Interactions of forests with secondary air pollutants – some challenges for future research.

J N Cape

Centre for Ecology & Hydrology, Bush Estate, Penicuik, Midlothian, EH26 0QB, UK

E-mail: jnc@ceh.ac.uk
Telephone (+44) 131 445 8533
Fax (+44) 131 445 3943

Abstract

The effects of ozone and other photochemical oxidants on individual trees have been studied for several decades, but there has been much less research on the potential effects on entire forest ecosystems. Given that ozone and other oxidants affect the production and subsequent fate of biogenic volatile organic compounds that act as signalling molecules, there is a need for more detailed study of the role of oxidants in modifying trophic interactions in forests. Deposition of fine particulates to forests may act as a source of nutrients, but also changes leaf surface properties, increasing the duration of surface wetness and modifying the habitat for epiphytic organisms, leading to increased risks from pathogens. Even where this pathway contributes a relatively small input of nutrients to forests, the indirect effects on canopy processes and subsequent deposition to the forest floor in throughfall and litter may play a more important role that has yet to be fully investigated.

Keywords

Ozone, biogenic VOCs, molecular signalling, surface wetness, aerosol deposition

Capsule

Secondary air pollutants may have indirect effects on forest ecology that have not yet been fully explored.

Introduction

Air pollution effects on forests have been documented as both local and regional problems since the early years of the 20th century, and were initially attributed to the obvious effects of soot (Rhine, 1924) and gases such as sulphur dioxide (Härtel, 1953). These were perceived as direct damage to foliage following deposition from the atmosphere. More recently, the debate on 'acid rain' in the 1970s and 1980s, particularly in Europe, led to hypotheses that attributed damage to trees through the acidification of forest soils, rather than a direct effect on foliage (Schulze et al., 1989). Responses to airborne pollutants were often interpreted in terms of nutrient imbalances caused by leaching of one or more essential metals (e.g. calcium, magnesium) from the rooting zones of forest soils. Nutrient imbalances are exacerbated by increased deposition of nitrogen, although its influence has also been implicated in an observed increase in stem growth and timber yield (Spiecker, 1999). The effects of photo-oxidants on trees, with ozone and PAN (peroxyacetyl nitrate) as particular gaseous pollutants, were recognised in the 1960s with the seminal studies in southern California and later throughout the USA (Karnosky et al., 2007a, Miller and McBride, 1999). Observed symptoms were largely ascribed to direct damage relating to foliar uptake by the tree canopy.

Although air pollution in much of Europe and North America is now less severe than in the 1980s (Cape et al., 2003, Lehmann et al., 2005), as a result of legislation to reduce emissions of sulphur dioxide (SO_2) and the ozone precursors, nitrogen oxides

(NOx) and volatile organic compounds (VOCs), the threat to forests from air pollution caused by the rapid industrialisation of other parts of the world (e.g. China, India) is a regional issue that translates the problems of last century in Europe and North America to different tree species and different climatic regimes in this century (Emberson et al., 2001). However, even in the areas where emissions of the primary pollutants (SO_2, NOx, VOCs) have been controlled by legislation and changing fuel types, the threat from secondary air pollutants has not been removed. 'Acid rain' and ozone are the most studied secondary pollutants, as far as forest effects are concerned, and while amounts of wet-deposited acidity (and sulphate and nitrate) have decreased, there are still large areas of Europe and North America that exceed the Critical Loads for forests (Hettelingh et al., 1995). Moreover, the increasing industrialisation of India, China and south-east Asia is leading to a gradual increase in the 'background' concentrations of ozone across the northern hemisphere, with several studies demonstrating that long-range (intercontinental) transport of ozone and/or its precursors is affecting annual average ozone concentrations across the whole hemisphere (Auvray and Bey, 2005, Derwent et al., 2006, Jaffe et al., 2003, Jonson et al., 2006, Oltmans et al., 2006, Vingarzan, 2004). This gradual increase in 'background' ozone is set against a pattern of decreasing severity of peak ozone concentrations during episodes, which can be attributed to the effects of emission controls, particularly on VOCs (Derwent et al., 2003). The predicted increase in 'background' ozone concentrations may be offset to some extent by climatic changes that are forecast to occur over similar time scales (decades). In particular, increased temperatures will lead to higher emissions of biogenic VOCs and larger water vapour concentrations in the atmosphere, which have opposing effects on the formation of ozone. The overall changes that can be attributed to the interactions between climate

