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Use of Dried Compressed Air to Generate Ozone in Vegetation Exposure Chambers: Quantification of Trace Nitrogen Oxidants Formed During Corona Discharge

Research Article

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Abstract

Corona discharge ozone (O_3) generators provide valuable data on the response of vegetation to O_3 exposures. Systems that use dried air as a feed gas, instead of pure or concentrated oxygen (O_2), are known to produce trace nitrogen (N) oxidant byproducts that may be toxic to plants. This study quantified the concentration of total N oxidants, including nitrogen oxides (NO_x, the sum of NO and NO_2), dinitrogen pentoxide (N_2O_5), and nitric acid (HNO_3), relative to O_3 levels in a continuous stirred tank reactor (CSTR). The CSTR was part of computer-controlled O_3 delivery and monitoring system used to study effects of O_3 on vegetation within a greenhouse with charcoal-filtered air. Ozone was generated via corona discharge with dried air as a feed gas, and the system was operated at different O_3 output levels and environmental conditions in seven separate trials. At O_3 levels up to 330 ppb, total N oxidant concentrations in the CSTR did not exceed 9.2 ppb, when averaged over 60-sec intervals. Across all trials, the relationship between total N oxidants and O_3 was described by the equation: $\text{N oxidants}(ppb) = 0.0108[O_3(ppb)] + 3.37$ ($R^2 = 0.46$; $n = 205$). In this system, trace N oxidant levels produced under typical experimental conditions are not expected to cause direct toxicity to vegetation. Therefore, corona discharge O_3 generators provide a suitable, inexpensive method of O_3 production for vegetation exposure studies.

Keywords: Air pollution; Ozone; Oxides of nitrogen; CSTR exposure chambers; Corona discharge

Introduction

Tropospheric ozone (O_3)

Ambient tropospheric O_3 is one of the most phytotoxic air pollutants in the U.S., if not the world [1-3]. Ozone is a secondary air pollutant formed from photochemical reactions of nitrogen oxides (NO_x, the sum of NO and NO_2) and volatile organic compounds (VOCs). The U.S. Environmental Protection Agency (EPA) has designated O_3 as one of six criteria air pollutants regulated by the National Ambient Air Quality Standards (NAAQS) to protect human beings, agricultural crops, forest ecosystems, and other resources in the U.S. from ambient exposure [4]. Ozone is of regional-scale importance in the U.S. due to its multi-day lifetime within slow-moving, stagnant high-pressure systems and, as a result, may cause damage to vegetation many miles downwind from the origin of its precursors, NO_x and VOCs [3].

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Exposing vegetation to O_3 in chambers

Ozone generators are important tools to study effects of O_3 on vegetation. Since O_3 cannot be stored, it must be created on-demand at the application site. In vegetation studies, O_3 generators have been essential for controlled studies evaluating the harmful effects of O_3 on vegetation [5,6], including the U.S. EPA's National Crop Loss Assessment Network, which established dose-response relationships between O_3 and crop yields using a network of open-top chambers [7]. Current research relies on O_3 generators to evaluate the impacts of O_3 on different crop species [8,9], at different times of day [10,11], and interacting with climatic changes [8].

Generation of ozone

Ozone generators dissociate molecular oxygen (O_2) into atomic oxygen (O). Subsequently, the O atoms produced by the generator combine with O_2 to form O_3 [12,13].

