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Measurement of NO_3 and N_2O_5 in a residential kitchen

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Abstract

We present direct indoor measurements of nitrate (NO_3) and dinitrogen pentoxide (N_2O_5) produced from combustion cooking emissions in a residential kitchen. When indoor ozone (O_3) concentrations were low (~ 4 ppbv), nitric oxide (NO) emitted from gas-stove combustion

suppressed NO_3 formation. However, at moderate O_3 levels (~ 40 ppbv), measured NO_3 concentrations reached 3 to 4 pptv, and the indoor NO_3 reactivity loss rate coefficient reached 0.8 s^{-1} . A box model of known chemistry agrees with the reactivity estimate and shows that moderate O_3 conditions led to a nitrate production rate of 7 ppbv h^{-1} . These indoor NO_3 production rates and reactivities are much higher than is typical outdoors. We conclude that at low O_3 levels indoor combustion suppresses nitrate chemistry, but when sufficient O_3 enters residences from outdoors or is emitted directly from indoor sources, gas stove combustion emissions promote indoor NO_3 chemistry.

Introduction

As humans commonly spend $\sim 90\%$ of their lives indoors, the chemical composition of indoor air is important for total human exposure.¹ Indoor air chemical composition is influenced by air change rates, outdoor air composition, indoor emissions, and indoor chemical transformation processes. Indoor-relevant atmospheric oxidants include ozone (O_3), hydroxyl radical (OH), and nitrate radical (NO_3). Among these, NO_3 abundance is least well characterized. Ozone is easily measured, has been broadly studied indoors, is transported indoors from outside, and in some cases is emitted directly indoors.² Knowledge about indoor OH is emerging, although few direct indoor air measurements have been published. Because of

its short lifetime, OH introduction from outdoors is insignificant. Production indoors may occur by ozonolysis of unsaturated volatile organic compounds (VOC), or by photolysis under certain lighting conditions.³⁻⁷

Nitrate could be relevant for indoor reactions involving unsaturated VOCs, such as monoterpenes.^{8,9} Monoterpene concentrations are often high indoors owing to emissions from cleaning products, air fresheners, citrus fruits, and other sources. Their oxidation is of particular interest because it leads to a variety of byproducts including secondary particulate matter.¹⁰ Nazaroff and Weschler (2004) compared expected reaction rates of indoor VOCs assuming 20 ppbv O₃, 5 × 10⁻³ pptv OH, and 1 pptv NO₃.¹¹ At these levels, for many terpenoids, indoor reactions with NO₃ would be more important than with O₃ or OH.

The NO₃ radical is produced from the reaction of O₃ with nitrogen dioxide:



In outdoor daylight, NO₃ is lost through reaction with NO and by photolysis. Indoors, and at night outdoors, if NO concentration is low enough, NO₃ reacts with NO₂ to form N₂O₅. This formation is in equilibrium with N₂O₅ thermal dissociation:¹²



The main fates of NO₃ are reaction with NO or with unsaturated VOCs, here denoted generically

as X:¹³



Ozone also reacts with NO to form NO₂:



Outdoors during daytime, sunlight rapidly photolyzes NO₂ leading to NO and O₃ regeneration.

At night, absent fresh emissions and photolysis, NO is quantitatively converted to NO₂ when O₃ is in excess. Competition between NO and VOC reactions then determine the importance of NO₃ as an indoor oxidant.⁶ Similarly, indoors in the absence of photolysis and in the presence of O₃, NO is depleted and NO₃ production increases. Thus, NO₃ is thought to be potentially important as an indoor oxidant.^{8,9}

There have been no direct measurements of NO₃ published for indoor air. Nøjgaard¹⁴ reported the sum of NO₃ and N₂O₅ between 1 and 58 pptv using an indirect technique in an office building. Those measurements could not discriminate between the two species.

