

ENVIRONMENTAL CONDITIONS

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ENVIRONMENTAL FACTORS AFFECTING REACTIVITY

Reactivity is, strictly speaking, not a constant, inherent property of a chemical species, since ambient conditions have a substantial influence on the amount of ozone that can be produced by a VOC within a specific airshed. The photolysis of atmospheric constituents, for example, depends on the overhead ozone column, the distribution of clouds, and the solar zenith angle. Chemical formation of ozone likewise depends on ambient pressure, temperature, humidity, the absolute VOC and NO_x concentrations, the VOC/NO_x ratio, and the overall supply of radicals (especially hydroxyl, which determines the atmospheric lifetimes of the majority of VOCs). These factors are in turn influenced by atmospheric transport to and from an airshed by prevailing winds, by horizontal and vertical mixing within the airshed, and by wet and dry removal processes. Anthropogenic and biogenic emissions of VOCs and NO_x themselves depend on wind, humidity, atmospheric stability, and temperature. Meteorology is therefore an important aspect of any discussion of the concept of reactivity. The familiar example of the Los Angeles basin, wherein so-called “inversion layers” of stable, warm air combine with the effects of local topography to produce frequent smog episodes, illustrates how critical the peculiar meteorological conditions of an airshed can be in accounting for ozone formation.

The central problem involving the impact of environmental factors on reactivity is whether or not a relative reactivity scale can be defined which is only weakly affected by

variations in environmental conditions within and among different airsheds, so that it can be applied on a national basis and with a reasonable expectation of effectiveness. For example, will the relative reactivity of VOCs within the Los Angeles basin differ substantially from that determined within the northeast corridor of the United States, where long range transport of ozone and precursors, as opposed to local trapping of air pollution, is an important phenomenon? A related issue is whether or not the scientific methodologies that have hitherto been used to examine this question are themselves capable of yielding an unequivocal answer.

The resolution of these difficulties depends partly on how the problem of ozone control is defined. Given that a change in the federal ozone standard (now 80 ppb averaged over 8 hours) has occurred, effectively giving more attention to chronic ozone exposure over large regions than to episodal peaks within urban airsheds, should reactivity be defined over multiple days and large regions rather than over single day urban episodes, as has previously been the case? If the answer to this last question is yes, then are the vital processes which may determine large-scale reactivity captured by current scientific models? The aim of this chapter is to enumerate and describe some of these vital processes so that models for environmental conditions can be appropriately evaluated, and the corresponding implications for future reactivity research identified.

ATMOSPHERIC STRUCTURE AND DYNAMICS

Before discussing the merits and demerits of any particular approach to reactivity, it is necessary to first understand the structural and dynamical features of the atmosphere that are vital to tropospheric ozone formation and transport. This includes the vertical stratification, stratospheric air intrusions, the boundary layer, atmospheric convection, the existence of westerly jet streams in the free troposphere, the role of large-scale weather (i.e., “synoptic” systems), microscale influences, and coastal meteorology.

The troposphere is defined as the region of the atmosphere immediately above the surface where temperature generally decreases with height. The top of the troposphere ranges from about 8 km at high latitudes to a maximum of about 16 km at the equator. The region of the atmosphere immediately above the troposphere and where the temperature generally increases with height is known as the stratosphere. The stratosphere is typically rich in ozone because of the equatorial maximum in photochemical ozone production at an altitude of about 35 km, and because of poleward and downward transport of ozone from this region. Occasionally, “tropopause folding” associated with certain weather events can result in stratospheric air intrusions into the troposphere (one aspect of so-called “stratospheric-tropospheric exchange”), during which downward transport of ozone-rich air produces sudden peaks in ground-level ozone (Danielsen, 1968; Ebel et al., 1991). This fact alone indicates the potential importance of downward subsidence throughout the depth of the troposphere in determining environmental conditions near the surface.

The troposphere itself is generally divided into the boundary layer, in which the frictional drag of the surface is important and where rapid vertical mixing occurs, and the free troposphere, in which the prevailing winds away from equatorial regions are determined largely by a balance between horizontal pressure gradients and the Coriolis force due to the earth's rotation (the so-called "quasi-geostrophic balance"). The height of the boundary layer increases with convective instability due to vertical temperature gradients, typically undergoing a diurnal variation and ranging from as low as 100 meters at night to as high as 3 kilometers during the day. This diurnal pattern can affect the VOC/NO_x ratio and radical density near the surface through changes in the effective diluting volume and through encroachment of free tropospheric air into the boundary layer.

