Table 2 Reported estimates of global meteorite accretion rate

Method used in estimate	Accretion rate (tons yr^{-1})	Ref.
Magnetic spherules from Pacific clay.	90	25
^{26}Al in Greenland ice	<100,000	26
^{26}Al in Pacific sediments	1.3×10^6	27
^{53}Mn in Antarctic ice	100,000	18
Iron in particles collected from stratosphere	<90,000	28
Ni in Pacific sediments	$(1-2)\times10^6$	29
	400,000	30
Ir in Mn nodules	20,000	31
	70,000	32
Ir in Pacific sediments	110,000	9
	78,000	23
Ir in Antarctic ice	400,000	19
Ir in Antarctic and Greenland ice	10,000–20,000	21
Ir in South Pole aerosol	6,000–11,000	This work
Co in Antarctic atmosphere	600	2
^{3}He/^{4}He ratio in Pacific sediments	2,000	33
Satellite, visual and radio-meteor studies	16,000	22

tons yr^{-1} by using the Co concentration in the South Polar aerosol. This unusually small flux estimate probably results from assumptions Cunningham and Zoller used to convert atmospheric meteorite concentration to a global flux value. When our model is applied to Co concentrations reported by Cunningham and Zoller, a flux value of 26,000 tons yr^{-1} is obtained. Temporal variations of Co at the South Pole suggest that Co may have a source other than crustal material and meteorites, probably volcanic or anthropogenic[5]. Consequently, the accretion rate estimated from Co concentrations is an upper limit rather than true flux value.

Takahashi *et al.*[21] measured the Ir concentration in the Antarctic snow as 3.1×10^{-16} g per g snow and estimated the meteorite flux as $(10-20)\times10^3$ tons yr^{-1}, both of which agree with our estimates. Ganapathy also measured the Ir concentration in the South Polar snow layers[19], obtaining an estimated flux of 100,000 tons yr^{-1}. (He then multiplied this value by 4 to account for uneven distribution of extraterrestrial material on the Earth's surface.)

Bibron *et al.*[18] measured ^{53}Mn activity in the Antarctic snow. The estimated accretion rate in this study was about 30,000 tons yr^{-1} assuming a uniform flux, but was later multiplied by a factor of 3 to approximate the global accretion rate.

Although our reported flux value can be compared with those from other studies of polar regions, comparison with accretion rate values from oceanic sediments is difficult. Because of the short sampling period in this work (1 yr), extraterrestrial particles collected on our filters are from the sporadic flux of material from solar dust cloud. Particles that make up this background flux are believed to have masses between 10^{-13} and 10^6 g (ref. 22). On the other hand, due to very slow accumulation rate, sediment samples used to estimate the flux of extraterrestrial material usually cover a time span of several million years. Samples that integrate such large time intervals, in addition to background dust particles, also include fragmentation products from large bodies. Extraterrestrial objects larger than 10^6 g do not frequently enter the earth's atmosphere, the impact probability dcreasing with increasing radius; however, over several million years, the impact of objects as large as 10^{17} g has a finite probability[23]. As the chemical methods used do not discriminate between background dust particles and fragmentation products from large bodies, a significant fraction of the flux estimated from sediment samples may be due to such large body impacts[23]. Satellite, visual and radio-meteor studies give a flux of background dust particles of around 16,000 tons yr^{-1} (refs 22, 24). Our estimate of 6,000 to 11,000 tons yr^{-1} for the particles smaller 10^6 g is in reasonable agreement with these studies.

Due to relatively fast snow accumulation rate in the polar regions (>10 cm yr^{-1}), the time interval covered by each snow and ice sample rarely exceeds 100 years. Since the contribution of large bodies is not significant for short time intervals, the accretion rate estimates from polar samples should be smaller than similar estimates from oceanic sediments.