and emissions have been studied in a global model by comparing the results of a model with fixed climate over the period 1990-2030 with results from a model with a varying climate (Stevenson et al., 2005), using the scenario of 'Current Legislation' to define precursor emissions. The overall conclusion was that climate-chemistry interactions as regards ozone formation appear to be largely negative, but year-to-year variability caused by changes in circulation patterns (e.g. ENSO) were at least as large as the variability in ozone that could be attributed either to changes in emissions or changes in climate. Increasing carbon dioxide concentrations may also influence biogenic VOC emissions (Pegoraro et al., 2005), but too little is known as yet to make quantitative predictions on a global scale.

Photochemical reactions of primary pollutants, including both anthropogenic and biogenic VOCs, lead to the formation of airborne particulates, adding to the burden of particulates emitted directly from combustion processes. Fine particulates, particularly those in the respirable size range (diameter < 10 μm, PM_{10}), have been associated with effects on human health (Englert, 2004), and reductions in visibility (Brewer and Adlhoch, 2005), but the potential effects of fine particulates on vegetation have received little experimental attention. Most studies on potential effects of airborne particulates have focussed on larger particles (soot, dust) from combustion or mechanical generation in quarries etc. which can occlude stomata or in extreme cases physically cover leaf surfaces and exclude light (Farmer, 1993, Grantz et al., 2003). Reductions in photosynthetically active radiation (PAR) on a regional scale in China, and consequent decreases in plant growth, have been attributed to the formation of fine particulates (ammonium sulphates and nitrate) in the atmosphere (Chameides et

106 al., 1999, Liang and Xia, 2005), but there is little information on potential direct
107 effects on trees and other vegetation. However, the impact of particulates on forests
108 may not be totally negative – one study suggests that although total irradiance may be
109 attenuated by fine particulates, diffuse irradiance may be enhanced, leading to a net
110 increase in photosynthesis (Misson et al., 2005).
111
112 This paper expands upon ideas presented to an international conference on the
113 impacts of air pollution and climate change on forest ecosystems, held in Riverside,
114 California in 2006 (Cape, 2007). Two aspects of secondary air pollution are
115 discussed: (1) the interaction of ozone and biogenic VOCs, in terms of affecting the
116 biogenic production of VOCs and their subsequent rates of oxidation, and the
117 potential consequential effects on forest ecosystems, and (2) the potential effects of
118 fine particulates on forests.
119
120 **Ozone and biogenic VOCs**
121 In the context of a slow but apparently inexorable increase in hemispheric ozone
122 concentrations (see above), the potential for direct effects of ozone on forest trees is of
123 continuing concern. Whereas the observed effects on Ponderosa pine and other
124 conifers in California were associated with peak ozone concentrations that exceeded
125 200 nl l^{-1} (ppbv) (Miller and McBride, 1998), more recent studies have emphasised
126 the overall increase in ozone concentrations outside major 'episodes', and the
127 potential for chronic injury (Coyle et al., 2003). There have been successful
128 experiments that have moved from the study of young trees (seedlings or saplings) in
129 the laboratory to the field-scale fumigation of adult trees with ozone, recognising that
130 the responses of small, immature plants in a controlled chamber environment may not