Unvented combustion from gas-fired stoves and ovens are generally the dominant indoor NO_x (NO + NO₂) sources in residences. Houses with gas-burning appliances often exceed outdoor air quality standards for NO₂.^{15,16} In residences without natural gas service, portable butane stoves are widely used, as in Asia for “hot-pot” cooking.¹⁷

We undertook this study to determine whether ordinary activity in a residence could lead to appreciable NO_3 production relevant for indoor chemistry. Specifically, we performed experiments in a kitchen with a butane stove that emitted NO_x . In some experiments O_3 was added, mimicking expected O_3 intrusion from outdoors. Here we report the results, including the first direct measurement of NO_3 indoors.

Experimental Methods

Site Description and Instrumentation. Experiments were done in January 2017 in the kitchen of a single-family house in Oakland, California as part of a comprehensive residential air chemistry study.¹⁸

A teakettle containing one liter of fresh tap water was placed on a portable butane stove (Turbo Portable Stove model TS-2500), which was then ignited and operated with a high flame. When the water boiled (after ~ 6 min) the stove was shut off and the kettle removed from the kitchen. Except for these brief visits by a researcher, all doors were kept closed to isolate the kitchen from the remainder of the house. As a control, the same experiment was carried out using the kitchen's built-in electric stove.

Between experiments the kitchen was ventilated to “background” conditions by opening the two interior doors and one exterior door. Experiments were done with and without deliberate

O₃ additions. An O₃ generator provided constant indoor emissions for the duration of the addition experiments, tuned to reach a stable concentration of 40 ppbv prior to the addition of NO_x from the butane stove.

Concentrations of NO₃ and N₂O₅ were measured by cavity ring-down spectroscopy.¹⁹⁻²¹ Background absorption due to NO₂, O₃, and water vapor was measured every 10 minutes via addition of excess NO to the inlet to chemically destroy NO₃ via reaction (4). The backgrounds were linearly interpolated between the zero measurement periods. If background conditions change rapidly (and nonlinearly) this correction may be invalid. Consequently, for periods with quickly changing conditions (i.e., until 20 minutes after stove is extinguished), we do not report NO₃ and N₂O₅ concentration measurements. Measurements of VOCs were by proton-transfer-reaction time-of-flight mass spectrometry (Ionicon PTR-TOF-MS 8000).¹⁸ Measurements of CO₂, NO and NO₂, and O₃ were by LICOR LI820, Thermo Scientific 42i, and Thermo Scientific 49i instruments, respectively. The decline of CO₂ concentrations after the stove was turned off was used to estimate the kitchen air-change rate during each experiment.

Results and Discussion

Six experiments were conducted over a two-day period; three used the gas stove without added O₃, two used the gas stove with added O₃, and one control used the electric stove with O₃

added. For the experiments without deliberate O_3 addition, the O_3 concentration prior to stove ignition was 5-10 ppbv and quickly dropped to below 1 ppbv following ignition. For experiments with no O_3 added, NO and NO_2 concentrations remained elevated for the duration of the experiment (at least 1 hour after stove ignition), and no NO_3 or N_2O_5 was detected. For the control in which O_3 was added, none of the measured species (NO, NO_2 , NO_3 , N_2O_5 , CO_2) showed any response to electric stove use.

For the two experiments with added O_3 the starting concentration was 40 ppbv, maximum NO concentrations were 117 and 101 ppbv, respectively, whereas the maximum NO_2 concentrations were 208 and 169 ppbv. These values are not solely indicative of the NO_2/NO_x ratio emitted from the stove, as the supplied O_3 converted some emitted NO to NO_2 . After NO was completely converted, the O_3 concentration began to rise, and N_2O_5 concentrations increased to maxima of 190 pptv in each run. Kitchen air-change rates for these runs were 1.4 and 1.0 h^{-1} .

During the first with-ozone experiment, 4 pptv of NO_3 was observed during the period from 45 min to 1 h after stove ignition. Rapid changes in background concentrations — and a 10-minute period in which NO, NO_2 , and O_3 were measured outdoors rather than in the kitchen — limit our NO_3 measurements to this interval. For the second experiment, we measured 3 pptv of NO_3 beginning 45 minutes after stove ignition. This experiment had a longer period of uninterrupted measurements allowing for more accurate NO_3 measurements. The results of this

experiment are used in later calculations.

