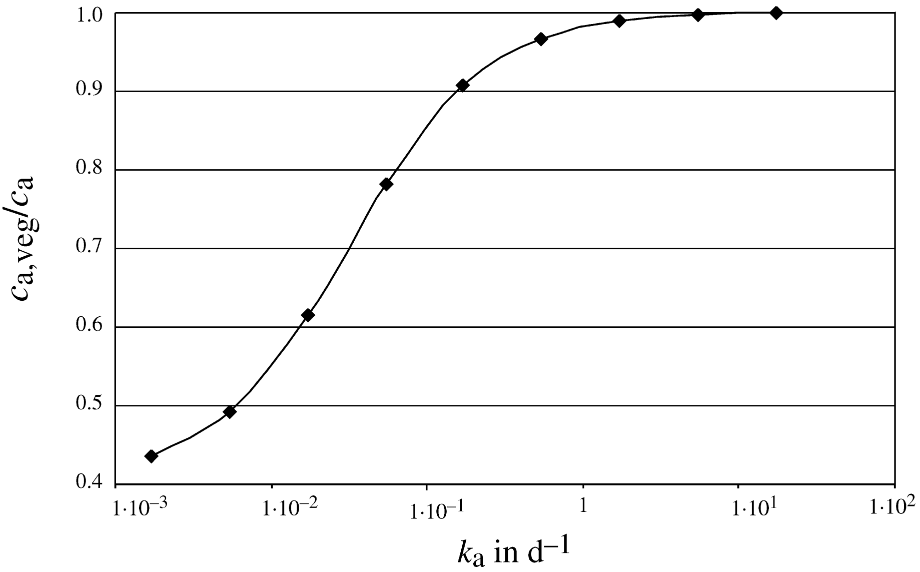

Fig. 2. Ratio of the concentrations in air in *VegeZoMo* and *NoVegeZoMo* vs. degradation rate constant in air, k_a. $k_{veg} = 1.72 \cdot 10^{-1}\ d^{-1}$

In the third step, the two degradation rate constants in air and vegetation are varied simultaneously between $1.72 \cdot 10^{-3}\ d^{-1}$ and $17.2\ d^{-1}$ (all other parameters as in the base case). Figure 3A shows that, with increasing degradation in air and vegetation, the concentrations' quotient first falls to a minimum of 0.82 at $k_a = k_{veg} = 1.72 \cdot 10^{-2}\ d^{-1}$ and then approaches one if the degradation rate constants are further increased. At high values of k_a and k_{veg}, degradation is the only relevant process in vegetation (leaf fall: 0.009% of total outflow; revolatilization: 0.27%; degradation: 99.7% at $k_{veg} = 17.2\ d^{-1}$). Since k_a equals k_{veg}, both vegetation and air are efficient sinks and the concentration ratio is one. The diffusive coupling between the air and the vegetation is ineffective because any substance transferred into the vegetation is degraded.

The minimum of the air concentration ratio can be explained by reducing the degradation rate constants in air and vegetation and analyzing the mass fluxes in the vegetation. If the two degradation rate constants are decreased (starting from the maximum value, $17.2\ d^{-1}$), two processes in air change: degradation becomes less important and, correspondingly, the transfer from air into foliage is enhanced. Although k_{veg} is lowered in parallel with k_a, the degradation mass flux within vegetation *increases* because transfer from the air into the canopy is increasing. At $k_{veg} = 1.72 \cdot 10^{-2}\ d^{-1}$, the degradation mass flux within the canopy is maximal and the minimal concentration ratio of 0.82 is observed. At even lower degradation rate constants, the degradation mass flux decreases and the revolatilization flux pushes substance back into the air (leaf fall accounts for a mass flux of only 3% of the revolatilization mass flux at all values of k_{veg} and k_a). At very low k_{veg}, the revolatilisation flux is the dominant pathway out of the canopy (97%), air and canopy are efficiently coupled by diffusive exchange, and the concentration ratio again approaches one (not shown in Fig. 3A).