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1. Lal, D., Peters, B. in *Handbuch Der Physik* Vol. 46(2) 551–612 (ed. Flugge, S.) (Springer, Berlin, 1967).
2. Cunningham, W. C. & Zoller, W. H. *J. Aerosol Sci.* 12, 367–384 (1981).
3. Maenhaut, W., Zoller, W. H. & Coles, D. G. *J. geopys. Res.* 84, 2421–2431 (1979).
4. Zoller, W. H., Parrington, J. R., Kotra, J. M. P. *Science* 222, 1118–1121 (1983).
5. Tuncel, G. thesis, Univ. Maryland (1985).
6. Parkin, D. W. & Tilles, D. *Science* 159, 936–946 (1968).
7. Fenner, F. D. & Presley, B. J. *Nature* 312, 260–263 (1984).
8. Taylor, S. R. *Geochim. cosmochim. Acta* 28, 1273–1285 (1972).
9. Crocket, J. H. & Kuo, H. Y. *Geochim. cosmochim. Acta* 43, 831–842 (1979).
10. Boutron, C. & Lorius, C. *Nature* 277, 1–3 (1979).
11. Legrand, M. R. & Delmas, R. J. *Atmos. Environ.* 18, 1867–1874 (1984).
12. Kumai, M. *J. atmos. Sci.* 33, 833–841 (1976).
13. Turco, R. P., Toon, O. B., Hammil, P. & Whitten, R. C. *J. geophys. Res.* 86, 1113–1128 (1981).
14. Sulek, A., M.S. thesis, Univ. Maryland (1979).
15. Thompson, L. G. & Thompson, E. M. *Science* 212, 812–814 (1981).
16. Mason, B. *US geol. Surv. Prof. Pap.* 440-B-1, (1979).
17. Brocas, J. & Piciotto, E. *J. geophys. Res.* 72, 2229–2236 (1967).
18. Bibron, R. R. *et al. Earth planet. Sci.* 21, 109–116 (1974).
19. Ganapathy, R. *Science* 220, 1158–1161 (1983).
20. Uematsu, M. & Duce, R. A. *Nature* (in the press).
21. Takahashi, H., Yokoyoma, Y., Fireman, E. L. & Lorius, C. *Lunar planet. Sci.* 9, 1131–1133 (1979).
22. Hughes, D. W. in *Cosmic Dust* (ed. McDonnell, J. A. M.) 123 (Wiley, Chichester, 1978).
23. Kyte, F. T. & Wasson, J. T. *Science* 232, 1225 (1986).
24. Grun, E., Zook, H. A., Fechtig, H. & Giese, R. H. *Icarus* 62, 244 (1982).
25. Murrel, M. T., Davis, P. A., Nishisumi, K. & Millard, H. T. *Geochim. cosmochim. Acta* 44, 2067–2074 (1980).
26. McGorkell, R., Fireman, E. L. & Langway, C. C. *Science* 156, 1690–1692 (1967).
27. Mulotak, V. I. *Kosmokhim. Metroid. 6th Mater. Vses. Symp.* 64–72 (1982).
28. Shedlowsky, J. P. & Paisley, S. *Tellus* 18, 499–503 (1966).
29. Patterson, H. & Rostchi, H. *Geochim. cosmochim. Acta* 2, 81–90 (1952).
30. Bonner, F. T. & Laurenco, A. S. *Nature* 207, 933–935 (1965).
31. Harris, R. C., Crockett, J. H. & Stainton, M. *Geochim. cosmochim. Acta* 32, 1049–1056 (1968).
32. Barker, J. L. & Anders, E. *Geochim. cosmochim. Acta* 32, 627–645 (1968).
33. Ozima, M., Tagayanagi, M. & Zashu, S. *Nature* 311, 448–450 (1984).

