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**EXAMINING THE GLOBAL IMPACT OF LOCAL/REGIONAL AIR POLLUTION: THE  
ROLE OF GLOBAL CHEMICAL TRANSPORT MODELS**

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**INTRODUCTION**

The environmental impact of chemically reactive air pollutants on both local air quality (smog) and the regional ecosystem (acid rain) is well established. The chemical and meteorological models used to study these problems are well known to most at this conference. On a larger scale are the potential impacts of air pollution on the global environment, both direct (air quality, sulfur and nitrogen budgets) and indirect (atmospheric reactivity, climate). Pollution sources of SO<sub>2</sub>, NO<sub>x</sub> and CO form a major component of the respective global budgets (e.g. Logan et al., 1981; Logan, 1983). Moreover, NO<sub>x</sub> concentrations, in both the polluted cities and the remote troposphere, play the dominant role in tropospheric ozone production (e.g. Isaksen, 1988), and indirectly control the oxidative power of the troposphere, i.e. its ability to cleanse itself of greenhouse gases such as methane. Gaseous sulfur levels over the ocean may have a major impact, via CCN levels, on global cloudiness and climate (Charlson et al., 1988).

We might expect the global impact of air pollutants to be greatly limited by their relatively short atmospheric lifetimes. However, with anthropogenic emissions being such a large fraction of the global budgets and natural levels so low in the unpolluted troposphere, even a small fraction of the emissions can play a major role. This discussion of global chemical transport models (CTM), will first focus on the major components of global transport and then examine three examples taken from recent simulations of the global transport and deposition of reactive nitrogen emitted from fossil fuel combustion.

**GLOBAL TRANSPORT**

A model of global transport has three major components: 1) An effective regional source that includes not only the actual emissions, but their chemical reactions and the meteorology responsible for mixing the surface emissions into the free troposphere; 2) Long-range advection by the collection of 3-dimensional meteorological events that comprise the transport climatology, frequently described in terms of the mean and eddy winds; 3) An effective removal function that includes the individual processes of wet and dry deposition, the chemical conversion among species of varying surface

reactivity and solubility and their transport into the boundary layer and to the ground. These components of global or long-range transport are discussed in some detail in a recent NATO-ASI publication (Isaksen, 1988) on tropospheric ozone and in a soon-to-be published NATO ASI publication (Knap et al., 1989) on long-range transport from the continents to the ocean.

### Effective Source

Emission. Global source functions for emissions from fossil fuel combustion are available on coarse  $5^{\circ} \times 5^{\circ}$  grids for  $\text{CO}_2$  (Marland et al., 1985) and  $\text{NO}_2$  (Hameed and Dignon, 1988) and a high resolution ( $1^{\circ} \times 1^{\circ}$ ) source is under development for  $\text{SO}_2$  and  $\text{NO}_2$  (Hameed, private communication). These are based on U.N. fuel use statistics and apportioned by population. A medium resolution ( $2.4^{\circ} \times 2.4^{\circ}$ ) global source function has been developed for the fossil fuel emissions of  $\text{NO}_2$  (Levy and Moxim, 1988) and high resolution regional sources for combustion gases have been developed for the U.S. and Canada (Middleton, 1987) and Europe (Eliassen et al., 1988). Where the data are available, the emissions are apportioned among the boundary layer levels according to the source type and according to the stack height for point sources. Area sources, generally autos and trucks, are released at the surface and are immediately subject to dry deposition. While there is extensive information about source type and stack height for U.S. and Canadian emissions, the data is more limited for Europe and essentially non-existent for the rest of the globe.

Chemistry. Once emitted, the fraction available for global transport, i.e. the effective source, is influenced by the rate of chemical conversion of the emissions to more soluble or surface reactive compounds that may be deposited in the emission region before being lifted into the free troposphere. In general, air with ppbv or more reactive nitrogen is polluted and has a complex chemistry involving the oxidative degradation of a wide range of reactive hydrocarbons, both natural and anthropogenic. Extensive gas-phase chemical reaction schemes for the polluted urban atmosphere have been developed and verified against smog chamber data (e.g. Leone and Seinfeld, 1985) and simplified versions have been recently employed in regional air pollution models (Stockwell, 1986; Chang et al., 1987; Hov et al., 1988). Chemical schemes for the polluted background continental atmosphere, with high levels of natural reactive organics, such as isoprene, have also been developed (e.g. Liu et al., 1987) and included in 3-D regional (Trainer, private communication) and 2-D global (Isaksen and Hov, 1987) models. A simplified scheme has been used in a quasi 3-D global model (Zimmermann, private communication).

The oxidation of  $\text{SO}_2$  by  $\text{H}_2\text{O}_2$  in cloudwater is a major  $\text{SO}_2$  oxidation mechanism (e.g. Chameides, 1984), and other heterogeneous reactions are believed to be important for oxidizing  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  to nitrate and nitric acid, particularly in the dark (Platt et al., 1984). While complex chemical reaction schemes have been developed for simplified cloud models, their use in 3-D regional/global transport models is limited (e.g. Carmichael et al., 1986). Instead, heterogeneous oxidation is generally treated as a simple first order process depending only on the gas phase concentration of the oxidant ( see Chang et al., 1987 for a recent discussion).

Boundary Layer/Free Troposphere Transport. Slow winds and surface removal make the long range transport of reactive gases unlikely in the boundary layer (B.L.). The meteorology producing transport out of the B.L. has an immense range of spatial scales: turbulence on the scale of meters; local convection on the scale of kilometers; cumulus clusters and fronts on the scale of tens of kilometers; and large scale frontal lifting and extratropical cyclones on the scale of hundreds of kilometers. While global

transport models now resolve extratropical cyclones and can be expected, in the future, to qualitatively resolve the vertical transport in fronts and cumulus clusters, neither global nor mesoscale models are expected to simulate small scale turbulence and convection. Such processes must be parameterized in terms of the model's resolved variables.

