Formation and Transport of Secondary Air Pollutants: Ozone and Aerosols in the St. Louis Urban Plume

Abstract. *Emissions from metropolitan St. Louis caused reduced visibilities and concentrations of ozone in excess of the federal ambient standard (0.08 part per million) 160 kilometers or more downwind of the city on 18 July 1975. Atmospheric production of ozone and visibility-reducing aerosols continues long after their primary precursors have been diluted to low concentrations.*

Metropolitan St. Louis is a major urban-industrial center, encompassing coal-fired power plants with a combined capacity of 4600 Mw, oil refineries with a combined capacity of 4.4×10^5 barrel/day (1 barrel = 160 liters), various other industries, and a population of about 2 million. It is surrounded by flat, predominantly agricultural terrain, the nearest neighboring city of 50,000 or more people being 135 km distant. Because St. Louis is so isolated, its impact on ambient air quality is relatively easy to identify; air that has been modified by the aggregate emissions of the metropolitan area forms an "urban plume" downwind. The Fate of Atmospheric Pollutants Study (FAPS) (*1–3*) has shown that this plume is often identifiable 80 or 120 km from the city.

As part of Project MISTT (Midwest Interstate Sulfur Transformation and Transport) (*4, 5*), pilot balloons and instrumented aircraft were used during the summer of 1975 to quantify the three-dimensional flow of aerosols and trace gases in the St. Louis urban plume. The plume was successfully tracked out to 240 km and was mapped in detail out to 160 km (distances are measured from the Gateway Arch). At these distances the plume was still well defined and on the order of 50 km wide. Our observations indicate that much of the pollutant background in the eastern United States may be due to the combined emissions of metropolitan areas far upwind.

During the summer sampling period, O_3 was a conspicuous indicator of the St. Louis urban plume. Daytime O_3 concentrations within the plume generally exceeded the federal ambient standard [0.08 part per million (ppm)], even in the most distant samplings. Peak concentrations in the plume were typically twice those in the unmodified background air and exceeded 0.15 ppm on most sampling days. It is estimated that one to two parts of O_3 were produced for each part (as carbon) of nonmethane hydrocarbons emitted by the city.

Reduced visibilities were a second characteristic of the St. Louis urban plume. Most of the light-scattering aerosol responsible for this reduction was of

