NITROGEN OXIDES FROM BURNING FOREST FUELS EXAMINED BY THERMOGRAVIMETRY AND EVOLVED GAS ANALYSIS

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ABSTRACT

Twelve forest fuels that varied widely in nitrogen content were burned in a thermo-gravimetric system, and nitrogen oxide production was analyzed by chemiluminescence. The effects of fuel nitrogen concentration, available oxygen, flow rate, and heating rate on nitrogen oxide production were examined.

Results show that fuel nitrogen is an important source of nitrogen oxides from the low-temperature ($<1000°C$) burning of forest fuels. The production of nitrogen oxides increases with, and is highly dependent on, fuel nitrogen content. Fuel nitrogen is significant at the 1% level for the production of both NO and NO_2. Conversion of fuel-bound nitrogen to NO, can occur readily in oxygen-depleted air.

INTRODUCTION

The Clean Air Act of 1970 identified nitrogen dioxide as one of the six pollutants that must be quantified in all source assessments of combustion. Nitrogen combines with oxygen to form several stable oxides, among which nitric oxide (NO) and nitrogen dioxide (NO,) have been identified as important pollutants in the lower atmosphere. Their participation in a series of chemical reactions in the photochemical smog cycle has led to their combined designation as NO,.

The Smoke Management Research and Development Program of the U.S. Forest Service is chartered to assess the impact of forest fire smoke on air quality. Foresters prescribe controlled bums for a variety of purposes including reduction of wildfire hazards, removal of logging debris, and Preparation of sites for reforestation. When planning a prescription fire, the forest manager must carefully consider the environmental impact of smoke. This has been judged primarily on the basis of visibility problems caused by suspended particulate matter. Less attention has been given to the gaseous Products of combustion (especially nitrogen oxides). This study is an attempt to identify the role of fuel-bound nitrogen in the production of NO, from the low-temperature combustion of forest fuels. It is a first step toward including NO, in broadly-based smoke-management strategies.

BACKGROUND

Because temperatures in prescribed forest burns are relatively low ($<800°C$) [1], some authors in the early nineteen-seventies predicted that NO, production from these fires would be negligible [2,3]. DeBell and Ralston [4] concluded that 99% of the nitrogen from forest fuels was released as nitrogen gas (N_2) and, therefore, was not returned to the soil as nutrients in precipitation. In a recent experiment in which coal with a low nitrogen content ($0.5-2.0\%$) was burned at low temperature, results strongly suggested that fuel nitrogen can produce environmentally significant quantities of nitrogen oxides [5].

Data on NO, production from forest fuel burning are scant and inconclusive. The most recent Environmental Protection Agency compilation of Air Pollution Emission Factors [6] assigns 2 g kg^{-1} for NO, from forest wildfires. That factor can be traced to the 1967 work of Gerstle and Kemnitz [7] on laboratory burning of landscape refuse (lawn clippings, leaves, and tree branches). More recently, Benner [8] reported NO, emission factors in the range 4-10 g kg-' from burning pine needles in small chambers.

Nitric oxide (NO) and nitrogen dioxide (NO,) are the major oxides of nitrogen emitted from combustion processes. NO is usually the initial product, and NO_2 is formed from it.

Combustion can form NO in three ways [9]:

reactions of atmospheric nitrogen (N,) with oxygen at high temperatures (thermal NO);

reactions of fuel-derived radicals with atmospheric nitrogen which ultimately lead to NO (prompt NO);

the oxidation of fuel nitrogen compounds at relatively low temperatures (fuel NO).

Thermal NO production occurs at temperatures above 1000 K, is strongly and non-linearly temperature dependent, and peaks around $1800-2000$ K [10]. When conditions are ideal, concentrations of several thousand p.p.m. of NO are often produced. Conditions suitable for formation of prompt NO are not well established.

Fuel nitrogen has been shown to be the major source of NO, emissions from the combustion of oil [11] and coal-derived liquid fuels [12]. In a recent study by Pershing and Wendt [13], pulverized coal containing $1-2\%$ nitrogen was burned in air and in mixtures of oxygen and argon. Results show conclusively that fuel nitrogen is the dominant source ($>80\%$) of NO, emissions during low-temperature pulverized coal combustion.