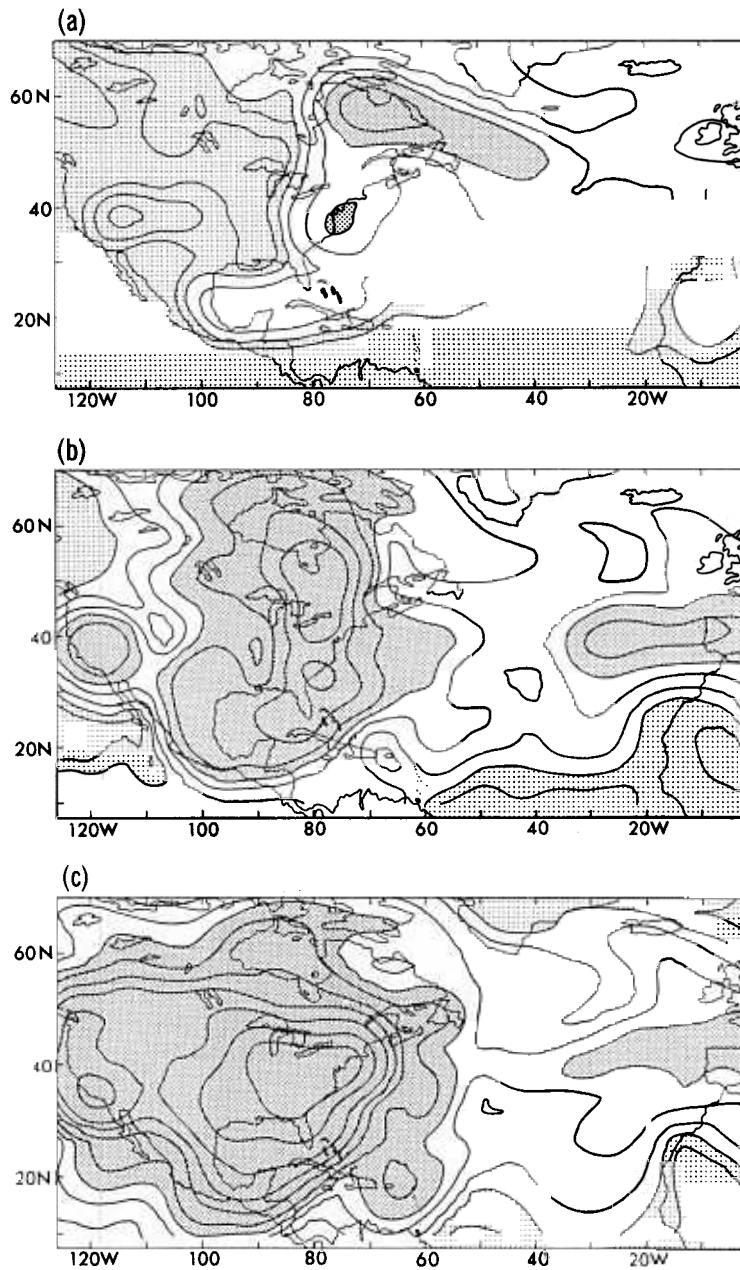


Fig. 1. NO<sub>y</sub> mixing ratios (ppbv) over North America and the Atlantic at 3 levels: (a) 500mb; (b) 835mb; and (c) 990mb. Log intervals 1-2-5. The light dots are less than 0.010ppbv and the dark dots are greater than 0.100ppbv.

Extratropical cyclones are an important mechanism for transport between the B.L. and the free troposphere, particularly in the winter and spring, and must be resolved by global models. As an example of this process, simulated instantaneous NO<sub>y</sub> fields resulting from the passage of a coastal storm over a polluted region (in this case NO<sub>x</sub> emissions) are shown in Fig. 1. As the storm progresses up the east coast of North America, the pollution is lifted in the rising air on the leading/precipitating side of the storm. While much of the soluble portion will be removed by the precipitation, some of the pollution remains in the lower troposphere (835mb) and is carried north into Canada. A portion is lifted higher into the middle troposphere (500mb) where it is caught in the strong westerly flow and swept across the North Atlantic. Once in the middle troposphere, the pollution moves quite rapidly and is protected from removal until it is swept down and caught in another storm system. This transport mechanism is supported by the isolated area of pollution at 835mb and 990mb over the Eastern Atlantic, which increases with height and is clearly disconnected from the main body over North America.

Cumulus convection, an important means of vertical transport, is the subject of a number of papers at this meeting. A relatively simple approach (Levy et al., 1982) identifies convective instability in the model atmosphere (via the bulk moist Richardson number) and employs a vertical diffusion that responds strongly to it. However, transport by individual cumulus clouds is not thought to be diffusive (e.g. Gidel, 1983; Chattfield and Crutzen, 1984). The details of parameterizations based on more realistic representations of a cumulus cloud, essentially lower dimension cloud models, will be discussed by others in this volume. In practice, the large mismatch of scales, 100's of km for the models and 1-10 km for the convection, makes it very difficult to connect the convection process to a global model in a physically meaningful way. Furthermore, while individual cumulus clouds may produce tracer vertical profiles that are inconsistent with eddy diffusion, the collection of processes associated with convection (strong updrafts, larger-scale subsidence and entrainment) may produce a net transport that appears to be diffusive when averaged over hundreds of kilometers.

Calculations of transport of a soluble and insoluble tracer in a 2-D anelastic cumulus cloud model (Lipps and Hemler, 1982) are presented in Fig. 2 (F. Lipps, private communication). The initial mixing ratio is normalized to 1.0 below 1.75km and set to 0.0 above. The boundaries are open and the only source of tracer is inflow at the sides, using mixing ratios from the initial condition for that height. Note that almost no soluble tracer reaches the mid-troposphere, though there is some vertical transport in the rain core. The average vertical profile for the complete domain could be represented by vertical diffusion. The vertical profile for the insoluble tracer is quite concave near the rain core with a deep minimum in the mid-troposphere, while it decreases rapidly with height out at the edges of the cloud. It is not clear that the vertical profile, when averaged over the domain, could not be represented by a 1-D eddy diffusion treatment of cloud transport. It does suggest that simple 1-D cloud models (Gidel, 1983; Chattfield and Crutzen, 1984), when applied to the large grids of global models, will exaggerate both the vertical flux of tracers and the concavity of their vertical profiles. Mass flux across the 6km level is essentially 0 for the soluble tracer and 2%/hr for the insoluble tracer. Preliminary calculations with a 3-D cloud model give qualitatively similar results with 1/3 of the 2-D mass flux. Clouds with reactive gases will be discussed by others in this volume.