131 be a good predictor of effects on forest trees growing *in situ* (Karnosky et al., 2007b,
132 Matyssek et al., 2007). This recognition of the importance of studying trees in the
133 context of their normal environment is a step towards thinking about potential effects
134 on the forest ecosystem as a whole and not just the major tree species that are the most
135 obvious components. Well-replicated field-scale experiments that recreate forest
136 conditions are beginning to provide information on the effects of ozone (and carbon
137 dioxide) on more than just trees (Percy et al., 2003).
138
139 Forest ecosystems, like other vegetation communities, rely on complex interactions
140 above and below ground, with a myriad of life forms, from epiphytic micro-organisms
141 on leaf surfaces (the phyllosphere) to the soil bacteria and fauna that process decaying
142 plant material in the soil – and everything in between (Figure 1). One of the primary
143 effects of ozone in plants is to interfere with signalling processes within the plant
144 (Evans et al., 2005), with consequences for the movement of water, nutrients and
145 photosynthate between root and shoot. However, there are other signalling processes
146 that operate between plant and plant, and between plant and animal, both atmospheric
147 and in the soil, and these may also be affected by exposure to ozone and other photo-
148 oxidants. In this context, it must be remembered that ozone is only one component of
149 a photochemically active atmosphere, that happens to be reasonably easily measured –
150 enhanced ozone concentrations are associated with greater free radical concentrations,
151 e.g. hydroxyl (OH) and nitrate (NO_3) radicals, which also have the potential to
152 interfere with biological processes (Cape, 1997).
153
154 Biogenic VOCs (BVOCs) have been recognised as a component of natural
155 undisturbed plant communities for several decades, although their physiological and

156 ecological roles, and the factors that control their emissions, are only now becoming
157 better understood. VOCs are energy-rich molecules, and production within a plant is
158 an expensive use of photosynthate. There has been considerable debate as to their role
159 (Holopainen, 2004, Kesselmeier and Staudt, 1999, Sharkey and Yeh, 2001), whether
160 inside the leaf (possibly acting to remove reactive oxygen species), or outside the leaf,
161 as signalling molecules. There is evidence for several different external roles, such as
162 signalling herbivory, attracting predators of herbivores, or triggering defence
163 responses in neighbouring plants (Ashmore, 2005, Du et al., 1998, Engelberth et al.,
164 2004). Herbivory has been shown to stimulate release of mono- and sesquiterpenes
165 (e.g. ocimene, linalool, farnesene) in crop plants (Pare and Tumlinson, 1999), and the
166 monoterpenes α- and β-pinene and δ-3-carene from conifers (Litvak et al., 1999).
167 Even though the ecological roles of such molecules are not fully understood, the
168 recent discovery that such biogenic molecules are chiral (i.e. are produced in a left-
169 handed or right-handed form) suggests an evolved specificity for their role as a
170 signalling agent that is different for tropical and Boreal forests (Williams et al., 2007).
171 Exposure to ozone and other oxidants has been shown to stimulate emissions of
172 signalling molecules (Heiden et al., 1999), presumably because the type of damage
173 caused mimics attack by herbivores or similar mechanical damage (Langebartels et
174 al., 2002). However, there may also be enhanced emissions of VOCs from forest
175 canopies in response to ozone that have a chemical rather than biological source
176 (Fruekilde et al., 1998) with no obvious ecological role.
177
178 Many biogenic VOCs that act as signalling molecules (examples are shown in Figure
179 2) contain double bonds that are susceptible to attack by ozone and oxidant free
180 radicals, and their role as signalling agents presumably evolved in atmospheres with

markedly less ozone than at present, or likely to be seen in the near future. What are the implications of increased oxidant concentrations in the atmosphere? A selection of reaction rates is presented in Table 1, which shows the lifetime with respect to oxidation by ozone under pre-industrial, current day, and possible future scenarios, and for comparison, the current lifetime relative to OH radical during daylight (based on a nominal 12 h daytime concentration).