Summertime conditions associated with the development of thunderstorms and cumulus towers can lead to a phenomenon known as penetrating or deep convection, wherein surface pollutants are rapidly (within an hour) lofted from the boundary layer into the free troposphere by intense convective plumes, and pollutants in the free troposphere are entrained into the boundary layer by a corresponding slow subsidence (within about 50 hours) in large regions around the convective plumes (Lelieveld and Crutzen, 1994). Thompson et al. (1994) showed that the central United States acts as a convective "chimney" for the country by venting large amounts of carbon monoxide and other ozone precursors from the boundary layer to the free troposphere, possibly contributing to high background levels of ozone in the eastern United States.

Once in the free troposphere, pollutants undergo faster eastward dispersion than they would otherwise near the surface, due to upper level winds associated with the climatological westerly jet stream centered at approximately 30 degrees north. The pollutants can then reenter the boundary layer either through convectively-induced subsidence and subsequent encroachment into the mixed layer, or within regions of subsiding air associated with traveling weather or "synoptic" systems. Carmichael et al. (1998) demonstrated using simulations of a 3-D Eulerian model and comparisons to observations, that strong downward fluxes of ozone from the upper troposphere associated with the passage of cold fronts can play a critical role compared to chemistry in accounting for variations in ozone near the surface. Cooper et al. (1998) likewise found evidence of strong ozone subsidence behind cold fronts from observations taken during the Atmosphere/Ocean Chemistry Experiment (AEROCE), together with indications that such post-frontal subsidence can bring substantial amounts of stratospheric ozone into the troposphere.

Within an urban airshed, environmental conditions are strongly affected by variations in the local heat balance, in air flow over topography, in source emissions, and in wet and dry deposition. During stagnant conditions, fast nocturnal winds can rapidly transport pollutants out of urban areas to rural regions (Banta et al., 1998; Meagher et al., 1998), whereas land-sea breeze circulations in coastal areas can re-circulate stagnant air back into an urban airshed, thus prolonging pollution episodes beyond a day and increasing the reactivities of slow-reacting compounds (McNair et al., 1994). It is also possible that in coastal cities such as Houston and Los Angeles, the presence of chlorine atoms from sea salt may account for more than 10% of initial VOC oxidation, thus significantly impacting ozone formation (Livingston and Finlayson-Pitts, 1991).

POTENTIAL IMPACTS OF LONG-RANGE TRANSPORT MECHANISMS

The coupling of the boundary layer and the free troposphere has important implications for long range reactivity because the lifetimes of some important ozone precursors such as PAN increase substantially in the colder, less humid environment of the free troposphere. Ozone itself lives considerably longer when not subject to surface deposition. Any transport mechanism, therefore, that lofts ozone or PAN into the free troposphere and then subsequently entrains it into the boundary layer may have an important chemical influence on surface air at large distances downwind of the jet stream. In addition, longer-lived organics such as methane and carbon monoxide can have a significant impact when transported downwind. Jeffries (1993) has shown that the majority of ozone formation in a typical urban airshed may actually be attributable to such longer-lived compounds, even though they are considerably less reactive than most VOCs when gauged by existing urban reactivity indices. McKeen et al. (1991) likewise showed using a 3-D regional model of the eastern United States that methane and carbon monoxide contribute significantly to regionally averaged net ozone formation. Given that air upwind of an urban area can have an ozone level already close to the new federal ozone standard (Valente et al., 1998), any ozone attributable to long-range transport will be of considerable importance.

A recent study by Berkowitz et al. (1998) examined airborne chemistry and meteorological measurements over the eastern seaboard of the U.S. using 4-D data assimilation within a mesoscale model, together with a Lagrangian particle dispersion model. They concluded that for a particular scenario on August 31, 1995, an elevated layer of ozone, PAN, and other ozone precursors just above the boundary layer was brought to the surface with the onset of convection. They further suggested that such elevated layers of pollutant frequently form over the northeastern United States due to lofting of pollutants into the free troposphere from distant sources, and that a significant portion of ozone at a particular location may be due to the entrainment of such layers into the convective boundary layer.

