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Physicochemical uptake and release of volatile organic compounds by soil in coated-wall flow tube experiments with ambient air

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Volatile organic compounds (VOCs) play a key role in atmospheric chemistry, because of their important impact on the atmospheric oxidation capacity and contribution to the formation of secondary organic aerosols (SOAs). Emission and deposition on soil have been suggested as important sources and sinks of atmospheric trace gases. The exchange characteristics and heterogeneous chemistry of VOCs on soil, however, are not well understood. In this work, we used a newly designed differential coated-wall flow tube system to investigate the long-term variability of bidirectional air-soil exchange of 13 VOCs at ambient air conditions of an urban background site in Beijing. Sterilized soil allowed us to investigate physicochemical processes and heterogeneous/multiphase reactions independently from biological activity. Most VOCs revealed net deposition with average uptake coefficients (γ) in the range of 10-7 – 10-6 (referring to the geometric soil surface area), corresponding to deposition velocities (Vd) of 0.0013 - 0.01 cm s-1 and soil surface resistances (Rc) of 98 - 745 s cm-1, respectively. Formic acid, however, was emitted at a long-term average rate of $\sim 6 \times 10$ -3 nmol m-2 s-1, suggesting that it was formed and released upon heterogeneous oxidation of other VOCs. The soil-atmosphere exchange of one individual VOC species can be affected by both its surface degradation/depletion caused by surface reactions and by competitive uptake or heterogeneous formation/accommodation of other VOC species. Overall, the results show that physicochemical processing and heterogeneous oxidation on soil and soil-derived dust can act as a sink or as a source of atmospheric VOCs, depending on molecular properties and environmental conditions.