PROGRAM B

Volatile organic emissions from eucalypts and other fuels measured using PTR-MS

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Outline

1. Background context (T Bell)
   a) atmospheric effects
   b) human health effects
   c) environmental effects
2. VOCs and the PTR-MS (S Maleknia)
   a) utility of PTR-MS
   b) current status of VOCs analysed by PTR-MS
   c) future plans for combustion analysis and field studies
3. Application and implications (M Adams)
   a) fire impacts on atmospheric chemistry
   b) fires and atmospheric carbon
   c) future collaborations and partnerships

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Volatile Organic Compounds (VOCs)

1. wide variety of organic compounds
   (e.g. benzene, naphthalene, toluene, methanol, formaldehyde, formic acid, acetic acid)
2. non-methane hydrocarbons
3. low molecular weight and boiling point
   many partitioned between gaseous and liquid or solid phase
4. produced abundantly from partial oxidation of fuels containing cellulose
5. little characterisation work has been done
   (Ward, WHO, 1999)

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Project B2.2 *rationale*

1. Stakeholder concern about smoke chemistry, especially from prescribed fires
2. Link to BOM studies, especially to develop understanding of atmospheric impacts and impacts on people and ecosystems
3. **Strong** emphasis on understanding background (i.e. without fire) rates of emission of specific compounds - vital context to studies of fires. Everyone is exposed to many, if not all, these compounds all the time.

For example, the Blue Mountains are blue due to continual VOC emissions

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Air pollution from cut grass: CSIRO Division of Atmospheric Research, Aspendale, Victoria

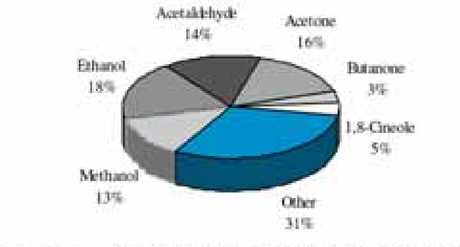

Figure 1. Approximate composition of VOCs from grass pasture as a percentage of total carbon (Kirstine *et al.* 1998).

Kirstine W, Galbally IE, Ye Y, Hooper MA, Emissions of volatile organic compounds (primarily oxygenated species) from pasture, 1998, *J. Geophys. Res.* 103, 10605-10620.

Atmospheric effects

1. VOCs naturally present in the atmosphere
   a) annual global emissions (Tg C): isoprene 175-503, monoterpenes 127-480, other reactive VOCs ~260 (*cf*: 120-510 CO and 11-53 CH_4 from biomass burning)
2. VOCs affect atmospheric chemistry
   a) formation of tropospheric ozone and photochemical oxidants
   b) contribute to formation of sulphuric, nitric and nitrous acids (acid rain)
3. VOCs affect climate
   a) formation of aerosols change light and heat in the biosphere (global warming)
   b) Act as cloud condensation nuclei

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Health effects

1. Several VOCs are major pollutants in smoke from biomass burning
   e.g. benzene, acrolein, formaldehyde
2. Many VOCs are strong irritants, others may be carcinogenic
   benzo(a)pyrene, benzo(e)pyrene, formic acid, acetic acid
3. Certain VOCs may act as markers for fire-related exposure but better characterisation is still needed (Mannino, WHO, 1999)

Environmental effects

1. VOCs produced in many different plant tissues for a variety of functions
   (e.g. defence, signalling, protectants, flammability)
2. Exposure of plants to VOCs
   a) effects as primary pollutants largely unknown (toxic or otherwise)
   b) indirect effect *via* involvement in formation of ozone, photochemical oxidants and acid deposition
   c) germination of seed by smoke (also stimulation of flowering, breaking of bulb dormancy and root initiation)

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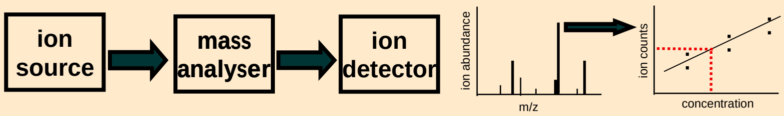
Analysis of VOCs