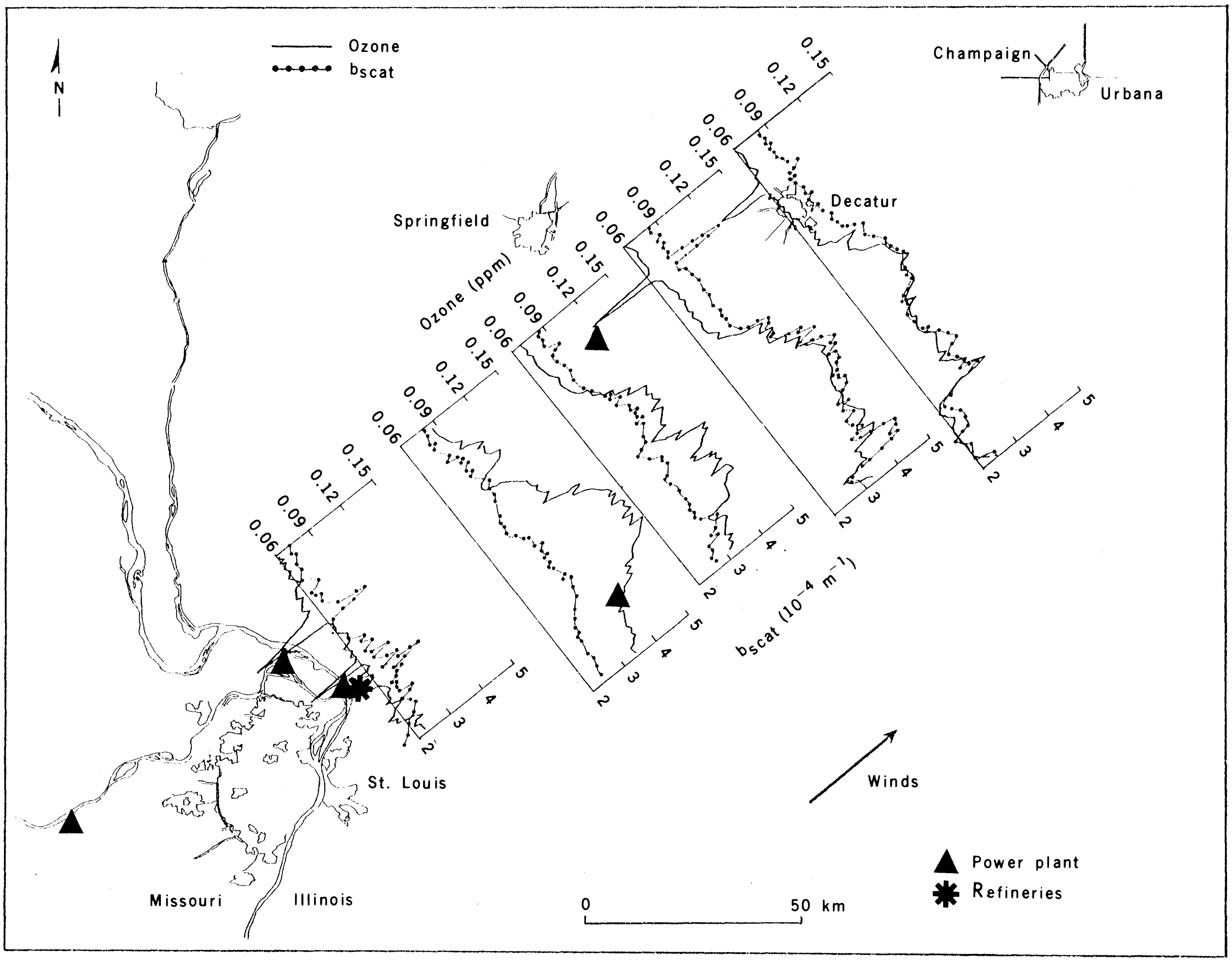

Fig. 1. Concentrations of O_3 and b_{scat} values downwind of St. Louis on 18 July 1975. Data are taken from horizontal traverses by instrumented aircraft, at altitudes indicated in Fig. 2A. Graph base lines show sampling paths; base-line concentrations are not zero.

secondary origin, and its production was observed farther downwind and later in the day than that of O_3. At 100 km or more downwind, the average light-scattering coefficient (b_{scat}) (*6*) within the plume was typically 50 percent above the background values on either side, with sulfate compounds accounting for most of the excess.

The results reported here generally corroborate those of FAPS on the identifiability and geometry of the St. Louis urban plume. The primary contribution of Project MISTT was to quantify the flow of material at increasing downwind distances so as to study the transformations that pollutants undergo in the atmosphere, at dilutions and time scales that are difficult to simulate in the laboratory.

Figure 1 shows O_3 and b_{scat} profiles recorded by the sampling aircraft (*7*) during selected crosswind traverses downwind of St. Louis on 18 July 1975. Each traverse path was flown at three different altitudes, as indicated in Fig. 2A, starting just downwind of St. Louis at 0900 C.D.T. and finishing near Decatur, Illinois, at 1900 C.D.T. These horizontal traverses, together with vertical soundings from 1500 m above mean sea level (MSL) to near ground level, documented a broad, shallow pollutant plume extending from St. Louis out past Decatur, 170 km to the northeast. The polluted airmass was about 50 km wide and deepened during the day, the mixing depth exceeding 1 km in the afternoon.

The concentrations of O_3 and light-scattering aerosols were the most prominent indicators of the aged plume 50 km or more downwind of St. Louis. Outside the plume, background concentrations of these contaminants were fairly uniform on 18 July, although some large-scale gradients were noted; O_3 concentrations were generally below 0.08 ppm, b_{scat} values were below 2.8×10^{-4} m^{-1}, and particulate sulfur (S_p) concentrations were below 3.6 $\mu g/m^3$ in the few passes made completely outside the plume. Within the plume, the measured O_3 concentration peaked at 0.17 ppm at 66 km, the measured value of b_{scat} reached 4.9×10^{-4} m^{-1} at 125 km, and S_p, averaged over an entire traverse, measured as high as 7.5 $\mu g/m^3$ at 125 km, corresponding to an estimated average in-plume concentration of about 15 $\mu g/m^3$. In contrast, SO_2 and NO_x (oxides of nitrogen) concentrations fell rapidly to within 0.03 ppm of background, away from major point sources.

The 18 July plume was mapped under hazy skies, with some scattered thundershowers appearing toward evening. The continued presence of a low-pressure trough over the western plains produced decreasing stability and strong southwesterly flow over the Missouri and upper Mississippi valleys, which was documented in the sampling area by a total of 36 pilot balloon observations carried out as part of Project MISTT. The mean transport vector lay between 230° and 243° during the middle of the day, at speeds of 20 to 36 km/hour. At these speeds, among the highest encountered during the program, emissions from the city would have aged roughly 5 to 7 hours by the time they were sampled in the farthest passes.