At the smallest scale we find turbulence, the great unsolved problem in fluid dynamics. Currently, there is neither a realistic physical model nor sufficient observational data to construct an empirical one. Furthermore, the spatial scales of boundary layer turbulence are so small that they are

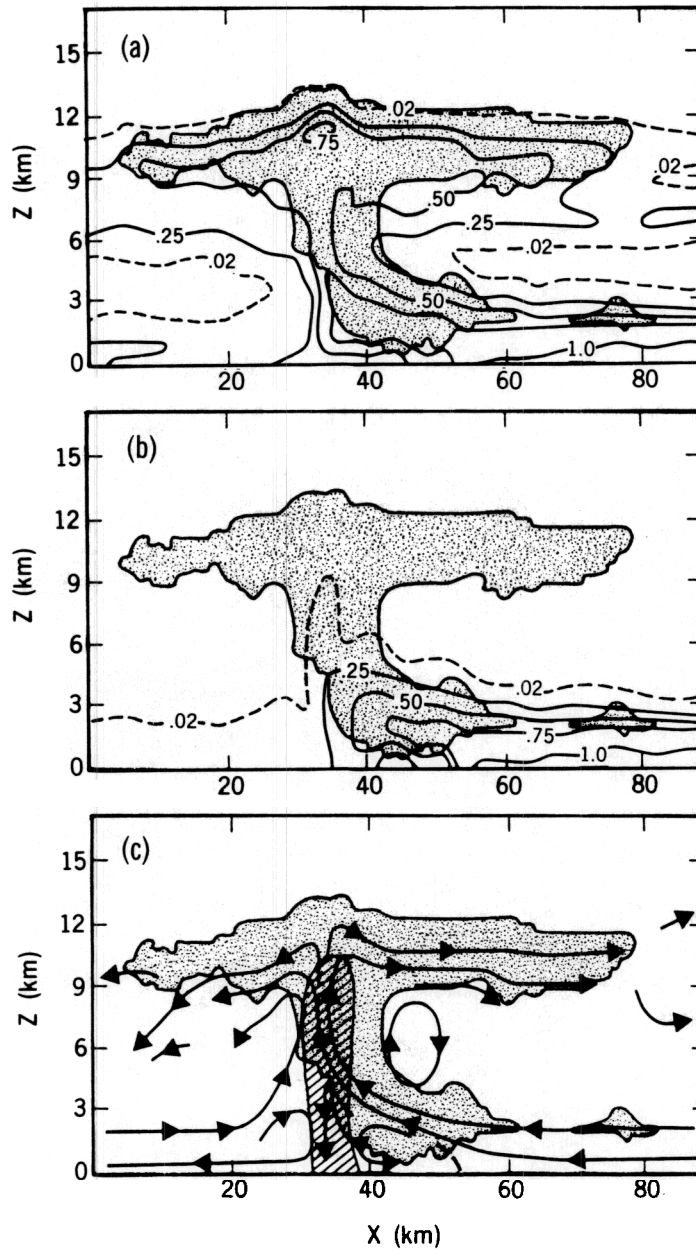


Fig. 2. Clouds are indicated by the stipled area. The hatched area indicates the vertical shaft with rain present. Concentration is in normalized units  
 (a) Distribution of insoluble tracer at 3 hours.  
 (b) Distribution of soluble tracer at 3 hours.  
 (c) Schematic plot of the flow field

effectively decoupled from the resolved stability of the highest resolution global model. As a result, sub-grid scale parameterization of boundary layer turbulence is the least satisfactory component of transport simulations.

The simplest treatment assumes a constant diffusion coefficient with atmospheric transport driven by the tracer gradient. While this has some statistical significance, it is non-physical. Atmospheric motions are independent of the gradients of trace gases, though the ultimate result of the ensemble of motions resembles diffusion in that it destroys concentration gradients. By adding wind shear dependence, we gain a connection to the mechanical source of turbulence. Such a term, with a height dependent diffusion coefficient, has been used to generate vertical mixing when the model's boundary layer is stable, for example over continents in the winter (Levy and Moxim, 1988). At the next level of complexity is a parameterization that reacts strongly when the model atmosphere is unstable, generally keying off of the model's Richardson Number (e.g. Levy et al., 1982). While this has been successful under conditions of large scale instability that can be diagnosed on the model grid, it provides no vertical transport when the atmosphere is stable on the large scale. At this time the only recourse, when the model is stable, is some form of constant eddy diffusion. More detailed treatments of turbulence have been developed (e.g. Mellor and Yamada, 1982) but have not been successfully applied to global/regional transport models.

#### Large-Scale Advection

Atmospheric transport is the result of many discrete and disparate 3-dimensional transport events. The ultimate simplification, "the highways in the sky" (Galloway, private communication), is to transport with time-averaged horizontal winds and ignore the vertical motion (Galloway and Whelpdale, 1987). An added sophistication is to combine the time-mean horizontal wind fields with a vertical diffusion field as in the MORGUNTIA model (Zimmermann, this volume). In all cases, the use of time-average winds neglects time varying meteorology, ranging from small scale convection, through meso-scale cyclones and including planetary scale eddies. The time varying component is important for such large-scale transport as interhemispheric exchange (Prather et al., 1987), and it is critical for short-lived trace species, which, because of large spatial gradients in their mixing ratio, have large local fluctuations in time. Unless the fluctuations of the winds and the trace species are randomly correlated, the mean wind will not generate the mean transport. To demonstrate this point more clearly, a series of idealized model experiments are performed for a short lived tracer with a surface source.

