Why Is Clean Air Clean?

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ABSTRACT

Air exhibiting very low concentrations of light-scattering aerosol particles is occasionally observed even in industrialized regions. Evidence is presented that this very clean air results from highly efficient removal of aerosol particles coupled to the removal of water in precipitation.

1. INTRODUCTION

One of the more remarkable atmospheric phenomena is the occurrence, even in industrialized regions of North America and Europe, of episodes of very clear air characterized by deep blue skies and distinct colors and sharply defined features of distant objects. The more usual situation in these regions—a whitish tinge to the sky, restricted visibility—is due to the presence of light-scattering accumulation-mode aerosol particles (diameter mainly 0.1 to 1 μm) attributable largely to combustion effluents. Yet occasionally we do experience very clean air that exhibits concentrations of light scattering aerosol particles two orders of magnitude lower than those characteristic of hazy air masses that can extend a thousand kilometers or more (Waggoner et al., 1981; Lyons and Husar, 1976). This paper assesses mechanisms that can lead to the occurrence of such very clean air.

2. POSSIBLE MECHANISMS LEADING TO VERY CLEAN AIR

The occurrence of very clean air in regions such as the northeastern United States often evokes questions regarding its source. However there are no sources of air—no matter how clean the air, it is not new air, freshly generated, but is, rather, old air from which particles have been highly efficiently removed. How then does air become clean? More specifically, in the context of this Conference, how can precipitation scavenging or dry deposition result in the nearly complete removal of accumulation-mode aerosol particles from the air in which they are imbedded.

Very clean air is frequently behind a cold front such that it has rather quickly travelled from the north, i.e., for observers in the northeast U. S., from Canada.

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This observation might suggest that the air is clean because it has recently been in a region of low emissions of aerosol particles or their precursors. However such an explanation is incomplete, since the absence of sources cannot in itself result in clean air. We still need a highly efficient cleansing mechanism.

Can this be achieved by dry deposition? The average or *e*-fold lifetime of particles against dry deposition can be estimated as the ratio of the height in the atmosphere over which the particles are distributed to their deposition velocity. For a box height of 3 km and a dry deposition velocity of 0.1 cm s^{-1}, Slinn (1983) calculates a lifetime of accumulation-mode particles of 35 days, corresponding to a removal rate of 3% per day. Clearly dry deposition while the air is in a source-free region cannot be the responsible process.

Very clean air is almost invariably dry, i.e., having a much lower humidity than the more heavily aerosol-laden air with which it is compared. A low relative humidity leads to a reduction in the size and light-scattering cross section of deliquescent particles (Charlson et al., 1984; d'Almeida et al., 1991), but this amounts to only about a factor of 3 between 30 and 95% relative humidity and thus cannot account for the increase in visibility and the reduction in particle concentrations associated with very clean air.

Alternatively the association of very clean air with dry air suggests that the process responsible for very clean air is precipitation scavenging. Since accumulation-mode aerosol particles are removed from the atmosphere primarily by precipitation scavenging (e.g., Slinn, 1983), it remains to be addressed how the removal process can be as complete as it sometimes seems to be. The existence of very clean air requires a process that can remove aerosol particles from air with great efficiency.

Water is of course unique in the atmosphere as the only condensible substance present in sufficient quantity to precipitate. This precipitation process, i.e., cooling of air to temperatures below the dew point of water followed by condensation of water and gravitationally induced motion of hydrometeors relative to the surrounding air, is therefore the only mechanism that is effective in removing material from the air in which it is embedded.

