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Industrial Dusts and Fumes in the Los Angeles Area

LOUIS C. MCCABE, PAUL P. MADER, H. E. MCMAHON, AND W. J. HAMMING

Los Angeles County Air Pollution Control District, Los Angeles, Calif.

A. L. CHANEY

Chaney Laboratories, Glendale, Calif.

Meteorological and topographical conditions in the Los Angeles basin cause the retention of dusts and fumes, frequently for several days. Eye irritation and limited visibility are characteristic of the resultant smog. Studies of the aerosols in this area have been undertaken by government and private laboratories. Methods and equipment used by the Los Angeles County Air Pollution Control District in identification of industrial contaminants are described. The roles of sulfuric acid mist and metallurgical dusts in smog formation are discussed.

IN THE Los Angeles basin the term smog is applied to the complex blue haze of air pollution which limits visibility and on 53 days of 1948 caused reports of eye, nose, and throat irritation. Natural gas is used for domestic heating, and natural and refinery gas and fuel oils are the principal fuels of industry. There is no appreciable use of coal.

Smoke, in the common usage of the word, is a minor source of nuisance although it is produced in burning combustible rubbish and in the improper firing of fuel oil. Many of these sources of smoke have been eliminated during the past year and current studies indicate that dust and fumes are the predominant aerosols.

METEOROLOGICAL ASPECTS

Temperature inversion and the local wind patterns aggravate the air contamination (1). The persistent temperature inversion limits the vertical distribution of the pollution by turbulence, and advec-

tion of the local winds distributes it beneath the inversion layer. Marked inversions are most prevalent in the summer months but sometimes occur in winter especially when a high pressure area develops over the Great Basin. There was an annual average of 262 days of temperature inversion in the Los Angeles area in the 3-year period, 1943 to 1945 (9). Figure 1 illustrates a characteristic period of inversion from August 16 to 19, 1948. This was a time of protracted low visibility and eye irritation.

The average wind velocity in the Los Angeles basin is 5 miles per hour in summer and 7 miles per hour in winter. Figures 2 to 4 are composite maps based on a study (10) made for the Los Angeles Air Pollution Control District in 1947 by the University of California at Los Angeles, which illustrate the diurnal changes of surface winds throughout the year. Figure 2 shows the location of the principal industrial areas and the direction of the sea breeze from 9:00 A.M. to noon in summer. The sea breeze pattern from noon to midnight in summer and from noon to 4:00 P.M. in winter is similar (Figure 3), although afternoon wind velocities are lower in the summer season. At night, in both summer and winter, a land breeze of 1 to 3 miles per hour moves down from the mountains toward the coast (Figure 4). This régime sets in at midnight in summer and continues until about 7:00 A.M., and begins around 7:00 P.M. in winter and continues until 10:00 A.M.

The sea wind reaches its highest velocity in mid-afternoon in both winter and summer as a true westerly (Figure 3). As it moves eastward from the coast it follows topographically lower elevations until the stream splits,

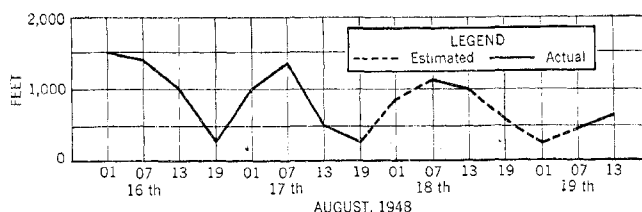


Figure 1. Variation in Base Temperature Inversion at U. S. Weather Bureau Station, Federal Building, Los Angeles, Calif.