Models and observations of the impact of natural hydrocarbons on rural ozone

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Large quantities of non-methane hydrocarbons (NMHCs) are emitted into the atmosphere from vegetation[1,2]. A recent inventory by Lamb *et al.*[2] indicates that the emission of natural hydrocarbons is significant compared to that of anthropogenic NMHCs in most regions of the United States. Because of their chemical activity, the natural NMHCs can play important parts in the formation of trace gases, such as ozone (O_3), peroxyacetyl nitrate (PAN) and oxygenated secondary hydrocarbons[3–5], which contribute to regional-scale air pollution[6] and may be harmful to crops and

forest[7–9]. The impact of natural hydrocarbons on the formation of O_3 in the atmosphere has been discussed previously[4–13]. In general, it has been concluded that their impact is small[14–16]. But lack of data on the ambient concentrations of key photochemical species and an incomplete analysis of the photochemistry has prevented a definitive evaluation of the impact of natural NMHCs on rural O_3. Here we report on concentrations of key trace gases measured concurrently at a rural site in the eastern USA during the summer of 1986 and a modelling study conducted to analyse these measurements. This study demonstrates that natural NMHCs can have a significant impact on ozone formation in rural air.

The field measurements were carried out at Scotia, Pennsylvania. The site is located in a forest preserve 10 km west of State College, remote from the influence of direct anthropogenic emissions. The site is a monitoring station of the National Acid Precipitation Assessment Program (NAPAP) with well-characterized meteorology. Trace gases measured at the site include NO, NO_2, HNO_3, PAN, NO_y (the sum of the reactive nitrogen species[17]), O_3, NO_3^-, SO_4^{2-}, individual HC up to C_{10} including the terpenes and isoprene, CH_2O and CH_3CHO.

Ozone shows a characteristic diurnal cycle at the site (Fig. 1). At night O_3 is suppressed due to surface deposition in a shallow inversion layer. In the morning hours O_3 increases following the breakup of the nocturnal inversion layer as air from above is mixed downward. During the day O_3 also increases due to photochemical formation. The highest O_3 concentrations at the site are observed under high-pressure conditions associated with low surface winds, high temperatures and predominantly clear skies. These high-pressure systems can persist for several days, allowing the accumulation of photochemically active trace compounds and the formation of secondary products. Accordingly, high-O_3 concentrations are frequently observed over large regions during these periods[18,19].

In particular, during 4–7 July 1986, central Pennsylvania was at the northern edge of a stagnant high-pressure system over the eastern USA. The O_3 concentration observed at Scotia during this 4-day period peaked at 110 p.p.b.v. Figure 2 shows the daytime average hydrocarbon mixing ratios observed at the site; the natural NMHC isoprene was the predominant hydrocarbon. Isoprene concentrations were low in the morning hours and increased throughout the day as the temperature increased, consistent with the expected temperature dependence of the emission rate[20]. Furthermore, the average isoprene concentration increased during the 4-day period as did the average daytime temperature. The anthropogenic NMHCs (sum of C_3–C_{10} HC) observed during this period were mainly alkanes, with propane, butanes and pentanes contributing 60% by mass to the C_3–C_{10} HC. The concentrations of more reactive anthropogenic NMHCs were low. For example, the concentration of ethene was 0.23 $\mu g\ m^{-3}$, while the propene concentration was $<0.1\ \mu g\ m^{-3}$. The high contribution of the less reactive light alkanes to the total burden of anthropogenic NMHCs is characteristic for a rural site[21].

To simulate this event a fine-resolution, one-dimensional planetary boundary layer (PBL) model developed by Trainer *et al.*[22] that includes isoprene photochemistry was used to evaluate the effect of natural NMHCs on the formation of rural ozone. The fine-height resolution is needed to model this event. Because the vertical mixing near the surface is slow and the photochemical destruction of the very reactive natural NMHCs is fast, the mixing ratios of the natural NMHCs decrease rapidly with altitude[23].

In the model calculations the temperature dependence of the isoprene emission rate was described according to measurements by Lamb *et al.*[20] at a forest site in eastern Pennsylvania. For the height at which the samples were taken (5 m) the maximum isoprene concentration predicted by the model is 5 p.p.b.v. or 15 $\mu g\ m^{-3}$, which is typical of the observed values.