The most common O_3 generation method, corona discharge, uses a high-voltage electric arc to split O_2 (i.e., similar to lightning), but if air is used as a feed gas instead of pure O_2, NO_x and N_2O_5 also form [14]. Corona discharge or high-voltage electric arc generators produce electrons that collide with and dissociate molecules of O_2 and N_2 in the air, resulting in formation of O and NO. As a byproduct, NO is then oxidized by O_3 until it reaches the highest possible oxidation states as N_2O_5 or HNO_3. If water vapor is present, the N_2O_5 is hydrated to HNO_3 [15]. Nitrous oxide (N_2O), another byproduct, is not formed via dissociation but rather from an excited N_2 molecule, which reacts with an O molecule. N_2O is chemically stable and not further oxidized [15]. To prevent byproducts, pure O_2 is the ideal feed gas for corona discharge, providing up to twice the O_3 output of dried air. In addition to compressed O_2, oxygen concentrators can be used to increase O_2 levels in a pressurized ambient air supply. However, both options raise production costs. Ambient air is therefore the least expensive feed gas but necessitates frequent corona cell maintenance. When ambient air is dried (i.e., to a dewpoint ≤-60 °C), O_3 output is more consistent, and maintenance needs are reduced relative to humid air [14,16].

In contrast, UV lamps use ambient air as a feed gas without generating trace N oxidants. Light emitted by mercury lamps, in the UV region at 185 nm, irradiates O_2 present in ambient air, similar to the photochemistry of the stratosphere, where O_2 absorbs radiation from 240 to 120 nm. In this process, one photon can generate up to two O_3 molecules when it dissociates one O_2 molecule to two single O molecules, which then primarily combine with O_2 to produce O_3 [12]. Other types of lamps, such as xenon excimers, are also capable of dissociating O_2 and have been studied for practical O_3 production [17]. However, mercury remains standard, and new coatings have been developed to increase lamp lifetime [18]. In spite of advances in technology for UV lamps, corona discharge generators provide the most efficient, durable O_3 production, particularly for studies requiring high flow rates of O_3 and distribution to multiple exposure chambers from a single source [19]. However, the cost of pure O_2 as a feed gas can be prohibitive for long-term studies [20].

Potential toxicity of N oxidants to vegetation

When using ambient air as a feed gas, it is important to quantify the potentially phytotoxic N oxidant compounds that result from passing O_2 and N_2 through a high-voltage dielectric field. These include NO and NO_2 [21], as well as HNO_3 [22] formed from hydrated N_2O_5 [15].

Under the Clean Air Act, EPA has maintained the secondary NAAQS, which protect public welfare, for NO_2 in the form of an annual arithmetic mean of 53 ppb, which is considered sufficient to protect vegetation from direct effects of gaseous NO_2 [23]. However, EPA [4] acknowledged the causal relationship between gaseous NO_x and injury to vegetation. Further, EPA concluded that, at ambient exposure levels for NO_2, exposure-response relationships were variable, due to differences in biological and environmental factors among experiments [24]. In some cases, low NO_2 levels increased growth, likely via foliar N fertilization. For continued (> 14 d) exposures of several hours per day, growth reductions generally appeared when NO_x levels exceeded 100 to 500 ppb, depending on the plant species [24]. EPA supported the conclusion that gaseous HNO_3 can cause "changes" to vegetation but did not find evidence of direct injury from HNO_3 exposure [4]. They noted that dry deposition of HNO_3 and resulting changes (e.g., degradation of epicuticular waxes) may increase adverse effects of other pollutants, such as O_3, on vegetation [25]. However, Mortensen and Jørgensen [20] suggested that trace N oxidants produced by corona discharge can also protect vegetation against O_3 damage. Few studies have been performed since the 1993 EPA summary [24], leading to a lack of information on the long-term effects of low concentrations of HNO_3 and total atmospheric oxidized N (NO_y) on plant species [4].

Terminology in this paper that defines inorganic N species is as follows:

$$NO_x = NO + NO_2$$

$$NO_y = NO_x + N_2O_5 + HNO_3$$

$$NO_z = NO_y - NO_x = N_2O_5 + HNO_3$$

Previous studies have measured the production of N oxidants relative to O_3 by corona discharge with dried air, as emitted directly from the generator. Notably, different systems and conditions (e.g., temperature, pressure) cause variation in relative yields [25]. Using infrared spectroscopy Harris et al. [14] and Kogelschatz and Baessler [17] estimated a molar ratio of HNO_3 to O_3 ranging from 0.007 to 0.010 per 1 mol O_3. Bubbling the generator air stream through water and measuring dissolved NO_3^- resulted in higher HNO_3: O_3 ratios, in the range of 0.020 to 0.025 [20,25].