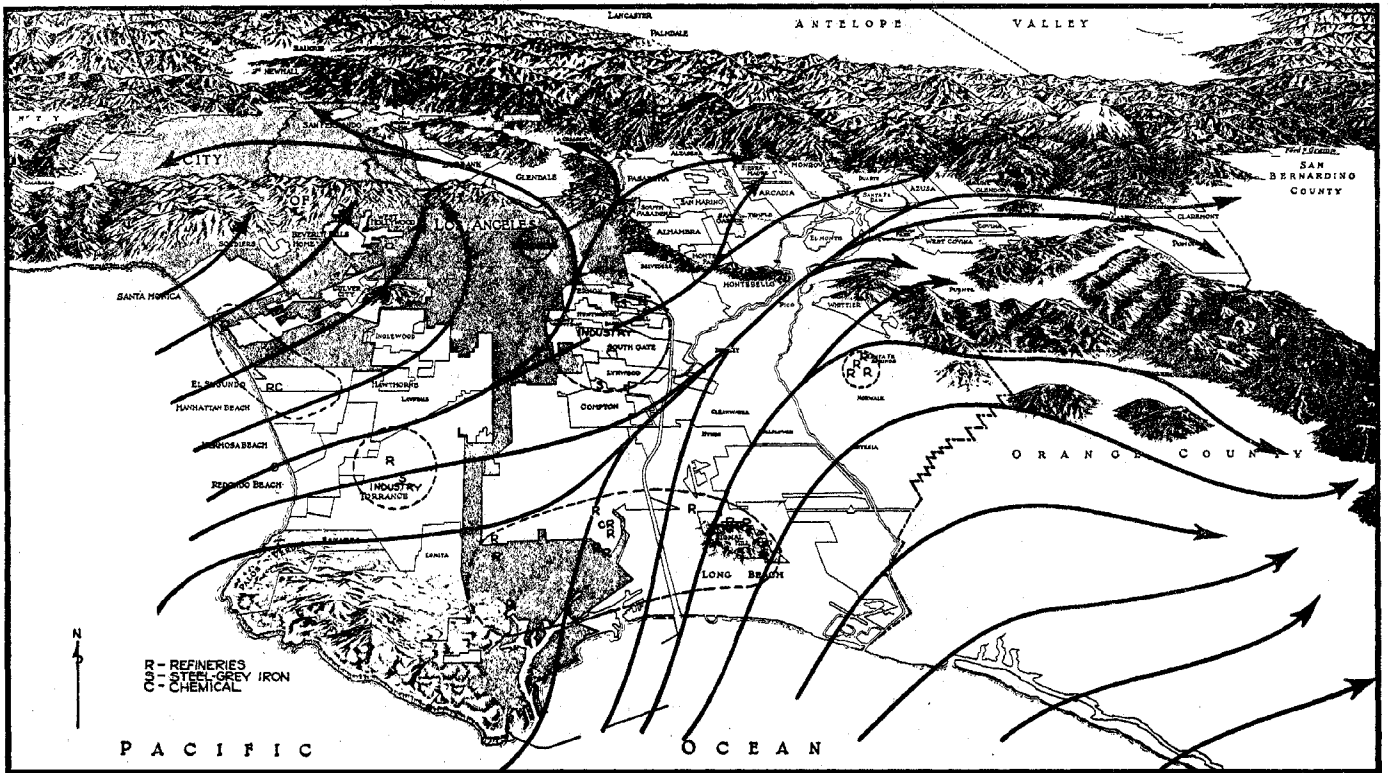


Figure 2. Wind Direction in Summer, 9 A.M. to Noon, County of Los Angeles, Calif.
Speed, 3 to 9 miles per hour

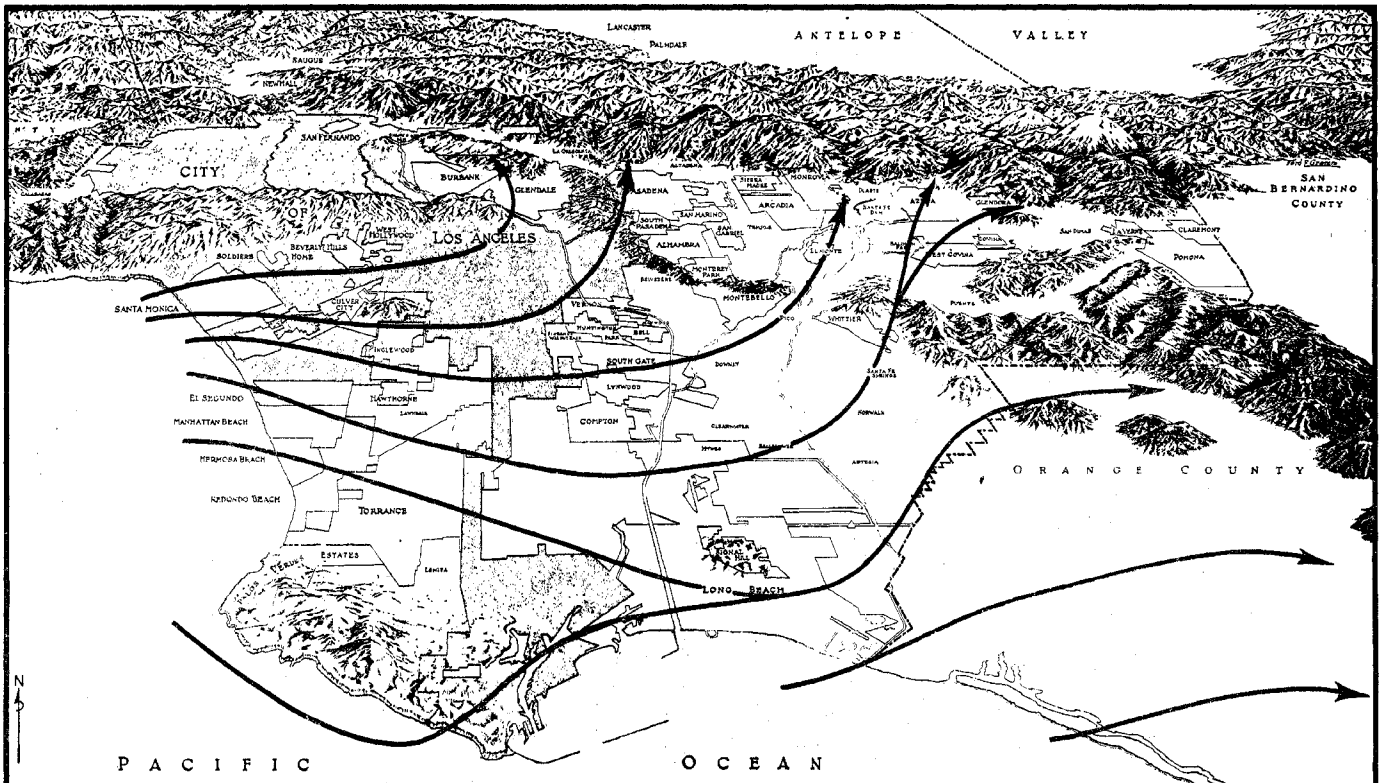


Figure 3. Wind Direction, Noon to Midnight in Summer and Noon to 4 P.M. in Winter, County of Los Angeles, Calif.
Speed, 7 to 12 miles per hour

