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Abstract

OBSERVATION BASED MODELS: PAST, PRESENT AND FUTURE

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ABSTRACT

The term "Observation-Based Model" was first used by Cardelino and Chameides (1995) to describe a particular modeling approach that relied on observed trace gas concentrations in order to predict the sensitivity of O_3 to changes in emissions of NO_x and hydrocarbons (HCs). This approach is only a few years old but already, the term observational based model has taken on a more general meaning. It is now used to refer to a variety of modeling approaches that rely on observed concentrations to make predictions on O_3 formation. It stands in contrast to an emissions based approach in which O_3 production is calculated from first principals starting from emissions of precursor compounds. The general thrust of the observational based model is that by bringing in the actual atmospheric concentrations, there is less reliance on ill-characterized emissions, computational demands are lessened, and an element of realty is imposed on the calculations.

In this presentation observational based models are reviewed. A taxonomy is suggested that puts models in 3 classes; past, present, and future, according to the quantities that are calculated. Examples are given for each category. A radical budget method is described that gives information about the present; the sensitivity of the O_3 production rate to changes in NO and HC. We show that NO_x (and HC) limited conditions are associated with high (and low) values of $(d[H_2O_2]/dt)/(d[NO_z]/dt)$. A connection is made to the indicator species approach of Sillman (1995) in which the sensitivity of O_3 to past emissions of NO_x and HC is specified by the concentration ratio; $[H_2O_2]/[NO_z]$.

Taxonomy

Measurements do not tell us all that we want to know about the atmosphere. The most interesting quantities cannot be directly measured, not even in principal. Among these quantities are rates for the chemical production and loss of O_3 (and other compounds), i.e., $P(O_3)$ and $L(O_3)$. Most of all, we want to know the sensitivity of the atmosphere to changes in O_3 precursors; for example, the quantities that represent the effects of an emission change: $\partial[O_3]/\partial E_{NOx}$ and $\partial[O_3]/\partial E_{HC}$. Note that these two derivatives are non-local. They represent the change in O_3 concentration at a particular location to an imposed change in emissions at some earlier time and some upwind region.

An operational definition for an observational based model is that it predicts the interesting non-observables in terms of things that can be measured. Three types of observational based models, called past, present and future can be defined according to the quantities that are predicted. Questions addressed, quantities predicted, and examples are:

Past:

How was O_3 formed?
$\partial[O_3]/\partial E_{NOx}$ and $\partial[O_3]/\partial E_{HC}$
"OBM" (Cardelino and Chameides, 1995); Indicator species (Sillman, 1995)

Present:

What's happening now?
$P(O_3)$, $L(O_3)$, $\partial P(O_3)/\partial[NO]$, $\partial P(O_3)/\partial[HC]$
Photostationary state; Radical budget (Kleinman et al., 1995);
Constrained steady state

Future:

What will air be like later?

$\Delta O_3 = O_3(t=later) - O_3(t=now)$

$\partial \Delta O_3/\partial[NO]$, $\partial \Delta O_3/\partial[HC]$

EKMA; Incremental reactivities (Carter, Jeffries);

O_3 - CO and NO_z correlations (Parrish, Trainer)

It is important to note that although there is a superficial resemblance between categories, $[O_3]$, $P(O_3)$, and ΔO_3 are different quantities as are NO and E_{NO}, and HC and E_{HC}.

Radical Budget

The radical budget approach is a member of the present tense family of observational models. In this approach the constraint that sources and sinks of free radicals must be equal is used to determine the production rate of O_3 in terms of measured concentrations of NO and free radical precursors (mainly O_3 and HCHO). Examples of this approach are given using data collected during the Southern Oxidant Study at Metter, GA (Kleinman et al., 1995) and during the North Atlantic Regional Experiment in Yarmouth, Nova Scotia. Ozone production rates at Metter, GA were also calculated from the photostationary state relations. The two methods agree to within the accuracy expected from measurement uncertainty.

The radical budget approach also yields an approximate analytic formula for the sensitivity of $P(O_3)$ to changes in [NO] and [HC]:

$$d\ln P(O_3)/d\ln[NO] = (1 - 3/2\, N/Q) / (1 - 1/2\, N/Q)$$
$$d\ln P(O_3)/d\ln[HC] = (1/2\, N/Q) / (1 - 1/2\, N/Q)$$

Relative sensitivities depend only on the variable "N/Q" which is the fraction of free radicals that are removed by reacting with NO_x, by $OH+NO_2$ and similar reactions. N/Q therefore determines whether peroxides or HNO_3 (and similar compounds) are the primary end products of the photochemistry. NO_x sensitive conditions occur when $d\ln P(O_3)/d\ln[NO] > d\ln P(O_3)/d\ln[HC]$ leading to peroxide formation. HC sensitive conditions occur when $d\ln P(O_3)/d\ln[NO] < d\ln P(O_3)/d\ln[HC]$ leading to HNO_3 formation. This association between NO_x and HC limited conditions on the one hand and production of peroxides and HNO_3 on the other hand is the basis for Sillman's indicator species technique, as he has noted (Sillman, 1995).

The above equations have a crossover from NO_x to HC sensitive conditions when 1/2 of radicals are removed by radical - NO_x reactions. NO_x is counter-productive to O_3 production when more than 2/3 of radicals are removed by reactions with NO_x. We have compared these equations to photochemical model calculations based on measurements collected during the SOS study of the Nashville urban plume. The radical budget approach captures all of the features obtained from the conventional calculations.

References

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