Time Mean Winds. After averaging time-dependent winds from a GCM (Mahlman and Moxim, 1978) over the four seasons, the distribution of combustion nitrogen emitted in North America is simulated with both the seasonally averaged (constant) winds and the full time-dependent winds. In both cases the deposition terms are adjusted to give the observed yearly integral of wet deposition over North America (~2 tg/yr) and realistic mixing ratios in the boundary layer. The seasonal distributions of NO<sub>y</sub> for the time-averaged winds are compared with those for the complete time-dependent meteorology in Figures 3 for winter and in Fig. 4 for summer.

In the winter the time-average winds confine the combustion nitrogen to the model's mean North Atlantic storm track at the surface and to a mid-latitude zonal belt in the free troposphere. Time-average winds greatly exaggerate transport to Europe while carrying almost nothing into the Arctic. The time-varying winds transport in a more diffuse pattern over the North Atlantic, the Arctic and Europe. In particular, the wintertime transport to the Arctic and most of the North Atlantic is dominated by eddy processes. In the summer, the time-mean winds carry less than 1pptv NO<sub>x</sub> over the Pacific to Hawaii, while both the time-dependent model winds and the real atmosphere transport much more (Levy and Moxim, 1988; Moxim, 1988). Because of the weak

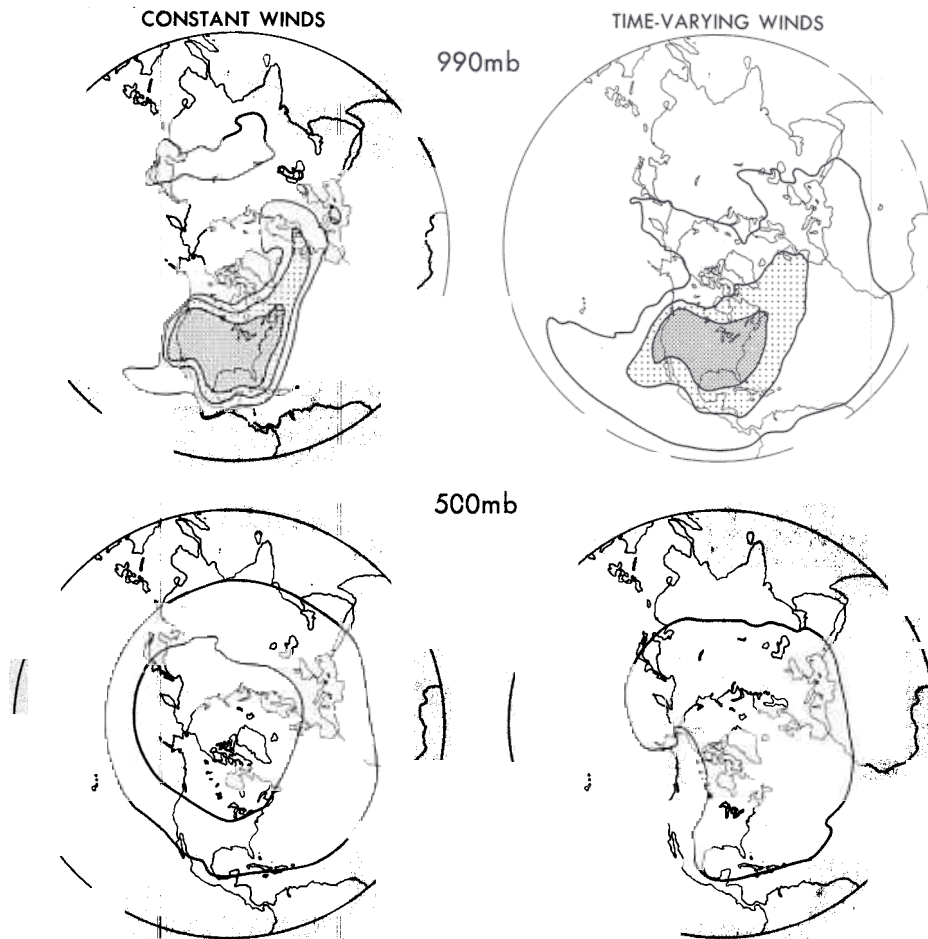


Fig. 3. Winter average  $\text{NO}_y$  mixing ratios (ppbv) on 990mb and 500mb surfaces. The clear contour is 0.01 - 0.1, the dotted area is 0.1 - 1.0, and the dark is 1.0 - 10.0

zonal flow and weak residual stationary features in the time-mean field. transport over the Atlantic is also greatly underestimated.

**Eddy Processes.** It should be clear from the previous section that transient processes, which are averaged out of the time-mean winds, play an important role in tropospheric transport. We briefly examine 3 synoptic-scale examples of the role of time-varying meteorology that were simulated by a global CTM.

Combustion nitrogen is not simply advected southwestward from the continental U.S. to Hawaii by surface winds circulating around the subtropical high over the Pacific, a major feature of the time-average meteorology in both the model and the real world. Rather, the transport of pollution from the west and Gulf coasts results from a complicated interaction of dry convection and synoptic-scale 3-D flow. This behavior is simulated by the model's time-varying winds as shown in the surface simulation in Fig. 4 and is observed in  $\text{HNO}_3$  measurements at Mauna Loa

(Galasyn et al., 1987). Detailed discussions of the transport of combustion nitrogen to Hawaii (Moxim, 1988; Levy, 1988) and to the North Pacific in general (Levy and Moxim, 1988) are presented elsewhere.