Objective

The objective of this study was to quantify trace N oxidants, as NO_y, present in a charcoal-filtered-air greenhouse during O_3 production via corona discharge. Specifically, the relationship between O_3 and NO_y concentrations within continuous stirred tank reactor (CSTR) treatment chambers [5], used to study the response of vegetation to O_3 [11] was of interest. Quantification of N oxidant byproducts under experimental operating conditions was necessary to ensure that the use of pure air as a feed gas for the corona discharge generator would not produce injurious levels of N oxide byproducts, potentially confounding the effects of O_3 treatment on vegetation.

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Material and Methods

Ozone was generated via corona discharge, with dried air as a feed gas, and distributed among 16 separate CSTRs, each with a volume of ~2.6 m^3, as described by Lloyd et al. [11]. Data were recorded within a single representative CSTR. In order to quantify NO_y, oxidation products were reduced via thermal dissociation at 650 °C to NO_2 and measured using chemiluminescence (Model 42i-TL; Thermo Environmental Corp., Franklin, MA) as NO, NO_2, and NO_x, with a 60-sec averaging time. The thermal dissociation column was constructed as described by Wooldridge et al.[26] and placed in one of the CSTRs. Measurements recorded when the thermal dissociator was at ambient temperature and when heated to 650 °C reflect NO_x and NO_y levels, respectively. Therefore, the difference between those quantities (i.e., $NO_y - NO_x$) gives an approximation for NO_z.

Results and Discussion

Across seven trials, background NO_x levels in the CSTR, prior to operation of the O_3 generator, ranged from approximately 2 to 5 ppb, with about 45% in the form of NO (data not shown). For comparison, across the U.S., the average annual NO_2 concentration for ambient air is ≈15 ppb [27]. Production of O_3 from the generator decreased the proportion of NO, since O_3 reacts with NO to form NO_2 [25]. The minimum levels of NO recorded during ambient conditions and O_3 production were 0.77 and 0.22 ppb, respectively (data not shown).

Background NO_x levels during operation of the O_3 generator (and thermal dissociation column) can be inferred from the intercept term of least squares regression, with a mean of 3.37 ppb across trials (Figure 1). Background NO_x was included in the analysis of the relationship between NO_y and O_3 to provide a maximum estimate of the level of NO_y plants may be exposed to in CSTRs.

Across all measurements, NO_y concentration was linearly related to both O_3 concentration and electric current, but electric current explained slightly more variation (R^2 = 0.54) than did O_3 (R^2 = 0.46, Figure 1). For the range of O_3 concentrations tested, up to 331 ppb, the maximum NO_y levels recorded did not exceed 9.2 ppb. Across the seven trials, the linear relationship between NO_y and O_3 in the CSTR was described by: NO_y (ppb) = 0.0108 [O_3 (ppb)] + 3.37 (R^2 = 0.46, n = 205 Figure 1).

For the seven separate trials, results of least squares regression are given in Table 1. R^2 values ranged from 0.32 to 0.95, slope coefficients ranged from 0.0074 to 0.0168 ppb NO_y·ppb O_3^{-1}, and intercepts ranged from 1.83 to 4.65 ppb NO_y. Notably, the number of individual measurements and overall time period varied among trials (Table 1). Based on least squares regression, there was no relationship between slopes or intercepts and air temperature, relative humidity, or photosynthetically active radiation (PAR) across the seven trials (R^2 = 0.01 to 0.04, data not shown).