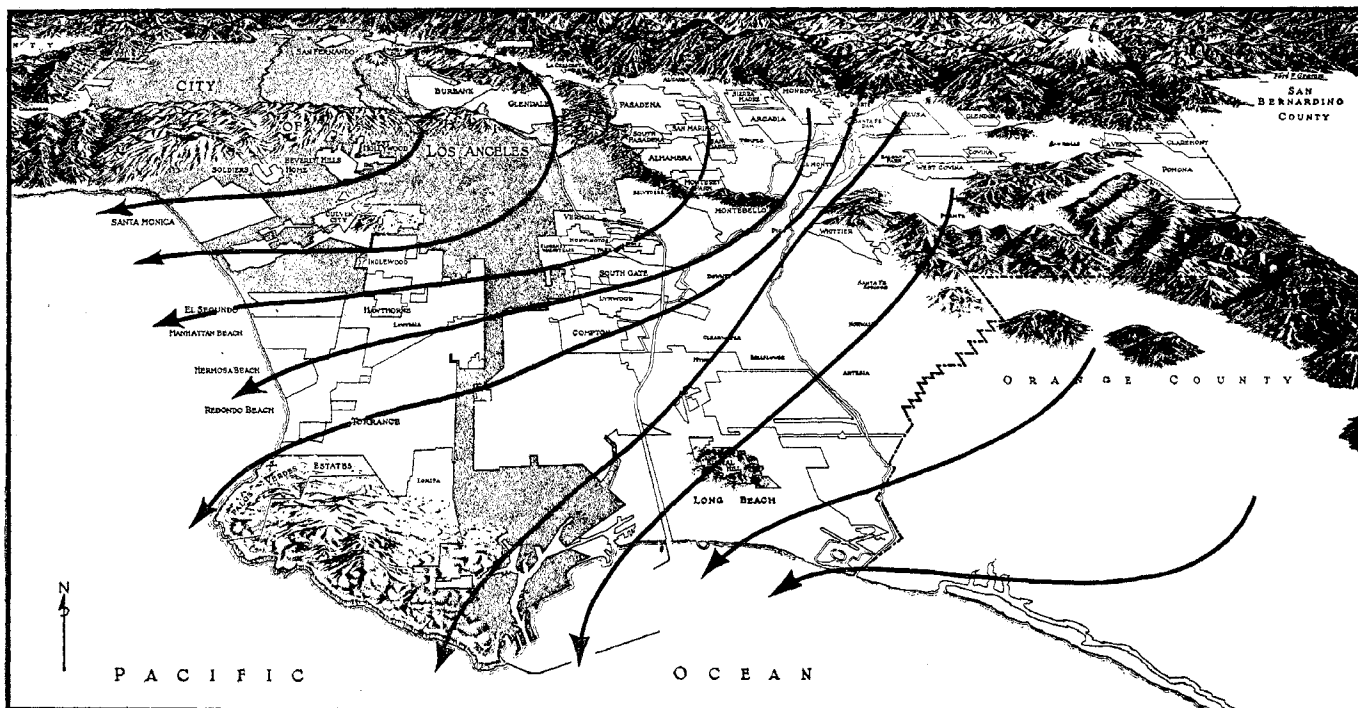


Figure 4. Wind Direction, Midnight to 7 A.M. in Summer and 7 P.M. to 10 A.M. in Winter, Los Angeles, Calif.
Speed, 1 to 3 miles per hour

one portion flowing up the San Fernando Valley and the other moving eastward along the foot of the San Gabriel and San Bernardino ranges toward San Geronimo Pass. Frequently in late afternoons in summer the smog may be seen streaming into the desert through this pass which is some 90 miles from Los Angeles.

The pattern of the smog stream for a 4-day period of temperature inversion during August 1948 is established by hourly observations of visibility at the Weather Bureau stations at Inglewood airport, downtown Los Angeles, and the Burbank airport (Table I and Figure 5).

Air pollution is greatest when the base of the temperature inversion approaches the ground. This is also the time of the greatest number of complaints of the irritating effects of the pollution. The time and location of complaints of eye irritation are shown graphically in Figure 6 for the last 6 months of 1948. This further illustrates the distribution of the smog by the surface winds.

COLLECTION OF THE AEROSOL

The recurrence of the smog nuisance has caused much speculation as to its origin, exaggerated claims regarding its physiological effects, and a strong public demand for its abatement. The first

step in the solution to the problem was the identification of the aerosol.

Development of equipment and techniques for collecting atmospheric samples were started in April 1948, soon after the district was fully staffed. Coincident with work on the aerosol, samples of industrial dusts were collected at their points of origin for chemical analysis and examination by electron microscope.

MODIFIED CASCADE IMPACTOR

Samples of the aerosol were first collected on August 14, 1948, with the cascade impactor originally designed by May (8) and modified by Sonkin (11).

The instrument provides a convenient means of measuring the concentration and size of air-borne solid and liquid particles. It consists of a series of four jets with progressively smaller cross-sectional areas. When a gas is drawn through the instrument, the velocity increases through each successive jet, and progressively smaller sized particles are impacted on glass slides which are mounted normally to the jet orifices at a distance of 1 mm.

The critical pressure required for such velocity is 16 inches of mercury; the critical air-flow rate is 20.8 liters per minute, but any convenient rate can be chosen. The dimensions of the jets,

Table I. Hourly Visibility during Inversion

Location	Date, August 1948	A.M.											P.M.							
		4	5	6	7	8	9	10	11	Noon 12	1	2	3	4	5	6	7	8		
Burbank	16	0.1875	0.3125	0.0625	0.125	1	1.5	1.75	1.5	2	4	5	5	6	6	7	7	6		
	17	3	4	4	4	3	3	2.5	2.25	3	6	6	9	12	15	15	12			
	18	5	6	6	4	3	3	3	1.5	3	4	5	12	20	15	15	15			
	19	10	10	8	4	4	4	4	2.5	3	5	8	12	15	15	20	15	15-		
Los Angeles City	16	2	0.75	0.625	0.625	0.75	0.75	0.75	1	2	2.5	3	4	4	5	4	3	5		
	17	3	0.75	0.75	0.5	0.5	0.5	0.75	1	2.5	4	7	10	10	8	10	10	15		
	18	3	2	1	0.625	0.625	0.75	0.75	2.5	5	4	2.5	10	10	10	15	15	20		
	19	8	7	5	2	1.5	1.5	2.5	1	3	4	6	7	12	15	15	15	15		
Los Angeles Airport	16	1.25	1	1	0.75	0.75	0.625	1.5	1	1.5	3	3	4	4	3	2.5	3	1.75		
	17	1.5	0.75	0.75	0.75	0.75	0.75	3	5	7	7	7	5	5	8	10	15	15		
	18	0.125	0.3125	0.0625	0.1875	1.25	2.5	4	5	2	1.75	10	10	12	20	20	15-	15-		
	19	5	2.5	1.75	1.5	2.5	3	3	4	7	8	10	20	25	25	30	15-	15-		