Figure 1 shows the concentration measurements during the second stove experiment with added O_3 . The stove was ignited at 17:30 when the O_3 concentration was 40 ppbv. The stove emitted NO and NO_2 , which quickly reacted with O_3 . Measurements of NO_3 are reported only after 18:05 to avoid changing conditions affecting the background determination; the N_2O_5 measurement suggest that NO_3 levels during and shortly after combustion remained very low. After NO has been almost completely reacted with O_3 to form NO_2 , O_3 levels began to increase, then N_2O_5 began to be observed, reaching a maximum of 190 pptv at 18:15, about 40 minutes after the stove is turned off. By 18:05, when background interferences are constant enough to make a reliable measurement, NO_3 is measured at a relatively stable concentration of 3 pptv over about 20 min duration.

The delay in peak concentrations of NO_3 and N_2O_5 following cooking with the gas stove has important implications for when NO_3 can be a significant indoor oxidant. Combustion-based cooking produces enough NO to rapidly react with and remove NO_3 , which will not rise to measurable concentrations until NO levels are reduced by dilution and oxidation via O_3 . In the case of the stove experiments with O_3 added, the NO_3 is not observed at a measurable level until ~15 minutes after the stove is extinguished as signaled by a rising N_2O_5 level.

The presence of NO suppresses the NO_3 mixing ratio in two ways: first, it directly

consumes NO_3 via reaction (4), and, second, the reaction between NO and O_3 (reaction (6)) alters the NO_3 production rate, P_{NO_3} , in reaction (1). For a given O_3 background, P_{NO_3} increases as reaction (6) converts NO into NO_2 until the NO_2 and O_3 mixing ratios are equal. Further conversion of O_3 into NO_2 (i.e., emission of NO equal to more than half of the available O_3) then reduces P_{NO_3} as NO emissions continue.

Because the presence of NO alters NO_3 production and loss, the ratio of NO_2 to NO from combustion sources influences the concentrations of NO_3 that may be reached indoors. Traynor et al. reported that 32% (+/- 18%) of NO_x emissions from gas stoves are in the form of NO_2 ($n = 522$ burners).²² Our measurements for the portable butane stove during the no O_3 added experiments fall in the upper portion of this range, with about half of NO_x observed as NO_2 .

Nitrate production has been predicted to occur indoors due to similarity of conditions with the outdoor environment at night (lack of NO_2 photolysis and low NO concentration), but only when O_3 is also available. Combustion increases the concentration of NO , which can directly react with NO_3 and thus suppress its concentration. With sufficient O_3 available, the NO_x emitted by combustion can lead to elevated NO_3 concentrations only after the combustion ceases to supply a fresh source of NO . The dominant source of indoor O_3 is typically transport from outdoors. In well-ventilated spaces, the indoor concentration is commonly reported to be 20-70% of the outdoor concentration.² Continuous influx of outdoor O_3 could potentially overcome the

NO produced from combustion and lead to elevated NO₃ concentrations. Such conditions might be particularly pronounced in high O₃ areas in urban and suburban areas where many people live. Additionally, NO₃ is always produced when O₃ and NO₂ are present— although NO reacts quickly to destroy NO₃, indoor VOC concentrations could be elevated enough to compete with NO leading to high rates of VOC oxidation despite low NO₃ concentrations.

Indoor NO₃ Reactivity. The concentration of VOCs indoors is always many orders of magnitude greater than the concentration of NO₃ (e.g. in the present study ~10⁵ times greater for total VOCs, and ~10² or more for monoterpenes alone). Consequently, the rate of reaction (5) can be approximated as

$$\text{Rate} = k'_x [\text{NO}_3] \quad (7)$$

where k'_x is the pseudo first-order rate constant for the reaction of NO₃ with VOCs. Examining Figure 1, one observes from 18:08 to 18:29 a steady NO₃ concentration of 3 pptv, implying that the production and loss rates of NO₃ are balanced:

$$P_{\text{NO}_3} = L_{\text{NO}_3} \quad (8)$$

Production of NO₃ occurs by O₃ reacting with NO₂ (reaction (1)). Loss of NO₃ can occur by two pathways: reaction with NO (reaction (4)) and oxidation of VOCs (reaction (5)). Including the equilibrium between NO₃ and N₂O₅, steady state can for NO₃ can be expressed as:

$$k_1[\text{NO}_2][\text{O}_3] + k_3[\text{N}_2\text{O}_5] = k_4[\text{NO}][\text{NO}_3] + k_2[\text{NO}_2][\text{NO}_3] + k'_x[\text{NO}_3] \quad (9)$$