Comparison of the trials on two dates with the highest R^2 values, 9 September and 31 August, helps explain the variation in slopes and intercepts. Relative to 31 August, the regression from 9 September produced a larger intercept (3.43 *vs.* 1.83 ppb NO_y) and smaller slope (0.0079 *vs.* 0168 ppb NO_y·ppb O_3^{-1}, Table 1). Figure 2 shows the O_3 concentration (ppb), ratio of O_3 (ppb) to NO_y (ppb), and power efficiency (ppb O_3·mA^{-1}) plotted relative to the elapsed measurement time (min) on both days. On 9 September, a larger number of measurements (n = 44 *vs.* 20) was recorded over a longer time period (185 *vs.* 67 min). On both dates, target O_3 levels in the CSTR were

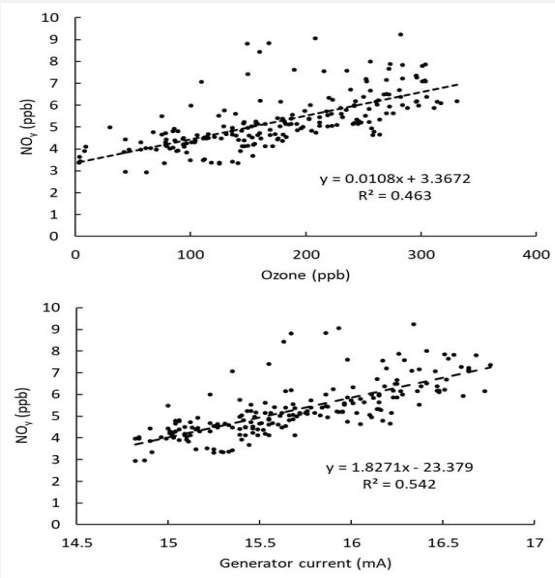

Figure 1: Relationship between NO_y and either O_3 concentration in a continuous stirred tank reactor (top) or electrical current supplied to the O_3 generator (bottom) across seven trials (n = 205). Equations and R^2 values are the result of least squares regression.

Table 1: Results of least squares regression, in order of decreasing R^2, for the relationship between NO_y and O_3 in a continuous stirred tank reactor, along with means for generator efficiency, relative humidity (RH), air temperature, photosynthetically active radiation (*PAR*), start and end times, and pattern of adjustment (decreased or increased concentrations) for O_3 target levels during each of seven trials.

					Efficiency	RH	Temp	*PAR*	Time		Ozone target
Date	n	R^2	Slope	Intercept	($ppbO_3 \cdot mA^{-1}$)	(%)	(°C)	($\mu mol \cdot m^2 \cdot s^{-1}$)	Start	End	adjustment
9 Sep.	44	0.95	0.0079	3.43	8.09	72	19	72	13:19	16:04	decrease
31 Aug.	20	0.73	0.0168	1.83	11.4	68	28	139	13:36	14:43	decrease
29 Aug.	51	0.67	0.0115	3.49	11.9	51	34	329	13:13	15:59	increase
5 Sep.	20	0.62	0.0110	3.91	11.9	75	28	0	19:26	20:38	increase
28 Aug.(A)[z]	24	0.56	0.0074	3.68	10.0	58	33	299	11:59	13:18	increase/decrease
30 Aug.	28	0.40	0.0077	3.20	10.8	74	26	168	8:35	10:24	increase
28 Aug. (B)[z]	18	0.32	0.0119	4.65	11.8	74	28	132	8:40	9:39	increase/decrease

[z]The relationship between O_3 and NO_y was tested at two separate times, "A" and "B", on 28 Aug.

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initially set at greater than 300 ppb and decreased over time. The rate was slower on 9 September than on 31 August, and the ratio of O_3: NO_y was less variable, as well as the generator power efficiency. These differences reflect inherent "noise" in the O_3 distribution and monitoring systems, which can result during computerized feedback when adjustment of electrical current to the generator overshoots target levels. The air in each CSTR is replaced (via a blower system) approximately once per minute, leading to a time lag between O_3 input from the generator, equilibration of the gas composition in the CSTR, and travel distance for a sample parcel to reach the O_3 monitor [11]. Figure 3 shows that the more rapid decrease in target O_3 concentration and resulting "bumps" in generator output caused underestimates of predicted NO_y at low O_3 levels and overestimates at high levels, relative to the expected values based on regression of the overall data set.