When ozone is entrained into the boundary layer, there is more formation of hydroxyl radicals, which then increases the local reactivity of VOCs. When PAN or other organic nitrates are entrained into the boundary layer, they act as potential sources, not only of radicals but also of NO_x, so that VOCs which form nitrates can act as remote sources of NO_x downwind. This effective remote supply of NO_x and radicals can therefore increase the long-range reactivity of parent VOCs, especially when the associated NO_x reservoirs are delivered to low-NO_x environments, where the efficiency of ozone formation is considerably greater than in urban areas (Lin et al., 1988), and where there is considerably less competition from in-situ NO_x sources.

In many areas of the country, local biogenic emissions of compounds such as isoprene may compete with or even dominate local anthropogenic sources of VOC, and some studies (e.g., Cardelino and Chameides, 1995) have used urban airshed models to deduce areas where local VOC control may be ineffective compared to NO_x control for such reasons. However, a mechanism by which VOCs contribute to the NO_x budget far downwind may conceivably allow remote urban VOCs which combine with intense mobile and stationary NO_x emissions to

compete effectively with in situ biogenic sources of VOCs as regional ozone precursors. Of course, biogenic emissions can themselves form transportable organic nitrates in addition to releasing radicals that contribute to local ozone formation. The wet and dry deposition rates of biogenic organic nitrates, however, may be such that they are actually an effective route for removal of NO_x from polluted air masses (O'Brien et al., 1995).

Measurements indicate that, even in remote regions of the troposphere, PAN and other organic nitrates may be contributing significantly to the total budget of reactive nitrogen (Atlas et al., 1992; Singh et al., 1992). A proper assessment of the role of organic nitrates in regional and global ozone pollution, however, will require a major improvement in both the analytical detection of organic nitrates and the accounting of organic nitrate degradation products within chemical mechanisms, including those that partition significantly in the aerosol phase.

Duncan and Chameides (1998) have recently examined the potential effects of urban control strategies on exports of ozone and ozone precursors from urban airsheds to the larger-scale troposphere using a simple urban plume model. They discovered that while NO_x reductions were always more effective than VOC reductions in controlling the direct export of ozone from urban areas, the relative importance of VOC and NO_x reductions in controlling the export of ozone precursors from the urban atmosphere was more complicated to describe. In particular, while NO_x reductions always reduced the exports of nitrogen oxide species and acetone, they enhanced the export of paraffins and significantly changed the speciation of the exported reactive nitrogen. Moreover, while VOC reductions decreased the export of PAN and other organic nitrates, they could also increase the export of NO_x and nitric acid. Duncan and Chameides (1998) concluded that a proper assessment of the impact of changing export rates of urban ozone precursors on tropospheric ozone can only be carried out with large-scale models.

The application of new-generation 3-D regional models to the assessment of reactivity becomes especially critical if long-range transport mechanisms involving boundary layer-free troposphere coupling are found to contribute substantially to the NO_x and ozone budgets in areas that are out of compliance with the new federal ozone standard. It will be important to determine the boundary conditions for such models accurately using hemispheric and global models, especially if hemisphere-wide transport significantly impacts regional background concentrations of ozone, nitrates, and long-lived organics. That this may in fact be the case is suggested by Jacob et al. (1993), who employed a 3-D regional model to study the effect of a 50% reduction in U.S. NO_x emissions. They found that this substantial emissions reduction led to a weak decrease in rural ozone over the eastern U.S. of only 15% due to the substantial import of ozone from outside North America. Moreover, they found that the total U.S. export of ozone and precursors to be about one-third that due to stratospheric-tropospheric exchange. The potential impact of such exports across the Atlantic is made clear in a study by Builtjes (1992), who concluded from experiments with the LOTOS 3-D model that persistently high regional ozone in Europe is affected by transport over the entire Northern Hemisphere.

VARIABILITY OF CURRENT REACTIVITY SCALES

Assessment of the urban reactivity scales defined by Carter (1994) are discussed in detail in a later chapter. We mention very briefly, however, some pertinent aspects of these assessments in order to point out the role that models play in examining the potential influence of environmental variability on reactivity scales.

