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B. Bonsang, M. Kanakidou, G. Lambert. NON METHANE HYDROCARBONS CHEMISTRY IN THE ATMOSPHERE OF AN EQUATORIAL FOREST' A CASE OF INDIRECT PHOTOCHEMICAL PRODUCTION OF OH RADICALS. *Geophysical Research Letters*, 1987, 14 (12), pp.1250-1253. 10.1029/gl014i012p01250 . hal-03545743

HAL Id: hal-03545743

<https://hal.science/hal-03545743>

Submitted on 27 Jan 2022

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NON METHANE HYDROCARBONS CHEMISTRY IN THE ATMOSPHERE OF AN EQUATORIAL FOREST:
A CASE OF INDIRECT PHOTOCHEMICAL PRODUCTION OF OH RADICALS.

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Abstract. An experiment was conducted in the Guyana forest in March 1985, during which $C_2 - C_6$ non methane hydrocarbons (NMHC) were measured in the air, together with CO_2 and its associated ^{13}C isotopic composition. Owing to the very high atmospheric stability, strong vertical concentration gradients were observed close to the soil surface. Simple assumptions allow showing that NMHC are mainly destroyed by OH radicals whose concentration seems to be surprisingly high, around 1×10^7 radicals cm^{-3} . An indirect photochemical production of these radicals is proposed.

On the other hand, the fluxes of the different NMHC emitted from the litter were found to be small, in the range of 10^{-7} to 10^{-6} g of carbon per hour and per m^2 .

Introduction

Although tropical forests comprise more than 50% of the continental biomass, their contribution to atmospheric trace gases budgets is poorly documented. In this respect, one problem relates to the strengths of sources and sinks associated with chemical species. More particularly we should be able to distinguish the exchanges between the atmospheric boundary layer and the top of the canopy from the emissions or absorptions by the litter. Another problem is to model chemical reactions that occur under the canopy i.e. that area screened from solar light. As a first step, an experiment was conducted in the Guyana forest in March 1985, during which $C_2 - C_6$ non methane hydrocarbons (NMHC) were measured in the air, together with CO_2 and its associated ^{13}C isotopic composition.

Sampling and measurements

Air samples were collected in 6 liter evacuated stainless steel canisters fitted with "NUPRO" bellow valves. For the NMHC, the sample analysis was performed in the laboratory by gas chromatography, using a micro-packed column of n-octane on porasil C, and a FID detector, according to a technique previously described [Zimmerman, 1977; Mindrup, 1978; Bonsang and Lambert, 1985]. Unfortunately this method did not effectively separate isomers of butene and pentene, and therefore air samples were also analysed on a Al_2O_3/KCl Porous Layer Open Tubular Capillary Column (Chrompack). As previous work has shown, storage efficiency of $C_2 - C_6$ NMHC in stainless steel canisters over a few weeks does not result in significant losses [Bonsang et al., 1986].

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Paper number 7L8022.

0094-8276/87/007L-8022\$03.00

CO_2 concentrations were measured in the same samples according to a technique described elsewhere [Komhyr et al., 1985; Bonsang et al., 1986].

Samples were collected, at twilight (6:30 p.m.), in the equatorial forest of French Guyana ($5.5^\circ N - 53^\circ W$), beneath the canopy at two distinct levels: 2cm and 120cm above the litter.

The NMHC are listed in Table 1. We note that acetylene was not detectable (< 0.020 ppbv), indicating a lack of anthropogenic influence and local contamination. On the opposite, the high CO_2 concentrations of the order of 445 ppm at soil level and 450 ppm at 1m height indicate strong natural biological sources. This point is supported by unusual isotopic $^{13}C/^{12}C$ compositions of -11.88% near the ground and -10.66% at 120 cm (P. Monfray; personal communication).

Interpretation

For the NMHC, we can distinguish the usual low reactive species (ethane and propane) which do not show any significant vertical concentration gradient, from the other species for which vertical concentration gradients were observed within the first metre above the soil surface. Moreover, these gradients were different for the different species: the concentration differences increased with their carbon number and their degree of unsaturation, i.e. their chemical reactivity.

Therefore, it is impossible to account for these experimental results by only a ventilation of the source into the atmosphere. In such a case, the concentration ratios between the two levels should be obviously identical for all the species. In contrast, the interpretation must combine together vertical slow eddy diffusion and chemistry.

Assuming that NMHC are principally removed through a first order chemical reaction, the hypothesis of a continuous soil production followed by a vertical diffusion leads, for short lived species, to a distribution of their mixing ratios versus height :

$$\partial C_z / \partial t = \partial / \partial z (K_z \cdot \partial C_z / \partial z) - \lambda C_z$$

where C_z is the mixing ratio of a given species at height z , K_z is the vertical diffusivity coefficient and λ the first order constant for chemical decay.

