

FIG. 3 Main figure, plot of emission current density (J) against electric field (F) characteristics of nitrogen-doped diamond. The threshold voltage is observed as low as $0.5 \text{ V } \mu\text{m}^{-1}$. Note that no linear relationship is observed in the J/F^2 versus $1/F$ plot (Fowler-Nordheim characteristics) inset.

shown in Fig. 3, indicating that the threshold field is less than $0.5 \text{ V } \mu\text{m}^{-1}$. When the distance between the cathode and the anode was changed, almost the same J - F characteristics were observed indicating that there is a linear relation between anode voltage and distance. Furthermore, no linear relation was observed in the J/F^2 versus $1/F$ characteristics (Fig. 3 inset) suggesting that the current limit is not dominated by the standard tunnelling theory proposed by Fowler and Nordheim¹². Although the total current density integrated over the entire anode area seems to be too low for the space-charge-limited current (SCLC) mechanism, if a much higher local current density occurs at the cathode, the current could be limited by the SCLC mechanism. In general, if the slope n of the J - F characteristics ($J = kF^n$) is 1.5, this confirms the Langmuir-Child law suggesting that the current is limited by SCLC in vacuum; if $n = 2$, the current is dominated by the SCLC in the diamond bulk. The value of n obtained from Fig. 3 is 1.75, and it is difficult at present to determine which mechanism is more probable. Defect/trap limited SCLC through the diamond is another possible reason for the current limitation, but the physical interpretation of this process still remains to be clarified.

Comparison of the emission properties of N-, phosphorus (P)- and boron (B)-doped diamond films are shown in Fig. 4. The surface morphologies of the P- and B-doped films were just the same as that of N-doped film shown in Fig. 2 inset^{11,13}, and there seems to be no large variation in the enhancement factor evaluated from the radius of curvature. This leads us to the view that

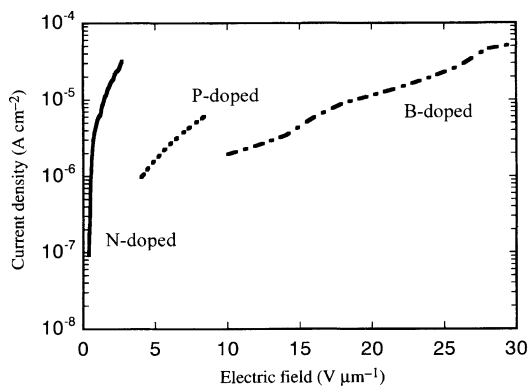


FIG. 4 Comparison of emission properties of nitrogen (N-), phosphorus (P-) and boron (B)-doped polycrystalline diamond films. The threshold field is much lower in the N-doped diamond film than P- and B-doped diamond films.

the difference in the emission properties must be fundamentally due to the difference in impurities introduced into the diamond films. It is clear from the figure that the threshold field is much lower in the N-doped sample than P- or B-doped samples, indicating that incorporation of N in diamond plays an important role in determining the emission characteristics.

As far as we know, such low-threshold emission has not previously been reported before for any type of diamond without caesium coating. If this material was used as the cathode in vacuum microelectronic devices, a single commercial 1.5 V battery would provide a current density of more than $10^{-6} \text{ A cm}^{-2}$ when the gap between the anode and the gate was $3 \mu\text{m}$ (a value which can be achieved readily with present technology). This will greatly simplify cathode switching as standard digital electronics could be used. Although bright luminescent displays with N-doped diamond cathodes can be realized with existing phosphors, with the achievement of such low electron-emission thresholds, the emphasis of research should be placed on obtaining stable phosphors that give enough brightness even when the electrons have significantly lower energies. □

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Increased UV-B penetration in a lake owing to drought-induced acidification

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CLIMATE change, acid deposition and increasing solar ultraviolet irradiance¹ have all combined to produce marked effects on lake waters and their ecosystems. Schindler *et al.*² have shown that both climate warming and lake acidification have led to decreases in dissolved organic carbon concentrations in North American boreal lakes, resulting in a markedly increased exposure of the upper water column to solar ultraviolet radiation. Here we report ten years of observations of rainfall and lake chemistry at Swan Lake, Canada, that suggest that a fall in dissolved organic carbon

concentrations can also occur by a different combination of climate change and acidification. In this boreal fresh water, a drought decreased lakewater levels, thus exposing to the atmosphere littoral sediments containing reduced sulphur from the previous atmospheric deposition of industrial sulphur dioxide into the lake and its catchment. This exposure caused a re-oxidation of sediment sulphur, resulting in a remobilization of acid into the lake water, and thus a decrease in dissolved organic carbon concentrations sufficient to increase by three-fold the depth to which ultraviolet radiation can penetrate.

