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What controls the diurnal variations of deuterium excess in atmospheric vapor?

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Diurnal variations of the isotopic composition of atmospheric vapor have been observed in many studies, especially for deuterium excess (d-excess), which sometimes displays diurnal amplitudes higher than day-to-day variations. It reflects the varying contributions of different vapor sources in the atmosphere, associated with the daily water and mass balance of the planetary boundary layer, which is driven by: i) entrainment of free atmosphere; ii) local evapotranspiration and iii) regional advection. These atmospheric processes have different spatial significances, but influence d-excess in the same direction. It thus is important to identify the main drivers of diurnal variations for interpreting the isotopic signal with respect to its relevant spatiotemporal scales. We propose an analysis of the daily cyclicity of δ18O and δD and d-excess in the atmospheric vapor of a Mediterranean coastal wetland during summer (Camargue, Rhône River delta, France). The mean composition of atmospheric vapor during the experiment is δ18O=-14.66‰ δD=-95.4‰ and d-excess = 21.9‰Ẇe show a clear separation of isotopic characteristics with respect to the air mass back trajectories, with the Northern air masses providing depleted compositions (δ18O=-15.83‰ δD=-103.5‰ compared to Mediterranean air masses (δ18O=-13.13‰ δD=-86.5‰. There is also a clear separation between d-excess corresponding to these different air mass origins, but not in the same direction as was previously evidenced from regional rainfall data, with higher values found for Northern air masses (23.2‰ than for Mediterranean air masses (18.6‰. Based on twenty-four average hourly data, we propose a depiction of the diurnal evolution of water vapor isotopic composition for the different climatic situations. We show that the increase in d-excess during daytime is due to a dominant control of evaporation, with more pronounced cycles for Mediterranean than for North Atlantic air mass origin, despite lower evaporation rates. We estimate the composition of the local vapor source that produces the day-time increase in d-excess, for the different air mass origins, and calculate the corresponding atmospheric water and isotopic mass balances. We compare our results with other case studies, with different amplitudes of diurnal variations, and where the entrainment of free atmosphere into the boundary layer was evidenced as the dominant driver of d-excess diurnal variations.