In steady state conditions, and assuming K_z constant within the considered altitude range, we have between z and the ground level for every NMHC (except ethane and propane):

$$C_z = C_0 \exp[(-\sqrt{\lambda/K_z})(z)] \quad \text{or:}$$

$$(\ln C_0 - \ln C_z) / z = \sqrt{\lambda/K_z} = \sqrt{k_x \cdot [X]/K_z} \quad (1)$$

Where $[X]$ is the concentration of the chemical

TABLE 1 : NMHC mixing ratios in the Guyana Forest.

Specie	N°	C _z level 1	C _z level 2	Flux from the litter in 10 ⁻⁸ g C m ⁻² h ⁻¹	Lifetime (hours)
C ₂ H ₂		< 0.020	<0.020	---	---
C ₂ H ₆		1.410	1.430	---	---
C ₃ H ₈		0.260	0.280	---	---
n C ₄ H ₁₀	(1)	0.095	0.070	4.5	14.8
isoC ₄ H ₁₀		< 0.020	<0.020	---	---
n C ₅ H ₁₂	(2)	0.106	0.064	9.5	5.3
isoC ₅ H ₁₂		0.053	<0.020	---	---
n C ₆ H ₁₄		0.030	<0.020	---	---
C ₂ H ₄	(3)	1.595	0.780	73	2.75
C ₃ H ₆	(4)	0.577	0.238	46	1.70
1-C ₄ H ₈	(5)	0.048	0.020	5	1.74
iso-C ₄ H ₈	(6)	0.134	0.044	16	1.10
1-C ₅ H ₁₀	(7)	0.392	0.086	69	0.60
1-C ₆ H ₁₂	(8)	0.083	0.014	19	0.42

Mixing ratios of aliphatic NMHC measured in the Guyana forest (in ppbv) at level 1 (soil) and level 2 (120 cm. height), and corresponding fluxes (in 10⁻⁸ g of carbon.m⁻².h⁻¹) and calculated lifetimes (in hours). Calculations assume $K_z = 3 \text{ cm}^2.\text{s}^{-1}$, which corresponds to a OH concentration of 10⁷ radicals cm⁻³.

species X, assumed to be that which reacts with the considered NMHC, and k_x is the corresponding first order kinetic constant.

To progress it is now necessary to examine what chemical species could be involved in the NMHC destruction.

It is well known that oxidation by OH radicals is the preponderant sink for NMHC, although alkenes also react, to a lower extent, with ozone. Furthermore, NO₃ radicals created through the reaction: $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$ can in some cases play a significant role in alkene oxidation reactions, particularly at night or when their destruction by photochemical processes is inefficient [Atkinson et al., 1984^{a,b,c}; Atkinson and Aschmann, 1984].

Therefore, under a canopy, where there is reduced sunlight, the contribution of OH oxidation is believed to be decreased, whereas that of ozone and NO₃ radicals could be comparatively enhanced. As the kinetic constants k_{O_3} and k_{NO_3} covary with the k_{OH} rate constant [Atkinson, 1985], the vertical gradients of NMHC observed could be accounted for by oxidation by any of these species.

However, it is possible to show that only OH radicals play a significant role in NMHC oxidation. In effect the ratios $[X]/K_z$, calculated for OH, O₃, and NO₃ from the vertical concentrations gradients, by using equation (1), are plotted in figure 1 versus the kinetic constants k_x . Clearly, the $[X]/K_z$ values obtained are scattered over an order of magnitude for ozone and over 3 orders of magnitude for NO₃ radicals. The only consistent result is obtained with OH radicals for which the ratio $[\text{OH}]/K_z$ is equal to $3.4 \pm 1.6 \times 10^6$ molecule. cm⁻⁵.s.

As samples were collected under very low wind conditions, the K_z value cannot be deduced from micrometeorological parameters. However, using Radon-220 as a tracer of ground emissions, Druil-

het [1966] has found that, under the canopy in conditions of high stability, K_z is in the range of 1 to 10 cm².s⁻¹. A figure of 3 cm².s⁻¹ will be utilized in the following discussion. Such a diffusivity coefficient would lead to a concentration of 1×10^7 OH radicals.cm⁻³ which will be discussed further. This figure leads to atmospheric lifetimes (1/λ, deduced from equation (1)) lower than half a day for those species for which a vertical gradient was observed (see table 1). As the dynamics of air mass exchanges in the equatorial forest follows a diurnal cycle [Clairac, 1986], a steady state can only be established for species with lifetimes of half a day or less.