Swan Lake (46° 22' N, 81° 04' W) is a small (area, 5.8 ha; maximum depth, 8.8 m), rapidly flushing (water renewal time of < 1 yr) lake located on the Canadian Precambrian Shield 13 km from the smelting complexes in Sudbury, Canada. The lake has a sparsely forested, uninhabited catchment. Swan Lake is one of the thousands of Sudbury lakes³ that have been acidified by the atmospheric deposition of industrial SO₂ emissions. Palaeolimnological reconstruction indicates that Swan Lake began to acidify 50 years ago, reaching a minimum in pH in the 1970s⁴. The measured pH averaged 3.97 in 1977⁵. Additional palaeolimnological, chemical and biological descriptions of Swan Lake are provided elsewhere^{4,6-9}.

During the early 1980s, the water quality of many Sudbury

lakes, including Swan Lake, improved in response to reductions in emissions of SO₂ from local copper/nickel smelters¹⁰. The SO₄²⁻ concentration of Swan Lake was 580 µequiv. l⁻¹ in 1977⁵, but dropped to 170 µequiv. l⁻¹ by 1985 (Fig. 1b). Concurrently, pH increased by almost 2 to 5.8 (Fig. 1c). However, 1986 and 1987 were extremely dry (Fig. 1a); in response, the lake surface area shrank by 18%, exposing large areas of littoral sediments to the atmosphere. In 1988, the wettest year since 1960⁶, the water level rose, the SO₄²⁻ concentration in Swan Lake increased to 400 µequiv. l⁻¹ (Fig. 1b), and lake pH dropped to 4.5 (Fig. 1c). Oxidation of reduced sulphur compounds in the exposed littoral zone and elsewhere within the catchment during the drought, followed by flushing in the subsequent wet year, is the likely cause of the SO₄²⁻ increase and resulting re-acidification^{6,11}, as there was no concurrent increase in SO₂ emissions from the smelters⁶.

In regions where the available base-cation pool exceeds the pool of re-oxidizable sulphur, drought may not lead to acidification¹²; however, the response of pH and SO₄²⁻ in Swan Lake is not unique. Bodo and Dillon¹³ reported that the 20-yr reversal of acidification in Clearwater Lake, near Sudbury, was interrupted in 1977 and 1988, the only years preceded by two-year droughts. In their annual survey, Keller *et al.*⁶ noted that the pH of 31 of 38 Sudbury lakes dropped in 1988, for the first time since 1980. Similarly, Kelso *et al.*¹⁴ recorded in 1988 a drop in average pH in 56 headwater lakes in north-central Ontario, 275 km west of Sudbury.

Concurrent with its acidification, the concentration of dissolved organic carbon (DOC) in Swan Lake decreased from 190 µmol Cl⁻¹ in 1987 to 63 µmol Cl⁻¹ in 1988 (Fig. 1e). Declines in DOC are an expected consequence of acidification^{2,15-18}. Although several factors may have contributed to this particular decline, two are most significant. The DOC decline may be a direct result of acidification to pH < 5 (ref. 15). Increases in aluminum concentration, a common consequence of acidification^{19,20}, can also lower DOC concentrations. In Swan Lake, the increase in Al in 1988 (Fig. 1d) produced concentrations exceeding the 1.4–2.8 µmol total Al per mg of DOC needed to saturate and flocculate DOC originating in wetlands²¹, the major DOC source for lakes on the Precambrian Shield²².