Consider the cycle of water as a trace atmospheric constituent. Water enters the atmosphere largely as vapor by evaporation of surface water or evapotranspiration of vegetation. In the absence of condensation and precipitation, water vapor would accumulate more or less uniformly in the atmosphere until the atmosphere was more or less saturated relative to the water vapor pressure at the surface. Different air masses would exhibit different mixing ratios of water vapor reflecting the vapor pressure of water at the surface with which the air was last in contact, and thus the surface temperature and the extent to which equilibrium had been achieved. An air parcel which was saturated at a given temperature that was subsequently cooled, e.g., by adiabatic expansion upon lifting, would become supersaturated, but in the absence of condensation there would be no mechanism for removal of this water vapor; the water vapor would simply travel with the air in which it was embedded.

Contrast this to the actual situation. When an air parcel is cooled to a temperature below the dew point, water vapor condenses to form liquid particles. With sufficient driving force provided by continued cooling, these particles grow by coalescence and/or vapor deposition to a size such that they have appreciable gravitational fall velocity relative to the surrounding air. As a

consequence water is removed from the air in which it has been present. The precipitating water is delivered to the surface, or perhaps to a lower, subsaturated level of the atmosphere where evaporation returns water to the gas phase. In any event, water is removed from the air in which it was present; i.e., the air is dried. This mechanism is the dominant process whereby water is removed from air, since alternative removal processes, i.e., dry deposition to surfaces, including dewfall, and chemical reactions are relatively slow. The drying process can occur quite rapidly (minutes to hours) and, because of the steepness of the dependence of saturation water vapor pressure on temperature, a substantial fraction of the water initially present in a given mass of air can be removed. It is the only mechanism for the production of dry air.

Now consider the cycle of atmospheric aerosol particles, with specific reference to accumulation-mode aerosol particles. These particles result from growth and coagulation of Aitken particles that derive from gas-to-particle conversion. Accumulation-mode particles (characterized by distributions peaking by number at ca. 0.07 μm diameter and by volume at ca. 0.3 μm diameter; Whitby, 1978) are long lived in the atmosphere with respect to either diffusional attachment to larger particles, which dominates loss of smaller aerosol particles, or gravitational settling, which dominates the loss of 10 μm-diameter or larger particles. Particles in this size range also appear to be relatively immune to below-cloud scavenging by precipitation elements because of their tendency to move with the air in which they are suspended and the resulting low scavenging efficiency (Pruppacher and Klett, 1978; Slinn, 1983). However, these particles are effective cloud condensation nuclei, and the great increase in their size and mass due to water condensation during cloud formation renders them much more susceptible to impactive scavenging by falling hydrometeors. This impactive scavenging is a key mechanism whereby rain forms and removes water from a given parcel of air (Pruppacher and Klett, 1978).

The thesis of the present discussion is that the removal of water from an air parcel by precipitation effects the removal of the cloud condensation nuclei, i.e., the accumulation-mode aerosol particles, and thus that dry air (i.e. air from which water has been removed) and clean air (air from which particles have been removed) are a consequence of the same process. However for this process to be responsible for the atmospheric cleansing leading to very clean air, the incorporation of aerosol particles into cloud water must be highly efficient.

3. FIELD OBSERVATIONS

Measurements of the distribution of material in clouds are difficult to conduct and interpret and have led to widely varying reports of the efficiency of incorporation of accumulation-mode aerosol particles into cloud droplets (Hegg and Hobbs, 1986; Leaitch et al., 1986; ten Brink et al., 1987; Gillani et al., 1992). Ten Brink et al (1987) reported that the excess light scattering coefficient above that due to Rayleigh scattering by air (b_{scat}) of interstitial air in nonprecipitating boundary layer stratus and stratocumulus clouds was generally 10% or less of that characterizing associated non-cloud air, indicating efficient uptake of light scattering particles into cloud droplets. However Leaitch et al. (1986) found indication that scavenging efficiency was not invariably so great, decreasing with increasing aerosol particle concentration, a finding reported also by Gillani et al. (1992).