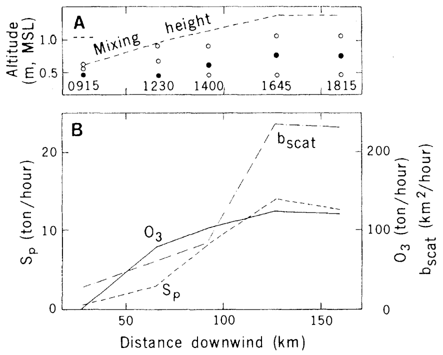

Fig. 2. Traverse altitudes and pollutant flow rates in the St. Louis urban plume on 18 July 1975. Data are plotted against distance downwind of the St. Louis Gateway Arch. (A) Location of horizontal traverses; closed circles correspond to traverses shown in Fig. 1. Mixing heights were determined from aircraft soundings. Approximate time (C.D.T.) of sampling is shown at the bottom. (B) Flow rates (in excess of background) of O_3, b_{scat}, and S_p.

The general direction of the airflow was corroborated by the alignment of power plant plumes in successive traverses. All of the major (greater than 1000 Mw capacity) power plants lying in and immediately upwind of the sampling area are noted in Fig. 1. The plumes from some of these plants can be identified (Fig. 1) by their O_3 "deficits," which result from the scavenging of ambient O_3 by plume NO. The Coffeen plant, 85 km west-northwest of St. Louis, is the only major downwind source that we know of that lay within the 18 July urban plume.

The MISTT plume mapping program was designed to characterize pollutant concentrations and winds over cross sections of the plume at discrete distances downwind from the sources. From these measurements, the horizontal mass flow rates F of pollutants at each distance can be calculated directly (*4*):

$$F = \int u_x(x,z) \int [C(x,y,z) - C_0(x,z)] \, dy \, dz$$

where x is the distance downwind, y and z are, respectively, crosswind and vertical coordinates, u_x is the wind speed (from pilot balloon observations), C is the pollutant concentration (from aircraft measurements), and C_0 is the average pollutant concentration outside the plume (from aircraft measurements). Figure 2B shows the flow rates of O_3, b_{scat}, and S_p on 18 July. These flow rates represent the contribution of metropolitan St. Louis (augmented slightly by the Coffeen power plant) to atmospheric loadings and are unaffected by cross-plume and vertical dispersion.

The flow rates of O_3, b_{scat}, and S_p all increased with distance downwind of St. Louis on 18 July, reflecting the secondary origin of all of the O_3 and most of the light-scattering aerosol. The O_3 flow rate leveled off at about 125 metric ton/hour, which can be interpreted as the rate at which O_3 was produced within the urban plume. The estimated annual emissions of nonmethane hydrocarbons in metropolitan St. Louis are about 1.6×10^5 ton/year (*8*); this value corresponds to 18 to 36 ton/hour, depending on whether emissions are spread out through the day or are concentrated in the daylight hours. Comparison of these two figures shows that a net one to two parts of O_3 was produced in the urban plume for each part (as carbon) of hydrocarbons emitted in the metropolitan area (*9*), much more efficient production than is found in most laboratory studies (*10*) which are conducted at higher reactant concentrations.

Most of the increase in the b_{scat} flow rate was observed downwind of the major increase in the O_3 flow rate, which is consistent with the finding in the laboratory studies (*10*) that aerosol production lags behind O_3 production. The calculated S_p flow rates are less accurate than those for O_3 and b_{scat}, particularly at the last two sampling distances, because of the more limited data available on background concentrations. The ratio of the flow rate of b_{scat} to the flow rate of S_p indicates (*11*) that sulfate compounds accounted for most of the new aerosol.

The St. Louis urban plume was mapped on a total of 8 days during the 15 July–15 August 1975 MISTT experiment. The object of Project MISTT was not to develop a climatology of the urban plume but to measure the plume in detail under favorable conditions, and sampling days were chosen according to this criterion. A plume of polluted air was always found downwind of the city, regardless of wind direction, confirming our attribution here of the excess concentrations to emissions from metropolitan St.

Louis rather than some upwind source. On 11 August, the plume again stretched out toward the northeast and was mapped in detail out to 145 km and tracked out to 240 km. Winds on this date were lighter than on 18 July but the plume was as well defined, and concentrations and flow rates were similar.