Equation (9) excludes loss due to dilution or heterogeneous reactions of NO₃ or N₂O₅, which are expected to be slow compared to gas phase chemistry for these conditions. Under conditions where reactions (2) and (3) are in balance, equation (9) can be further simplified as:

$$k_1[\text{NO}_2][\text{O}_3] = k_4[\text{NO}][\text{NO}_3] + k'_x[\text{NO}_3] \quad (10)$$

By examining the ratio [N₂O₅]/([NO₂][NO₃]) for the experiment depicted in Figure 1, we determined that equilibrium was reached at 18:13 and continued until 18:30. The NO concentration was below the detection limit (and therefore assumed to be negligible) during this period. Rearranging equation (10) yields a solution for the pseudo first-order reaction rate constant of NO₃ with VOCs:

$$k'_x = k_1[\text{NO}_2][\text{O}_3] / [\text{NO}_3] \quad (11)$$

Using measurements from 18:13 to 18:30, we find an indoor NO₃ reactivity with VOCs of $k'_x = 0.8 \text{ s}^{-1}$. This value is an order of magnitude higher than determined for outdoor air in a forested mountain site with urban influence.²³ The inferred reactivity rate would be consistent with 330 pptv terpinolene, or 180 pptv of α -terpinene, monoterpenes commonly found in household cleaning products.¹¹ Total monoterpene concentrations of 700 pptv were measured in the kitchen by PTR-TOF-MS during the time when NO₃ reactivity with VOCs was calculated.

With indoor O₃ and NO₃ of 40 ppbv and 3 pptv, respectively, the pseudo first-order rate constant for the reaction of terpinolene with NO₃ is about 4× faster than the rate of reaction with

O₃ ($7.2 \times 10^{-3} \text{ s}^{-1}$ compared to $1.9 \times 10^{-3} \text{ s}^{-1}$), making NO₃ the dominant oxidant in this case. Both rates are significantly faster than loss by air change at 1 h^{-1} ($2.8 \times 10^{-4} \text{ s}^{-1}$).

Box Model A box model was constructed to match the experimental conditions of the O₃ added experiment. Initial NO and NO₂ levels were set to match the conditions of the kitchen after the stove was extinguished. The rate of continuous O₃ addition was set so the O₃ concentration 30 min after the stove was extinguished matched the experimental conditions (40 ppbv). Dilution was set to match the decay of the NO_x species over the experiment. A rate constant of $1 \times 10^{-4} \text{ s}^{-1}$ was applied for heterogeneous loss of N₂O₅ to produce HNO₃.

A constant d-limonene level of 700 pptv was assumed present over the course of the experiment, yielding 0.2 s^{-1} of NO₃ reactivity. An additional 0.6 s^{-1} of VOC reactivity was needed to reach experimentally observed steady state NO₃ concentration, bringing the total NO₃ reactivity with VOC in the model into agreement with the experimentally derived value, 0.8 s^{-1} .

Figure 2 shows the model output for the production rate of NO₃ (P_{NO_3}), the fractional NO₃ loss, and the concentration of the products from NO₃ loss. Production of NO₃ begins immediately after the stove is extinguished and rises as O₃ concentrations increase. However, NO competes for the majority of the NO₃ produced early in the experiment. For this experiment, only after sufficient NO has been consumed by O₃ do oxidation sinks for NO₃ compete for its loss, oxidizing and reducing the concentrations of d-limonene and the unspecified VOC. Peak

NO₃ production is realized when most of the NO_x is NO₂ rather than NO. The O₃ concentration grows, and it can only react with NO₂ to form NO₃, or with d-limonene to form the ‘O₃+MT’ oxidation product. The peak NO₃ production rate, 7 ppbv h⁻¹, is high compared to most reports from outdoor environments, where P_{NO_3} has been reported in the range 0.01 to 1.2 ppbv h⁻¹.²⁴ The model illustrates that NO₃ production does not contribute significantly to oxidation of VOCs until NO is removed and VOC reactions compete for the available NO₃.