Plee [14], working with NH_3-doped gaseous fuels and flat flames, suggests the following general mechanism for fuel NO formation

$$\text{fuel } N(NH_3) \rightarrow NH_i \rightarrow HCN \rightleftharpoons CN \underset{N_2}{\overset{NO}{\diagdown}} \qquad (1)$$
$$\downarrow$$
$$\dot{N}O$$
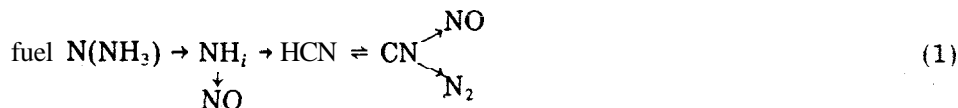
Thus, it has been found that fuel nitrogen is the dominant source of NO from low-temperature flame combustion. Atmospheric nitrogen is the dominant source at temperatures above 1000 K.

TABLE 1

Fuel components selected for NO, study

Fuel	Fuel-bound nitrogen (W)
Slash pine wood	0.20
Slash pine bark	0.28
Slash pine limbs (< 7 mm)	0.31
Slash pine needles (dry)	0.50
Slash pine needles (green)	0.80
Saw palmetto foliage (green)	1.10
Pine needle standard (NBS) [a]	1.20
Saw palmetto foliage (dry)	1.20
Loblolly pine needles (green)	1.23
Gallberry foliage (green)	1.23
Organic soil	1.49
Orchard leaves standard (NBS) [a]	2.66

[a] National Bureau of Standards.

METHOD

Survey experiment

In **an initial** survey, the magnitude of NO, production from the low-temperature burning was measured for 12 fuels (Table 1). These fuels were selected to provide a range of nitrogen contents from 0.2 to more than 2.5%.

AH samples were ground in a Wiley mill to pass through a 60-mesh sieve. All fuel samples were air-dried *to* facilitate grinding. Prior to burning, each fuel was analyzed for total nitrogen by the Kjeldahl method. A 9-mg fuel sample was loaded in the sample pan of a Perkin-Elmer TGS-2 * thermogravimetric (TG) balance, heated to $100°C$, held until dry, and weighed. The furnace was programmed to heat at 40°C min^{-1} to 1000°C and then allowed to **cool** at maximum rate. The ash was weighed at 100°C. The purge gas was air, flowing at 125 cm^3 min^{-1}.

Samples of the gaseous combustion products diluted with purge gas were first filtered through a glass fiber filter and then collected in an aluminized gas collection bag attached to the upper exit port of the glass furnace tube. The gas bag was massaged gently for l-2 min to assure good mixing and analyzed immediately for nitrogen oxides with a Thermoelectron 14D chemiluminescence analyzer (CLA). Rapid analysis was required to prevent sample degradation.

Nitrogen oxides (NO and NO_2) can be routinely measured with a CLA, which employs the gas-phase chemiluminescence reaction of ozone with NO. Major advantages of this technique over some wet chemical methods are a **high-precision selective response** to NO, ability to detect several parts per billion, wide **linear dynamic range,** and rapid response time. The CLA also mea-

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* **Mention of trade names throughout this paper does not constitute endorsement by the U.S. Department of Agriculture.**

TABLE 2

Factors and levels involved in two-level four factor (2^4) unreplicated factorial arrangement

Factors	Levels	
	Low	High
Heating rate (°C min^{-1})	20	80
Flow rate (cm^3 min^{-1})	45	205
Oxygen concentration (%)	2.0	20.0
Fuel nitrogen (%)	0.2	2.66

sures NO_2 by passing a portion of the sample through a molybdenum converter which quantitatively reduces NO_2 to NO. The total NO (i.e., the original NO plus the reduced NO,) is then reacted with ozone, and the chemiluminescence emission is recorded as total oxides of nitrogen (NO,). Electronic subtraction of the NO signal from the NO, signal yields the amount of NO_2 present in the sample.

Interferences are negligible in the detection of NO. However, when the instrument is measuring for *NO,*, some nitrogen-containing compounds other than NO, may reduce to NO. Hence, estimates of NO_2 are too high. In this analysis, use of a low-temperature molybdenum converter in lieu of a high-temperature stainless steel converter minimizes the problem. Furthermore, NO predominates over NO_2 in most combustion processes.