The emission rate for NO_x was chosen to reproduce the observed diurnal pattern of NO_x. During the 4-day period, NO_x showed a sharp peak in the morning that lasted 1–2 h and coincided with the breakup of the nocturnal inversion layer (Fig. 3). The NO_x concentrations during the day were ~1 p.p.b.v. As there are no appreciable local NO_x sources, the NO_x is probably transported to the site from distant sources. To simulate this phenomena a continuous NO_x emission rate was assumed for the height range from 200 to 800 m. The exact range is not important provided that it is above the nocturnal inversion layer. During the night-time the vertical mixing is slow and NO_x accumulates in this emission layer. The surface, where the measurements are taken, is isolated from the air aloft during the night by the shallow inversion layer. In the morning, when the inversion breaks up, downward mixing of NO_x leads to the sharp early morning rise in the near-surface NO_x mixing ratio. The subsequent decline in NO_x is due to dilution as the PBL height increases during the daytime and due to photochemical conversion of NO_x to PAN and HNO_3.

The rate of the NO_x emission, chosen to reproduce the observed diurnal variation, is $4\times10^{15}\ m^{-2}\ s^{-1}$. This value agrees with the average NO_x emission rate estimated for western Pennsylvania[24]. The emission rates of the anthropogenic NMHCs were chosen to reproduce the concentrations observed at the site. The ratio of the anthropogenic NMHCs to NO_x emission rates (by volume) was 1.2 with the following partitioning: C_2H_6, 38%; C_3H_8, 25%; C_2H_4, 6%; C_3H_6, 6%. Butane was taken as the surrogate for the C_4–C_{10} hydrocarbons.

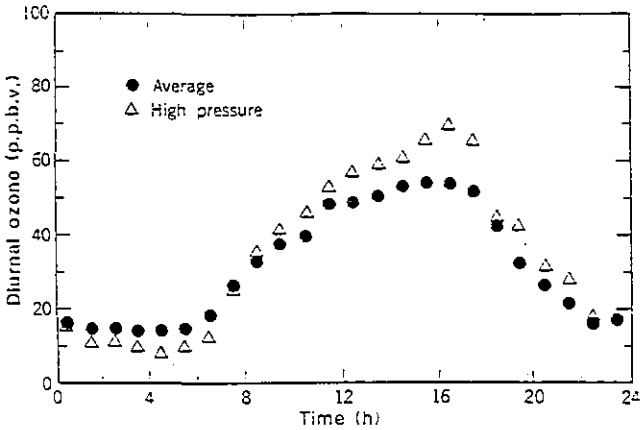

Fig. 1 Average diurnal ozone mixing ratio at Scotia, Pennsylvania, for 25 June–26 July 1986 (circles) and for times when the surface pressure was larger than the average pressure of 970 mbar (open triangles). The sampling height was 5 m above the ground.

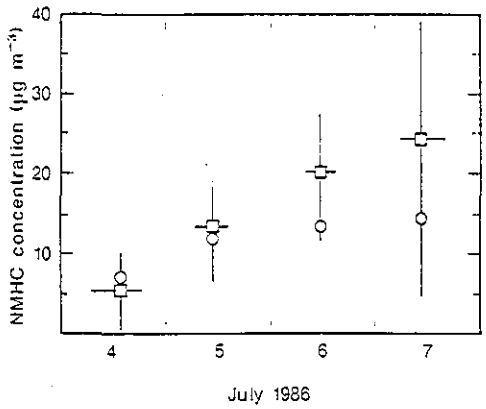

Fig. 2 Average isoprene (squares) and anthropogenic C_3–C_{10} HC (circles) mixing ratios at Scotia, for 4–7 July 1986. Horizontal bars, times during which several individual samples were taken; vertical bars, variation of isoprene throughout the time.

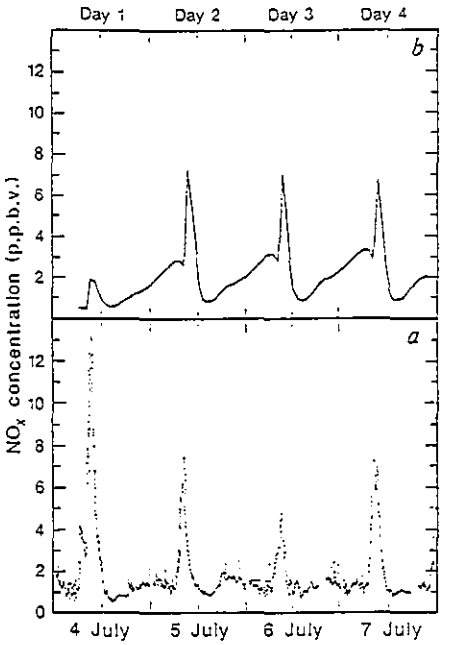

Fig. 3 *a*, Observed variation of the NO_x mixing ratio at Scotia for 4–7 July; 1986; *b*, the variation of the NO_x mixing ratio during a 4-day period as calculated by the model for the emission model described in the text.

