

## Chapter 13

### New Directions: VOCs and biosphere–atmosphere feedbacks

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Shallcross and Monks (New Directions: A role for isoprene in biosphere-climate-chemistry feedbacks, *Atmospheric Environment*, Vol. 34 (2000) pp. 1659–1660) recently summarised the importance of biogenic isoprene in a biosphere-atmosphere system under constant change. In this article, we expand this synthesis to include the biophysical feedbacks between plants that produce volatile organic compounds (VOCs) and the overlying atmosphere.

Plants produce a wide range of hydrocarbons including isoprene, terpenes, hemiterpenes, oxygenated species, and cuticular waxes. At the global scale it is estimated that vegetation emits  $1.2 \times 10^{15}$  g C per year, an amount equivalent to global methane (CH<sub>4</sub>) emissions.

There has been little direct experimental research on how global environmental change can affect emissions of phytogetic hydrocarbons. A broad-based research programme is needed because VOCs rapidly react with hydroxyl radical (OH), ozone (O<sub>3</sub>), and nitrate (NO<sub>3</sub>). Such reactions lead to the formation of secondary chemical species (e.g., formaldehyde, peroxy radicals, carbonyl compounds, etc.) that can enhance O<sub>3</sub> and other oxidant levels in locales rich in nitrogen oxides. The reaction of VOCs and OH can lead to enhanced CH<sub>4</sub> levels, as OH is the major atmospheric sink for CH<sub>4</sub>. Poisson and co-workers (*Journal of Atmospheric Chemistry*, Vol. 36, (2000) pp. 157–230) estimated that VOC emissions have the global effect of increasing the lifetime of CH<sub>4</sub> by 15% and enhancing background O<sub>3</sub> levels, by 18%. Once reacted, terpene compounds can also generate carbonaceous aerosols whose impacts may include feedback mechanisms in the Earth radiation balance. Finally, VOCs constitute a source of atmospheric carbon and can thus play key functions in the global carbon budget and cycling.

The potential for feedbacks among global environmental change, phytogetic hydrocarbons, and associated atmospheric chemistry, requires coordinated research efforts. In particular, new research is required to ascertain how environmental changes occurring at the global scale might affect VOC emissions from ecosystems to the atmosphere. This research should take into account: (1) warming from increased greenhouse gas concentrations and from other perturbations, (2) elevated carbon dioxide (CO<sub>2</sub>) levels, (3) increased deposition of nitrogen, and (4) conversion of land from unmanaged to managed ecosystems.

Warming can augment emissions of phytogetic hydrocarbons. As isoprene and terpene production strongly depends on temperature, the temperature increases predicted by global climate models suggest that VOC emissions may increase exponentially. This change could, with the increase in reactive nitrogen oxides that result from fertilisation and fossil fuel combustion, lead to increasing levels of tropospheric carbon monoxide and O<sub>3</sub>: both important pollutants and greenhouse gases.

Similarly, as elevated CO<sub>2</sub> increases productivity in terrestrial systems, the standing biomass available to produce VOCs will also rise, and emissions may increase proportionally. Elevated CO<sub>2</sub> may also increase the relative availability of carbon to nitrogen in ecosystems and this will lead to a proportional increase in the production of carbon-based compounds such as isoprenoids, but experiments are only beginning to examine this possibility.

An environmental change that is occurring locally and across the globe, and that may be of great relevance to biogenic VOC production, is the increased deposition of reactive nitrogen. Nitrogen could serve to 'fertilise' ecosystems and lead to large increases in productivity. Experiments show that plant monoterpene and isoprene emissions respond strongly to nitrogen fertilisation (see,

for example, Litvak and co-workers writing in *Plant, Cell and Environment*, Vol. 19 (1996) pp. 549–559). Increases appear to occur as a result of both enhanced carbon fixation and increased activity of enzymes responsible for isoprenoid production. Nitrogen deposition may also alter VOC emissions through its impact on biological diversity. It is not yet known whether nitrogen deposition will tend to favour hydrocarbon-producing species or not, but effects could be profound.

Perhaps, the single most important change in the global environment that is occurring with respect to VOCs is the expansion of agriculture, especially in tropical regions, and the resulting conversion of forest to cropland, pasture, and then secondary forest. In addition, some of the most important species in modern agroforestry, poplars and eucalyptus, emit large quantities of VOCs. These land-use changes have the potential to dramatically shift both regional and global budgets of biogenic VOC emissions.

