cell regeneration observed in adult recovery from bone-marrow aplasia that is mainly composed of memory CD4+ T cells (18). The trend toward normalization of CD4+ T cells displaying the CD28 co-stimulatory molecule (8) observed in our studies reflects the lower CD4+ T cell activation and might allow for some recovery from enhanced sensitivity to apoptosis or anergy (19). The loss of memory CD4+ T cell reactivity to recall antigens was indeed reversible under efficient antiviral therapy. This latter observation contrasts with the limited benefit for CD4+ T cell function reported with ritonavir alone, where a weaker reduction in viral load (−1 log) could only increase preexisting CD4+ T cell responses but failed to restore a lost T cell reactivity to recall antigens (20). The significant but partial restoration of CD4+ T cell proliferation to recall antigens that we report might participate to the progressive regeneration of mature peripheral CD4+ T cells observed after the first month of treatment, in agreement with murine models (21, 22).

This sequence of events suggests that, in the natural course of a productive infection, HIV activity per se is the driving force for chronic immune stimulation; the latter would take part in the defects in antigen-specific CD4+ T cell activation and proliferation noted in HIV-infected patients (6, 7). Because such functions are required for a normal homeostasis of mature peripheral T cells in adults (21), their alteration would appear as a key mechanism in HIV-induced CD4+ T cell depletion. This impairment of the mature CD4+ cell repopulation process was, in part, reversible under effective antiviral treatment, although the balance between CD4+ and CD8+ subsets was not yet normalized with CD8+ counts still higher than normal and CD4+ counts remaining below normal thresholds. Earlier or stronger therapeutic interventions should reasonably achieve better reversibility.

**REFERENCES AND NOTES**


9. B. A. Furt et al., data not shown.


23. We thank the clinicians participating in the therapeutic trial: A. Saimot, I. Gorin, G. Pialoux, and P. De Truchis, V. Calvez for analyzing HIV-1 plasma viral load; J. P. Chauvin from Abbott Laboratories for sponsoring the clinical trial; D. Faudoit and M. Hirn from Coulter/Immunotech for kindly providing reagents; and SIDACTION and the Agence Nationale de Recherches sur le SIDA for financial support.

12 February 1997; accepted 7 May 1997

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**Chemical Coupling Between Atmospheric Ozone and Particulate Matter**

Z. Meng, D. Dabdub, J. H. Seinfeld*

A major fraction of ambient particulate matter arises from atmospheric gas-to-particle conversion. Attempts to reduce particulate matter levels require control of the same organic and nitrogen oxide (NOx) emissions that are precursors to urban and regional ozone formation. Modeling of the gas-aerosol chemical interactions that govern levels of particulate components showed that control of gas-phase organic and NOx precursors does not lead to proportionate reductions of the gas-phase–derived components of atmospheric particles. The chemical coupling between ozone and particulate matter has implications for strategies to achieve the new ozone and particulate matter standards proposed by the U.S. Environmental Protection Agency.

Ozone has historically been regarded as the principal urban and regional air quality problem in the United States (1). Epidemiological evidence that urban mortality rates are correlated with mass concentration of fine particulate matter has now focused intense interest on reducing levels of airborne particles (2). In November 1996, the U.S. Environmental Protection Agency (EPA) proposed new ozone (O3) and particulate matter air quality standards (3). Because exposure to lower O3 concentrations over longer periods of time than the current standard (0.12 parts per million averaged over a 1-hour period) is deemed to be of primary relevance, EPA proposed to lower the O3 standard to 0.08 ppm averaged over an 8-hour period. EPA also proposed to revise the existing particulate matter (PM) standard to add two new PM2.5 (particulate matter of diameter less than or equal to 2.5 µm) standards set at 15 µg m⁻³ for the annual mean, and 50 µg m⁻³ over a 24-hour period. Hundreds of counties in the United States in addition to those already in violation of the current standards are estimated to violate either or both of the new O3 and PM standards (4).

