Atmospheric science

Ultraviolet light and leaf emission of NO_x

Nitrogen oxides are trace gases that critically affect atmospheric chemistry and aerosol formation[1]. Vegetation is usually regarded as a sink for these gases, although nitric oxide and nitrogen dioxide have been detected as natural emissions from plants[2,3]. Here we use *in situ* measurements to show that solar ultraviolet radiation induces the emission of nitrogen oxide radicals (NO_x) from Scots pine (*Pinus sylvestris*) shoots when ambient concentrations drop below one part per billion. Although this contribution is insignificant on a local scale, our findings suggest that global NO_x emissions from boreal coniferous forests may be comparable to those produced by worldwide industrial and traffic sources.

We measured the amount of NO_x emitted from *P. sylvestris* (NO_x flux) at the SMEAR II station in southern Finland[4] by enclosing individual young shoots inside a specially equipped chamber[5,6]. The cover of each chamber was made of ultraviolet-transparent quartz glass (which has a transmittance of over 90% for ultraviolet A and B light) so that the plants were exposed to solar ultraviolet radiation. The chambers were closed 2–3 times every hour for 60 s while the gas concentration inside was being monitored.

We used a mass-balance equation to determine the rate of change in NO_x concentration inside the chamber during a single chamber closure. To calculate the NO_x flux, the solution to the mass-balance equation was fitted to the measured values[6].

The NO_x concentration increased during closure in an empty chamber, but increased faster when the chamber contained a shoot (Fig. 1a). Ultraviolet radiation also caused a small amount of NO_x emission from the chamber walls, which was taken into account in applying the mass-balance equation.

NO_x flux from the shoots occurred when they were exposed to solar ultraviolet light: when the shoots were removed from their ultraviolet-transparent chambers, the NO_x flux decreased, but was restored when the shoots were replaced (Fig. 1b). We repeated this experiment using two chambers during three sunny days in summer 2001, and found that the measured reduction in NO_x emission after removing the shoots, and the increase after inserting the shoots, were statistically significant on each occasion ($P = 0.00004$).

We confirmed that ultraviolet radiation was inducing NO_x emission from the shoots by replacing the quartz covers on the chambers with ultraviolet-opaque methacrylate (plexiglass) covers (negligible transmittance at 290–320 nm). NO_x emission decreased from shoots inside chambers with opaque covers, and removing the plants had no effect on NO_x flux (Fig. 1c). Swapping the covers had no effect on photosynthesis, which uses visible light.

The uptake of NO_x by plants increases as its atmospheric concentration increases, so a compensation point[7] is frequently detected[2,3,8,9]. NO_x concentrations at the SMEAR II station are usually below 1 part per billion (p.p.b), but in May 2001 they rose to 6 p.p.b. during an episode when the weather was cloudy and ultraviolet radiation was low (mostly $< 10\ W\ m^{-2}$), causing NO_x deposition. This varied linearly with the ambient concentration, and the compensation point was estimated to be around 1 p.p.b.

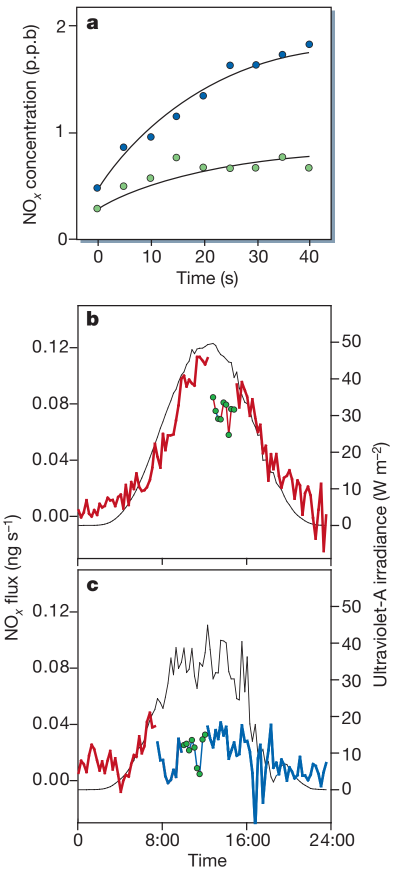

Figure 1 Ultraviolet radiation induces emission of nitrogen oxides from Scots pine (*Pinus sylvestris*) shoots. **a,** Increase in NO_x concentration inside an experimental chamber with an ultraviolet-transparent quartz cover, measured during closure (see text). Blue circles, NO_x concentrations measured inside a chamber containing a single shoot; green circles, NO_x concentrations inside an empty chamber. Curves are solutions to the mass-balance equation used to determine NO_x flux. Shoots were 1 yr old and 10–15 cm high. **b,** Representative experiment showing the change in NO_x flux (red) and ultraviolet-A irradiance (black) in an ultraviolet-transparent plant chamber over 24 h on 28 June 2001. Green circles, NO_x flux in the absence of the plant, which was removed at 12:40 and replaced at 14:50. **c,** Similar experiment, except that the transparent cover was replaced with an ultraviolet-opaque one (blue line) after 07:30 and the shoots were outside the chamber from 10:10 to 12:15.

As ultraviolet radiation induces NO_x emission from *P. sylvestris* shoots, it must also influence the compensation point. Assuming a linear relationship between exposure to ultraviolet light and NO_x emission, and between the ambient concentration of NO_x and its deposition, the compensation point is above 3 p.p.b. at maximum ultraviolet irradiance. In previous NO_x-exchange studies[3,8,9], ultraviolet radiation was excluded either by the chamber material or from the light source, causing the compensation-point estimates to be too low.

We do not yet know the origin of the emitted NO_x. It may come from plant metabolism[2] or be released from pine-needle surfaces as a result of ultraviolet irradiation, in a reaction similar to the one that occurs at the chamber walls. Gas-phase NO_x is produced from snow by photolysis of nitrate[10] — a reaction that would enable NO_x emissions to recycle reactive nitrogen on foliage.

The NO_x emission induced by ultraviolet radiation was 1 ng m^{-2} of pine-needle surface per second under conditions corresponding to a pre-industrial time, when the ambient NO_x concentration was less than 0.5 p.p.b. A flux of this magnitude is sufficient to influence the availability of nitrogen to plants and may affect the atmospheric NO_x budget[11].

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