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Outdoor smog chamber experiments in Mexico

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Abstract

Towards the end of the 1940s the air's contamination began in Mexico. It just happened when Mexico starts its industrial growing. During these years the population increased notably. Industrial growing in the 1950s was carried through an urbanization process (Restrepo, 1992). Mexico City was the first because it had industries, services, government offices, culture attractions and higher education. It was followed by suburbs of the State of Mexico, which are close to the Mexico City. Nowadays it is called Mexico City's metropolitan area (MCMA) and it lies in a high valley surrounded by mountains located 2240 meters above the sea level capable of holding in pollutants released by its more than 20 million inhabitants. This altitude causes a fuel's incomplete combustion because of low oxygen concentration in the air. In addition to average low velocities (< 1.5 m/s) almost during 7 months in a year (Martínez, 1996). Due to that, MCMA has a behavior close to a smog chamber and has suffered during the past two decades from increasingly severe smog events with very high ozone (O_3) levels. On the other hand, the major non-methane hydrocarbons (NMHC) components and nitrogen oxides (NOx) of the contaminated atmospheric mixture proceed from the approximately 3 million vehicles in the MCMA and of industrial operation (inventario de emisiones, 1996).

Taking in account this problem was necessary to do research look into the ambient air the conditions under it was happening. Some papers were consulted in order to begin an investigation. The ozone formation depends not only on the HC and its atmospherics reactions, but also on the conditions of the system where the HC are reacting (Carter, 1994). So with a budge cut out, it was decided to looking for ozone control strategies under real conditions. Several experiments were conducted to simulate potential O_3 control strategies involving the effect of adding NMHC or NOx and reductions of them in outdoor smog chambers. It was made a similar experiment as Nelson A. Kelly carried out in Los Angeles (Kelly and Gunst, 1990).

captive-air irradiation (CAI) was used to evaluate the effects of HC and NOx changes on peak springtime O_3 levels. The experiments were performed at the Mexican Petroleum Institute (IMP). It is located in northwest of Mexico City near large sources of HC and NOx emissions. At this site. The CAI experiments were run on 17 days between 3 April and 22 April in 1995.

The experimental program was designed with the primary objective of finding out the response of maximum ozone levels, O_3 (max), to changes in the initial concentrations HC and NOx. The experimental design consisted of four levels each for HC and NOx; two levels of reduction below the ambient level (-25% and -50%). The ambient level, and one level of increase above the ambient level (+25%). So that, 16 HC-NOx experiments were possible each day, however only eight chambers could be operated each day. The eight HC-NOx combination to be tested on a given day were selected to meet two objective more: to provide replicates, with identical prepared mixtures and to minimize the confounding effects of day to day variations. In this scheme, at least one unperturbed chamber was included each day. The selection of the chamber to be used for each experiment in an eight-chamber block of experiments was made randomly during the study. A total number of 136 experiments were performed on 20 days. Control chamber experiments were run every day. Those experiments comprised the largest fraction of the total.

Every day was prepared by filling the eight chambers with morning ambient air at the same time. After that, each chamber was prepared with the experiment according to the experimental program: (1) replacing some ambient air with clean air from a cylinder (dilution), and /or (2) adding HC and/or NOx. The clean air diluent was HC-free air with a few ppbC of hydrocarbons. The NOx spike gas was 10,000 ppm NO in N_2 and the HC spike gas was a 39,060 ppmC in N_2. The HC mixture was made of propane, n-butane, toluene and propylene with the proportion 40.6:30.1:27.4:1.9, respectively in ppmC. This hydrocarbons proportion is typical of MCMA. Filling Hamilton syringes from the cylinders, and then adding the gas to the flowing stream of clean or ambient air filling the chambers added spike gases.