The current use of reactivity within the United States is an outgrowth of attempts to solve the urban ozone problem as it was defined and understood during the 1970s through the major part of this decade, when controlling episodal peaks in ozone above 120 ppb near urban cores was the primary goal of air quality strategies. Carter's reactivity scaling approach acknowledges the role of environmental variability within this framework by averaging reactivities calculated with a simple box/trajectory model over 39 U.S. cities. Among the 39 scenarios, it is possible for a compound to go from being fairly reactive to having a negative reactivity (e.g., toluene), although the basic trend in the reactivity of most organics is maintained (i.e., highly/poorly reactive compounds under one scenario generally remain highly/poorly reactive under another). The impact of environmental variability is apparently lessened when relative rather than absolute reactivities are used, and when high NO_x conditions are assumed within each scenario (Carter, 1994). The assumption of high NO_x conditions, however, does not necessarily correspond to conditions under which exceedances of the new federal ozone standard may occur, particularly outside urban areas.

The issue of environmental variability has been further explored in comparisons between reactivities computed using the box model approach and those computed using 3-D Eulerian models, which cover domains with a wide range of environmental conditions, from NO_x-rich urban centers to VOC-rich areas downwind. The studies of Russell et al. (1995) and Bergin et al. (1995) showed that, with some notable exceptions such as aromatics and photoreactive species, multi-day reactivities derived from the CIT 3-D urban airshed model were in good agreement with Carter's box model-derived single-day reactivities in the Los Angeles basin. The CIT model, however, shares a common deficiency with Carter's box model, in that it is largely confined to the boundary layer. This feature eliminates the transport mechanisms involving the coupling of the boundary layer to the free troposphere referred to in previous sections. A similar criticism applies to the Photochemical Ozone Creation Potential (POCP) scale of Derwent and Jenkin (1991), which like the reactivity scales of Carter, is computed using a box/trajectory model, but for longer trajectories over multiple days. It is therefore not yet known whether the apparently good correlation between box/trajectory model reactivities and more sophisticated 3-D Eulerian model reactivities is retained when the vertical and horizontal domains of the 3-D model are expanded and the appropriate transport mechanisms considered, particularly for areas such as the Ozone Transport Assessment Group (OTAG) region, where long-range transport is a key factor.

SUMMARY AND RECOMMENDATIONS

Current urban reactivity scales presume that air near the surface moves slowly and is confined to the boundary layer. They do not consider long range transport mechanisms involving the coupling of the boundary layer to the free troposphere, wherein ozone and its precursors are rapidly vented aloft and quickly transported downwind of the mid-latitude jet stream, where they can be re-entrained into the boundary layer. If reactivity scales are to be relevant to the new ozone standard of 80 ppb averaged over 8 hours, then they must account for such transport mechanisms for the following reasons:

- Long-range transport of ozone and ozone precursors via the free troposphere has the potential to influence the level of radicals in remote urban and rural areas, thereby influencing the local reactivities of VOCs in those areas.
- Long-range transport of ozone precursors via the free troposphere has the potential to influence the NO_x budget in remote rural areas, through reservoir species such as PAN and other organic nitrates that do not easily rain out of the atmosphere.
- Long-range transport of ozone precursors via the free troposphere has the potential to produce significant quantities of ozone in remote urban and rural areas when compared to the difference between the new federal ozone standard (80 ppb) and the level of background tropospheric ozone (30 ppb).

Regional, 3-D Eulerian models that adequately resolve both the boundary layer and the free troposphere are the only tools that can properly account for long-range transport mechanisms involving boundary layer-free troposphere coupling. We therefore recommend that their use in reactivity research be expanded to properly design regulatory controls based on reactivity and to assess their effectiveness in achieving and maintaining compliance with the new federal ozone standard on a national basis.

We further recommend research in the following areas to better address the issues raised in this chapter:

- The role of upper and lateral boundary conditions for ozone and ozone precursors in determining the reactivities of VOCs in urban and rural airsheds.
- Improved representations of convective, mesoscale, and synoptic-scale transport in large-scale reactivity models, including deep convection, frontal motions, and tropopause folding events.
- More complete representation of radical sources in reactivity models, including chlorine radicals from sea salt in coastal airsheds.
- Better resolution of organic nitrates in chemical mechanisms, including both soluble multi-functional organic nitrates that may deplete NO_x from polluted air masses and non-soluble organic nitrates that can deliver NO_x to remote rural environments.

- Rigorous measurements of the total reactive nitrogen budget in urban and rural areas within the United States to provide more extensive ground truth for both chemical mechanisms and airshed models.
- More emphasis on evaluating export-oriented approaches to reactivity.
- Large-scale 3-D modeling assessments of the effectiveness of existing and alternative reactivity-based control strategies.

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