1. mass spectrometry is used to identify and quantify VOCs
2. advantages of MS: direct analysis of mixtures; suited to a variety of compounds; structural information; low level detection (ppt)
3. mass spectrometer is an instrument that produces charged molecules (ions) and separates the ions in vacuum according to their mass-to-charge ratio (*m/z*)



Ionisation of VOCs

1. electron ionisation (EI) - gaseous sample molecules are bombarded with a stream of electrons (70 eV)

$$\text{VOCs} \xrightarrow{e^-} \text{VOC}^{+\cdot} + \text{fragments } (\text{V}^{+\cdot}\ \ \text{VO}^{+\cdot}\ \ \text{OC}^{+\cdot})$$

2. chemical ionisation (CI) - ionise reagent molecules (water, methane) and subsequently ionise sample molecules through typically proton-transfer reactions

$$H_2O \longrightarrow H_3O^+ + H_3O^+(H_2O)_n \text{ clusters}$$

$$\text{VOCs} + H_3O^+ \longrightarrow (\text{VOC+H})^+ + \text{some fragments}$$

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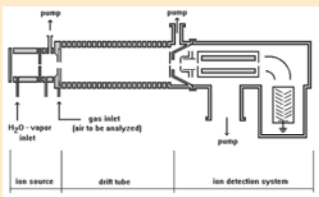
Proton Transfer Reaction Mass Spectrometer

identifies & quantifies VOCs in real-time with low detection limit of a few pptv

H_3O^+ ions from water vapor ionise VOCs with a higher proton affinity than water (165.2 kcal/mol)

O_2 100.6; N_2 118; CO_2 129.2; CH_4 132; CO 141.7 (< H_2O <)
methanol 180.3; acetic acid 190.2; acetone 195.1; isoprene 198.9; ammonia 204.1

PTR-MS: Ionicon, Austria
High-Sensitivity PTR-MS
UNSW
February 2006



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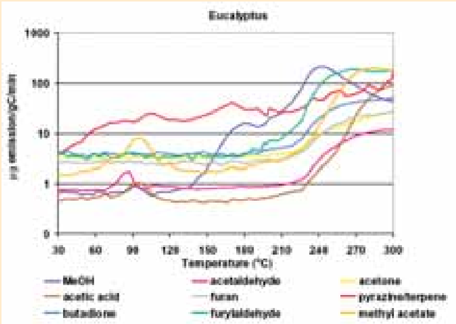
VOCs of Eucalyptus leaf identified by PTR-MS



Greenberg JP, Friedli H, Guenther AB, Hanson D, Karl T;
Volatile organic emissions from the distillation and pyrolysis of vegetation,
Atmos. Chem. Phys. 6, 81-91, 2006.

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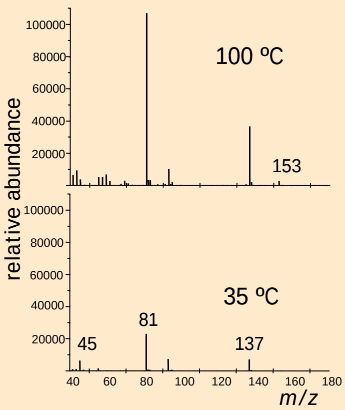
Temperature effects on Eucalyptus leaf VOCs

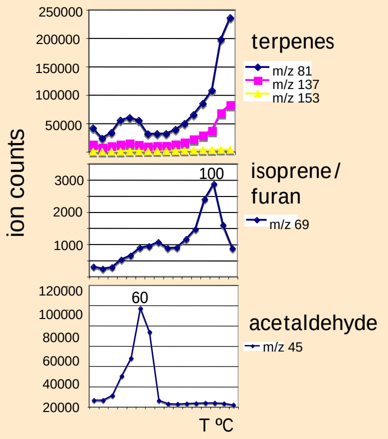


acetaldehyde (45)
acetic acid (61, 43)
isoprene, furan (69)
pyrazine (81 also terpenes)
terpenes $C_{10}H_{16}$ (137, 81)
$C_{10}H_{16}O$ (153, 137, 81)