Although most studies of VOC emission impacts have focused on changes in atmospheric redox potential, there is emerging evidence that these VOCs can also affect local radiative balance. In areas with active photosynthesis and relatively dry air masses, VOCs contribute to elevated atmospheric emissivities and thus retard nocturnal cooling (Hayden, *Philosophical Transactions of the Royal Society of London, B*, Vol. 353 (1998) pp. 5–18). In such regions, minimum temperatures are significantly higher than the dewpoint, but in regions without vegetation, the average daily minimum temperatures are close to the dewpoint.

Field observations by Garstang and co-workers (*Journal of Experimental Biology*, Vol. 200 (1997) pp. 421–431) show that extreme nocturnal inversions can exist over surfaces covered by high terpene emitters (e.g., mopane – *Colophospermum mopane*). Temperatures at 50 m can be  $\sim 10^{\circ}\text{C}$  warmer than at the surface. This extreme positive lapse rate may be the result of two concomitant processes.

Firstly, hydrocarbons such as  $\alpha$ -pinene and  $\beta$ -pinene effectively ( $\sim 90\%$ ) absorb thermal energy within the ‘atmospheric window’ (8–13  $\mu\text{m}$ ) of the electromagnetic spectrum. These hydrocarbons, in place of water vapour, act as greenhouse gases thereby elevating minimum temperatures. Note that for this greenhouse effect to be detectable, the ambient abundance of VOCs must be high, with mixing ratios perhaps reaching parts per million (ppm) levels. Utilising the meteorology data reported by Garstang and co-workers together with vegetation characteristics and reported emissions for mopane, we estimate ambient terpene mixing ratios ranging from 10 to 50 ppm. Haze layers near the surface, observed near sunset as the nocturnal inversion forms, suggest trapping of emissions and formation of visible aerosols close to the surface. These aerosols, ranging in size from 0.01 to 0.4  $\mu\text{m}$  (Hoffmann and co-workers, *Journal of Atmospheric Chemistry*, Vol. 26 (1997) pp. 189–222), can form at rel-

ative humidities above 60% on particulate hydrocarbons, resulting in “wet” haze particles.

Secondly, the release of latent heat of condensation can increase the heat content of a thermally insulated atmospheric column  $1 \text{ m}^2 \times 100 \text{ m}$  by as much as 30 K at relative humidities greater than 60% ( $> 10 \text{ g (water) per kg of air}$ ). Although such extreme heating is never realised in the open atmosphere, owing to the presence of turbulent diffusion and radiative flux divergence, this process requires further investigation.

The regional implications of this VOC heating within the atmospheric surface layer is that there can be a tendency to change the atmosphere from the dry adiabatic state to more stable conditions, and hence statically stable regimes can be augmented at night. As a consequence, the lapse rate of the atmospheric boundary layer becomes less negative, and thus the static stability is increased. We propose as a working hypothesis that the biogenic hydrocarbon ‘greenhouse effect’, combined with latent heat of condensation released to the environment due to water condensation onto hydrocarbon-derived aerosols, can retard heat losses and add heat to the lower atmosphere and alter the thermal structure of the atmospheric boundary layer.

We therefore propose here a framework of vegetation controlled atmosphere dynamics consisting of three linked feedback loops, operating on different time scales. First, Loop I represents the vegetation-nocturnal temperature feedback. Vegetation produces isoprene (day), as well as terpenes and other chemical species (day and night). Under low humidity levels, these compounds strongly absorb terrestrial radiation and elevate nocturnal minimum temperatures above the dewpoint. Feedback Loop II comprises VOC conversion to aerosols on which water vapour condensation occurs. Such condensation produces latent heat, which is converted to sensible heat throughout the atmospheric boundary layer. The resulting vertical change in temperature with height gives rise to increased atmospheric static stability. With this stability comes increased residence time of gaseous VOCs, aerosols, increased haze, and hence additional heating. We believe that this feedback operates at time scales ranging from days to weeks, and at spatial scales from the ecosystem to synoptic levels. All these processes lead to the long-term feedback Loop III, which operates at time scales of years to decades.

We propose that vegetation adjusts to these atmospheric dynamics in a synergistic manner. For Loop III, we further propose that with these elevated nocturnal temperatures, neo-tropical plant species become more successful at higher latitudes with photosynthetic and VOC production capabilities over a longer portion of the year. These systematic changes give rise to altered plant species assemblages, biodiversity changes, and shifted ecotones. If land-use changes increase the proportion of VOC plant emitters then this positive feedback will be amplified.

To address the processes described here co-ordinated and integrated research efforts are required involving atmospheric scientists, ecologists, and atmospheric chemists.