Recently Kleinman and Daum (1991; see also Kleinman et al., 1992) reported measurements up to an altitude of about 10 km of the mixing ratio (i.e., concentration normalized to the mass concentration of dry air) of water vapor and accumulation-mode aerosol particles, the latter expressed as number of particles per standard cubic centimeter of air. The measurements were made in non-cloud air in the vicinity of convective storms. Such storms are quite effective in transporting boundary layer air to such altitudes, as has been demonstrated by measurement of concentrations of insoluble pollutants such as carbon monoxide, ozone, and nitrogen oxides (NO_y), which are quasi-conservative tracers of boundary layer air (Dickerson et al., 1987).

Measurements of particle and NO_y mixing ratios during a horizontal traverse at ~9 km are shown in Figure 1. The peaks in NO_y mixing ratio are indicative of parcels of boundary layer air (NO_y ~2 ppbv) transported to the upper troposphere with a dilution, by entrainment, of a factor of 2 to 3, superimposed on a lower background level of ~0.2 ppbv. The particle mixing ratio exhibits variation coherent with that of NO_y, indicative of vertical transport of particles as well. However the particle mixing ratios are a factor of 50 lower than in the boundary layer, as may be seen in to Figure 2, which shows the vertical profiles for particle and water vapor mixing ratios, both of which decrease by almost two orders of magnitude from the boundary layer to 10 km. The strong decrease in water

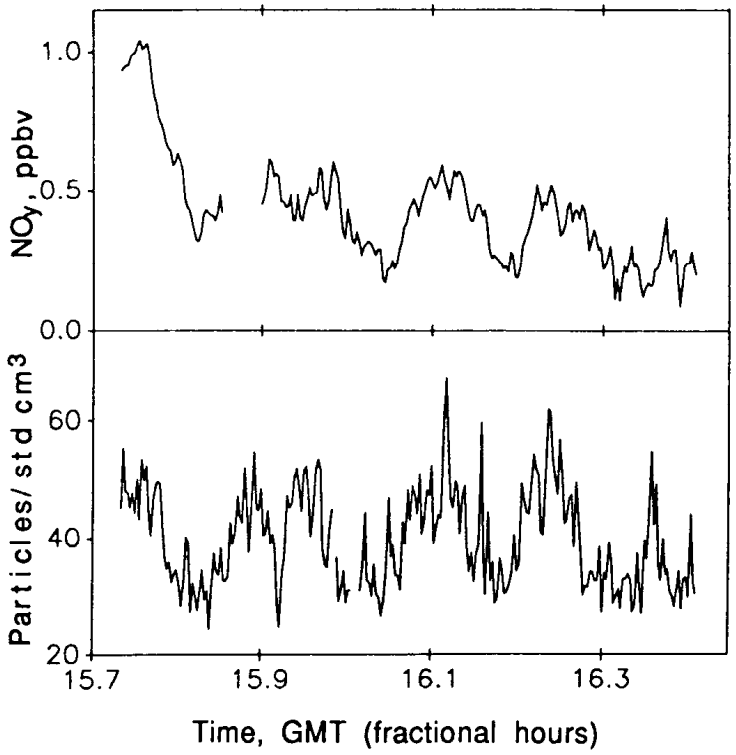

FIGURE 1. Portion of a trace of mixing ratios of nitrogen oxides NO_y (parts per 10^9 by volume, ppbv) and accumulation-mode (0.1 to 1 μm) aerosol particles (number per standard cm^3 of air) during horizontal flight at ~9 km in the vicinity of Columbus Ohio, June 9, 1987. Adapted from Kleinman and Daum (1991).

vapor mixing ratio is of course expected, since temperature decreases with increasing altitude and since the saturation vapor pressure of water decreases strongly with decreasing temperature; a decrease in water vapor mixing ratio such as this can be achieved only by condensation and precipitation. The similar strong decrease in particle mixing ratio, which contrasts with that for nitrogen oxides, must therefore be ascribed to highly efficient removal of particles from air concurrent with removal of water by precipitation.