It is significant that no data exist for one of the more important of the recognised signalling molecules, E-β-farnesene, although α-farnesene is reported to be more reactive than monoterpenes (Joutsensaari, 2005). The decreased lifetime of such molecules as ozone concentrations increase implies a shorter dispersion path in the atmosphere and a reduction in the spatial effectiveness of the signalling. Despite the possibility that ozone (and other oxidants) might interfere with atmospheric signalling processes (Vuorinen et al., 2004), there is also limited evidence that less reactive biogenic VOCs may act as signalling molecules, and be relatively unaffected by oxidants (Pinto et al., 2007). Similarly, the effects of ozone on the production of signalling molecules may not require an atmospheric pathway, but may nevertheless have a direct influence on herbivore behaviour (Mondor et al., 2004).

Potential direct effects of ozone and other oxidant air pollutants below canopy, whether on flora or fauna, have not been clearly established from field measurements, partly because of interactions with sunlight penetration, water and nutrient supply, and the lower air concentrations of pollutant gases below the canopy than above (Krzyzanowski, 2004). However, there is some evidence of air pollutant effects on the understorey (Allen et al., 2007). The role of other oxidants, such as the nitrate radical

206 (NO_3), under the low-light conditions below forest canopies, has still to be explored in
207 detail (Cape, 2002).
208
209 **The challenge** is for more research to investigate the ecological impacts of the effects
210 of ozone and associated oxidants on signalling processes between different
211 components of forest ecosystems.
212
213 **Secondary aerosol particles**
214 The oxidation of biogenic VOCs can be an important first step in the generation of
215 secondary organic aerosol (SOA) particles (Joutsensaari et al., 2005, Rohr et al.,
216 2007), a process that has long been associated with forests, leading to the
217 characteristic 'blue haze' observed over forested areas. Reactions with sesquiterpenes
218 (e.g. farnesene) are particularly rapid, leading to depletion of the BVOC and
219 generation of SOA within the forest canopy (Lunden et al., 2006). The initial
220 formation of SOA, with diameters of 10 nm or less, leads to the eventual formation of
221 larger particles, through coalescence, until the 'accumulation mode' is reached, with
222 diameters up to 1000 nm. This size range of particles is only slowly removed from the
223 atmosphere by turbulent deposition, and consequently can be long-lived, travelling
224 long distances in the atmosphere. The continuing oxidation of SOA leads to
225 progressively more polar functional groups, and an increasing affinity of the SOA
226 particles for water, which condenses and enhances the particle size, leading to faster
227 deposition rates. Increased oxidation rates, from higher oxidant concentrations, and
228 increased emissions of BVOCs (in response to ozone stress), can therefore lead to
229 enhanced rates of formation of SOA, which in turn lead to a decrease in visible range
230 and a direct contribution to the risk to human health of respirable particles in the PM_1

231 to PM_{10} size range. Forests contribute to the 'background' PM concentrations, even in
232 the absence of other pollutant emissions, and may therefore contribute directly to the
233 exceedance of regulatory thresholds for PM concentrations.
234
235 The preceding section dealt with forests as a source of SOA, which contributes to
236 particulate matter in the atmosphere. Forests are also a sink for particulates, albeit
237 rather inefficient (in terms of the deposition velocity) compared to the sink for
238 reactive gases such as ozone and sulphur dioxide. However, in regions with high
239 atmospheric concentrations of ammonium salts (nitrates and sulphates) the deposition
240 of nutrients to forest canopies as fine particulates cannot be ignored. For example, a
241 deposition velocity of 1 cm s^{-1}, which is typical for fine particulate deposition to
242 forests (Gallagher et al., 1997), and an air concentration of around 6 μg N m^{-3} as
243 measured in parts of China (Aas et al., 2007, Wang et al., 2006) would give an annual
244 N deposition greater than 15 kg ha^{-1}, close to the Critical Load for forests used in
245 Europe (Hettelingh et al., 1995) before any consideration of other atmospheric sources
246 of N deposition, such as wet deposition or dry deposition of N-containing gases.
247
248 Even in areas with smaller air concentrations, however, the effects of particle
249 deposition to forests may be seen not simply in terms of nutrient input, but in terms of
250 the effects of such particles on the leaf surfaces of the canopy. Ammonium salts are
251 hygroscopic, absorbing water vapour from the atmosphere to form solutions at
252 relative humidities (RH) well below saturation (100%). Pure ammonium sulphate is
253 hygroscopic at 70% RH; mixtures of different ammonium salts are likely to become
254 hygroscopic at lower RHs. Consequently, the deposition of ammonium salts on leaf
255 surfaces will lead to the generation of liquid water even in air which is unsaturated,