Table II. Dustfall Summaries

City	Year	Average Monthly Dustfall, Tons/Sq. Mile/Month											Monthly Av. for Year	
		Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.		Dec.
Los Angeles, Calif.	1946	32.0	24.6	28.1	38.5	35.5	26.0	28.2	21.8	24.7	24.9	26.4	21.2	27.7
	1947	34.3	25.8	29.1	38.0	31.0	29.7	34.8	28.8	27.7	27.9	41.5	42.1	32.6
	1948	41.0	45.4	26.8	36.4	35.2	24.3	25.8	26.8	27.7	36.6	92.2 ^a	40.4	33.3
Cincinnati, Ohio	1946	46.6	48.6	39.5	39.6	23.0	26.6	27.1	26.1	29.1	32.5	31.5	36.4	34.0
	1947	45.8	49.1	46.6	35.5	34.0	26.3
Rochester, N. Y.	1941	25.0	31.2	33.5	36.9	29.8	23.3	19.7	17.8	38.2	19.1	26.6	26.9	27.3
	1942	31.7	25.4	37.6	34.9	26.9	20.9	20.4	19.5	17.2	21.4	23.0	26.6	26.4
Chicago, Ill.	1946	76.2	62.7	68.3	74.8	62.9	64.5	59.7	53.9	64.8	62.6	68.4	63.7	65.2
	1947	99.2	80.4	57.9	73.2	58.5	61.9	32.2	50.5	51.5	49.6	53.3	59.6	61.2
Detroit, Mich.	1945	76.7	31.9	36.8	65.8	..	48.4	59.5	67.9	65.4	56.5
	1946	62.4	40.9	36.6	48.0	..	62.0	42.4	54.8	68.3	51.7

^a Very heavy dust storm—not included in average.

the air speed through them, and the approximate size of the impacted particles were:

Jet No.	Dimension of Jets, MI.	Approx. Air Speed through Jets, M.P.H.	Approx. Size Range of Droplets, μ
1	1.1 X 0.1	60	0.7
2	0.9 X 0.08	90	1.5-0.25
3	0.7 X 0.05	180	1.1-0.15
4	0.63 X 0.015	770	0.7-0.1

Recently a second instrument, much more efficient than the first, was constructed of glass. Imperfections in the jets of the first impactor made it impossible to obtain the velocities described by Sonkin but the experience gained made it possible to build the second to the specifications originally described. A third instrument has been constructed of brass (Figure 7). In this instance, meticulous honing was necessary to obtain the required velocities in the jets.

The aerosol appears as a faint smudge on the fourth slide. On heavy smog days a satisfactory sample for microscopic examination is impacted on the slide after passing 1 or 2 cubic feet of air. In excess of this quantity the aerosol builds up until the particles coalesce and lose their form. Figure 8 illustrates the liquid droplets collected on the fourth slide of the impactor. These particles measure 1.2 microns in diameter after impaction. The diameter of the particle before impaction computed by May's factor (8) is about 0.6 micron. The particles do not coalesce or evaporate on standing for several days.

Some solid particles are deposited on all four slides. Examination with the petrographic microscope shows some of these to be crystalline. The relative quantities of solid particles and liquid droplets deposited on the slides have not been determined, but microscopic observation indicates a preponderance of the liquid phase from collections made during dense smog conditions. Immediately following rain the liquid droplets are not collected but solid particles are deposited on all four slides.

TECHNIQUE OF MICROCHEMICAL ANALYSIS

A sample containing appreciable amounts of the liquid phase of the aerosol was collected on the glass slide and dissolved in a small droplet of 3 N hydrochloric acid. The mixture was agitated with a small glass rod and the solution drawn into a 0.5-mm. capillary tube. Care was exercised to pick up only the clear supernatant fluid. To this solution barium chloride-hydrochloric acid reagent was added by touching the end of the partially filled tube with a small reagent drop on a clean microscope slide. The curvature of the tube made the direct microscopic examination of the contents of the capillary impossible for optical reasons. This difficulty was largely overcome by mounting the tube in a drop of cedar oil and viewing it under a cover glass. In this manner barium sulfate crystals, made in a blank test by using 0.002 N sulfuric acid in place of the sample, were clearly visible in the tube.

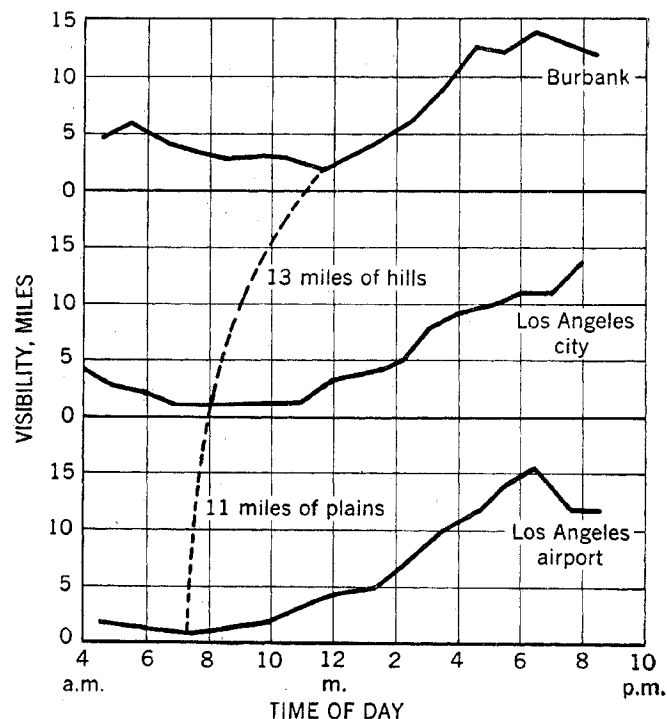


Figure 5. Hourly Visibility during Inversion

The unknown, however, was still too dilute to yield a decisive deposit of barium sulfate crystals in the capillary. Attempts to concentrate the sample solution by evaporation in the capillary placed in an oven at 100° C. proved unsuccessful. The sample was invariably ejected from the hot capillary. The sample was effectively concentrated, however, by allowing the capillary tube containing the solution to stand for 24 hours in an evacuated desiccator. An 8-ml. length of liquid in the capillary was thus concentrated to 2 mm. or less. An equal volume of barium chloride-hydrochloric acid reagent was added. This treatment of a sample, obtained from the impingement of 20 cubic feet of air, formed crystals of barium sulfate which could easily be seen with a magnification of 100X when the capillary was mounted in a drop of cedar oil.

Air samples collected on slides with the cascade impactor, as already described, were submitted for analysis to A. J. Haagen Smit of California Institute of Technology. Chemical analysis of the deposits, collected on days when heavy air pollution existed, revealed the presence of sulfates in the atmosphere by the sodium rhodizonate method (3).