In the Kleinman-Daum data set as a whole (12 flights during June 1987) particle mixing ratios in the upper troposphere (~9 km) were typically 2 per cent of those in the boundary layer and never exceeded 5 percent of their boundary layer values, corresponding to particle removal efficiencies of 95 to 98 per cent. In contrast, upper tropospheric mixing ratios of NO_y and CO were 35 and 50 percent of their boundary layer values, respectively, on average, and occasionally very close to values in the boundary layer. These measurements argue persuasively on behalf of highly efficient scavenging of accumulation-mode aerosol particles by condensation and precipitation of water associated with the convective storms that transport boundary layer air to the high troposphere.

Model calculations of the efficiency of incorporation of accumulation-mode aerosol particles into cloud droplets and precipitation are highly sensitive to assumptions and approach (Jensen and Charlson, 1984; Flossmann et al., 1985; Hänel, 1987; Ahr et al., 1989; Alheit et al., 1990). Scavenging of particles in a convective storm typical of those in the vicinity of the Kleinman-Daum measurements has been examined in model simulations (Kleinman et al., 1992). Although the results are somewhat sensitive to assumptions concerning particle nucleation efficiency, the calculations support the picture outlined here, namely

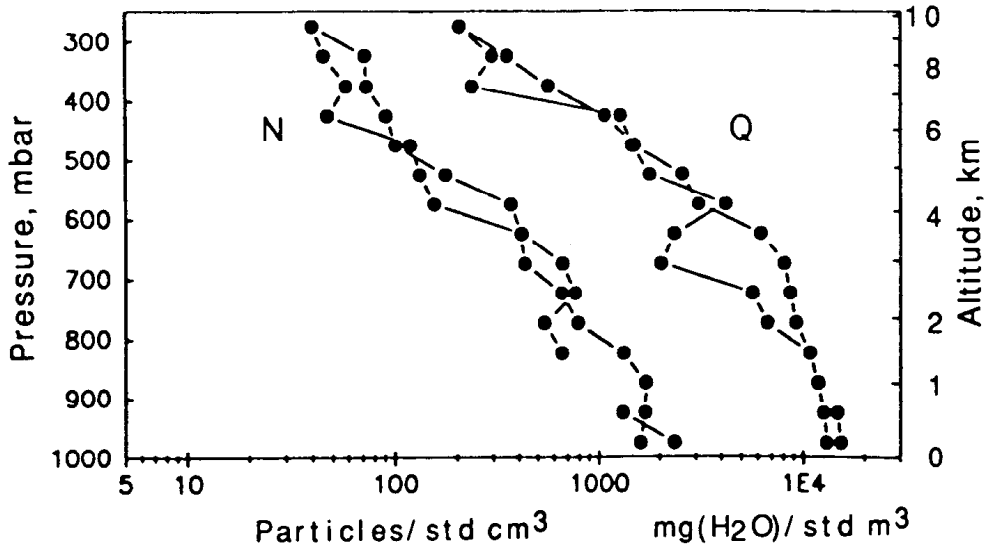

FIGURE 2. Vertical profiles on June 9 of mixing ratio of accumulation-mode aerosol particles N and water vapor Q as a function of pressure (left axis); the approximate corresponding altitude is shown on the right axis. Points denote average values for 50-mbar altitude bins, with ascending and descending flight segments presented separately. Adapted from Kleinman and Daum (1991).

that the drying of air by the precipitation process results in highly efficient removal of aerosol particles from the air.

4. CONCLUSION

How do these findings bear on the question of why clean air is clean? In brief clean air is clean because it has been dried. The condensation and precipitation process associated with convective upward transport of boundary layer air is highly efficient in removing from the ascending air not only water, but also light-scattering particles, leading to air that is highly cleansed of its aerosol burden. Moreover this is very likely the only mechanism capable of cleansing air with such efficiency. When such air is ultimately returned to the boundary layer it is responsible for the remarkably clear air that it is occasionally our joy to experience.

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