The conditions of our experiment correspond to a case where the classical Fick's law of diffusion can be applied. Thus, the production F of an NMHC per unit area is given by:

$$F = -K_z (\partial C_z / \partial z).$$

The fluxes are therefore proportional to K_z . The values given in Table 1 correspond to a figure of 3 cm².s⁻¹ for K_z . These data show that alkenes are the major contributor (94%) to the C₂-C₅ NMHC fluxes in forest with values approaching 2.5×10^{-6} gC m⁻².h⁻¹. This flux is small relative to the figures published for continents and oceans [Ehhalt and Rudolph, 1984; Bonsang and Lambert, 1985; Blake and Rowland, 1986; Bonsang et al., 1986]. Ethylene appears to be the major NMHC released from the litter. The degradation of organic matter by microbial activity, is the likely mechanism responsible for these emissions according to Van Cleemput et al. [1982], and Sawada and Totsuka [1986]. The "signature" of this source is comparable to that of other natural processes occurring in surface seawater [Lamontagne et al., 1973; Bonsang et al., 1986], but this is probably different from that of trees

Fig. 1 : Oxidizer concentration to diffusivity ratios calculated for different NMHC in the case of OH, O_3 , and NO_3 . See caption Table 1 for the name of the species. K_{OH} from Atkinson et al. [1979] and Atkinson and Aschmann [1984]; K_{O_3} from Herron and Huie [1974], Atkinson et al. [1984^b] and deduced from Atkinson [1985]; K_{NO_3} from Atkinson et al. [1984^{a,b,c}] and deduced from Atkinson [1985].

emissions characterized by a preponderance of isoprene and terpenes [Greenberg and Zimmerman, 1984; Lamb et al., 1985].

Discussion

Only one set of samples was obtained and measured in this experiment. However, owing to the consistency of all the above mentioned results on NMHC vertical gradients, CO_2 concentrations and isotopic compositions, there is a compelling evidence that the OH radicals concentration was surprisingly high under the canopy of this equatorial forest. In effect, the figure of $3 \text{ cm}^2 \text{ s}^{-1}$, here adopted for K_z , corresponds to 1×10^7 OH radicals per cm^3 , which is close to the highest values mentioned for the free troposphere [Hewitt and Harrison, 1985; Crutzen, 1982].

Though, this OH concentration is consistent with the existence of vertical gradients within 1 metre. It is important to note that the smallest acceptable value of K_z is the molecular diffusivity of gases in air i.e. $0.1 \text{ cm}^2 \text{ s}^{-1}$ and therefore the OH concentration could by no way be smaller than 3×10^5 OH radicals per cm^3 .

One fundamental problem relates to how OH radicals can be generated in conditions of low

photochemistry, where the usual process for OH production through the photolysis of ozone followed by the reaction of oxygen radicals with water vapour is unimportant. An indirect mechanism of OH production from NO and HO_2 radicals (through the reaction: $NO + HO_2 \rightarrow NO_2 + OH$) has been proposed by Hard et al. [1986] to explain the presence of OH radicals at night in urban areas. In the case of the forest, model calculations show that, even at night, the air above the canopy should be very rich in HO_2 radicals produced by the oxidation of organic species: isoprene, terpenes, aldehydes, CH_4 [Lopez et al., 1987]. A value of $7 \times 10^7 \text{ } HO_2 \text{ rad. cm}^{-3}$ deduced from the diurnal variations given by Logan et al. [1981] at $15^\circ N$, and Lopez et al. [1987] can be used here as the lowest acceptable figure. On the other hand it has been shown by Kaplan et al. [1986] and Kirchoff et al. [1986] that equatorial forest soil is an important source of nitric oxide (NO) which accumulates below the canopy during the persistence of the inversion layer. Typical concentrations reported by these authors are of the order of 10 ppbv ($25 \times 10^{10} \text{ molecules cm}^{-3}$). Providing that there is an intrusion of tropospheric air beneath the canopy, mixing of NO and HO_2 rich air masses could lead to an indirect OH production at twilight according to the above reaction with a kinetic constant of $8 \times 10^{-12} \text{ cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}$ [Hard et al., 1986]. Assuming that the major sinks for OH radicals are the oxidation of CH_4 , CO, and C_5H_8 (isoprene) whose mixing ratios are respectively of 1.7 ppmv (this work), 80 ppbv and 2.5 ppbv [Gregory et al., 1986], a classical calculation with the kinetic constants generally admitted for these consumption processes [Logan et al., 1981; Atkinson, 1985] leads to a figure of $2 \times 10^7 \text{ OH rad. cm}^{-3}$ consistent with our observations.

In conclusion, the measurements reported in this study, despite their small number, strongly suggest the existence, in the Guyana tropical forest, of an indirect photochemical process of OH radicals production, which could be important in similar areas.

Acknowledgements. This research was supported by CNRS, CEA, PIREN and Ministère de l'Environnement. The authors are grateful to Dr. P. Blanc from Laboratoire de Botanique Tropicale (University of Paris VI) for samplings in Guyana forest and to P. Monfray (CFR) for CO_2 measurements. They also thank the Greek State Organisation for Scholarship for financial support of M. Kanakidou. CFR contribution N° 889.

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(Received June 30, 1987;
accepted October 8, 1987.)