Tellus (1989), *41B*, 474–477

SHORT CONTRIBUTION

High HONO atmospheric concentrations during vegetation burning in the tropical savannah

By ALBERTO RONDON[1] and EUGENIO SANHUEZA, *Instituto Venezolano de Investigaciones Cientificas (IVIC), Apartado 21827, Caracas 1020-A, Venezuela*

(Manuscript received 15 June 1988; in final form 29 August 1988)

ABSTRACT

Using a denuder technique, high HONO concentrations (up to 1 ppb, for 12 h average) were observed at night in the Venezuelan savannah region during the vegetation burning period. The levels in the rainy season were always below 0.05 ppb. It is likely that HONO is directly emitted from the fires.

1. Introduction

The hydroxyl radical plays an important rôle in the destruction and production of many atmospheric gases. In clean atmospheres, the OH radical is mainly produced by the following reactions:

$$O_3 + h\nu(\lambda \lesssim 310 \text{ nm}) \longrightarrow O(^1D) + O_2(^1\Delta g) \quad (1)$$

$$O(^1D) + H_2O \longrightarrow 2OH. \quad (2)$$

The photolysis of HONO also produces OH radical:

$$HONO + h\nu(\lambda \sim 290\text{–}400 \text{ nm}) \longrightarrow OH + NO. \quad (3)$$

During daylight hours, HONO is formed largely by the reaction:

$$OH + NO \xrightarrow{M} HONO. \quad (4)$$

Reactions (3) and (4) lead to steady-state concentration of HONO and no net production of OH radicals. However, other sources of HONO will result in a net production of OH radicals.

An increase in HONO concentration during the night has been observed in polluted urban atmospheres (Perner and Platt, 1979; Platt et al., 1980; Harris et al., 1982; Sjödin and Ferm, 1985). The cause of this night-time buildup of HONO is presently not well established. According to Pitts et al. (1984b), it appears that a combination of heterogeneous formation via the hydrolysis of NO_2

$$2NO_2 + H_2O \xrightarrow{het} HONO + HNO_3 \quad (5)$$

and direct HONO emission are responsible for the formation of HONO at night. Direct detection of gaseous nitrous acid in exhaust emissions from light duty motor vehicles has been reported (Pitts et al., 1984a).

In this paper, we report a significant increase of the atmospheric concentrations of HONO during the vegetation burning season in the tropical savannah.

2. Field measurements and results

The sampling was made from April to December 1987 at Chaguaramas (9°23′N, 66°15′W), Guarico State, in the savannah region of Venezuela. The HONO was collected by the sodium carbonate denuder sampling technique, described in detail by Ferm and Sjödin (1985). The annular denuders used were similar to the

[1] Present address: Department of Meteorology, University of Stockholm, 10691 Stockholm, Sweden.

one designed by Possanzini et al. (1983), and were operated with a flow rate of 20 l/min. In order to establish the efficiency of our system, in several runs, two denuders were connected in series. The analysis of the extract was made spectrophotometrically using a diazotization reaction.

Our sampling site was located in an area protected from fires and therefore we were always out of dense plumes. We believe that we sampled relatively well-mixed air.

Table 1 summarizes the results. Most of the samples are for 24-h periods, however, some separate day and night measurements were also made. The diffusion coefficient was calculated following the procedure given by Possanzini et al. (1983).