Ozone and PM have traditionally been considered as separate problems. However, O3 and PM are chemically coupled, and this coupling is of profound importance in understanding processes that control the levels of both. Urban and regional ozone abatement strategies have, for more than a decade, been evaluated with three-dimensional atmospheric models by the EPA and state and local agencies (1). We report here the application of a three-dimensional, size- and chemically resolved gas-aerosol model to examine how the chemical coupling that exists between O3 and PM influences joint control of the two classes of pollutants. The common components of atmospheric particles, such as sulfate (SO4²⁻), nitrate (NO₃⁻) ammonium (NH₄⁺), organic compounds, crustal material, and water, reach the particulate phase by several different processes (Fig. 1). Aside from the direct emission of particles into the atmosphere, gas-to-particle conversion processes play an essential role in determining the mass of airborne PM. Such processes depend intimately on the organic
and NO₃ gas-phase chemistry that generates ozone (Fig. 2). Gas-phase organic and NO₃ chemistry is driven by the hydroxyl (OH) radical, the levels of which depend on the mixture of organics and the organic/NO₃ relative concentrations (5). Gas-phase conversion of SO₂ to aerosol sulfate occurs by means of the reaction SO₂ + OH, which leads to H₂SO₄ vapor molecules that rapidly transfer to the particulate phase by nucleation or condensation on existing aerosol surfaces (6, 7). In the presence of fogs or clouds, aqueous-phase conversion of SO₂ to sulfate takes place, for example, by dissolved hydrogen peroxide (H₂O₂) or O₃ (8), and H₂O₂ concentrations depend indirectly on the OH concentration. Hydrogen peroxide is itself a gas-phase product of the HO₂-HO converts. A dominant termination reaction in the photochemical O₃ system is the production of nitric acid

\[ \text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3 \]  

(1)

As the most ubiquitous basic gas in the atmosphere, ammonia provides a route for the formation of particulate-phase nitrate by means of the reversible reaction (9)

\[ \text{NH}_3(g) + \text{HNO}_3(g) \rightleftharpoons \text{NH}_4\text{NO}_3(p) \]  

(2)

where (g) denotes gas phase and (p) denotes particulate phase. Secondary organic aerosol results when a parent organic molecule A reacts with OH, O₃, or NO₃ to yield semivolatile products that partition themselves between the gas and aerosol phases (10).

The major gas-phase sinks of NO₃ are HNO₃ and peroxyacetyl nitrate (PAN), CH₃C(O)OOONO₂. Because of its reversible formation through reaction of peroxyacetyl radicals CH₃C(O)OO (sometimes denoted RCOO⁻) and NO₂,

\[ \text{CH}_3\text{C(O)OO} + \text{NO}_2 \rightleftharpoons \text{CH}_3\text{C(O)OOONO}_2 \]  

(3)

PAN serves as a temporary NO₃ reservoir. Once formed, HNO₃ may either be removed by deposition or, in the presence of NH₃, form particulate NH₄NO₃. Gas-phase photochemistry determines the relative amounts of HNO₃ and PAN formed, and the amount of NH₃ present governs the subsequent split between HNO₃ loss by deposition and particulate NH₄NO₃ formation.

Gas-phase HNO₃ has a relatively high affinity to deposit on virtually any surface, a process termed dry deposition. A layer of HNO₃ uniformly distributed up to a height of 1 km has a half-life of about 3 hours (11). Particulate NH₄NO₃ on the other hand, has an affinity for dry deposition that is about an order of magnitude less than that of HNO₃ (12). Consequently, for a layer of NH₄NO₃ particles uniformly distributed up to a height of 1 km, the half-life is an order of magnitude larger than that of HNO₃ vapor. In its role in converting HNO₃ to NH₄NO₃, ammonia therefore exerts a direct influence on the airborne lifetime of nitrate. At low NH₃ concentrations, more of the nitrate remains in the gas phase as HNO₃ where it is subject to dry deposition. In contrast, at higher concentrations of NH₃, more of the total nitrate is converted to particulate NH₄NO₃, and because of the lower dry deposition rate of particles, the overall atmospheric lifetime of nitrate is increased. As HNO₃ is removed by dry deposition, the HNO₃/NH₃/NH₄NO₃ equilibrium can be shifted back toward the gas phase, causing NH₄NO₃ to evaporate. Converting NH₄NO₃ back into HNO₃, which is subject to an enhanced rate of dry deposition, serves to shorten the overall atmospheric lifetime of oxidized nitrogen.

Three-dimensional urban and regional ozone models have been in existence for two decades (13). We report here on the application of a three-dimensional Eulerian urban and regional atmospheric model designed to study the dynamics of trace gases and aerosols (14). Gas-to-particle conver-

**Fig. 1.** Routes of incorporation of chemical species into atmospheric particulate matter. OC and EC denote organic and elemental carbon; other species are defined in the text.

