

## Is there a “forest filter effect” for organic pollutants?

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***Question 1:***

The short answer to question 1 is yes, but with qualifications. We interpret the word filter in “forest filter effect” to refer to an irreversible removal of a chemical from a specified environmental system due to the presence of vegetation. Although vegetation can accumulate or scavenge semi-volatile organic chemicals (SVOCs) from the environment (Buckley 1982), it remains unclear how or even if vegetation influences the ultimate fate of a chemical. Because published research related to the exchange of SVOCs between the atmosphere and forest ecosystems is limited (Brorstrom-Lunden and Lofgren 1998; Horstmann and McLachlan 1998), we focus our response mainly on theoretical and modeling aspects.

In regional multimedia models with a forest compartment, chemical partitioning into vegetation will affect the retention capacity of a given region, which in turn will influence the overall residence time of the pollutant. But is this a filter effect? Yes and no – Under transient conditions, any increase of retention capacity will remove or dampen the relatively high frequency (short residence time) components of the system response. Such an effect will influence concentrations in compartments having short residence times (i.e., the lower atmosphere) more than in compartments with longer residence times (i.e., soil). In this sense the vegetation would appear to be filtering chemical out of the atmosphere. However, under steady-state conditions, the presence of vegetation will not necessarily alter the mass-balance of organic chemicals unless there is also some form of chemical sink (i.e., degradation, metabolism, sequestration) associated with the vegetation.

Crosby et al. (1977) suggested that cuticle wax may enhance the degradation of some organic environmental pollutants and recent work supports this suggestion (McCrary and Maggard 1993; Schynowski and Schwack 1996; Schuler, Schmid et al. 1998). However, plant tissue may also

reduce a chemical's degradation rate constant relative to that in the atmosphere (Larson and Weber 1994, page 383). Although the potential importance of degradation in vegetation is recognized, little is known about actual reaction or degradation processes in the forest canopy for most chemicals. Thus, our response to question 1 is that if loss pathways are associated with the forest compartment then one would expect to see a filter effect but our experience indicates that the magnitude of this effect will be relatively small compared to uncertainties typically associated with regional fate models.

***Question 2:***

We base our response to question 1 on a modeling exercise designed to evaluate the importance of chemical transformation in vegetation using what we believe to be a representative regional mass-balance model. Given the lack of knowledge about reaction rates in vegetation, we set up a simple bounding exercise using the CalTOX version 4.0 model to evaluate the possible influence of reaction processes in vegetation. The characteristic travel distance (CTD) defined by Bennet *et al.* (1998) was used as a surrogate for evaluating changes in environmental fate. The CTD is a measure of the distance that a chemical will travel in the environment before its atmospheric concentration is reduced by 63% under *steady-state* conditions, so this simulation evaluates the impact of forests on the steady-state transport of pollutants. In the absence of data on reactions in vegetation, we use the first-order reaction rate constants for air ( $k_a$ ) as a proxy to pose the question: if reaction rate constants in vegetation ( $k_v$ ) were some multiple of  $k_a$ , how would that influence a chemical's CTD?

Figure 1 shows, for a set of SVOCs, the decrease in CTD with increasing  $k_v$  for values ranging from  $0.01k_a$  to  $100k_a$ . Increasing the  $k_v$  beyond  $\sim 100k_a$  does not result in further reduction of

CTD. This maximum filtering effect is reached because mass transfer at the plant-air interface or deposition to the vegetation ultimately becomes rate limiting in the model. Figure 2 illustrates the magnitude of the filter effect reported as maximum percent reduction in CTD (when  $k_v = 100k_a$ ) for a set of 307 organic chemicals. For most chemicals, even when the first-order reaction rate constant in vegetation is set to a hundred times that in air, the vegetation compartment has little influence on CTD. However, for chemicals in the log  $K_{oa}$  range of  $\sim 7$ - $11$ , reaction processes in or on vegetation can reduce the CTD. The magnitude of this effect is chemical dependant but we find that the reduction in CTD is typically less than a factor of three. Whether this influence will be important in the context of regulatory decision-making, given the large uncertainties that exist in environmental models and modeling inputs, remains to be determined. Nevertheless, this exercise shows that including reaction processes in the "forest" compartment can influence the regional mass-balance of organic chemicals but only for chemicals in a limited range of log  $K_{oa}$ , and only to the extent that mass transfer to the forest compartment is not rate limiting.