256 leading to conditions similar to those which promote the formation of dew (Burkhardt
257 and Eiden, 1994). Areas on leaf surfaces close to sources of water vapour (transpiring
258 stomata) will remain 'wet' for longer than in the absence of the particle deposition.
259 This mechanism has been suggested as a possible explanation for increased water loss
260 from forest canopies (Burkhardt, 1995) and enhanced deposition rates of water-
261 soluble gases (Cape, 1996), and may also be responsible for decreased CO_2 uptake by
262 leaf surfaces that stay wet for longer in the morning (Misson et al., 2005). Perhaps as
263 important are the implications for biological activity on leaf surfaces exposed to
264 ammonium salts. Apart from the ready availability of N as a nutrient source for micro-
265 organisms, enhanced periods with liquid water availability could lead to enhanced
266 ion-exchange and leaching across the leaf surface (Tukey, 1970), and may also affect
267 the deposition and reaction of ozone (Altimir et al., 2006). The more favourable
268 conditions for micro-organism growth lead to increased risks of pathogen attack
269 (Huber and Gillespie, 1992). Even in the absence of pathogenic activity, the
270 proliferation of algae on a canopy that is well supplied with nitrogen and water may
271 lead to situations where primary photosynthesis by the leaf is inhibited (Cape et al.,
272 1989). Certainly, the processing of nitrogen within forest canopies is still not well
273 described or understood – transformations from inorganic to organic forms can occur,
274 and organic N can be retained within the canopy, either by epiphytic microbes or by
275 the leaf itself (Hill et al., 2005, Piirainen et al., 1998). In the latter case, the long-term
276 ecological implications of a transfer of the pathway for N uptake from roots to
277 canopies (Rennenberg and Gessler, 1999), although recognised as a problem because
278 of the changes in signalling hormones within the plant, have not been fully explored.
279 Similarly, changes in the chemical form of deposited N reaching the forest floor as
280 throughfall, interacting with understorey vegetation and entering the forest soil, have

implications for the storage and transport of N within and beyond the forest. Changes in the canopy may also affect leaf composition in a way that changes litter decomposition rates (Magill and Aber, 2000), with further long-term implications for nutrient availability, accumulation and transport.

The challenge is to understand the long-term implications of the deposition of hygroscopic fine particulates to forest canopies, in terms of leaf surface wetness, ion exchange, effects on epiphytic organisms, and nutrient pathways in the trees themselves and also in the forest floor.

Conclusions

Secondary air pollutants such as ozone and fine particulates are the products of chemical reactions in the atmosphere. The time taken for their production from primary pollutant emissions means that they can be transported over long distances, and therefore can affect forests (and other types of vegetation) far from the original pollution source. Although the direct effects on forest trees of ozone and other photochemical oxidants has long been recognised, most studies have relied on examination of the direct effects on the forest canopy. At much larger scales, studies of the potential effects of ozone on water status at the catchment (watershed) scale (McLaughlin et al., 2007) show the broader implications of ozone effects on forests. Although the interaction of ozone with biogenic VOCs, both in terms of effects on molecular signalling, and SOA formation, have been identified, little is known quantitatively of the long-term ecological effects of increasing atmospheric oxidant concentrations in forest ecosystems.