**Fig. 2.** Chemical coupling in the atmospheric gas, particle, and droplet phases. Cycling in the OH-H₂O₂ system generates tropospheric ozone (O₃) and hydrogen peroxide (H₂O₂), which are principal oxidants of dissolved SO₂. Hydroxyl (OH) levels determine the rates of oxidation of SO₂ and NO₂ to sulfuric and nitric acids, respectively, which are gas-phase precursors to aerosol sulfate and nitrate. Hydroxyl (and ozone) attack on organic molecules (denoted by RH in the figure, where R is an organic group) containing seven or more carbon atoms can generate semivolatile secondary organic aerosol, Dₚ is particle diameter and hν is energy of a photon.
emissions. Numbers in parentheses are percentage changes compared with the base case. No NH$_3$
maximum 1-hour average HNO$_3$ (13.8 parts per billion) occurred at noon. Measurements were reported as 4-hour
downtown (central) Los Angeles and Riverside, California, on 27 to 28 August 1987.

We performed an extensive test of the performance of the model in simulating available data on gases and aerosols in the South Coast Air Basin from 27 to 28 August 1987, a period during the Southern California Air Quality Study (SCAQS) that experienced exceedingly high ozone and PM levels and for which a comprehensive gas-aerosol database exists (16).

Performance of the model in simulating the 27 to 28 August 1987 episode was analyzed by Meng et al. (17). Figure 3 shows the observed and predicted levels of O$_3$ and PM$_{2.5}$ NO$_3^-$ at the Central Los Angeles and Riverside monitoring stations. A question critical to model application is the degree of uncertainty in predictions as a result of uncertainties in model inputs. It is well established that the most uncertain input in Los Angeles air pollution modeling is the volatile organic compound (VOC) inventory (18). Varying the total area-wide VOC emissions by ±25% produces little change in PM$_{2.5}$ levels, so input uncertainties do not appear to affect the use of the model to explore the phenomenology of joint control of ozone and PM.

The sensitivity of PM levels to emission reductions of organics and NO$_x$ can be assessed by systematically changing source emissions by prescribed factors. We considered a matrix of control strategy cases (Table 1). Entries in the table indicate maxi-

<table>
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<th>NO$_x$ reduction</th>
<th>Chemical species</th>
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<th>25%</th>
<th>50%</th>
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<tr>
<td>0%</td>
<td>O$_3$ (ppb)</td>
<td>180*</td>
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<td>119</td>
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<td>HNO$_3$ (ppb)</td>
<td>13.8*</td>
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<td>16 (+17%)</td>
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<td>13.7*</td>
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<td>PM$_{2.5}$ NO$_3^-$ (µg m$^{-3}$)</td>
<td>97*</td>
<td>119 (+23%)</td>
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<td>173 (+18%)</td>
<td>175 (+19%)</td>
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<td>25%</td>
<td>O$_3$ (ppb)</td>
<td>175 (-2.6%)</td>
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<td>13 (-6%)</td>
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<td>134 (-9%)</td>
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<td></td>
<td>PM$_{2.5}$ mass (µg m$^{-3}$)</td>
<td>120 (-18%)</td>
<td>133 (-9%)</td>
<td>124 (-15%)</td>
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</table>

*These entries are the model-simulated values at Riverside, California, on 28 August 1987 for base-case emissions inventory. Correspondence between the simulated and measured values of O$_3$ and PM$_{2.5}$ NO$_3^-$ is shown in Fig. 3. The maximum 1-hour average HNO$_3$ (13.8 parts per billion) occurred at noon. Measurements were reported as 4-hour averages; from noon to 4 p.m. the observed 4-hour average HNO$_3$ was 5.4 ppb, as compared with the predicted 4-hour average of 6.5 ppb. Maximum total measured PM$_{2.5}$ mass (4-hour average) was 120 µg m$^{-3}$, as compared with the maximum 1-hour average prediction of 146 µg m$^{-3}$.