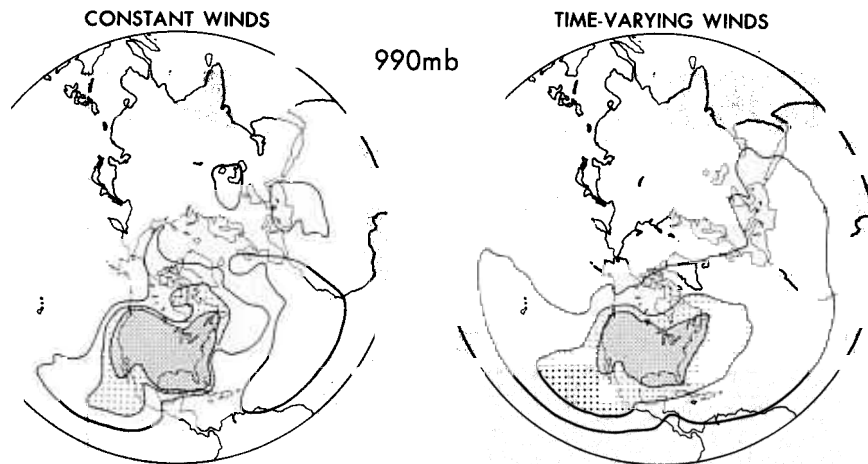


Fig. 4. The same as Fig. 3 except for summer averages

As we can tell from Fig. 3, there is essentially no wintertime transport from the U.S. to Bermuda by the time-mean winds. However, the simulated time series of NO<sub>y</sub> at Bermuda (see Fig. 5) for the time-varying winds is highly variable with peak values of 3 ppbv. Specifically, we consider the period (Feb 22-24) when a storm is moving up the East Coast from North Carolina to Nova Scotia. The 3-D back-trajectory for the February 24th peak originates at ~780mb over the Ohio Valley. The nitrogen emissions are carried to Bermuda in air descending in a southeasterly direction behind the storm as it moves up the coast. This and other simulated transport events will be the subject of a future paper.

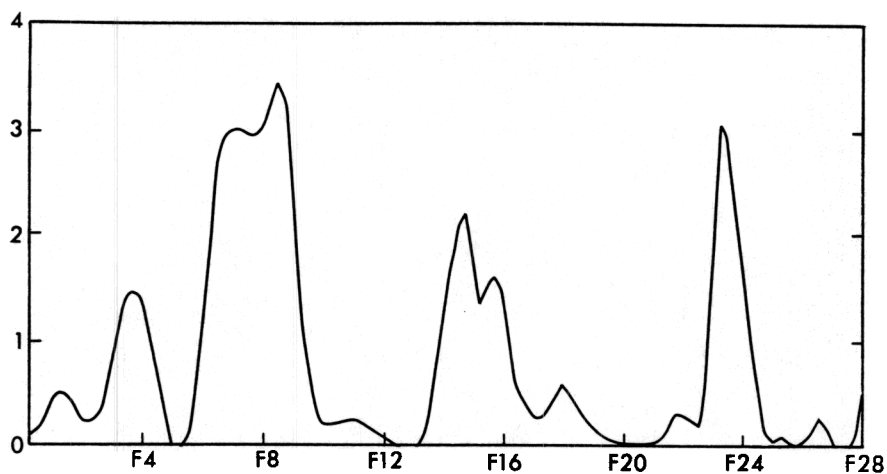


Fig. 5 Simulated boundary layer NO<sub>y</sub> (ppbv) for the month of February over Bermuda



Transient meteorology can also affect deposition. Our simulations predict and recent analysis confirms (Dana and Slinn, 1988) that, over the source region where local sources, not transported emissions, control the local mixing ratio, deposition and precipitation are highly correlated. However, at clean sites the local mixing ratio is strongly influenced by transported emissions and the deposition depends, not on the magnitude of the precipitation, but on the history of the air mass preceding the event. An example is given in Figure 6. Over Nova Scotia, Canada, a region that is strongly affected by transported NO<sub>x</sub> from the west and southwest, the deposition of acid nitrogen is not at all correlated with the intensity of precipitation. The heavy rainfall of a strong coastal storm produces little nitrogen deposition because the preceding flow of air was off the ocean and relatively clean. However, the light rain of a frontal passage results in heavy nitrogen deposition because the northward flow ahead of the front brought polluted air up from the Eastern U.S..

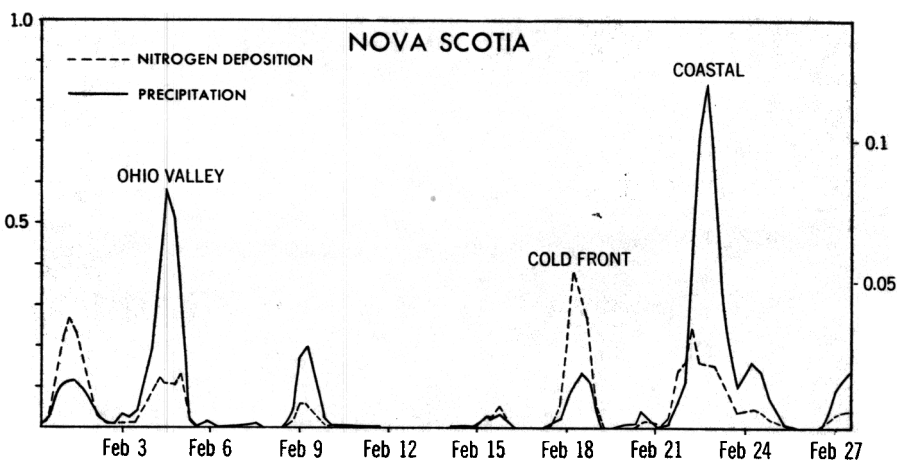


Fig. 6. Simulated time series of wet deposition of nitrogen ( $\text{mMole}/\text{m}^2$  - right axis) and precipitation (cm - left axis) for the month of February.

### Effective Removal

The simulation of effective removal for hydrocarbon pollutants requires their oxidation to non-reactive end products, CO<sub>2</sub> and H<sub>2</sub>O, and depends on the same photochemical models discussed earlier. The effective removal of O<sub>3</sub> can be described as dry deposition though it may, in fact, result from chemical destruction in the boundary layer. The case for NO<sub>x</sub> and SO<sub>2</sub> emissions is more complicated since effective removal either involves their oxidation to soluble forms and removal in precipitation, or their conversion to surface reactive forms and transport to the ground. In both cases we must model both chemistry and transport in either clouds or the B.L.. A number of papers in this volume will discuss cloud processes in detail.