Increased fine particle concentrations in the atmosphere, whether from combustion, or secondary oxidation of inorganic pollutants or VOCs, have not been seen as a direct threat to forests, except perhaps in relation to reduced photosynthesis because of light exclusion. However, the hygroscopic nature of fine particulate matter may have long-term impacts on forest health because of the changed conditions (increased incidence of surface wetness) on canopy surfaces and consequent interactions with pathogens and other epiphytic organisms. The input of nutrients as fine particulate matter may also be of importance in some regions, whether as direct input to the canopy, or through changing the composition of throughfall and input to the forest floor.

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544 Table 1. Atmospheric lifetimes of selected monoterpenes and sesquiterpenes with
545 respect to different concentrations of ozone and OH radical, based on
546 published reaction rates (Atkinson and Arey, 2003)
547

Biogenic VOC	Pre-industrial O_3 (20 nl l^{-1})	Current O_3 (40 nl l^{-1})	Future O_3 (60 nl l^{-1})	Current daytime OH (2 x 10^6 cm^{-3} / 12 h)
α-pinene	6.5 h	3.3 h	2.2 h	2.6 h
β-pinene	1.6 d	19 h	12 h	1.8 h
3-carene	16 h	7.8 h	5.2 h	1.6 h
ocimene	1.0 h	31 min	21 min	33 min
linalool	1.3 h	39 min	26 min	52 min
farnesene	No data ?<1 h*	No data	No data	No data ?< 30 min**

548 * (Joutsensaari, 2005) **(Kwok and Atkinson, 1995)
549
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551
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553 Captions to Figures
554 Figure 1. Schematic diagram of the interactions and pathways of ozone and other
555 oxidants with biogenic VOCs, and of the role of airborne particulates, in forest
556 ecosystems.
557 Figure 2. Examples of biogenic VOCs that have been shown to act as signalling
558 molecules.
559