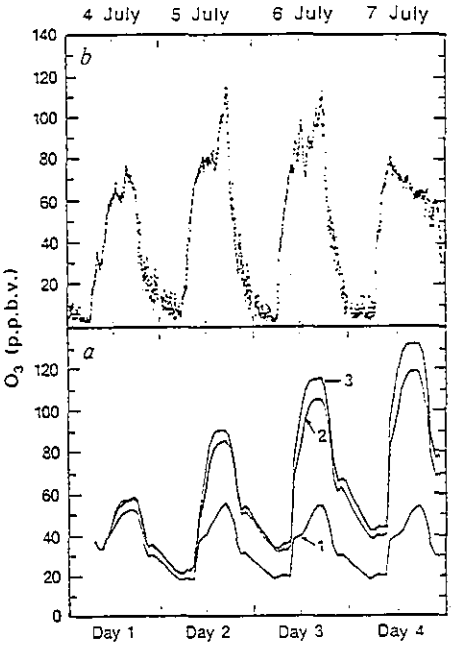

Fig. 4 *a*, Model-calculated variation of the O_3 mixing ratio during a 4-day period for the following models: 1, CO, CH_4 oxidation only; 2, additional isoprene emission; 3, additional isoprene and anthropogenic NMHC emission. *b*, Observed variation of the O_3 mixing ratio at Scotia, 4–7 July 1986.

Figure 4*a* shows the predicted ozone variation for a 4-day period at a height of 5 m for the NO_x emission rate and three models: only CO and CH_4, with isoprene, and with anthropogenic NMHCs. The model that includes all the hydrocarbon emissions simulates the observed peak ozone concentrations well except for 7 July. The decline in O_3 observed on 7 July may indicate an approaching cold front and change of air masses at the site. This effect needs to be investigated in more detail. If no hydrocarbons are emitted and only CO and CH_4 oxidation are considered in the model (Fig. 4*a*, curve 1), the daytime maximum ozone values are ~55 p.p.b.v. When isoprene emission is added (Fig. 4*a*, curve 2), the concentrations of HO_2 and organic peroxy radicals are substantially increased, resulting in a strong build-up of ozone during the 4-day period. In this context we note that carbonyl compounds such as methylvinylketone, methacrolein and formaldehyde are major intermediates in the production of HO_2 and organic peroxy radicals from isoprene. These intermediates and other byproducts such as PAN, H_2O_2 and organic peroxides are increased substantially due to the oxidation of isoprene[22]. If there is an efficient heterogeneous removal of these intermediates, the build-up of peroxy radicals and thus ozone would be significantly curtailed.

Additional inclusion of the emission of anthropogenic hydrocarbons (Fig. 4*a*, curve 3) shows only a small additional increase in the ozone production in these conditions. The system is in a strongly nonlinear regime where an increase of the hydrocarbon emission rate does not lead to a corresponding increase in the ozone production rate. Consequently, the model evaluation of the impact of natural NMHCs depends on the way the question is posed. For example, in a calculation that includes first the emission of anthropogenic NMHCs and then the addition of isoprene, most of the ozone increase (~70%) is due to anthropogenic NMHCs. Many previous studies that considered only this model may have therefore underestimated the contribution of natural NMHCs to rural ozone formation.

The comparison of model prediction and observation indicates that the oxidation of NO_x, which is mainly of anthropogenic origin, in the presence of naturally emitted isoprene, at levels observed at this rural site, can lead to high ozone concentrations during a stagnant high-pressure period. If high ozone in rural areas is of concern, a reduction of the emission of anthropogenic hydrocarbons will probably not reduce the ozone formation substantially in rural air. Consideration has to be given to a reduction of the anthropogenic NO_x emissions.