Dry Deposition. The loss of gases and particles by their reacting with the earth's surface and its vegetation as well as their absorption by that same vegetation is a continuous process called dry deposition. This process depends on the surface mixing ratio of the individual trace gas,  $R_{\text{surf}}$ , and its deposition velocities,  $w_0$ .

Assuming that the bottom half of the lowest model level is in steady state with surface deposition balanced by turbulent flux, we can write

$$R_{surf} = R_{11} / [1 + (w_0 / C_d |V_{eff}|)] \quad [1]$$

$C_d$  is a globally averaged surface drag coefficient,  $R_{11}$  is the mixing ratio in the lowest level and  $|V_{eff}|$  is the model's effective surface wind speed. For more details on [1], see Levy et al. (1985). For a more detailed discussion of turbulent mixing, see Walcek et al. (1986).

Measurements of  $w_0$  exist for ozone and a number of nitrogen and sulfur species for a variety of surfaces and seasons (see Walcek et al., 1986 and Voldner et al., 1986 for recent reviews). Over land, deposition is most rapid over growing vegetation and slowest over barren ground. Over water, only soluble species have a significant net-deposition and only nitric acid and nitrate are deposited to snow and ice. The limited available measurements, while generally bound within a range of .02 cm/sec to 2 cm/sec, are highly variable on spatial scales much smaller than those resolved by any global model. This degree of variability appears to be true for most biologically related phenomena. The modeling of dry deposition is further limited by a lack of deposition velocity data and a lack of a realistic model of turbulent transport. For the highly reactive gases such as  $O_3$  and  $HNO_3$ , turbulent transport is the controlling step, while surface deposition dominates for less reactive gases, which remain essentially well mixed throughout the B.L.

Wet Deposition. An intermittent process acting throughout the tropospheric column, it is most simply expressed as a first order loss term,  $\Phi$ , as shown in [2]

$$\Phi = N B [RAIN/RAIN^G] \quad [2]$$

where RAIN is the model's column precipitation,  $RAIN^G$  is the global average precipitation,  $1/B$  is a lifetime that, based on observations of the vertical distribution of rainfall production, ranges from 20 days at the lowest level to 60 days at the 8.7km level (Mahlman and Moxim, 1978), and  $N$  is a global empirical parameter (Levy and Moxim, 1988) that depends on the solubility of the species being removed and has been used for radioactive debris from nuclear tests in the stratosphere ( $N=1$ ) and combustion nitrogen ( $N=9$ ). This formulation does not treat the vertical transport occurring during convective rain, though such transport may be present implicitly in sub-grid scale vertical diffusion that responds to convection. A refinement would be to use the model's precipitation at each level.

A much more complex formulation based on Henry's Law solubility and a 1-D cloud physics parameterization, including rainout in the cloud and washout below, reduces to a form similar to Eq. [2] for highly soluble gases (private communication, W.L. Chameides). However, instead of an empirical parameter  $N$ , there is the more physical Henry's Law coefficient. Again there is no explicit treatment of the vertical transport occurring during convective rain. While such treatments may be adequate for cases of "stable" rain which are associated with slow large-scale lifting, there is the possibility that convective rain, rather than removing soluble gases from air at the height of the condensation, is actually removing trace gases from boundary layer air that has been lifted to that height.

The next level of treatment recognizes the disparity in scales between convective clouds and the model grids and apportions a fraction of the grid to rapid vertical lifting and wet removal with the remaining fraction slowly descending and dry(e.g. Chang et al., 1987). The ultimate approach is to

incorporate a realistic precipitating convective cloud model, or some highly parameterized version thereof, along with the appropriate cloud chemistry, in the larger model. Other papers in this volume will discuss such attempts.

#### GLOBAL IMPACT OF COMBUSTION NITROGEN

As an example of the use of global CTM's, we present recent studies, both published (Levy and Moxim, 1988) and unpublished, of the hemispheric/global impact of NO<sub>x</sub> emissions from fossil fuel combustion on the distribution and deposition of reactive nitrogen.

##### Arctic Haze

An excellent example of the hemispheric impact of pollution is Arctic haze, first reported in the scientific literature by Mitchell (1956). Its association with mid-latitude combustion was demonstrated by Rahn et al. (1977) and a number of studies have since been reported (see Barrie (1986)). The wintertime Arctic has a very stable boundary layer, little precipitation, a low temperature and a snow or ice covered surface, where HNO<sub>3</sub> and NO<sub>3</sub><sup>-</sup> are deposited slowly (Johansson and Granat, 1986), and PAN, NO, NO<sub>2</sub>, SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> all have very long lifetimes. With the European emissions almost 20° north of those in North America and with significant European emissions inside the Arctic Circle, we might expect them to be the major cause of Arctic haze. Model simulations (e.g. Barrie et al., 1988; Iversen, 1987) find this to be true for sulfate, though the relative importance of emissions north and south of the Arctic Circle is still an issue.

Table 1 The Percentage Contribution to NO<sub>y</sub> in the Arctic by Source Region

Source	R990mb (%)	R940mb (%)	R835mb (%)	R685mb (%)
Global	100	100	100	100
Europe S of 60°N	30	44	50	46
North of 60°N	49	25	10	6
North America	10	15	26	37
Asia S of 60°N	11	16	14	11

The impact of nitrogen emissions from fossil fuel combustion on the average winter NO<sub>y</sub> mixing ratios in the Arctic boundary layer are shown in Fig. 7 and further detail is given in Table 1. This work has been reported in greater detail in an earlier paper (Levy and Moxim, 1988), and only the highlights are given here. Emissions inside the Arctic are responsible for half of the total NO<sub>y</sub> at the surface, while both European and North American emissions play important roles at higher levels. Transport to these levels in the Arctic is the result of winter extratropical cyclones that generally form over the northern U.S. and Canada, the North Atlantic and northern Europe. The model predicts a strong longitudinal gradient with NO<sub>y</sub> mixing ratios lower than .1ppbv in northern Alaska and greater than 1ppbv in northern Scandinavia and the Soviet Union. These general patterns are consistent with previous simulations for sulfur (Iversen, 1987; Barrie, 1986). Bottenheim and Gallent (1986) report .25 - .35 ppbv NO<sub>y</sub> at Alert in late winter, mostly PAN, while the model only gives .15 - .20 ppbv of NO<sub>y</sub>. However, when surface deposition is shut off, the simulated levels of NO<sub>y</sub> exceed the observations. While the model overestimates dry deposition in the winter Arctic and lacks explicit transport for PAN, the qualitative pattern of distribution and the dominance of the European sources is robust.