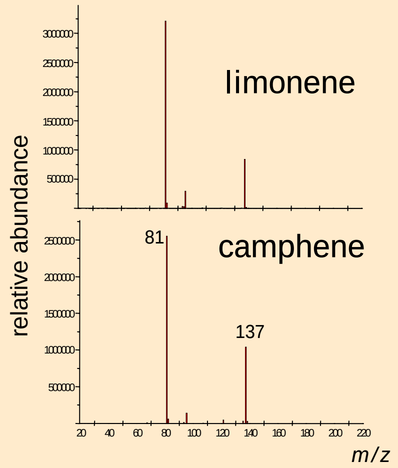
pyrazine.H^+ 81.070425
$C_6H_9^+$ 81.045273
R = m/Δm = 3200
isoprene/furan
R = 1900

VOCs from 0.2g eucalyptus leaf analyzed by PTR-MS, UNSW

Temperature effects on Eucalyptus leaf VOCs



PTR-MS of references



Current plans & future directions

1. Temperature studies of VOCs from plant tissues by PTR-MS (ambient to 300 ºC)
2. PTR-MS analysis of VOCs as standards to identify characteristic ions and quantify VOCs
3. Identify unknowns in spectra - investigate their significance
4. Design & construct a chamber for combustion studies
5. Plan field studies for controlled burns in collaboration with CSIRO

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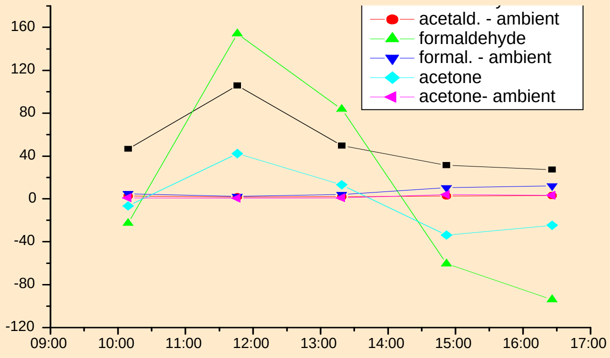
Typical diurnal emissions of carbonyl compounds from *Eucalyptus camaldulensis* in the Barmah Forest, Victoria



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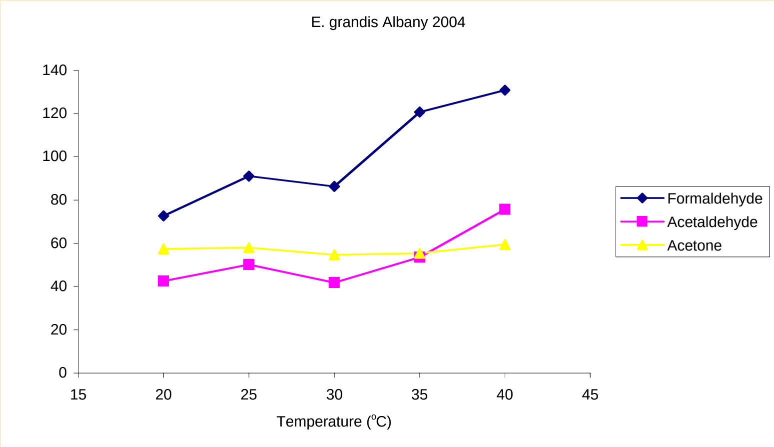
Relationship to temperature of carbonyl emissions from *Eucalyptus grandis* at Albany, Western Australia