3. Discussion

Good efficiencies were obtained when two

Table 1. *Nitrous acid atmospheric concentrations at Chaguaramas, during 1987*

Sampling period	HONO (μg)		HONO (ppb)	D ($cm^2\ s^{-1}$)
	1st denuder	2nd denuder		
25 April, 24 h	26.5	—	0.61[a]	—
26 April, 24 h	12.5	—	0.35[a]	—
27 April, 24 h	26.7	2.5	0.65	0.152
28 April, 24 h	16.9	—	0.45[a]	—
06 May, 12 h N	26.7	6.8	1.07	0.115
07 May, 12 h N	21.7	5.8	0.91	0.101
08 May, 12 h D	1.4	<0.5	0.05	—
08 May, 12 h N	17.2	3.2	0.70	0.142
09 May, 17 h[b]	9.5	1.8	0.24	0.147
17 June, 21 h[b]	8.2	0.5	0.21	0.171
18 June, 21 h[b]	0.9	<0.5	0.03	
08 July, 24 h	0.6	—	0.01	—
09 July, 24 h	1.0	—	0.02	—
13 July, 11 h N	<0.5	<0.5	<0.02	—
14 July, 12 h D	0.5	<0.5	0.01	—
14 July, 09 h N	0.9	<0.5	0.05	—
15 July, 10 h D	0.6	<0.5	0.03	—
15 July, 12 h N	0.5	<0.5	0.02	—
17 July, 24 h	0.5	—	0.01	—
18 July, 24 h	<0.5	—	<0.01	—
20 July, 48 h	<0.5	—	<0.01	—
05 August, 24 h	0.6	—	0.01	—
06 August, 24 h	0.5	—	0.02	—
08 August, 10 h D	<0.5	<0.5	<0.02	—
08 August, 12 h N	0.5	<0.5	0.01	—
09 August, 10 h D	<0.5	—	<0.01	—
10 August, 24 h	<0.5	—	<0.01	—
15 October, 24 h	<0.5	<0.5	<0.01	—
16 October, 24 h	0.7	<0.5	0.01	—
17 October, 24 h	<0.5	—	<0.01	—
18 October, 24 h	<0.5	—	<0.01	—
10 December, 24 h	<0.5	—	<0.01	—
11 December, 24 h	0.5	—	0.01	—
12 December, 24 h	1.8	<0.5	0.04	—
13 December, 24 h	0.5	<0.5	0.01	—

[a] Corrected for an efficiency of 80%.
[b] 12-h daytime.

denuders were connected in series (Table 1) showing that we were mainly collecting HONO (Ferm and Sjödin, 1985; De Santis and Di Palo, 1985). The diffusion coefficient is 0.139 ± 0.028 cm^2 s^{-1} ($n = 6$), in good agreement with the values of 0.125 obtained near Rome (De Santis et al., 1985), and 0.13 found in Gothenburg, Sweden (Ferm and Sjödin, 1985).

The results show that during the vegetation burning period (April, May and to some extent June), much higher concentrations of HONO were observed compared with the levels measured in the rainy season (July to October) and early dry season (December). Therefore, HONO must be emitted directly from fires and/or formed by reaction in the atmosphere from precursors emitted during the burning. Other studies by our group (Sanhueza et al., 1987; Sanhueza and Rondón, 1988) have also shown that higher levels of suspended particles are produced in the Venezuelan savannah region during the vegetation burning period.

The results also show that during the period of high HONO, the night-time average concentrations were much higher (up to 1 ppb) than daytime concentrations. As expected, HONO photolyzes with daylight and accumulates in the night. Obviously, the night-time HONO concentration build-up is also favored by a shallower nocturnal mixing height. The HONO levels should increase throughout the night and concentrations much higher than 1 ppb should be produced at dawn, comparable to what happens in the heavily polluted Los Angeles atmosphere (Harris et al., 1982).

Unfortunately, no measurements of NO_2 were made during the heavy burning period (April–June). However, in the early burning period (late February), the NO_2 levels were "relatively" low with concentration around 1 ppb and 2.5 ppb for day and night, respectively (Johansson et al., 1988). These concentrations are much lower (10 to 50 times) than the NO_2 reported in polluted atmosphere where nocturnal increase of HONO have been observed (Perner and Platt, 1979; Harris et al., 1982; Sjödin and Ferm, 1985).

It is important to point out that in the woodland-savannah, where the measurements were made, large NO emission from soils after heavy rain produce high NO_2 atmospheric concentrations (up to 25 ppb) in the night (Johansson and Sanhueza, 1988). However, during the rainy season, high HONO concentrations were never observed; in the course of 14–17 July, it rained every day with a total rainfall of 35 mm.