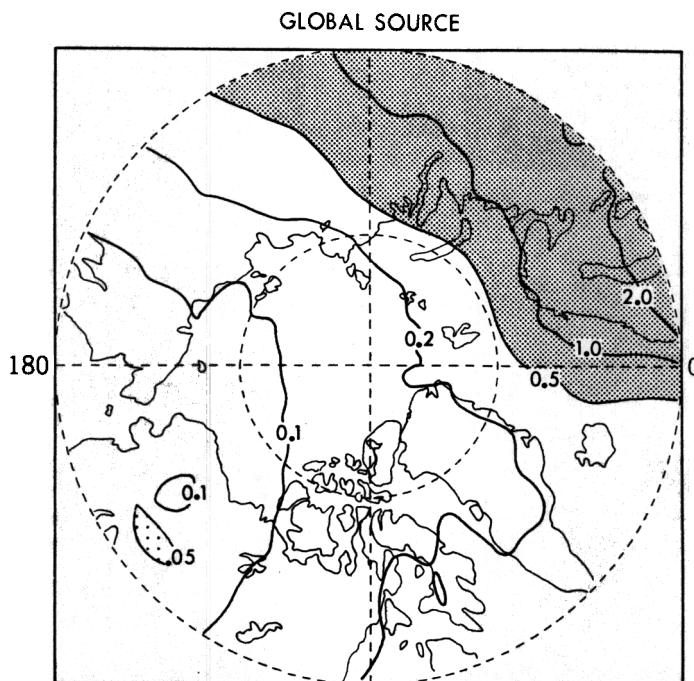


Fig 7 Average winter mixing ratios for boundary layer NO<sub>y</sub> (ppbv) in the Arctic. The light dots have < 0.05ppbv and the dark shading has > 0.50ppbv.

#### Regional Budgets

Just as was simulated (Levy and Moxim, 1987) and estimated from observation (Galloway and Whelpdale, 1987) for North America, acid rain over the world's other major source regions, Europe and eastern Asia, accounts for a small portion (~30%) of the combustion emissions of nitrogen, while dry deposition over the source regions accounts for ~45% and export, mainly over the oceans, for the remaining ~25%.

Most of the NO<sub>y</sub> exported from Asia is deposited in the North Pacific (0.75tg N) as one would expect from the prevailing westerlies (see Levy and Moxim, 1988 for details). This is in excellent agreement with a recent estimate by Savoie, (1989). 70% of the NO<sub>y</sub> exported from North America is deposited in the North Atlantic, 10% is deposited in the North Pacific and the remainder reaches Latin America and Europe. While most of the emissions exported from North America travel over the North Atlantic, only 25% of the nitrogen in acid rain at Adrigole on the west coast of Ireland comes from North America and less than 3% or .2tg N reach continental Europe (Levy and Moxim, 1987). Similar conclusions are reached by Galloway (1989) and Galloway and Whelpdale (1987) for sulfate. The European export is more complex with ~1/3 deposited in both Asia and the North Atlantic and the remaining 1/3 reaching the Arctic, the Mediterranean, North Africa, and even the North Pacific.

### Global Distribution and Deposition

We recently simulated the distribution of the single largest term in the global nitrogen budget, fossil fuel combustion (Levy and Moxim, 1988). Key results are summarized in Fig. 8 which shows the simulated surface concentration of NO<sub>y</sub> resulting from fossil fuel combustion and in Table 2 which compares measured and simulated surface concentrations and wet deposition at remote sites in the Southern Hemisphere. As noted previously (Levy and Moxim, 1987), little is transported between the hemispheres, with the Southern Hemisphere NO<sub>y</sub> levels seldom exceeding .05ppbv. The small stratospheric source of NO<sub>y</sub>, predicted to support zonal averages of .01 - .03 ppbv in the boundary layer and .03 - .05 ppbv in the free troposphere (Levy et al., 1980), appears to be more important than fossil fuel combustion over most of the Southern Hemisphere and the upper troposphere of the Northern Hemisphere.

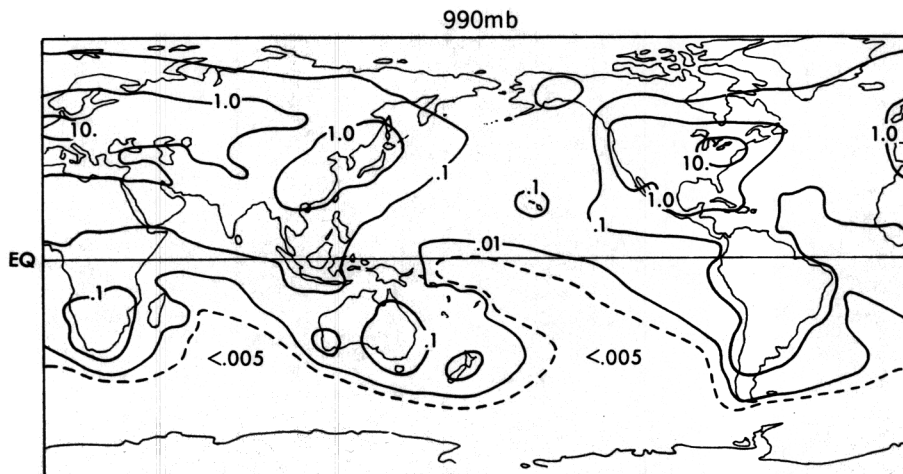


Fig. 8. Yearly average NO<sub>y</sub> mixing ratio (ppbv) at 990mb

Examining the remote Southern Hemisphere sites in Table 2, we see that the model can explain at most 10% of the observed background depositions of ~2mMole/m<sup>2</sup>yr (Galloway, private communication) and surface concentrations of ~.04ppbv (Savoie et al., 1988). We are left with three likely explanations for the background nitrogen (Prospero et al., 1985; Savoie et al., 1988):