Finally it is interesting to note that, in the absence of anthropogenic NO_x emissions, isoprene contributes little to ozone formation. Model calculations that assume only a biogenic surface emission of NO_x with a flux of $2\times10^{14}\,m^{-2}\,s^{-1}$ (ref. 25) indicate that isoprene has little effect on the production of ozone and even can lead to a slight reduction in O_3. The conversion of NO_x to PAN and possibly other organic nitrates in the photo-oxidation of isoprene plays a critical part in moderating the PBL photochemistry[26].

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1. Zimmerman, P. R. *EPA Rep. No.* 904/9-77-028 (US EPA, 1979).
2. Lamb, B., Guenther, A., Gay, D. & Westberg, H. *Atmos. Envir.* 21, 1695–1705 (1987).
3. Demerjian, K. L., Kerr, J. A. & Calvert, J. G. *Adv. envir. Sci. Technol.* 4, 1–262 (1974).
4. Graedel, T. E. *Rev. Geophys. Space Phys.* 17, 937–946 (1979).
5. Dimitriades, B. *J. Air Pollut. Control. Ass.* 31, 229–235 (1981).
6. Environmental Protection Agency *Investigation of Rural Oxidant Levels as related to Urban Hydrocarbon Control Strategies* Rep. No. 450/3-75-036 (1975).
7. Heck, W. W. *et al. J. Air Pollut. Control Ass.* 34, 729–735 (1984).
8. Wang, D., Bormann, F. H. & Karnosky, D. F. *Envir. Sci. Technol.* 20, 1122–1125 (1986).
9. Skärby, L. & Selldén, G. *Ambio* 13, 68–72 (1984).
10. Lonneman, W. A., Seila, R. L. & Bufalini, J. J. *Envir. Sci. Technol.* 12, 459–463 (1978).
11. Sandberg, J. S., Basso, M. J. & Okin, B. A. *Science* 200, 1051–1054 (1978).
12. Arnts, R. R. & Meeks, S. A. *Atmos. Envir.* 15, 1643–1651 (1981).
13. Isaksen, I. A., Hov, Ø & Hesvedt, E. *Envir. Sci. Technol.* 12, 1279–1284 (1978).
14. Lurmann, F. W., Lloyd, A. C. & Nitta, B. *Atmos. Envir.* 17, 1951–1963 (1983).
15. Lurmann, F. W., Nitta, B., Ganesan, K. & Lloyd, A. C. *Atmos. Envir.* 18, 1133–1143 (1984).
16. Altshuller, A. P. *Amos. Envir.* 17, 2131–2165 (1983).
17. Fahey, D. W. *et al. J. geophys. Res.* 91, 9781–9793 (1986).
18. Vukovich, F. M., Bach, W. D. Jr, Grissman, B. W. & King, W. J. *Atmos. Envir.* 11, 967–984 (1977).
19. Guichert, R. & van Dop, H. *Atmos. Envir.* 11, 145–155 (1977).
20. Lamb, B., Westberg, H., Allwine, G. & Quarles, T. *J. geophys. Res.* 90, 2380–2390 (1985).
21. Sexton, K. & Westberg, H. *Atmos. Envir.* 18, 1125–1132 (1984).
22. Trainer, M. *et al. J. geophys. Res.* (in the press).
23. Hov, Ø, Schjoldager, J. & Wathne, B. M. *J. geophys. Res.* 88, 10679–10688 (1983).
24. National Acid Precipitation Assessment Program *Second Annual Acid Deposition Emission Inventory Symposium* EPA Rep. No. 600/9-86-010 (1986).
25. Williams, E. J., Parrish, D. D., Buhr, M. P., Fehsenfeld, F. C. & Fall, R. *Eos Trans. AGU* 67, 892 (1986).
26. Jacob, D. J. & Wofsy, S. C. *J. geophys. Res.* (in the press).