Simulating the Effects of Intermittent Rain in a Dynamic Environmental Fate and Transport Model

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Introduction

Multimedia environmental fate and transport models combine a series of mass-balance equations to simulate the partitioning and transfer of chemicals among various homogenous environmental compartments such as water, soil, and the atmosphere. Among the uses of such models is the assessment of a chemical's environmental persistence and long-range transport potential. Many models are steady state, and most assume that precipitation occurs as continuous light drizzle. It is increasingly recognized that these models fail to appropriately describe the atmospheric fate of organic chemicals that are efficiently scavenged by precipitation[1]. In particular, they may greatly underestimate the atmospheric residence time, and thus the long-range transport potential[2], of chemicals with a low air-water partition coefficient and chemicals that sorb strongly to atmospheric particles.

We have modified a dynamic environmental fate model of regional scale to allow for the occurrence of randomized intermittent precipitation. The average length, frequency, and intensity of precipitation events can be specified by temporally variable parameters, providing the possibility to define complex and more realistic precipitation regimes. Evaluative simulations for three chemicals (α-HCH, pentachlorophenol, and PBDE-209) are performed to quantify the effect of various intermittent precipitation scenarios on chemical fate. We further quantify the agreement between linearly time-weighted averages of concentrations obtained with scenarios of constant-rain and no-rain and the mean of concentrations obtained in intermittent rain scenarios, and how this agreement depends on both precipitation characteristics and chemical properties.

Method

The model used for this work is CoZMo-POP, a fugacity-based Level IV model describing a coastal region[3]. Whereas the model previously used a constant yearly precipitation rate defined by the user, it was changed to apply user-defined parameters describing the average rain event duration (TinHrain, defined in hours), frequency (U3fr, a number between 0 and 1), and precipitation rate (U3, in m/h) during an event. In CoZMo-POP these parameters can also be defined individually for every month of the year, allowing seasonal variations in the type and amount of rainfall.

In the CoZMo-POP simulations, temporal variations of other environmental parameters were temporarily removed to focus on the temporal variability in chemical fate caused by the precipitation scenarios. In particular, the forest coverage of the drainage basin was set to 0%, to remove seasonally variable chemical uptake by foliage. All other environmental model parameters with temporal variations, from temperature to OH radical concentration, were set to remain constant throughout the year.

The atmospheric fate of three sample chemicals was investigated with the modified CoZMo-POP model: α-HCH, a volatile and relatively water soluble chemical; pentachlorophenol (PCP), which has a similar volatility as α–HCH, but is slightly more water soluble; and PBDE-209, a very involatile chemical that is mostly associated with atmospheric particles. α–HCH and PCP are so volatile that they tend to be in the atmospheric gas phase. At 25 °C, the logarithm of the air-water equilibrium partition coefficients for α–HCH, PCP, and BDE-209 are -3.5, -4.9 and -5.1, respectively, and thus fall in the range where precipitation scavenging starts to become an important fate process[4,5].

Results and Discussion

When simulating intermittent rain with CoZMo-POP, the air concentrations of PCP and BDE-209 show similar behaviour, dropping rapidly during rain events and rising again during intermittent dry periods (Fig. 1). α-HCH air

concentrations are much more stable and are not obviously influenced by the intermittent rain events. More comprehensive calculations involving variations of both rain frequency and duration show that the air concentrations of all three chemicals are reduced either by increasing the fraction of time it rains, or by increasing the length of the rain event (Fig. 2). Maximum air concentrations occur in situations with no rainfall, and lowest concentrations when heavy rainfall is simulated.

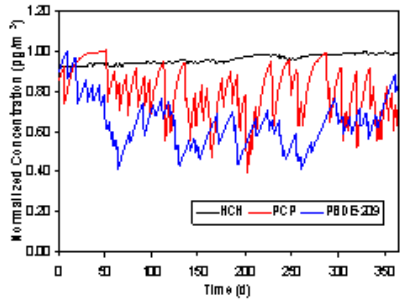
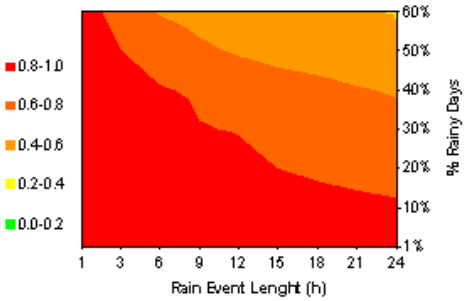
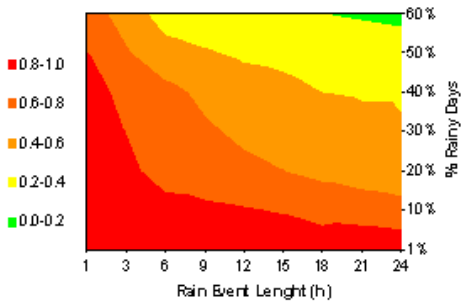


Figure 1: Typical air concentration variability of the three sample chemicals during a one year period simulated with CoZMo-POP in a situation with 10% rain, 6 h rain events, and 0.001 m/h precipitation rate.