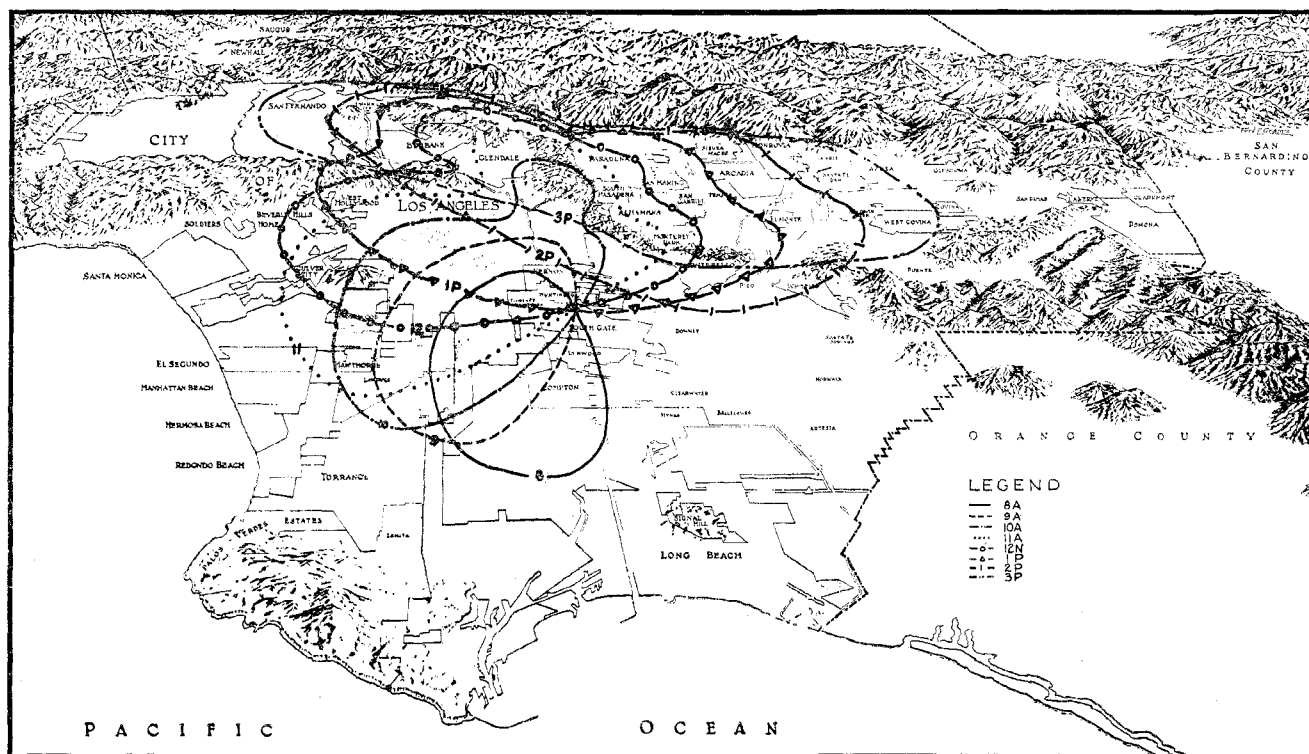


Figure 6. Position of Area of Eye Irritation at Various Times of Day
County of Los Angeles, Calif., 8 A.M. to 3 P.M.

DUSTFALL

A country-wide dustfall survey was initiated in 1946. The monthly averages of dustfall per square mile are shown in Table II, together with similar monthly averages from other large industrial and residential cities of the United States. Rochester, N. Y., and Cincinnati, Ohio, have comparable dustfall; other industrial cities have a much heavier dustfall than Los Angeles.

Lapple (7) states that conditions which constitute only a local nuisance in one locality may cause a serious general pollution problem in another. It is very probable that if the industrial fumes and dust which remain in suspension over Los Angeles