Finally, the quotient of the vegetation-covered soil concentration divided by the bare soil concentration is plotted in Fig. 3B. The vegetation-covered soil has a higher concentration than the bare soil if degradation is slow because of the higher input by leaf fall. Leaf fall is responsible for 26% of the total inflow into the

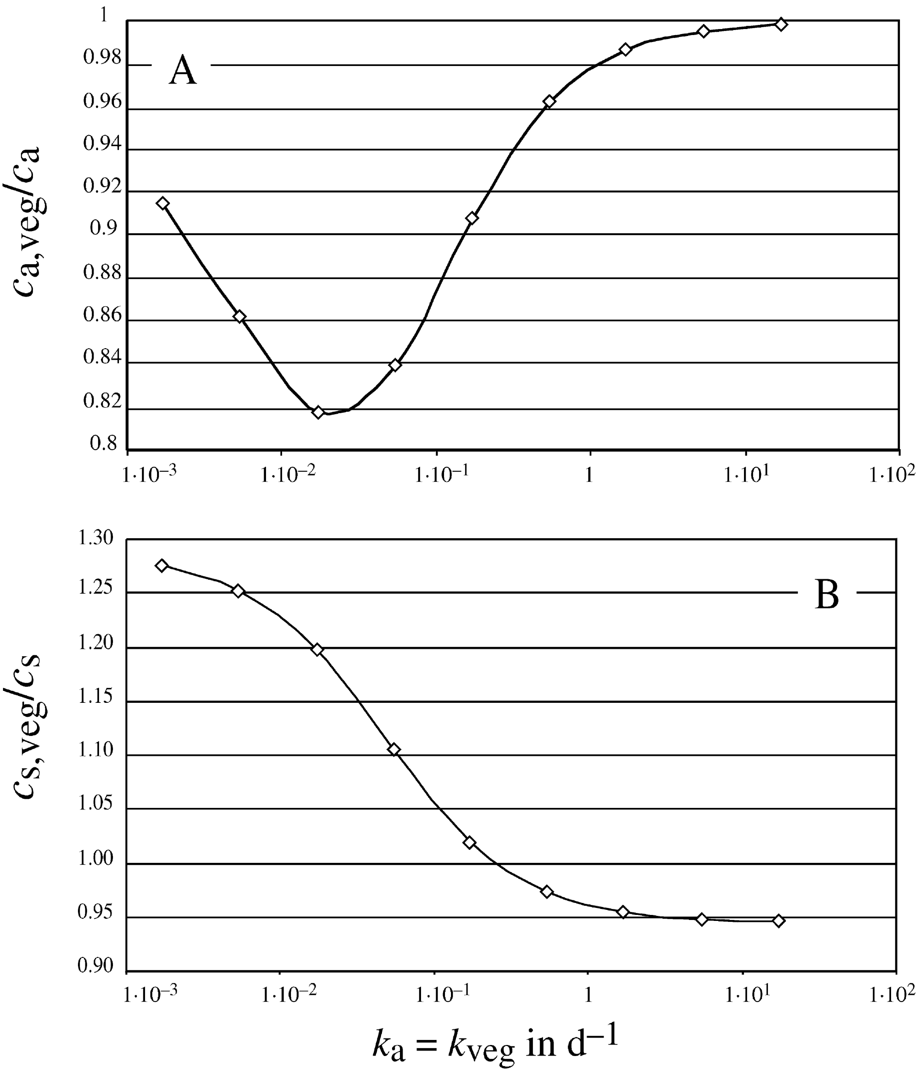

Fig. 3. **A** Ratio of the concentrations in air in *VegeZoMo* and *NoVegeZoMo* vs. degradation rate constants in vegetation and in air, $k_{veg} = k_a$. **B** Ratio of the concentrations in vegetation-covered soil in *VegeZoMo* and in bare soil in *NoVegeZoMo* vs. degradation rate constants in vegetation and in air, $k_{veg} = k_a$

vegetation-covered soil at $k_{veg} = 1.72 \cdot 10^{-3}$ d^{-1}, whereas it contributes only 0.1% of the total inflow at $k_{veg} = 17.2$ d^{-1}.

In conclusion, we generally find a filter effect in our model. However, the effect is not as pronounced as in regional models. Variation of the degradation rate constants k_a and k_{veg} shows the whole range from a shielding effect to a significant filter effect. Our results indicate a need for reliable degradation rate constants, especially in air and vegetation.

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