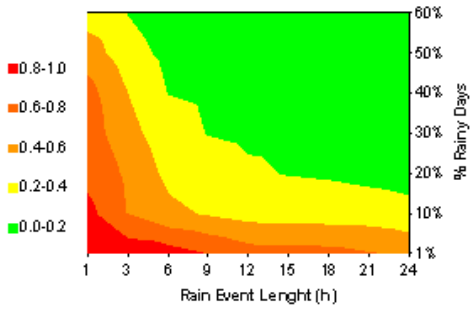
α-HCH shows the least decline in air concentrations, which do not fall below 40% of the maximum value even with heavy simulated rainfall (Figure 2a). PCP shows a more rapid decline in air concentrations, where the normalized values are approaching zero under heavy simulated rainfall (Figure 2b). BDE-209 (Figure 2c) shows the most dramatic decline in air concentration under high rain conditions. The normalized concentrations approach zero with any simulated precipitation above 20%. BDE-209 is so involatile that it is essentially completely particle-bound in the atmosphere. Since particles are efficiently removed from the atmosphere by rain, BDE-209 air concentrations quickly fall with increased rain – whether from longer rain events or higher event frequency. The air concentrations of PCP demonstrate a similar sensitivity to precipitation (Figure 2c). In contrast to PBDE-209, PCP is removed from the air by gas scavenging[4], but the occurrence of precipitation still quickly reduces the PCP air concentration. The air concentration of α-HCH shows a much lower sensitivity to precipitation than either of the other chemicals. Because α–HCH air concentrations still decrease with higher amounts of precipitation (Figure 2a), we can conclude that while PCP is scavenged efficiently from the atmosphere even by short rain events, α–HCH air concentrations are affected by the long-term average amount of rain.



a)α-
HCH



b) PCP



c) BDE-209

Figure 2: Normalized average annual air concentrations of a) α–HCH; b) PCP; c) BDE-209 calculated with CoZMo-POP with intermittent rain parameters. The air concentrations are plotted on the Z-axis of surface maps, i.e. the Z-axis is perpendicular to the page. Above 50% rain, the chemicals' concentrations approach minimums (near zero for α–HCH and PBDE-209).

Hertwich[1] suggested that the time-weighted average of the air concentrations calculated under constant-rain ($C_{air\ (CR)}$) and no-rain ($C_{air(NR)}$) conditions may serve as a simple estimate of a chemical's air concentrations under intermittent rain conditions. Values for $C_{air(CR)}$ and $C_{air(NR)}$ were obtained from CoZMo-POP by simulating air concentrations with 100% and 0% rain, respectively. By linearly extrapolating between these values we obtain a regression where the estimated air concentration is dependent on the fraction of time it rains. (Fig. 3). We can then compare the concentrations obtained for each sample chemical to the concentrations simulated for that chemical by CoZMo-POP with intermittent rain across the range of rain frequency and duration. Such a comparison for BDE-209 is shown in Figure 4.

For both α–HCH and PCP, the air concentrations simulated with intermittent rain in CoZMo-POP are very similar to those calculated by the linear regression shown in Figure 3, differing only by a maximum factor of two. In contrast, the BDE-209 air concentrations are greatly overestimated by the linear regression, even when using mild precipitation simulations, as is shown in Figure 4. As both rain event length and % of rainy days increase, the linear regression becomes less and less accurate at approximating the simulated air concentrations. At 20% rainy days and 12 hour rain events, a relatively common rain scenario, the time-weighted average method underestimates BDE-209 air concentrations by a factor of 2, and this error increases to a factor of 5 at the limits of our simulations.

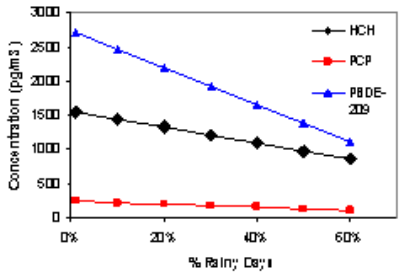


Figure 3: Linear time-weighted average air concentrations modeled under constant-rain and no-rain conditions.

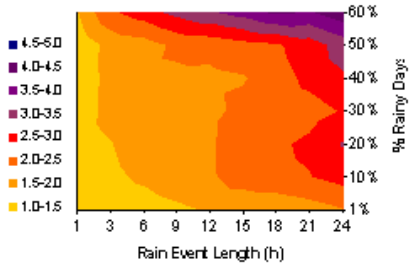


Figure 4: Ratio of time-weighted BDE-209 air concentrations to the concentrations simulated with variable rain parameters in Cozmo-POP.

Conclusion

By using a time-weighted average of chemical air concentrations based on the concentrations in no-rain and constant-rain situations, we can approximately estimate the air concentrations of α–HCH and PCP simulated by a Level IV model with randomized intermittent rain. However, the same approximation underestimates the amount of BDE-209 removed from the atmosphere by rain under heavy rain conditions. The air concentrations of particle-bound substances such as BDE-209 are most sensitive to changes in the types of rain events modeled, as they are efficiently scavenged from the atmosphere by rain. Gaseous compounds such as PCP are also efficiently scavenged by rain, although not to the same degree as particle-bound substances.

Simulations with intermittent rain suggest that for less volatile chemicals bound to particles, and semi-volatile chemicals in the gas phase, LRT is dependent on the movement of dry air, and is decreased by the occurrence of rain events. α–HCH shows a large variation in air concentration based on different types of rain, but is sensitive mainly to the long-term average amount of rain simulated, meaning that for volatile, water soluble chemicals, LRT is mainly affected by the overall amount of rain occurring in the environment.

References

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