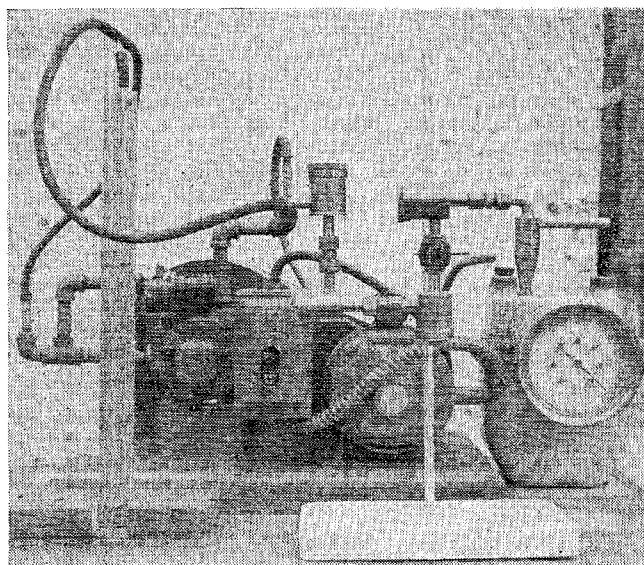


Figure 7. Microimpactor Constructed of Brass

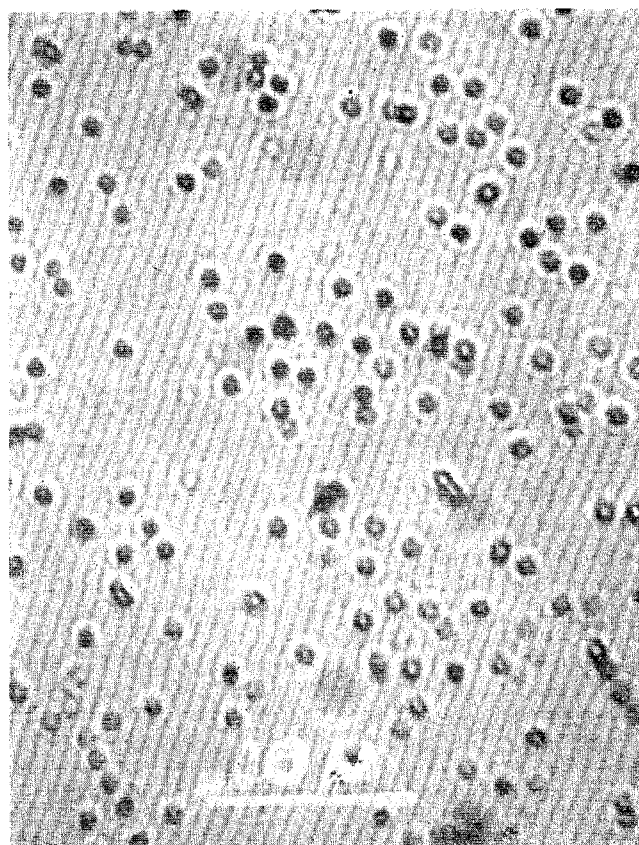


Figure 8. Liquid Droplets Collected from Atmosphere with Cascade Impactor

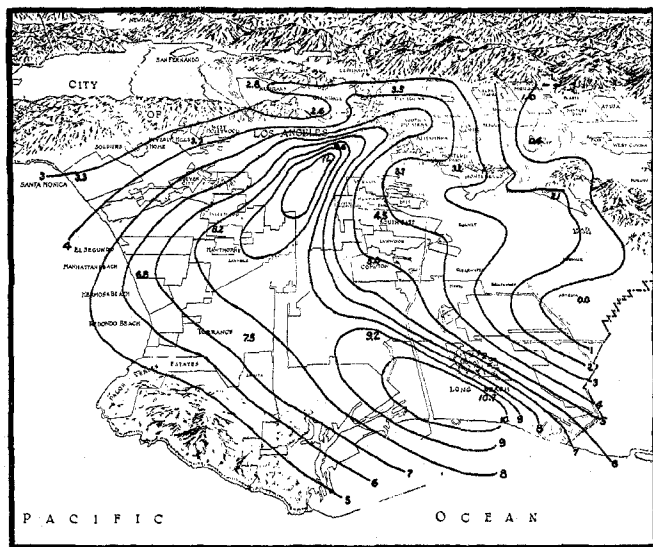


Figure 9. Lines of Equal Concentration of Acidity as Sulfur Dioxide, Mg./Jar/Month

1947 average from dustfall stations, County of Los Angeles, Calif.

were moved out of the area by air currents daily, the heavy pollution would not occur.

The monthly dustfall survey in the Los Angeles basin gives an average tonnage of settled solids much lower than would be expected for such an industrial area. Standard dustfall measurement represents only the coarser particles in the atmosphere (7) and probably only those particles larger than 1 micron. In normal sedimentation of solid particles in still air Stokes' law does not hold below 3 microns and Cunningham's modification (2) must be used in calculating the rate of fall. With an increase in wind velocity and gustiness, particles larger than 1 micron in diameter would be affected and a wider deviation from the true dustfall would result. However, the low wind velocity and calm periods which mark the change in wind direction in Los Angeles provide better conditions for sedimentation than in any other large industrial area. These conditions produce a dustfall value that is more representative than the values obtained in an industrial area of high wind turbulence.

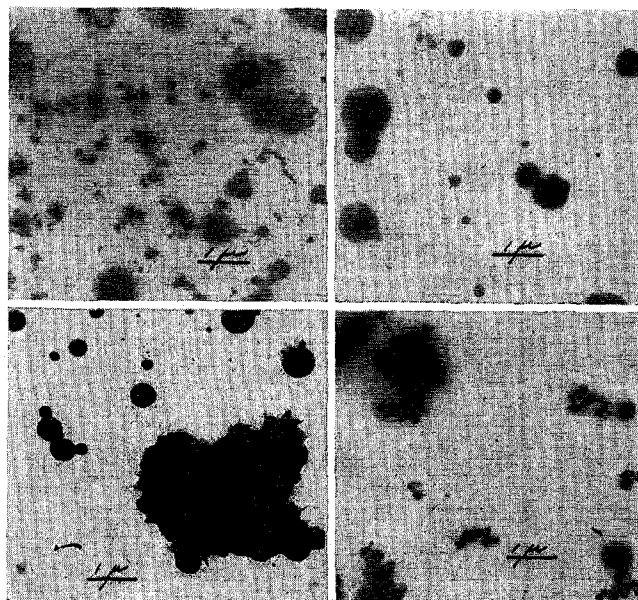


Figure 10. Fumes from Electric Furnace Making Alloy Steels

Johnstone (5) states that the characteristic blue haze, which in high concentrations causes low visibility in the Los Angeles area, is usually associated with aerosols of very small particle size—that is, 0.3 to 0.5 micron. Little or none of this material is found in dustfall collections. However, as Johnstone points out, the effect of an increase in humidity on the particle size of a hygroscopic aerosol is to increase the particle size and to stabilize the aerosol. Solid particles may serve as nuclei of hygroscopic aerosols and dissolve partially in the condensed moisture. Sulfur dioxide and other toxic gases in the air are absorbed in solutions of this type, and under these conditions sulfur dioxide readily oxidizes to sulfuric acid.

The relative humidity increases in the evening and during the summer months fogs are quite frequent. Conditions for an increase in particle size of the aerosol then prevail. In general, these aerosols are not associated with the blue haze. The blue haze is not apparent during foggy days, but on days of early morning fog, as the humidity decreases and the fog dissipates, it remains.

Since the particle size of natural fog ranges between 5 and 50 microns, aerosols formed under these conditions are probably collected in dustfall jars. Sulfur dioxide and sulfuric acid may enter the dustfall jar in this way. Their distribution as shown in Figure 9 reflects origin, wind pattern, and topography, and perhaps the time necessary for oxidation of sulfur dioxide in the atmosphere. Evidences of water-soluble organic compounds have been detected on several occasions in dustfall studies.

EXAMINATION OF SUBMICRON DUSTS

In order properly to assess the relative importance of different sources of air pollution, as much as possible must be learned about the characteristics of the individual particles, as to average shape and size, as well as to their chemical composition. In this range of particle size, from 0.01 to 1 micron, the appearance of individual particles can at best only be inferred with the optical microscope, but the electron microscope makes a genuine contribution to this information.