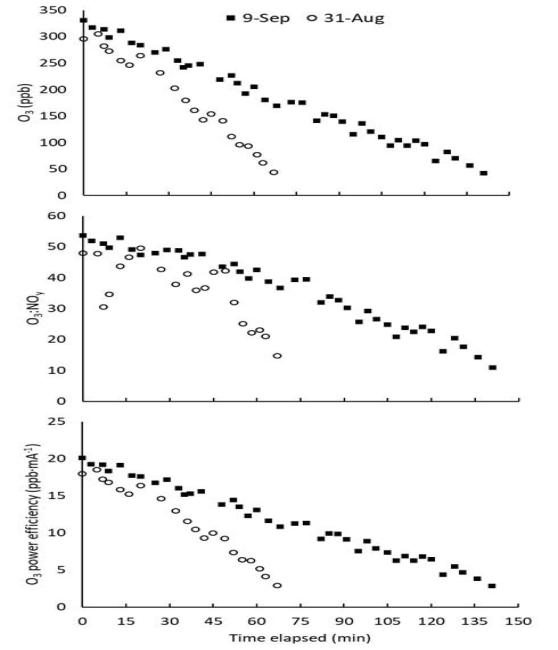

Figure 2: Trends in O_3 concentration (top), the ratio of O_3: NO_y (middle), and generator power efficiency (bottom), based on O_3 and NO_y concentrations in a continuous stirred tank reactor, relative to elapsed time in two trials: 9 Sep. (n = 44) and 31 Aug. (n = 20).

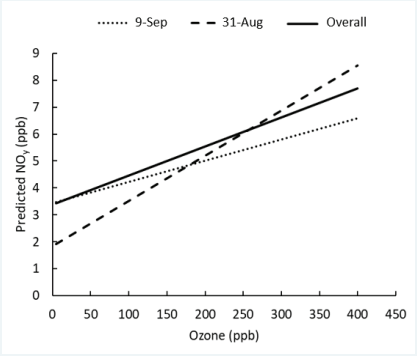

Figure 3: Predicted NO_y relative to O_3 concentration based on least squares regression of data collected on 9 Sep., 31 Aug., and across seven trials, including 9 Sep. and 31 Aug.

The slope obtained via linear regression of all CSTR observations (0.0108 ppb NO_y·ppb O_3^{-1}) falls within the range of prior measurements (0.007 to 0.025), confirming that present observations of NO_y were within reported values [14,15,20,25].

Using the predictive equation derived from all seven trials, at a CSTR O_3 level of 300 ppb, the expected NO_y concentration was ≈6.6 ppb. With maximum CSTR concentrations far lower than the secondary NAAQS for NO_2, set at 53 ppb [24], direct plant injury is unlikely. Further, Stripe et al. [22] treated two snap bean *(Phaseolus vulgaris L.)* genotypes with HNO_3 during the daytime for 6 weeks. Exposure to peak daily HNO_3 concentrations of 80 to 100 ppb did not significantly affect bean plant biomass. Therefore, NO_2 and HNO_3 generated by corona discharge in the CSTR system are unlikely to incite direct phytotoxic effects.

Conclusion

The system-specific estimates of NO_y production *via* corona discharge, with dried air as a feed gas, are in agreement with other studies, and these levels are not expected to be directly phytotoxic in the form of NO_2 or HNO_3. Notably, Taylor et al. [28] suggested that elevated levels of both O_3 and HNO_3 are representative of ambient conditions in the outdoor growth environment. However, O_3 has a much higher phytotoxicity than NO_x [24]. Therefore, studies employing this method of O_3 generation should produce valid results testing the effect of O_3 treatment on vegetation, though actual N by product outputs will vary among exposure systems.

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