Temporal changes in the diffuse vertical attenuation coefficient (K_d) of UV-B radiation in Swan Lake were estimated from the measured changes in DOC concentration (Fig. 1e) using an empirical model based on 16 North American lakes²³, including Swan Lake. The model inferred that the re-acidification of Swan Lake substantially increased UV-B penetration. The median modelled annual K_d decreased by three-fold between 1987 and 1988, from 2.54 to 0.86 m⁻¹. This corresponded to an increase in the depth of lake waters exposed to 1% of lake surface UV-B irradiance, from 1.8 m in 1987 to 5.6 m in 1988 (Fig. 1f), the latter corresponding to 94% of the lake's volume.

In Swan Lake, the change in DOC concentration was linked to climate through drought-induced acidification. In other lakes, more direct linkages are possible. The DOC concentration may decline during droughts in response to decreased DOC export from catchments, and/or more efficient removal from the water column over the longer water renewal times^{2,18} (Fig. 2).

Manabe and Wetherald²⁴ estimate that soil moisture content in eastern North America, the region of highest atmospheric sulphur deposition on the continent, will decline by 10–40% if atmospheric CO₂ concentrations double. One likely consequence of such reductions in soil moisture is an increase in the amount of strong acid exported from sulphur-enriched catchments¹¹. The size of the reservoir of reduced sulphur that would supply this acidity, a legacy of a century of elevated industrial SO₂ emissions²⁵, has not been quantified. If the drought-induced increase in export of acid from catchments exceeds the decrease attributable to the anticipated reductions in anthropogenic emissions of SO₂ (ref. 26), then many lakes will acidify. Rapidly flushing lakes that have wetlands in their catchments and are in high sulphur

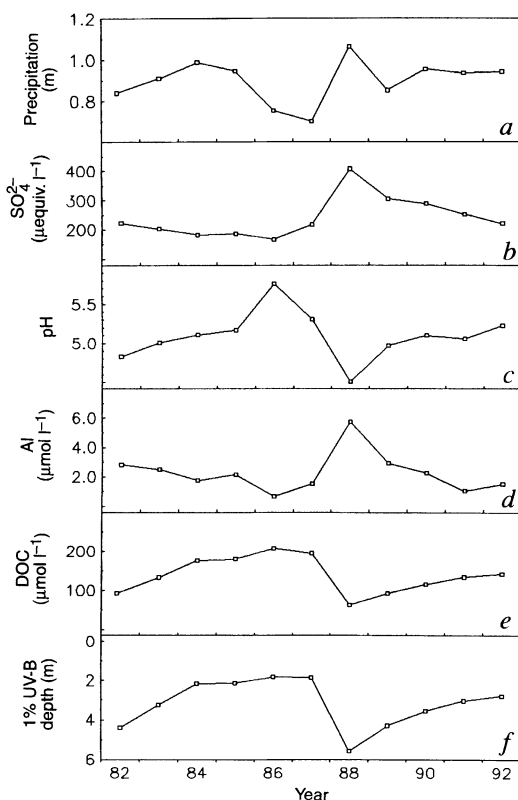
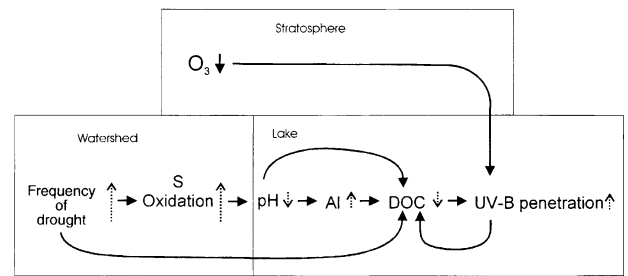


FIG. 1 a, Annual precipitation depths measured at the Sudbury airport. b–e, Measured quantities in Swan Lake as follows: b, sulphate concentration; c, pH; d, total Al; e, DOC concentrations. f, Calculated depth of 1% of surface UV-B irradiance. The 1% depth was calculated from the diffuse vertical attenuation coefficient (K_d) using the relation: $K_d = 0.60 + 0.389\text{DOC}^{1.873}$, $r^2 = 0.97$, which was constructed from the open-lake profiles data in ref. 23 (DOC in mg l⁻¹, as ref. 23). Chemical analyses were performed on bathymetrically weighted composite samples made from water collected at 1-m intervals through the water column. Composites were generated on alternate weeks throughout the seven-month ice-free season. DOC concentrations were determined by automated colorimetric titration of the inorganic carbon produced by photo-oxidation of DOC after first removing inorganic carbon from the samples by acidification and gas flushing²⁸.