The first step in tracing the origin of particles, as they are found in smog itself, is a catalog of photographs of particles of various kinds, taken at source. An important known source of particles of this range is known as metallic fume; it originates in the industrial processes of smelting, refining, and casting of nonferrous metals and in the production of cast iron and steel in

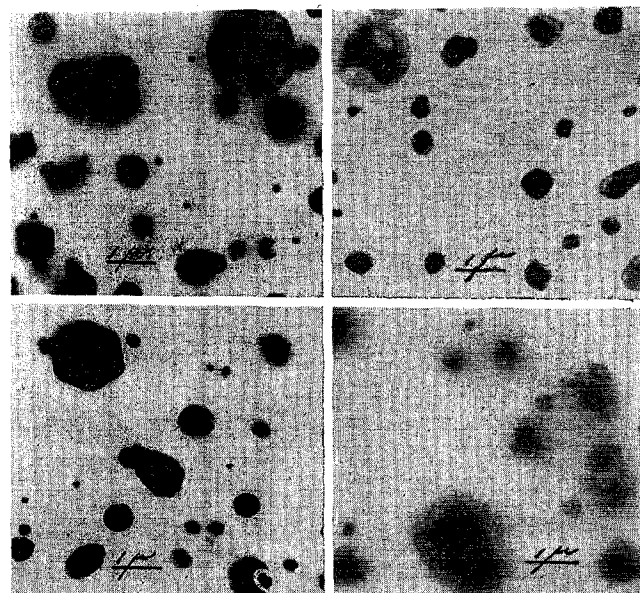


Figure 11. Dusts from Open Hearth Steel Furnace

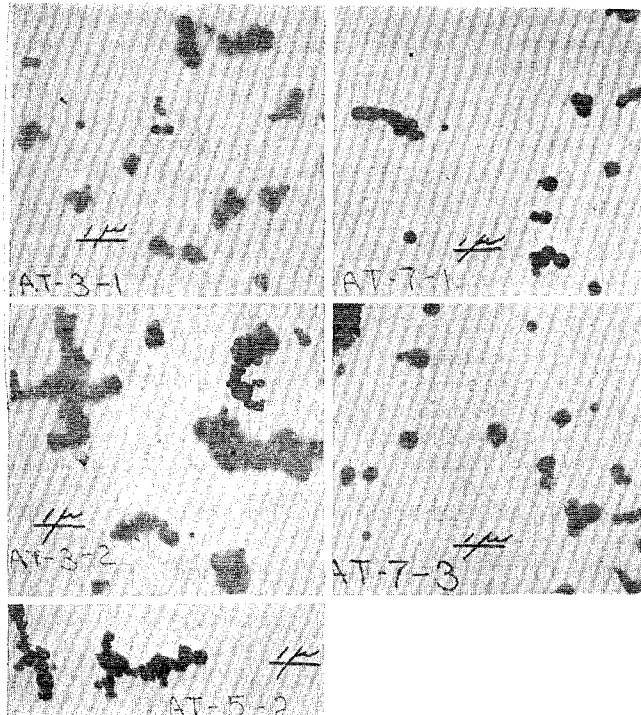


Figure 12. Fumes from Lead Smelting Process

blast furnaces and electric furnaces. These processes have in common temperatures sufficiently high to vaporize significant quantities of metal. The fume consists of the condensed vapor or its oxidation products. The material presented here consists accordingly of a series of electron microscope studies of metallic fumes in the form in which they are released as atmospheric contaminants.

To prepare the fume samples for examination under the electron microscope, it is necessary to collect them with as little alteration as possible from the state in which they exist in the atmosphere. For this purpose, the thermal precipitator (4, 6) has outstanding advantages, since the particles are collected at low velocity with no solvent contact, and agglomeration or frag-

mentation is minimized. In addition, the collection efficiency is high over the whole particle size range.

The principle of thermal precipitation is that suspended particles in an air stream flowing over a wire heated to a low temperature are repelled by the wire, and if a suitable surface is present a few tenths of a millimeter away from the wire, the particles will be deposited on this surface. The collecting surface used was the thin supporting membrane on the metallic screens which are used for sample examination in the electron microscope. These supporting films should be as thin as possible to permit the best resolution with the microscope. If the fume concentration is high, a few milliliters of air drawn through the precipitator will cause a deposit of suitable density on the supporting membrane.

To obtain fumes of known origin and characteristics, samples were drawn directly from the stacks of typical industrial establishments representing the principal sources of metallic fumes from both ferrous and nonferrous metals available in the Los Angeles area. An examination of the electron photographs reveals, in addition to the particle size, other information which can be used for identifying the particles.

The fume shown in Figure 10 was collected from an electric furnace making alloy steels. About 95% of these particles are below 0.5 micron in diameter. They are almost all circular in appearance, indicating a spherical shape. Chemical composition is principally iron oxide. The concentration of fume in the stack from this furnace was approximately 0.3 grain per cubic foot.

In contrast to the spherical particles shown from the electric furnace, the particles produced by the open hearth process are shown in Figure 11. This process involves the use of scrap containing considerable nonferrous metals, and the fuel as well as the metal contains considerable sulfur. Chemical analysis of the fume showed the presence of a high percentage of sulfates, presumably lead and zinc. The interesting features shown by this material are the somewhat larger particle size averaging about 0.5 micron, and the presence of a fair percentage of crystalline forms, usually of hexagonal shape. Some of the particles show fine structural detail and interesting transition from globular to hexagonal form.

In the nonferrous field relatively pure lead fume was available in a smelting process, and its characteristics are shown in Figure 12. The average particle size is about 0.3 micron, and most forms are spherical.