There are a number of other environmental processes related to the forest canopy that were not considered in the above discussion but might contribute to a forest filter effect. For example, from studies on ecosystem carbon fluxes we know that forests can influence mass transfer between the atmosphere and soil by increasing aerodynamic resistance through the canopy air. To evaluate this resistance, we applied the LSM1 model (Bonan 1996) which was developed to estimate energy, carbon, and water exchanges between ecosystems and the atmosphere. From a simple exercise comparing a forest canopy to a grassland canopy, we estimate that overall daytime canopy resistance can be 3-5 times greater in the forest than in the grassland. This relatively larger resistance might enhance the ability of the forest to trap chemicals that are transferred through the canopy to the forest floor by precipitation, litterfall, or cuticle erosion.

Further, current state-of-the-art models of contaminant exchange with ecosystems are unable to simulate the impact of diurnal variations in soil and canopy temperatures, moisture, and resistances. Nighttime aerodynamic resistances between the atmosphere and canopy air and between the canopy air and ground surface can be ten times greater than midday values. In addition, nighttime conditions can influence reaction rates and partitioning characteristics of chemicals in the canopy or forest soil. The net effect of this diurnal variation is difficult to discern, but we hypothesize that it will enhance the forest's ability to remove contaminants from the atmosphere.

Given the limitations and uncertainties associated with existing models, understanding the importance of the forest filter effect will ultimately require the combined and iterative use of careful field observations, laboratory experiments, and models.

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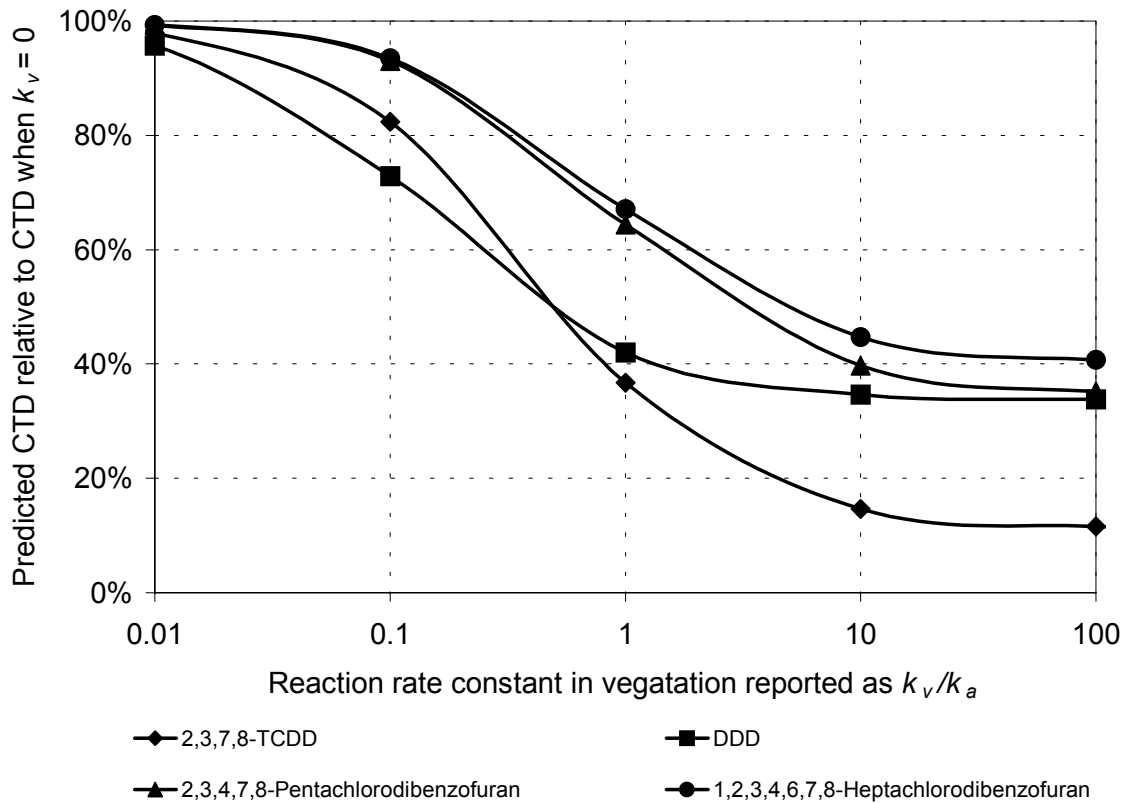