All experiments were performed in 500 liters chambers constructed from 0.5 mm FEP-Teflon. Nine chambers were mounted on nets in a 3 x 3 matrix to 1 m above a wood platform. The middle chamber was a control chamber used for HC, Carbonyl and Temperature measurements. The eight chamber around the control chamber were used for HC-NOx different mixtures.

Every day, the chambers, which contained air from the day before, were evaluated at 6.00 h in the morning for leaks. Each damaged chamber was changed, The chambers were evacuated, refilled with 30 liters of clean air, reevacuate and then filled. After that, the mixtures were prepared, the measurements started almost ever at 9.00 h in the morning. The measurements reported are HC, NOx, O_3, ultraviolet flux and temperature. HC samples were taken in canisters from the control chamber beginning the experiments in the morning and at the end of them in the afternoon. The HC samples were analyzed by using gas chromatography. The initial HC of each chamber was calculated from the treatment it received and the analysis of hydrocarbon in the control chamber. The NOx was measured each 58 minutes in each chamber until 17.00 h using a Thermoenvironment 49 analyzer equipped with a nylon filter to remove nitric acid. Ambient and chamber temperatures were measured with aspirated thermocouple. Ultraviolet flux was measured with an Eppley ultraviolet radiometer.

Experiments in addition to those related strategy control, were conducted to check chambers-wall-loss and line loss determination for NOx and O_3, and to study meteorological variables like temperature an ultraviolet flux. The first two types of experiments showed that wall and line losses were negligible. The meteorological variables presented a linear correlation with the O_3 formed in surrogate HC-NOx - clean air mixtures on different days.

All experimental database consists of hourly measurements of NOx and O_3, initial and end HC in a control chamber, and temperature and ultra violet flux in ambient air outside the chambers. The database comprises 136 experiments run on 20 days. The initial HC and NOx concentrations, temperature and ultra violet flux were taken in count as independent variables; the independent variable was O_3(max). This database was used to determine the adequacy of the experimental program, to assess the experimental error, and to find out an empirical model for O_3(max).

The effects of perturbations on the O_3 profiles followed a sigmoidal kinetics curve, which is typical of an autocatalytic reaction. An initial induction period was followed by a sharp increase to O_3 (max), and then by very little change O_3 (max) occurred between 14.00 h and 16.00 h.

To estimate the experimental uncertainty attributed to random error 50 % of the experiments were replicates. A quantitative estimate of the random measurement error variability as a percentage of the mean was only 4.27%.

Day to day variations in initial HC and NOx were very different. So that, the induced perturbation expanded the experimental region slightly. It included the curvature in the isopleths and the NOx -inhibition region. The daily variability in the control chamber was large; HC varied from 1500 to 6000 ppbC and NOx varied from 38 to 345 ppb. The HC/NOx ratio in the control chamber ranged from 9 to 32 with an average of 20.6. The day to day variations in O_3 (max) in chambers without perturbations (ambient morning air to generate O_3 in the chamber) ranged from 175 to 684 ppb.

To study the temperature effects on the rates of thermal reactions and ultraviolet flux effects on the rates of photochemical reactions were performed surrogate HC-NOx-clean air irradiation. In this experiments, perturbations of the initial HC and NOx concentration were controlled, but the variations in temperature and ultraviolet flux were no controlled. These important variables were assessed using two chambers containing clean air plus 1500 ppbC the three-component HC-spike mixture and 150 ppb NOx. These replicate mixture were prepared and irradiated on 3 days. The difference between O_3 (max) for same-day replicates average only 7.5%. Those experiments allowed to confirm that O_3 (max) was directly proportional to the average temperature and ultraviolet flux of each day.