Table 2 Yearly Average NO<sub>y</sub> Surface Mixing Ratio and NO<sub>y</sub> Wet Deposition for Remote Locations

Station	NO <sub>y</sub> Mixing Ratio (ppbv)		NO <sub>y</sub> Wet Deposition (mMole/m <sup>2</sup> )	
	Obs	Model	Obs	Model
Fanning	.058	011		
Nauru	.058	004		
Funafutti	.040	003		
Samoa	.043	003		
Rarotonga	.042	004		
Amsterdam Is.			1.9	0.1
Cape Point, SA			1.6	0.2
Katherine, Australia			4.0	0.2
Torre de Paine, Chile			0.2	0.1

(1) explicit long-range transport of insoluble end-products such as PAN; (2) alternative local and regional sources of NO<sub>y</sub>; (3) downward transport from the lower stratosphere and upper troposphere. While lightning and long-range transport of nitrogen emissions from biomass burning in the tropics are both possible, past calculations of downward transport from the stratosphere (Levy et al., 1980) will explain at least half of the background. An interesting point is the qualitative similarity between the seasonal cycles measured at Samoa for O<sub>3</sub> (Oltmans, 1981) and NO<sub>y</sub> (Savoie et al., 1988). The observed seasonal cycle for O<sub>3</sub> was reproduced by a numerical simulation whose sole source was transport from the stratosphere (Levy et al., 1985).

#### SUMMARY

Global atmospheric chemistry modeling is currently an exciting and highly relevant field of research. Furthermore, the field is just developing and awaits energetic scientists with new ideas. Both 3-D models of large-scale advection and the complex gas-phase photochemical models are being developed and combined to form realistic CTM's. However, while realistic 3-D cloud models exist, they have yet to be coupled with complex cloud chemistry and physics, and no realistic sub-grid scale parameterization has been developed for CTM's. The treatment of sub-grid scale turbulent mixing in CTM's is also quite primitive, particularly for conditions of large-scale stability.

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## DISCUSSION

D.A. HANSEN

Research on 2-D modeling of rainbands, including chemistry and microphysics, that EPRI has sponsored at Univ. of Washington indicates that less than 50% of sulfur and nitrogen ingested into the clouds are deposited in precipitation. Is this consistent with your modeling results indicating essentially complete removal of ingested nitrogen in the precipitation?

H. LEVY

In the global model with the parameterized wet deposition, there is not complete removal. In fact, the parameter requires that the wet removal agree with the observed total yearly deposition, and the model's transport to relatively clean sites, such as Bermuda, Hawaii, Newfoundland and the west coast of Ireland, agrees well with observation. In the cloud model, two idealized cases were considered, the soluble tracer corresponding to nitric acid and the insoluble tracer corresponding to NO<sub>x</sub>. The complete removal of a soluble tracer such as nitric acid seems quite reasonable and is discussed in the answers to questions 3 and 4. If you combine the two studies to approximate the observations of total nitrogen and sulfur in rainbands, you would not have complete removal. However, the cloud model does predict that you should observe almost

complete removal of the soluble portion of the total sulfur and nitrogen that is ingested into the clouds.

J.C.R. HUNT

1. Please can you explain your result about the concentration rising in the cloud. I assume that was a time average result, with rapid entrainment on the sides, below the cloud and not much mixing in the cloud top?

2. Comment: You concluded that for chemical and cloud effect it is preferable to model a sequence of actual flow realisations rather than using flow models based on a mean velocity and fluctuation. I would like to comment that this is similar to recent approaches in engineering fluid mechanics for combustion and chemical reaction. These studies show that different characteristic flow patterns have different effect depending on the speed of the reaction.

H. LEVY

1. All three figures are based on the third hour of the simulation when the convection is well developed and quasi-steady. There was considerable turbulent mixing at the cloud top. The relatively narrow stem of tracer in the mid-levels reflects both rapid entrainment at the sides and the narrowness of the vertical core that advects the tracer upward.

2. We concur.

P.J. MASON

I am concerned that your nearly complete washout of a soluble species may neglect the fact that in most convective clouds a significant part of the rain evaporates before it reaches the ground.

H. LEVY

In both cases, very little tracer remains in the boundary to the left of the cloud because the initial tracer has been advected out and the initial boundary layer air replaced by air from higher levels containing very little tracer. We do not continuously supply the boundary layer with tracer from the surface. Rather, it can only flow in through the side boundaries, in this case from the right.

There is no evaporation of the soluble tracer unless all rain in a grid box evaporates. Therefore, we may underestimate the effect mentioned by Mason, though not for sulfate and nitric acid.

A. VENKATRAM

You said that soluble species are not transported efficiently in the vertical by cumulus clouds. This is plausible only if the efficiency of water removal by rain is close to unity. As these efficiencies for cumulus clouds are typically very small, I am not sure that your conclusions can be justified.

H. LEVY

In the 2-D and 3-D cloud models of warm cumulonimbus, the efficiency is ~40%, which we believe is consistent with warm cumulonimbus clouds in the real world. Furthermore, highly soluble gases entering at cloud base are immediately captured by the cloud water which is quickly converted to rainwater. Thus very little of the cloud water formed at cloud base is transported beyond 4-6 km. Most of it either falls out as precipitation or evaporates in the lower levels. The reduction in condensa-

tion efficiency is largely due to evaporation of cloud water at cloud top and cloud sides where very little tracer is present. Evaporation of rainwater containing tracer is also present, but that is smaller, occurs primarily in the boundary layer and is not relevant to the vertical transport of tracer to higher levels.