<Figure 3. Observed (data points) and predicted (solid line) concentrations of O$_3$ and PM$_{2.5}$ NO$_3^-$ at downtown (central) Los Angeles and Riverside, California, on 27 to 28 August 1987.>

<Figure 4. Peak 1-hour average PM$_{2.5}$ nitrate levels achieved at Riverside, California, on 28 August 1987 as dependent on the degree of emissions reduction from the base conditions of the episode.>

Table 1. Maximum 1-hour average concentrations simulated at Riverside, California, on 28 August 1987 for various combinations of VOC and NO$_x$ reduction from base estimated 1987 basinwide emissions. Numbers in parentheses are percentage changes compared with the base case. No NH$_3$ emission reduction is assumed.
dicted to lead to a slight decrease in peak NOx reduction in NOx nitrate; a 50% increase in maximum PAN, and a 10% decrease, but one that is proportionate to the Basin being in an overall NOx-rich state. Reductions in VOC emissions alone lead to more significant decreases in maximum O3 levels than equivalent reductions in NOx.

An important feature of the predicted response to VOC and NOx reductions is the behavior of HNO3, PAN, and PM2.5 nitrate as either NOx or VOC emissions are reduced. A 25% reduction in NOx emissions at the base VOC level is predicted to lead to only a 3% reduction in peak HNO3, a 4% increase in maximum PAN, and a 10% reduction in peak PM2.5 nitrate; a 50% reduction in NOx leads to a 5% increase in PAN and a 21% reduction in maximum PM2.5 nitrate. When total NOx is reduced, less NO2 is available to produce either HNO3 or PAN (reactions 1 and 3). If OH and RCO3 radicals remain unchaged as NOx is decreased, reactions 1 and 3 predict that both HNO3 and PAN should decrease accordingly. However, because HNO3 decreases less than proportionately and PAN actually increases, decreases of NOx lead to increases in both OH and RCO3 levels, a behavior that is consistent with the region being in an NOx-rich condition. If RCO3 increases considerably more than OH, then PAN levels increase while HNO3 levels exhibit a modest decrease, but one that is proportionately less than the NOx reduction. As VOC levels are decreased, at any given NOx level, PAN concentrations decrease as a result of the diminished availability of RCO3 radicals. As less RCO3 is available to convert NO2 to PAN, more NOx is available to react with OH to form HNO3 (though overall OH levels are less than in the base case). Because of this increase in HNO3, PM2.5 nitrate also increases. When production of RCO3 cannot compensate for the NOx reduction, PAN decreases also [compare PAN levels at each of 25 and 50% VOC control at 25 and 50% NOx control (Table 1)]. Whereas our calculations are specific to the South Coast Air Basin of California, these conclusions can be expected to hold generally for any region having similar relative VOC/NOx levels.

Maximum 1-hour PM2.5 nitrate levels at Riverside for emission reductions of NOx only, NH3 only, and NOx and NH3 together (Fig. 4) illustrate the response of particulate nitrate levels to NH3 emissions changes, which is indicative of the extent to which NH3 controls the fixation of HNO3 vapor to NH4NO3. For reductions of up to 50%, PM2.5 nitrate reductions are essentially the same for individual reductions in NOx or NH3; at the 75% control level, formation becomes somewhat more NH3 controlled. That PM2.5 nitrate levels are substantially decreased when NOx and NH3 are jointly reduced indicates that neither HNO3 nor NH3 individually dominates nitrate formation under current conditions.

Reduction of VOC and NOx emissions to meet the proposed new standards for O3 and PM in those areas that are in violation will require expenditures of billions of dollars. Control strategies need to account for the intricate coupling that exists between O3 and PM. The results presented here indicate that control of gas-phase VOC and NOx precursors generally does not lead to proportionate reductions of the secondary components of ambient particulate matter.

REFERENCES AND NOTES


14. The first three-dimensional, gas-aerosol, urban-scale model was that of C. Pilinis and J. H. Seinfeld [Atmos. Environ. 22, 1985 (1988)]. Development of the simulation equations on which the current model is based is given in (17). A full description of the current model used in this study, together with a detailed evaluation of the model’s performance in simulating the August 1987 episode considered here, will appear in (17).


19. We would like to acknowledge support by the Electric Power Research Institute, the IBM Environmental Research Program, the U.S. Environmental Protection Agency Center on Airborne Organics, the State of California Air Resources Board, and NSF.

29 April 1997; accepted 17 June 1997
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Science 277 (5322), 116-119.
DOI: 10.1126/science.277.5322.116