In the model, ozonolysis of d-limonene occurs at about half the rate of this compound’s reaction with NO₃. The dominant source of oxidation products comes from NO₃ reacting with the unspecified VOC. Heterogeneous loss of N₂O₅ to form HNO₃ is small throughout.

In summary, we have shown that in an indoor environment with moderate O₃ levels, routine combustion emissions of NO_x can lead to significant production and measurable concentrations of NO₃ and N₂O₅. Furthermore, the inferred NO₃ production rates are high compared to outdoors, and, when NO₃ is elevated, it may become the dominant indoor oxidant for some VOCs, including certain terpenoids.

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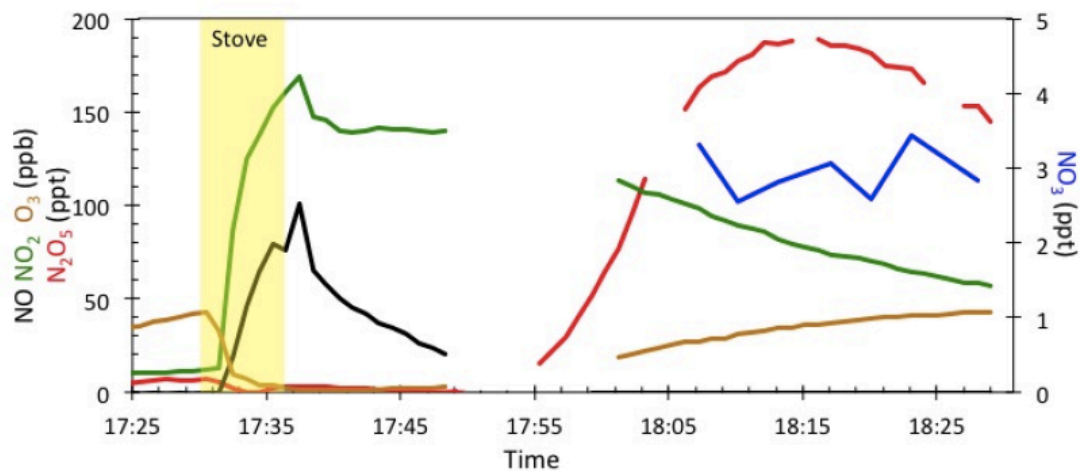


Figure 1: Concentrations of NO, NO₂, NO₃, N₂O₅, and O₃ during an ozone-added stove experiment. The yellow shaded region indicates when the stove was on.