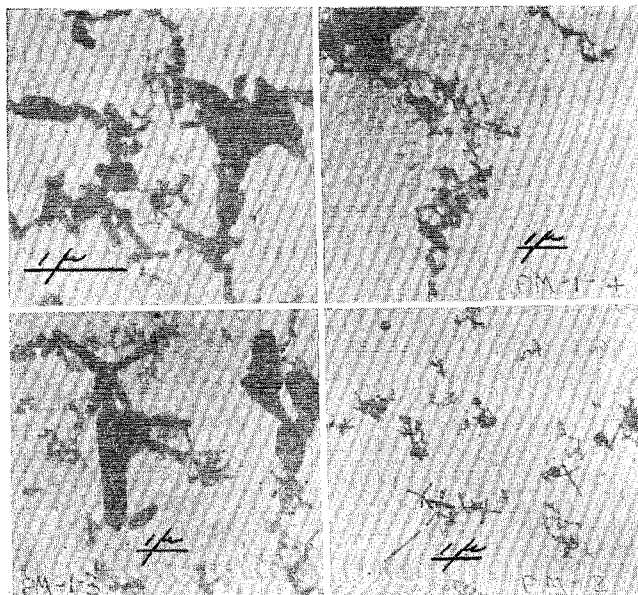


Figure 13. Fumes from Zinc Smelting

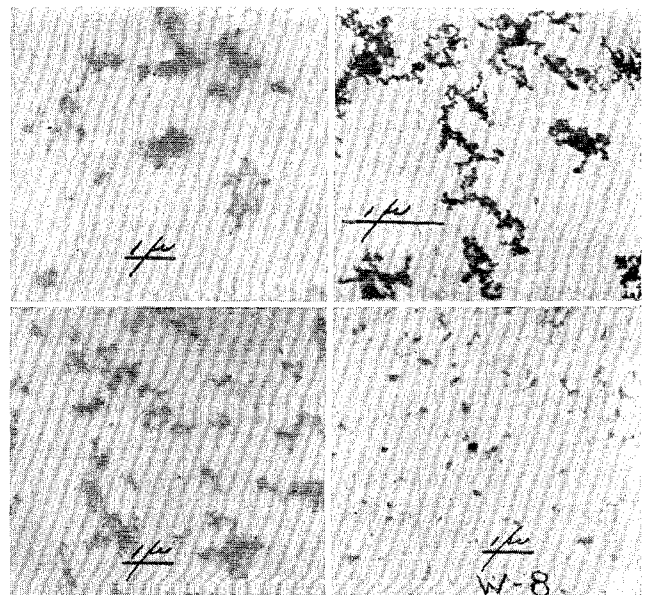


Figure 14. Fumes from Red Brass Furnace

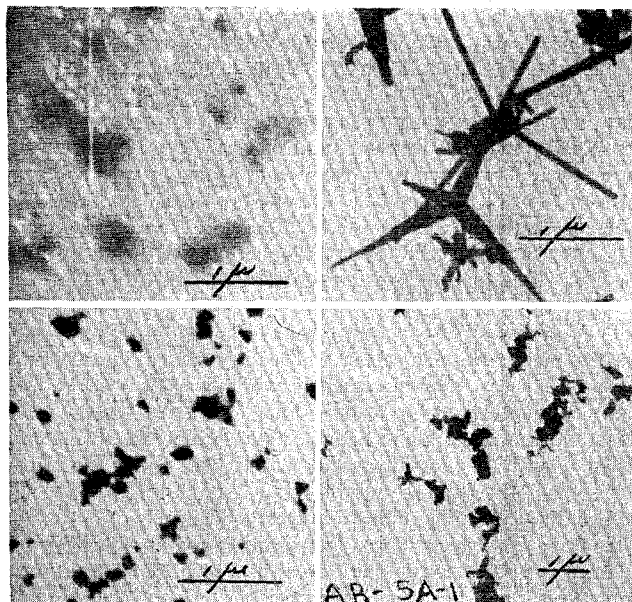


Figure 15. Fumes from Yellow Brass Furnace

The most characteristic crystal forms in the nonferrous field are obtained where zinc oxide is a major constituent. Figure 13 shows the characteristic zinc oxide obtained in zinc smelting. The forms are all crystalline and of a great range in size.

In the melting of red and yellow brass as it occurs in typical foundries, the fume has a more complex chemical composition, and it no longer shows the characteristic crystalline form associated with the pure metals. Figure 14, showing fume from a typical oil-fired furnace producing red brass, has some interesting

and distinct characteristics. The first of these is the extremely small average particle size, about 0.01 micron, and the second is the marked tendency for the agglomeration of these fine particles into chains or clumps.

The final example, Figure 15, is a yellow brass which, at some stages of the melting cycle, shows the characteristic zinc oxide crystals; many of these, however, are less distinctly formed than in the case of the zinc smelter.

Because of the individual characteristics of the fume produced by these different industrial processes, their importance as contributors to the resultant haze should be readily ascertained by electron-microscope studies of the haze itself. In addition, the information obtained with regard to the shape and size of particles and their tendency toward agglomeration is of great assistance in the design of equipment for collecting the fume at the source and preventing its appearance as an aerosol in the atmosphere.

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Recovery of Fluorine from Stack Gases

T. P. HIGNETT AND M. R. SIEGEL

Tennessee Valley Authority, Wilson Dam, Ala.

A process was developed on a pilot plant scale for recovery of fluorine from stack gases that are evolved in the thermal processing of rock phosphate to produce fused tricalcium phosphate. The recovery process consists in absorbing the fluorine, which is present as hydrogen fluoride, in a bed of lump limestone at temperatures above the dew point of the stack gas. The calcium fluoride reaction product separates from the limestone lumps in the form of fines; portions of the bed are withdrawn from the tower at intervals, screened to remove the fines, and the oversize (partially reacted limestone) is recycled to the tower together with fresh make-up limestone. The pilot plant product contained 80 to 95% CaF_2 , which is comparable in grade to commercial fluorspar. Fluorine recovery in the pilot plant using a 4-foot depth of packing was as high as 96% for extended periods of operation and was governed principally by the rate of removal of the

reaction product. Calculations indicated that virtually complete recovery could be obtained by increasing depth of tower packing to about 9 feet. A large scale unit was constructed which utilizes this process for recovering fluorine from stack gases in the TVA demonstration scale plant in which fused tricalcium phosphate is produced by fusion and defluorination of rock phosphate.

FLUORINE is present in all continental formations of rock phosphate, usually in amounts equal to or somewhat greater than that stoichiometrically required to form fluorapatite [$\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$] with the phosphorus contents of the rocks. All commercially used methods for processing rock phosphate to produce fertilizer materials result in volatilization of some of the fluorine.