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Reactions of ozone at simulated plant surfaces

J.N. Cape (1), R. Hamilton (1,2), M.R. Heal (2)

(1) Centre for Ecology & Hydrology, Penicuik, UK, (2) School of Chemistry, University of Edinburgh, UK (jnc@ceh.ac.uk / Fax: +44 131 445 3943)

Field measurements of the dry deposition of ozone to natural vegetation, crops and forests have shown that the non-stomatal flux (i.e. the deposition of ozone to external plant surfaces, soil, or reaction within the plant canopy) can account for over 50% of the total measured flux. The fate of the deposited ozone is not known, although the temperature dependence has been described in terms of an activation energy of around 40 kJ mol^{-1} . In order to investigate the reactions of ozone at surfaces a stainless steel reaction chamber (0.25 m^3) was used inside a controlled environment cabinet over a range of temperatures and humidities, supplied with ozone at around 180 ppby, and operated as a CSTR. The difference between inlet and outlet concentrations, measured using a UV photometric ozone analyzer, was used to infer reaction rates within the chamber. Deposition to the empty chamber at steady state was slow, equivalent to a deposition velocity of around 10^{-6} m s⁻¹, but showed a temperature dependence similar to that observed in the field. Different surfaces were introduced into the chamber, as surrogates for plant leaves. Deposition to aluminium foil coated with paraffin wax (to simulate the plant cuticle) was faster than to steel, but deposition to beeswax, which contains unsaturated hydrocarbons, was much more rapid, indicating reaction of ozone with the surface wax. The possible interaction of ozone at the surface with biogenic VOCs emitted from plants was studied for α -pinene; losses of ozone in the presence of known inlet concentrations of the VOC implied reaction rates slightly faster than those quoted in the literature for purely gas-phase reactions, either because of heterogeneous wall reactions or secondary reactions of ozone with the initial oxidation products. Inclusion of wax surfaces, pre-equilibrated with the VOC, led to no significant increase in reaction rates, suggesting that dissolution and concentration of biogenic VOCs in plant surface waxes is not a major pathway for subsequent reaction with ozone.