FIG. 2 Illustration of linkages among drought, acidification, DOC concentration and UV-B penetration depth in lakes. Solid-headed arrows link processes; open-headed arrows indicate changes in frequency, intensity or concentrations of constituents or processes. DOC concentration is affected by the mechanisms discussed in the text including acidification, Al increase and hydrological change (drought), but may also be affected by changes in DOC decomposition rate induced by changes in UV-B penetration depth. In Swan Lake, the principal mechanism for DOC decline in 1988 (Fig. 1e) was drought-induced acidification.



deposition zones are most at risk. This increased acidity will be accompanied by a decline in DOC concentrations, if the pH of the lake drops to ≤ 5.0 , as happened in Swan Lake. In consequence, the depth of underwater UV-B penetration will increase; this will compound the stress already on biota from the increased acidity.

The level of UV-B irradiation of hundreds of thousands²⁶ of eastern North American lakes has increased because of stratospheric ozone depletion^{1,27}. Further increases, especially in the shorter, more photochemically active UV-B wavelengths, are expected over the next six decades¹. Precipitation is also most acidic in the eastern region of North America²⁵. Despite recent declines in anthropogenic SO₂ emissions²⁶, deposition rates of sulphur in this region will exceed those in non-industrialized areas for the foreseeable future²⁶. Because global emissions of greenhouse gases will also continue to increase for some time, the detrimental interaction of global climate change, acid deposition and increased UV-B irradiation described here will persist in this region. □

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A latitudinal gradient in carbon turnover times in forest soils

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ATTEMPTS to model the global carbon cycle, and anthropogenic modifications to carbon flow between the atmospheric, oceanic and terrestrial carbon reservoirs, commonly rely on values assumed for the ¹³C/¹²C ratio and 'bomb-spike' ¹⁴C signature of carbon in each reservoir^{1,2}. A large proportion of the carbon in the terrestrial biosphere resides in the soil organic carbon (SOC) pool³, most of which is derived from plants that assimilate carbon via the C₃ photosynthetic pathway⁴. Here we report measurements of the ¹³C and ¹⁴C signatures of particulate organic carbon from surface soils of C₃ biomes from a global distribution of low-altitude, non-water-stressed locations. We find that there is currently a latitudinal gradient in the signature, with low-latitude soils being relatively depleted in ¹³C. The ¹⁴C signatures indicate that today's gradient is due to a latitudinal gradient in the residence time of the soil organic carbon, coupled with anthropogenic modifications to the ¹³C/¹²C ratio of atmospheric CO₂ (for example by fossil-fuel burning⁵). The long residence times (tens of years) of particulate organic carbon from high-latitude soils provide empirical evidence that if fluxes of carbon from vegetation to the soil increase, these soils have the capacity to act as a carbon sink on decadal timescales.

The mechanisms by which isotopic fractionation occurs during photosynthesis in C₃ plants are well known⁶. In addition, several studies have demonstrated how environmental factors (such as water availability⁷, irradiance⁸, altitude⁹ and respired-CO₂ reutilization¹⁰) can affect the δ¹³C value of C₃ plant tissue, in some cases at the ecosystem level⁷. In contrast, there have been few attempts to examine how these factors affect the isotopic composition of organic carbon in the much larger SOC pool, or to place observational constraints on the isotopic composition of the SOC pool at a global level.

Balesdent *et al.*¹¹ have shown that there is no carbon-isotope fractionation during the early decay of fallen plant material. Therefore, the δ¹³C value of surface soil also provides a useful proxy for the 'bulk' δ¹³C value of the overlying vegetation where SOC turnover times are short, by smoothing out variations due to species-specific and tissue-specific fractionation effects which occur between individual plants, as well as reducing effects on

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