Does rain smell?

Have you ever made the following observation? At the beginning of a rainfall event following an extended period of dry weather, there is a characteristic 'earthy/muddy' smell in the air. This phenomenon occurs both in urban as well as rural areas. In forests, this 'earthy' smell is caused by terpenes, a certain class of tree-derived natural organic molecules. So, the question is: Why would we smell more of these terpenes at the beginning of a rainfall event and not before or after? In the TV broadcast 'Kopfball' (http://www.kopfball.de) the following explanation was given:

"Terpenes that are emitted from trees can move to higher altitudes in the air. When it rains, these terpenes are washed out in the higher atmosphere layers and transported back to atmospheric layers close to the surface. This leads to an increase in the concentrations of terpenes near the ground, which is picked up by our nose".

This explanation violates some of the fundamental rules of partitioning thermodynamics and therefore must be incorrect. What is incorrect in this line of argument? Neglect potential temperature effects.

Help: Assume that there is partition equilibrium of the terpenes between air and rain water in the higher atmospheric layers (this is the 'best' case with regard to raining out of the terpenes). Now, imagine that the terpene-loaded water is brought in contact with a certain volume of fresh air near the ground. Let the system re-equilibrate. Clearly, the highest concentration of terpenes in air that can develop is the respective equilibrium concentration in air. How high can this concentration be compared to the concentration in air in the higher altitude where the rain took up the terpenes?

Answer: Under dry weather conditions, all kinds of organic molecules that smell (i.e., semi-volatile organic compounds) adsorb to some extent to mineral surfaces in soils. Water molecules typically have a much higher affinity to these surfaces than the organic compounds. As a consequence, when it starts to rain, the organic compounds are displaced from these surfaces by water. The terpene molecules that got displaced re-partition between all other phases, including the rain water and the air. Our nose picks up this increase in the concentration of terpenes in the air. Such a competition effect of various molecules for the same sites on a surface (or in a phase) can make an equilibrium partition situation quite difficult to understand. Fortunately this does not occur in too many situations that are relevant for environmental chemistry. More detailed information on the effect of humidity on the adsorption

to mineral surfaces can be found in the script (Chapter V.3.2).

Question: Why does the smell disappear in extended rain events?

Answer: Because over time, almost all terpene molecules partition to the rain water and the concentration in the air decreases.