Reactions of ozone at simulated plant surfaces

J Neil Cape[1], Richard Hamilton[1,2], Mathew R Heal[2]

[1]*Centre for Ecology & Hydrology, Bush Estate, Penicuik EH26 0QB, UK*
[2]*School of Chemistry, University of Edinburgh, West Mains Rd, Edinburgh EH9 3JJ, UK*
E-mail: jnc@ceh.ac.uk

BACKGROUND

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 annual measured flux, and up to 80% in winter. The fate of the deposited ozone is not known. Reaction is possible at the leaf or soil surface, with organic or inorganic reactants, or may involve (catalysed) decomposition. Some of the losses measured in the field as 'deposition' may involve gas-phase reactions inside the plant canopy. This poster describes experiments designed to study the reaction (loss) of ozone on simulated plant surfaces in the laboratory, in an attempt to understand the processes involved. The main hypothesis to be tested was that reaction with biogenic hydrocarbons (e.g. isoprene, terpenes), in addition to reactions in the gas phase, may also occur at leaf surfaces, where such molecules are likely to accumulate in the surface waxes. If this type of reaction occurs, it could help to explain why the rate of removal of ozone by vegetation is relatively rapid, even when stomata are closed.

Experimental design

- Stainless steel reaction vessel, 0.25 m^3
- Ozone generated by electrical discharge in pure O_2
- Dynamic operation, with flow through at ca. 20 litre min^{-1}
- Internal fan to ensure mixing
- Ozone measured by UV absorption (O_3 analyzer)
- Housed within controlled environment cabinet
- All measurements made in darkness
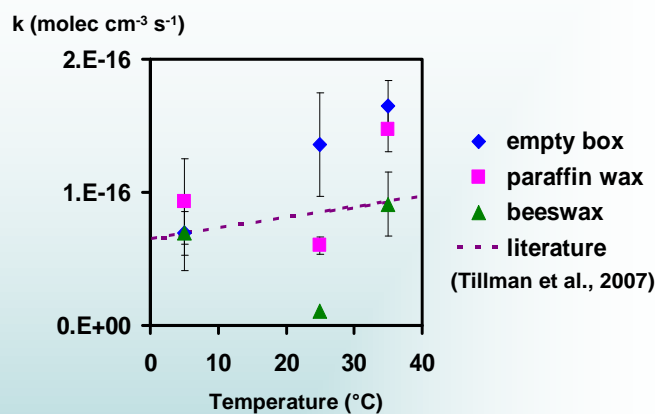- Reactive VOCs generated using a diffusion source

RESULTS: Reactions of ozone with simulated leaf surfaces: 'inert' surfaces

Reaction of ozone with the empty box (stainless steel) increased as temperature increased, i.e. the surface resistance decreased with increasing temperature. From this relationship the activation energy (Ea/R) for ozone reaction is calculated to be 40 kJ mol^{-1} (Figure 1). Leaf surfaces of higher plants are covered with waxes which are relatively inert to chemical reaction with ozone, being mostly long-chain aliphatic hydrocarbons, alcohols and esters. These were simulated by spraying a solution of paraffin wax onto an Al foil which was placed in the reaction chamber. Resistances were significantly lower than for stainless steel (i.e. faster reaction rate), but similar to aluminium foil (Figure 1). The temperature dependence was similar, but with smaller Ea/R. The greater reaction rate may reflect a larger surface area at the molecular scale. A beeswax surface, which contains ozone-reactive components, showed even smaller surface resistances, but still 30 times greater than vegetation surfaces in the field. Although the temperature dependence is similar for all the surfaces, the absolute surface resistances are 3000 times greater for stainless steel than for field vegetation. There must be more to ozone reaction at vegetation surfaces than a simple heterogeneous decomposition.
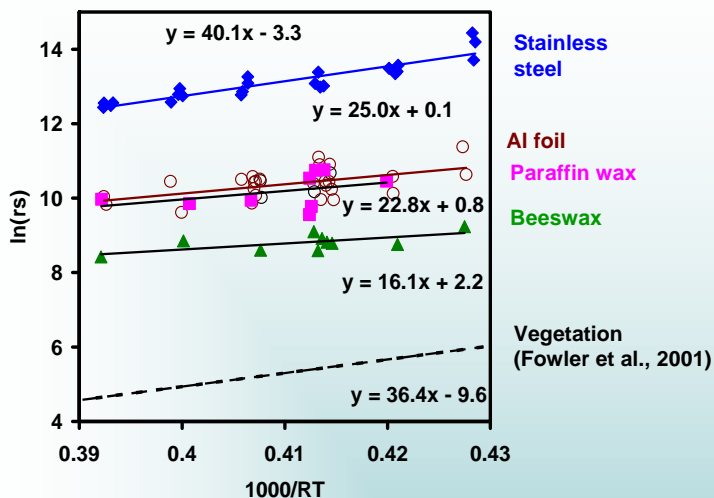
Figure 1: variation of reactivity of different surfaces with temperature between 10°C and 35°C, expressed as change in $\log_e$(surface resistance). The fitted slope is equivalent to an Arrhenius activation energy (kJ mole^{-1}).

