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- Margalef, R. *Our Biosphere* (Ecol. Inst., Oldendorf, 1997).
- Boyd, P. W. *et al. Science* **315**, 612–617 (2007).
- Blain, S. *et al. Nature* **446**, 1070–1074 (2007).

- Morel, F. M. M. & Price, N. M. *Science* **300**, 944–947 (2003).
- Martin, J. H. *Paleoceanography* **5**, 1–10 (1990).
- Sigman, D. M. & Boyle, E. A. *Nature* **407**, 859–869 (2000).
- Sunda, W. G., Swift, D. G. & Huntsman, S. A. *Nature* **351**, 55–57 (1991).
- Frew, R. D. *et al. Glob. Biogeochem. Cycles* **20**, doi:10.1029/2005GB002558 (2006).
- Hutchins, D. A. & Bruland, K. W. *Nature* **393**, 561–564 (1998).

ATMOSPHERIC CHEMISTRY

A forest air of chirality

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A sophisticated survey of certain volatile organic compounds in the air over forest ecosystems shows how such work can reveal varied emission patterns of different chiral, or mirror-image, forms of these compounds.

An unseen component of forest ecology is the emission, by both plants and animals, of a cocktail of volatile organic compounds into the atmosphere. Emissions from plants exceed those from animals by several orders of magnitude, and have various purposes, such as repelling herbivorous animals or attracting specific insects for pollination. A little-understood aspect of the chemistry of these compounds is the possibly different emission patterns of different chiral (mirror-image) forms, known as enantiomers, of the same compound. With a Lear jet as one of their platforms, Williams *et al.*¹ have undertaken an ecosystem-scale sampling of air over tropical forest. As they report in *Atmospheric Chemistry and Physics*, they find distinct differences between the enantiomeric composition of a common volatile compound emitted by tropical forest compared with boreal forest.

Plant emission of volatile organic compounds occurs on a vast scale, estimated at 1,150 Tg carbon (1 Tg = 10¹² g) annually². Many of these compounds are built up from isoprene (C₅) subunits and are traditionally given the collective name terpenes³. Together, isoprene and its monoterpene derivatives (C₁₀H₁₆) make up 55% of the estimated emissions². Many monoterpenes are produced in two enantiomeric forms: α -pinene, a common example, occurs as both (+)- α -pinene and (–)- α -pinene.

The light-induced oxidation of natural and man-made volatile organic compounds affects the chemical and physical properties of the atmosphere^{4,5}. But although the importance of different enantiomers for the biological activity of a compound is well known, the implications for atmospheric chemistry have not been established⁶. Indeed, the global effect of compounds such as monoterpenes has been estimated by measurements and models that consider the enantiomeric forms as one². The work of Williams *et al.*¹ is an attempt to use a detailed enantiomeric characterization of monoterpene

patterns in the atmosphere as a tool to enable a better understanding of the mechanisms underlying their emission from plants.

This is where the Lear jet came in. Williams *et al.* took air samples from an aircraft making flights of 3 hours, with a range of 1,800 km, over the tropical forest of the northeast coast of South America, and subsequently analysed the monoterpene content. They also sampled ambient air at the level of the forest canopy at a site in Suriname, within the region surveyed. The other sites of investigation were boreal pine forest in Finland, samples being taken at a height of 8 m from the ground, and the greenhouse of the botanical garden of the Johannes Gutenberg University in Mainz, Germany, where 8,500 plant species from all over the world are cultivated.

Most notably, monoterpenes emitted from the tropical forest showed an excess of the (–) enantiomer of α -pinene, and also of the (+) enantiomer of β -pinene. The monoterpene emissions from a mixture of three tropical species in the greenhouse of the botanical garden likewise showed an excess of (–)- α -pinene. Laboratory studies⁶ have shown that both enantiomers of α -pinene react at the same rate with atmospheric oxidants (hydroxyl radicals and ozone). So the dominance of one enantiomer over the other does not imply preferential atmospheric removal of one of them. Rather, the explanation probably lies in the factors influencing emissions by plants. In that respect, studies of leaf chemistry² have shown that the strength of isoprene emission is a function of both light and temperature. In contrast, although monoterpene emission rates increase with temperature, plant species show differential sensitivity to temperature; different monoterpenes can also exhibit differing temperature dependence.

To interpret their observations, Williams *et al.* compared the concentrations of isoprene, (–)- α -pinene and (+)- α -pinene measured over tropical forest. They observed a surprising

correlation between (–)- α -pinene and isoprene, but no correlation between its mirror image (+)- α -pinene and isoprene. The converse applied to emissions from the boreal forest: there was a clear predominance of (+)- α -pinene and (–)- β -pinene. A previous study⁷ conducted in the same boreal forest showed that rates of emission of non-enantiomerically resolved α -pinene were temperature dependent. On the basis of both their own results¹ and this earlier work⁷, Williams and colleagues propose that over the tropical forest, emission of (–)- α -pinene is — like that of isoprene — light-dependent, whereas that of (+)- α -pinene over the boreal forest is temperature-dependent.

Volatile organic compounds have a fundamental role in the coexistence of the flora and fauna in ecosystems. But there is still much to learn about the relationships and interactions between species that can be related to an effect of naturally produced compounds such as monoterpenes. Studies⁸ of the biosynthesis and the enantiomeric composition of monoterpenes in forest trees has shown that different enzymes (terpene cyclases) are responsible for the production of the two enantiomers. This supports the observation that enantiomeric composition varies in different tissues and in different individual trees⁸. Research aimed at correlating the enantiomeric composition of monoterpenes from different parts of specific trees with the corresponding enantiomeric composition of emissions by the same trees under specific environmental conditions — light, temperature and humidity — will be necessary for a fuller understanding of the mechanisms of the emission of volatile organic compounds into the atmosphere.

Microbial degradation and plant metabolism might be selective towards a specific enantiomer; but processes in the atmosphere such as photo-oxidation are not. So chiral analysis will be a powerful additional tool in atmospheric chemistry for investigating the sources of emission and the fates of chemical compounds in various environments⁹. The main message of Williams and colleagues' work is that ecosystem-scale field studies involving sophisticated sampling and analytical techniques are required to make sense of the biochemistry and ecology of these natural emissions, and of other physical and chemical observations in the atmosphere. ■

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- Williams, J. *et al. Atmos. Chem. Phys.* **7**, 973–980 (2007).
- Guenther, A. *et al. J. Geophys. Res.* **100**, 8873–8892 (1995).
- Ruzicka, L. *Proc. Chem. Soc.* 341–360 (1959).
- Andreae, M. O. & Crutzen, P. J. *Science* **276**, 1052–1058 (1997).
- Kavouras, I. G. *et al. Nature* **395**, 683–686 (1998).
- Nunes, F. M. N. *et al. Atmos. Environ.* **39**, 7715–7730 (2005).
- Tarvainen, V. *et al. Atmos. Chem. Phys.* **5**, 989–998 (2005).
- Norin, T. *Pure Appl. Chem.* **68**, 2043–2049 (1996).
- Harner, T. *et al. Environ. Sci. Technol.* **34**, 218–220 (2000).