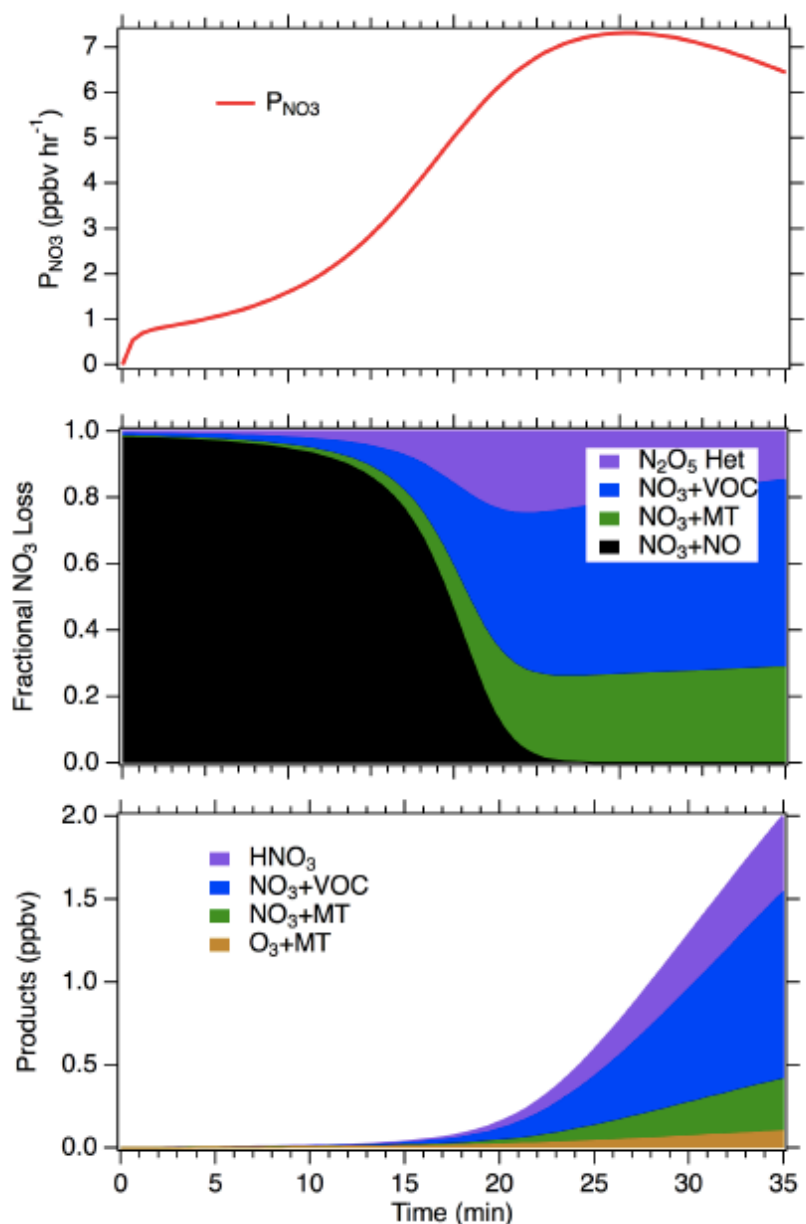


Figure 2: Box model outputs of NO_3 production rate (top), fractional time dependent losses of NO_3 and N_2O_5 (middle), and mixing ratios of reaction products (bottom). Note that time $t=0$ corresponds to the extinguishing of the stove. The center plot shows fractional NO_3 losses for 4 reaction pathways: heterogeneous reaction of N_2O_5 to form HNO_3 (N_2O_5 Het), NO_3 oxidation of the ‘generic’ VOC ($\text{NO}_3 + \text{VOC}$), NO_3 oxidation of d-limonene ($\text{NO}_3 + \text{MT}$), and NO_3 consumption by NO ($\text{NO}_3 + \text{NO}$). The bottom plot shows the concentration of the NO_3 loss products, as well as the concentration of products from ozonolysis of d-limonene ($\text{O}_3 + \text{MT}$).

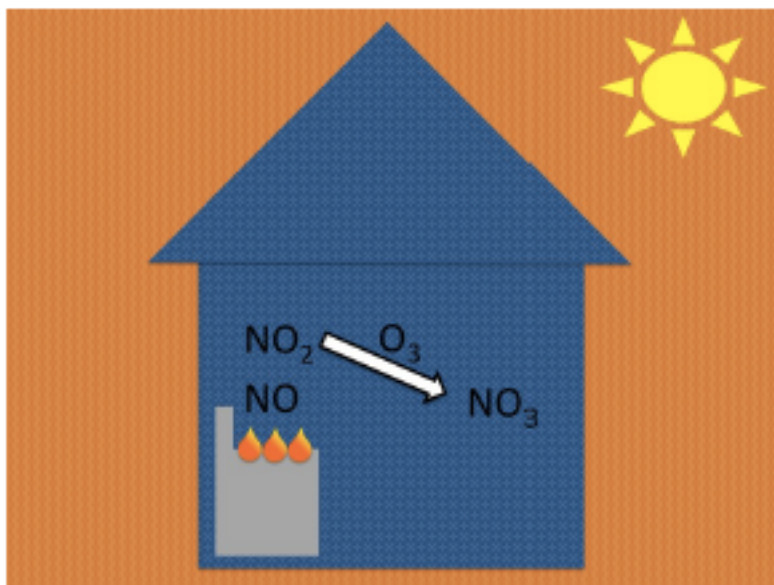


Figure 3: TOC Art