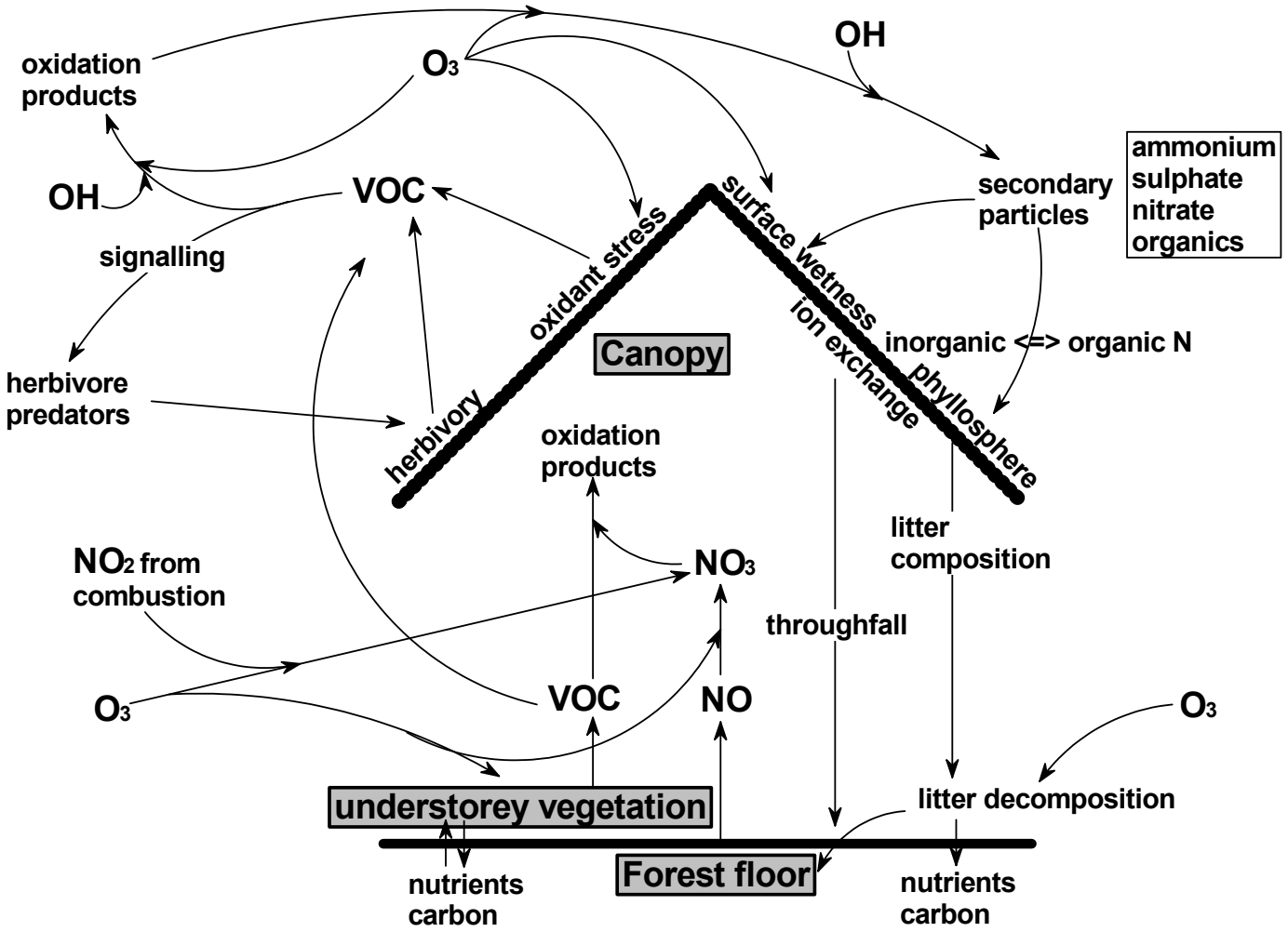
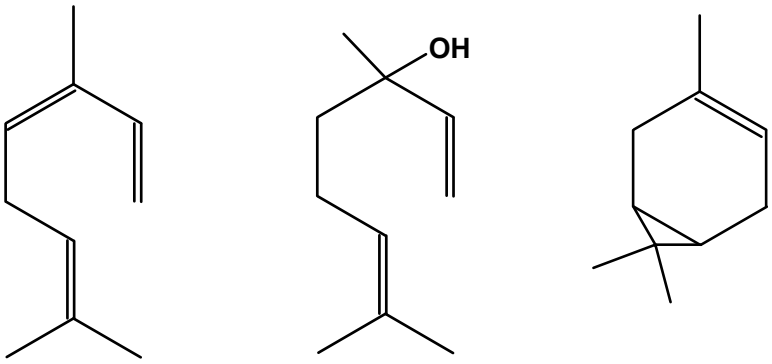

oxidation products
O3
OH
OH
VOC
secondary particles
ammonium sulphate nitrate organics
signalling
oxidant stress
surface wetness
ion exchange
inorganic <=> organic N
Canopy
herbivore predators
herbivory
phyllosphere
oxidation products
litter composition
NO2 from combustion
NO3
throughfall
O3
VOC
NO
O3
understorey vegetation
litter decomposition
Forest floor
nutrients carbon
nutrients carbon

Figure 1. Schematic diagram of the interactions and pathways of ozone and other oxidants with biogenic VOCs, and of the role of airborne particulates, in forest ecosystems.

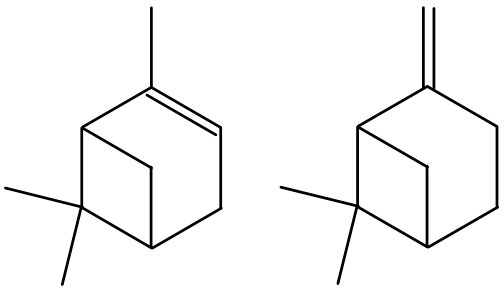
Figure 2. Examples of biogenic VOCs that have been shown to act as signalling molecules.

Monoterpenes

ocimene **linalool** **3-carene**



α-pinene **β-pinene**



Sesquiterpene **E-β-farnesene**