Factorial experiment

This experiment was designed to determine whether nitrogen content of fuel, heating rate, purge rate, and oxygen concentration influence the production of nitrogen oxides. Two levels of each factor were tested in a factorial design (Table 2). The 16 treatments (2^4) were not replicated. Slash pine wood and orchard leaves standard (NBS) were selected for the low- and high-nitrogen content fuels. Nitrogen and oxygen were metered by pressure regulators and needle valves through a mixing tee to obtain selected concentrations and flow rates. Procedures for treating samples were the same as in the survey experiment, except for the listed changes in the levels of factors examined.

The experimental design was completely randomized, and results were evaluated by analysis of variance for fixed effects. The main effects of each factor and all first-order (two-factor) interactions were analyzed. The sums of squares for the third-order and all second-order interactions were pooled and used as an estimate of error.

RESULTS

Survey experiment

As expected, amounts of NO, emission were greatest from the fuels with the highest bound-nitrogen contents and lowest from fuels with the lowest

TABLE 3

Emission factors of nitrogen oxides and % conversion of nitrogen to NO, by heating fuels to 1000°C in air

Fuel	NO_x	NO (g kg^{-1})	NO_2	Conversion to NO, (%)
Slash pine wood	0.40	0.23	0.06	6.1
Slash pine bark	1.54	0.97	0.06	17.1
Slash pine limbs (< 7 mm)	2.44	1.49	0.17	24.3
Slash pine needles (dry)	2.19	1.33	0.15	13.3
Slash pine needles (green)	5.58	3.42	0.36	21.2
Saw palmetto foliage (green)	8.99	5.39	0.76	24.7
Pine needle standard (NBS)	8.12	4.91	0.61	20.6
Saw palmetto foliage (dry)	9.47	5.98	0.34	24.0
Loblolly pine needles (green)	7.01	4.29	0.45	17.3
Gallberry foliage (green)	11.29	6.79	0.93	28.1
Organic soil	20.40	11.58	2.70	41.7
Orchard leaves standard (NBS)	32.52	16.50	7.32	37.2

ᵃ Calculated as NO_2

bound-nitrogen contents. These results are shown in Table 3, in which the weight of NO,, NO, and NO_2 emitted are reported per kilogram of oven-dry fuel weight. In this table, NO, weights are computed as NO,. This is a standard procedure because NO in ambient air eventually converts to NO,. As a result, however, the value shown for NO, in the table is somewhat greater than the sum of NO and NO_2.

Simple linear regressions indicate that nitrogen oxide emissions were closely related to the bound-nitrogen content of the fuel (N_f)

NO = -3.0 + 13.3 N_f *R = 0.96*

NO, = -7.7 + 25.6 N_f *R = 0.95*

NO_2 = -3.0 + 5.3 N_f *R = 0.57.*

The high R values indicate close linear relationships between emission rate and fuel nitrogen content. The relatively low R value for the NO_2 regression is due in part to its determination as a difference between NO, and NO readings. The error in NO_2 measurement, therefore, is the sum of the errors for NO, and NO measurements.

We also computed the percentage of fuel nitrogen that was converted to NO, and called this value the conversion efficiency (E_N). Cursory scanning of the efficiencies shown in the final column of Table 3 indicates that efficiency increased with fuel nitrogen content. Regression analysis tends to confirm this conclusion. However, additional work is needed to better define this relationship.

The ratio of NO to NO_2 was generally as expected. Exceptions were the wood sample, in which experimental error may have been high because nitrogen concentrations were low, and the organic soil and orchard leaves. We have no explanation for the unusually high NO_2 values for organic soil and

orchard leaves. Results reported by Merryman and Levy [15] indicate that these values were probably real and not just artifacts of the CLA.

F-tests show that the influence of fuel nitrogen on NO and NO, emissions was statistically significant at the 1% level. Heating rate was significant at the 5% level. Also appearing as significant effects **at** the 5% level are flow rate on the production of NO, and the first-order interaction, heating rate X fuel nitrogen, on the formation of NO. NO, formed at approximately the same rate whether the purge gas contained 2 or 20% oxygen. This result indicates that conversion of fuel-bound nitrogen can occur readily in oxygen-depleted air.