Figure 1 content:
- $y = 40.1x - 3.3$ — Stainless steel
- $y = 25.0x + 0.1$ — Al foil, Paraffin wax
- $y = 22.8x + 0.8$ — Beeswax
- $y = 16.1x + 2.2$
- $y = 36.4x - 9.6$ — Vegetation (Fowler et al., 2001)
- Y-axis: $\ln(r_s)$
- X-axis: 1000/RT

Figure 2: calculated second-order rate coefficient for reaction of ozone with α-pinene between 5 and 35 °C.

Figure 2 content:
- Y-axis: k (molec cm^{-3} s^{-1})
- X-axis: Temperature (°C)
- Legend: empty box; paraffin wax; beeswax; literature (Tillman et al., 2007)

RESULTS: Adding a reactive hydrocarbon (α-pinene)

Reactive hydrocarbons such as α-pinene are emitted by plants. In addition to reaction in the gas phase, it is possible that reaction of VOCs with ozone at the leaf surface (where VOC concentrations may be high because of adsorption) is an important pathway for ozone deposition. Reaction of α-pinene with ozone in the empty steel box gave results consistent with the published reaction rate (Figure 2). Reaction rates in the presence of a wax-coated foil were no greater than in the empty box, showing that there was no enhanced reaction of ozone with α-pinene at the wax surface. If anything, the reactive loss of ozone in the presence of wax surfaces was less than in the empty box, suggesting removal of α-pinene from the gas phase into the wax layer, leading to a smaller gas-phase concentration, and a smaller apparent gas-phase reaction rate than that based on the inlet concentration of α-pinene.

CONCLUSIONS – the bottom line

- **The reaction of ozone with 'inert' surfaces increases with temperature, and depends on surface structure and chemistry, but is much slower than apparent reaction rates of ozone with vegetation in the field.**

- **Reaction rates of ozone with α-pinene are not enhanced by the presence of a wax surface in which the VOC can dissolve.**

- **Some other explanation for the (relatively) rapid loss of ozone to plant surfaces must be found.**

The fine print – if you're interested in the details

Deposition to the internal surfaces of the box is expressed in terms of the surface resistance (r_s), derived from the measured ozone flux, the outlet ozone concentration (reflecting the concentration in the well-mixed box) and the transfer resistance measured using a 'perfect' sink for ozone – paper soaked in acidified KI solution.
The measured transfer resistance (r_{tr}) was 210±20 sm^{-1}.

Surface resistance r_s = concentration($g\,m^{-3}$) / flux($g\,m^{-2}s^{-1}$) – r_{tr}

The surface resistance decreased with increasing temperature, but was much greater (>10^5 sm^{-1}) than for typical field conditions (300 sm^{-1}). An effective Arrhenius activation energy can be calculated from the variation of $\log_e(r_s)$ with 1/RT; this value was in the range 15-40 kJ mol^{-1} for all the surfaces studied (Figure 1), even though the absolute 'reaction rates' varied greatly. There was no consistent dependence on humidity (relative or absolute).

Ozone concentrations used for all experiments were around 180 ppbV; α-pinene concentrations (from a diffusion source) were 15-60 ppbV.

Surface resistance at 25°C (s m^{-1})	stainless steel 4.0×10^5	Al foil 2.7×10^4
	paraffin wax 2.1×10^4	beeswax 5.8×10^3
cf. moorland vegetation with closed stomata 2-3 $\times 10^2$ s m^{-1}		

REFERENCES:
Fowler, D., Flechard, C., Cape, J.N., Storeton-West, R.L., Coyle, M., 2001. Measurements of ozone deposition to vegetation quantifying the flux, the stomatal and non-stomatal components. Water Air and Soil Pollution 130 (1-4), 63-74.
Tillmann, R., Mentel, T.F., Kiendler-Scharr, A., Brauers, T., Saathof, H., 2007. Temperature dependent rate coefficients of the a-pinene + ozone reaction. Geophysical Research Abstracts 9, 09179.