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6. The quantity b_{scat} gives the rate (fraction per distance) at which a beam of light is scattered in all directions and is the main determinant of visual range in the atmosphere. In polluted urban air, b_{scat} is roughly proportional to the mass concentration of aerosol particles in the diameter range from 0.2 to 2.0 μm, those inhaled most deeply into the lungs [see R. J. Charlson, N. C. Ahlquist, H. Selvidge, P. B. MacCready, Jr., *J. Air Pollut. Control Assoc.* **19**, 937 (1969)].
7. The sampling aircraft was instrumented to measure O_3, NO, NO_2, and SO_2 concentrations, aerosol size distribution, b_{scat}, electrical charge acceptance and condensation nuclei count, temperature, relative humidity, dew point, and turbulent dissipation, as described by W. H. White, J. A. Anderson, W. R. Knuth, D. L. Blumenthal, J. C. Hsiung, and R. B. Husar [Final Report No. MR176-FR-1414, Meteorology Research, Inc., Altadena, Calif., 1976]. Submicrometer aerosol samples were collected for sulfate analysis as described by J. D. Husar, R. B. Husar, and P. K. Stubits [*Anal. Chem.* **47**, 2062 (1975)].
8. Data supplied by the U.S. Environmental Protection Agency and the Illinois Environmental Protection Agency.
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Electrochemical Growth of Highly Conducting Inorganic Complexes

Abstract. *The formation of single crystals of highly conducting inorganic complexes, for example,* $K_2Pt(CN)_4X_{0.3} \cdot 3H_2O$ *(X = Cl, Br),* $K_{1.75}Pt(CN)_4 \cdot 1.5H_2O$*, or* $K_{1.64}Pt(O_2C_2O_2)_2 \cdot 2H_2O$*, has been effected via electrochemical growth from concentrated aqueous solutions of potassium tetracyanoplatinate(II) and potassium bis(oxalato)platinate(II).*

In recent years there has been a great interest (*1*) in the chemical and physical properties of highly conducting molecular complexes. This interest has resulted from observation of a number of unusual anisotropic physical phenomena (for example, high conductivity, metallic state, metal-insulator transition, charge density wave, superconductivity) and chemical properties (for example, novel structures containing infinite chains with short interplanar spacings, mixed valency, and homogeneous nonstoichiometric compositions) directly associated with numerous one-dimensional systems (*2, 3*). In order to measure the intrinsic physical properties of such complexes, it is necessary to have high-quality single crystals suitable for various measurements. Typically, various highly conducting materials containing a transition metal form fibrous needles that are difficult to analyze by single-crystal techniques. Furthermore, because of the pseudo one-dimensionality of such systems, impurities or defects, or both, will strongly influence various physical properties and, in particular, the electrical transport (for example, conductivity) properties of such materials. Thus, because large single crystals of $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$ (KCP) have been available, this material has been the most extensively studied highly conducting inorganic one-dimensional system to date.

Single crystals of highly conducting inorganic complexes have traditionally been grown by crystallization from solution (*2*). However, the electrical properties of such materials can be utilized to grow single crystals via electrolysis at an anode. Upon nucleation at the anode, growth proceeds primarily along the conducting axis of the crystal such that the introduction of an impurity or defect will impede the current flow and crystal formation. However, as a result of microscopic reversibility, defects may be eliminated and growth may proceed, thereby making possible the fabrication of a high-quality crystal. Such electrochemical synthesis has been effected with the use of aqueous ~0.2*M* solutions of $K_2Pt(CN)_4$ and ~ 0.02*M* $K_2Pt(O_2C_2O_2)_2$ in an electrolysis cell comprised of a platinum anode and cathode. Application of a 1.5-volt potential (*4*) causes nucleation and growth of needle crystals of $K_{1.75}Pt(CN)_4 \cdot 1.5H_2O$ and gas evolution at the cathode. This process is consistent with the following anodic and cathodic half cell reactions:

$$1.5H_2O + 1.75K^+ + Pt(CN)_4^{2-} \xrightarrow{H_2O} K_{1.75}Pt(CN)_4 \cdot 1.5H_2O + 0.25e^-$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

In the presence of halide ions, that is, Cl^- or Br^-, KCP nucleates by an alternate anodic reaction:

$$0.3X^- + 2K^+ + Pt(CN)_4^{2-} + 3H_2O \xrightarrow[X\,=\,Cl,\ Br]{H_2O} KPt(CN)_4X_{0.3} \cdot 3H_2O + 0.3e^-$$

In a similar manner, other highly conducting inorganic complexes can be grown. For example, anodic oxidation of potassium bis(oxalato)platinate(II) results in the formation of the cation-deficient species $K_{1.64}Pt(O_2C_2O_2)_2 \cdot 2H_2O$ presumably via the anode reaction:

$$1.64K^+ + Pt(O_2C_2O_2)_2^{2-} \xrightarrow{H_2O} 0.36e^- + K_{1.64}Pt(O_2C_2O_2)_2 \cdot 2H_2O$$

A typical electrochemical growth is shown on the front cover.

Thus, electrochemical growth provides an attractive alternate technique for the synthesis of highly conducting pseudo one-dimensional inorganic complexes. Furthermore, evaluation of the electrochemical parameters makes it possible for us to probe for the first time the stoichiometric, kinetic, and thermodynamic features of these systems.

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