From the discussion above, it seems likely that HONO is directly emitted by biomass burning. Field and/or laboratory experiments to evaluate this source are needed. It is important to indicate that because of higher wind velocities, the fires are widespread during day-time, and consequently larger HONO emissions (compared with night-time) should occur in the day.

Compared with temperate regions, larger amounts of OH radical are produced in the tropics (Crutzen, 1987). If HONO is either emitted or formed in the atmosphere, its photolysis will increase the production of OH in the savannah region during burning periods, magnifying the reactivity of the tropical atmosphere.

REFERENCES

Crutzen, P. J. 1987. Role of the tropics in atmospheric chemistry. In: *The geophysiology of amazonia, vegetation climate interactions* (ed. R. E. Dickinson). Chichester: John Wiley and Sons, 107–131.

De Santis, F. and Di Palo, V. 1985. Determination of atmospheric HNO_3, HNO_2, HCl and SO_2 by the annular denuder system. *Proc. of Workshop on Measurement of Atmospheric Acidity* (Commission of the European Communities). Mohtelibretti, Italy, 14–19.

De Santis, F., Febo, A., Perrino, C., Possanzini, M. and Liberti, A. 1985. Simultaneous measurements of nitric acid, nitrous acid, hydrogen chloride and sulfur dioxide in air by means of high-efficiency annular denuders. *Proc. E.C.E. Workshop on Advancements in Air Pollution Monitoring Equipment and Procedures* (Federal Ministry of the Interior). Freiburg, FRG, 68–75.

Ferm, M. and Sjödin, A. 1985. A sodium carbonate coated denuder for determination of nitrous acid in the atmosphere. *Atmos. Environ. 19*, 979–983.

Harris, G. W., Carter, W. P. L., Winer, A. M., Pitts, J. N. Jr., Platt, U. and Perner, D. 1982. Observations of nitrous acid in the Los Angeles atmosphere and implications for predictions of ozone-precursor relationships. *Environ. Sci. Technol. 16*, 414–419.

Johansson, C., Rodhe, H. and Sanhueza, E. 1988. Emission of NO in a tropical savanna and a cloud forest during the dry season. *J. Geophys. Res. 93*, 7180–7192.

Johansson, C. and Sanhueza, E. 1988. Emission of NO from savannah soils during rainy season. *J. Geophys. Res.*, in press.

Perner, D. and Platt, U. 1979. Detection of nitrous acid in the atmosphere by differential optical absorption. *Geophys. Res. Lett. 6*, 917–920.

Pitts, J. N. Jr., Biermann, H. W., Winer, A. M. and Tuazon, E. C. 1984a. Spectroscopic identification and measurements of gaseous nitrous acid in dilute auto exhaust. *Atmos. Environ. 18*, 847–854.

Pitts, J. N. Jr., Sanhueza, E., Atkinson, R., Carter, W. P. L., Winer, A. M., Harris, G. W. and Plum, C. N. 1984b. An investigation of the dark formation of nitrous acid in environmental chambers. *Inter. J. Chem. Kinet. 16*, 919–939.

Platt, U., Perner, D., Harris, G. W., Winer, A. M. and Pitts, J. N. Jr. 1980. Observations of nitrous acid in an urban atmosphere by differential optical absorption. *Nature 285*, 312–314.

Possanzini, M., Febo, A. and Liberti, A. 1983. New design of a high-performance denuder for the sampling of atmosphere pollutants. *Atmos. Environ. 17*, 2605–2610.

Sanhueza, E. and Rondón, A. 1988. Particle size distribution of inorganic water soluble ions in the Venezuelan savannah atmosphere during burning and non-burning periods. *J. Atmos. Chem.*, in press.

Sanhueza, E., Rondón, A. and Romero, J. 1987. Airborne particles in the Venezuelan savannah during burning and non-burning periods. *Atmos. Environ. 21*, 2227–2331.

Sjödin, A. and Ferm, M. 1985. Measurements of nitrous acid in an urban area. *Atmos. Environ. 19*, 985–992.