DISCUSSION AND CONCLUSIONS

The nitrogen content of forest fuels can range from 0.1% in logs and branches to 1 or 2% in needles, leaves, and other foliage [1,16]. If you assume that a composite forest fuel with a mean nitrogen content of 0.5% is burned with only 25% conversion, an NO, emission factor of 4.3 g kg^{-1} would still result. Thus, the significance of fuel nitrogen is apparent when viewed in terms of the current 2 g kg-' figure now used in EPA emission factor reports.

Results of these experiments clearly show that environmentally significant amounts of nitrogen oxides were formed by forest fuels burned in a TG furnace. The NO, emission factors found for slash pine bark, limbs, and dry needles agree with the 2 g kg-' **value** reported by Yamate [3] for lawn clippings, leaves, and tree branches. Green needles of slash and loblolly pines, green gallberry leaves, and both green and dry palmetto fronds produced NO, emission factors in the 4-10 g kg-' range reported by Benner [8] for small-scale pine needle fires.

In the factorial TG experiment, production of nitrogen oxides was primarily dependent on the nitrogen content of the fuel, but heating rate and flow rate of purge gases were also important.

Production of nitrogen oxides by prescription fires in the forest cannot be dismissed as negligible solely on the basis of low combustion temperatures. When the nitrogen content of the fuel is either known or can be readily determined, it should be possible to predict the amount of NO, produced. These predictions, however, will not be reliable for high-intensity fires with massed woody fuels where temperatures above 1400°C have been reported [17,18]. In those cases, monitoring is required because thermal NO may be plentiful.

ACKNOWLEDGEMENTS

REFERENCES

1 L.S. Davis and R.E. Martin, USDA For. Serv. Res. Note SE-148, Southeast. For. Exp. Stn., Asheville NC, 1960.
2 J.A. Hall, USDA For. Serv., Pacific Northwest For. Range Exp. Stn., 1972, 44 pp.
3 G. Yamate, EPA 450/3-73-009, U.S. Environ. Prot. Agency, Office of Air and Water Programs, Office of Air Quality Planning and Stand., Research Triangle Park, NC, 1973.
4 D.S. DeBell and C.W. Ralston, reprinted from Soil Sci. Soc. Am. Proc., 34 (1970) 936.
5 R.A. Vogt and N.M. Laurendeau, J. Air Pollut. Control Assoc., 28 (1978) 60.
6 U.S. Environmental Protection Agency, Office of Air and Waste Manage., Office of Air Quality Plann. and Stand., Research Triangle Park, NC (U.S. Dept. Commerce, National Technical Info. Serv. PB-264-194, unnumbered pages), 1976.
7 R.S. Gerstle and D.A. Kemnitz, J. Air Pollut. Control Assoc., 17 (1967) 324.
8 W.H. Benner, Ph.D. dissertation, University of Florida, Gainesville, FL, 1977, 202 pp.
9 National Academy of Sciences, work performed pursuant to Contract No. 68-02-1226 with Environmental Protection Agency, Washington, DC, 1977, 333 pp.
10 C. MacKinnon, J. Air Pollut. Control Assoc., 24 (1974) 237.
11 D.W. Turner, R.L. Andrews and C.W. Siegmund, Combustion 44 (1972) 21.
12 J.E. Haebig, B.E. Davis and E.R. Dzuna, ACS Div. Fuel Chem. Reprints, 20 (1975) 203.
13 D.W. Pershing and J.O.L. Wendt, in 16th Symp. (Int.) Combust., The Combustion Institute, 1977, p. 389.
14 S.L. Plee, MS. Thesis, School of Mech. Eng., Purdue Univ., Lafayett, IN, 1975.
15 E.L. Merryman and A. Levy, in 15th Symp. (Int.) Combust. The Combustion Institute, 1974, p. 1073.
16 W.A. Hough, Chemical Composition of Above-ground Material in Stands of Slash Pine, Saw, Talmetto, and Gallberry, Official Correspondence on File, Southeast. For. Exp. Stn., Asheville, NC, 1977.
17 C.M. Countryman, USDA For. Serv., Pacific Southwest For. Range Exp. Stn. Res. Pap. PSW-19, 1964, 53 pp.
18 C.W. Philpot, USDA For. Serv., Pacific Southwest For. Range Exp. Stn. Res. Note PSW-90. 1965.