Figure 1: Characteristic travel distance (CTD) plotted as a function of reaction rate constants in vegetation. The travel distance is expressed as a percent of the maximum CTD for the chemical as estimated when  $k_v = 0$ . The ordinate axis is given as the ratio of the reaction rate constant in vegetation relative to that in air. For example, a value of 1 on the x-axis indicates that the rate constants in air and vegetation are equal.



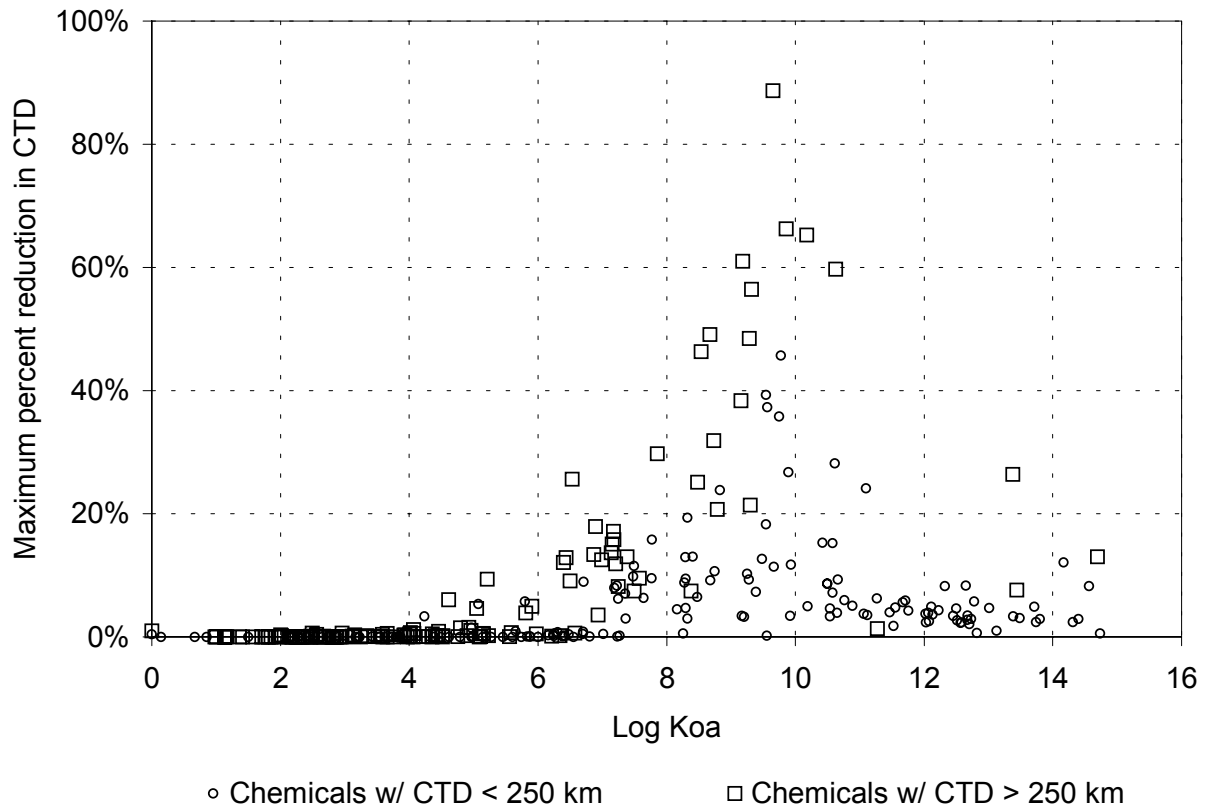


Figure 2: Maximum percent reduction in CTD due to chemical reaction in vegetation plotted as a function of the octanol air partition coefficient ( $K_{oa}$ ). Chemicals with CTD greater than 250 km are plotted as squares.