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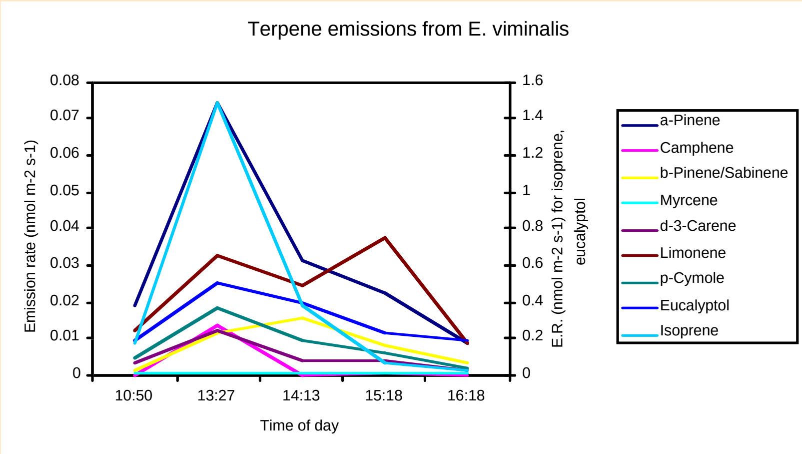

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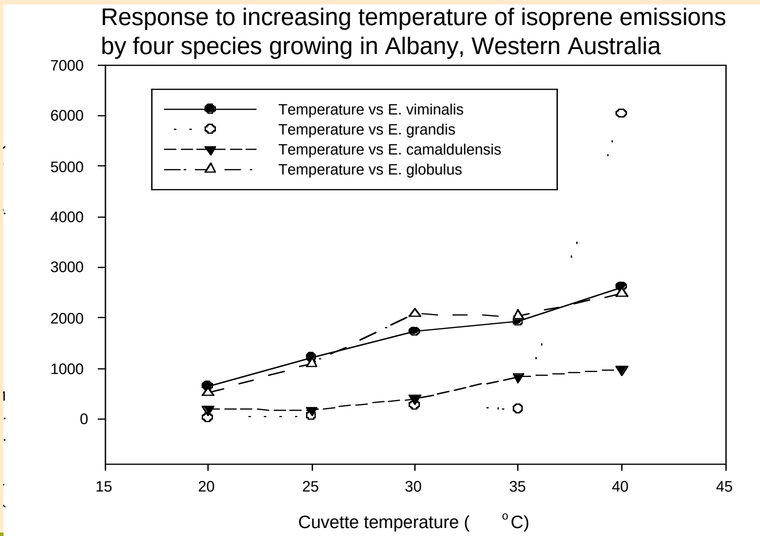

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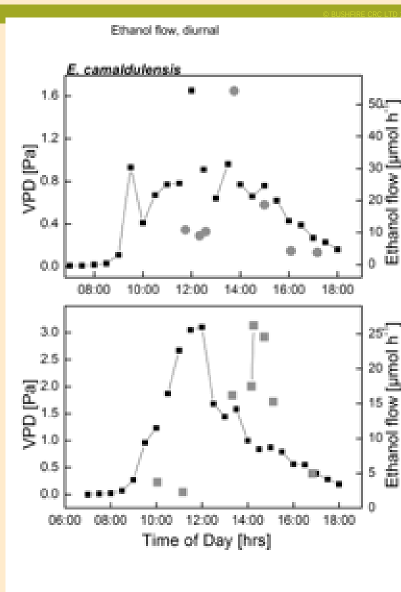
How and where are VOC emissions produced?

In fact, many of the precursors are produced in roots and transported to the foliage



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Current plans & future directions

1. Partnership with CSIRO in a range of studies of atmospheric impacts of VOCs, with and without fire
2. Continue work with IFU Garmisch to develop understanding of production of VOCs by plants. Link to BOM atmospheric chemistry studies and smoke plume and dispersion models
3. Continue discussions with range of stakeholders to develop utility of PTR-MS. VOCs are major causes of concern, for example, to the grape industry. PTR-Ms offers the most sensitive real-time analysis presently available
4. Publish, publish, publish