The most of the experimental dates were used to determine a functional relationship between O_3(max), and the initial HC and NOx concentrations,

temperature and ultraviolet flux. Multiple regression modeling was used for it. Some combinations of predictor variables were investigated by including terms in the mathematical model such as HC^x, and NO^y_x, where x and y = 0.5,1,2 and 3. Cross products and ratios, such as HC^x. NO^y_x, HC^x/NO^y_x, and NO^y_x/ HC^x, were also considered. These terms express interactions between HC and NOx. The effects of temperature and ultraviolet flux were investigates by including T(avg.), T(max). u.v.(avg.) and u.v.(max) in linear form. The coefficient of determination, R^2, was the statistical criterion considered. The empirical model, for O_3(max) found out, can generate similar isopleths in shape to those generated by a mechanistic model. Thus, the empirical model is consistent with the chemical phenomena shown to be responsible for O_3 formation under laboratory conditions.

Regression modeling was used to determine the empirical model for O_3(max) and considering the R^2 statistics as well:

$$O_3(max) = 195.063 + 1.12\ NO_x - 0.5\ NO^2_x/HC + 0.115(T_{avg} - 26.98)$$

was chosen as the empirical model for O_3(max) (the average temperature was 26.98 ^oC). It contains two terms to fit the dependence of O_3(max) on the initial HC and NOx precursor concentrations, and one term to fit the temperature dependence.

Using the equation for T_{avg} = 26.98 ^oC an O_3 isopleth was generated. The isopleths were similar in shape to those generated by a mechanistic model. Thus, the empirical model was consistent with the chemical phenomena shown to be responsible for O_3 formation under laboratory conditions.

This model predicts the NOx-inhibition region and the horizontal flattening in the lower right hand portion region. Between the NOx-inhibition and HC-saturation regions there is a highly curved region. Where O_3(max) will respond to changes in HC and/or NOx within the knee region. Those region provide the foundation for discussions of O_3 control strategies.

Ozone control strategies can be evaluated with the empirical model developed from the experiments. Of course the CAI are not exact simulations of real atmosphere, because of in the real atmosphere there are HC and NOx emissions into an air parcel throughout the day. Thus, this difference between the chambers and the atmosphere should be unimportant for elucidating control strategies. By the way, we focused on control strategies to reduce O_3(max) by 50%; specifically, changes in O_3(max) from 600 to 300 ppb in the chambers. Those end-points were selected because they bracket the average O_3(max) observed. In the experiments (450 ppb), and they represent a 50% decrease in O_3(max).

O_3(max) control strategies were evaluated for initial HC/NOx ratios of 12, 16 and 20. The ambient HC/NOx ratio that was measured in the 90% of the control chambers. For all calculations T_{avg} was taken as 26.98 ^oC.

O_3(max) response to simultaneous HC and NOx reductions. The ozone changes are in the HC-saturation region. 50% reductions in O_3(max) required 73.5 % simultaneous reductions in HC and NOx for HC/NOx ratios in the range 12-20. Here the change in O_3(max) is linear with the change in precursors and independent of the HC/NOx ratio.

O_3(max) response to HC reductions. These HC reductions cause changes from the HC saturation region to the knee region. 50% reduction in O_3(max) requires 95-97% reductions in HC for initial HC/NOx ratios of 12-20. There is a marked non-linear in the response of O_3(max) to reductions in HC alone after 80% reductions.

O_3(max) response to NOx reductions. These NOx reductions cause changes into the HC-saturation region. 50% reductions in O_3(max) requires 75% roughly NOx reductions in NOx for initial HC/NOx ratios of 12-20. Here the change in O_3(max) is linear and independent of the HC/NOx ratio.

Ambient air in Mexico City (the control chambers) usually had a HC/NOx ratio in the HC saturation region. That means that a change in HC does not reduce la O_3 significantly. But a change in NOx moves the system into the HC saturation region where the O_3 is reduced in an important way. Changes in both pollutants move the system throughout the HC saturation region. Thus, the current emissions control on HC only may be responsible for the lack of progress in reducing O_3 in Mexico City. the best O_3-control strategy is to reduce the NOx pollutant.

Of course, while the NOx reduction strategy is the most efficient on average, no single strategy is the best every day due to the variability in HC/NOx.

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